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STRUCTURE OF GRIGNARD REAGENTS
IN DIETHYL ETHER

by

PAUL TERGIS

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Faculty in Chemistry in partial fulfillment
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1976

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

STRUCTURE OF GRIGNARD REAGENTS
IN DIETHYL ETHER

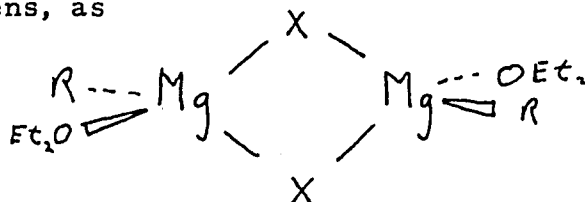
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Paul Tergis

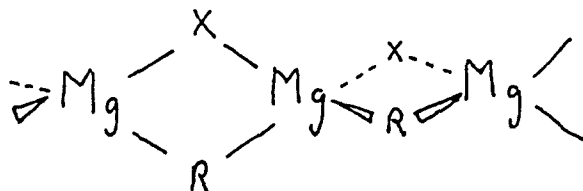
Adviser: Professor Bernard Bulkin

The Raman spectra of varying concentrations of Grignard reagents (RMgX , $\text{R} = \text{Me}$, Et , and $\text{X} = \text{Br}$, I) at room temperature were studied. The spectra were interpreted in conjunction with association data of Ashby¹ who demonstrated by ebullioscopic studies that Grignard species in diethyl ether form monomers at low concentration which associate to form multimers with increasing concentration.

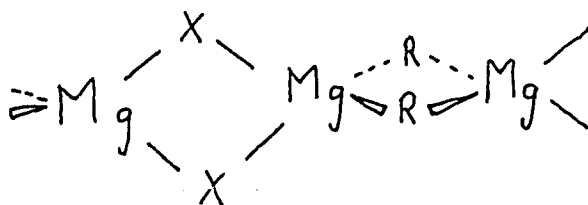
The spectra are interpreted to indicate that the magnesium atom in Grignard species has a coordination number of four with an approximate T_d arrangement of ligands. They associate, via bridging halogens, as



As the concentration becomes greater alkyl bridging also takes part in bridging. There is evidence that alkyl groups may singly bridge magnesium atoms, alone or with halogen such as

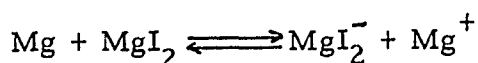
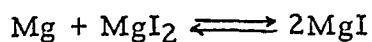


or may doubly bridge such as



No bands are assigned to Mg-O stretching although a shift in equilibrium is observed from trans-trans (TT) conformers to trans-gauche (TG) conformers as the Grignard concentration increases. The $TT \rightleftharpoons TG$ conformer shift provides an additional method of diethyl ether conformer determination which generally agrees with intensity vs. $1/T$ studies.

We looked for univalent magnesium in the reducing system Mg/MgI_2 in diethyl ether. Some authors have proposed the following possible equations involving univalent magnesium:



An alternative apparatus for ebullioscopic measurements of air and water sensitive compounds was designed and constructed to determine the extent of the above possible reactions. The apparatus uses two boiling chambers, each with a Cottrell pump and condenser. The design of the boiling chamber is similar to one used by Walker and Ashby.² In our system one boiling chamber has solution while the other contains pure solvent. Both chambers are connected and have the same pressure. Because the solution and solvent have almost identical pressure dependencies, ΔT has a negligible dependence on pressure and a precision manometer is unnecessary. This substantially reduces the cost of the apparatus, simplifies the operation, while maintaining precision.

We found no significant difference in association (apparent molecular mass/formula mass) vs. concentration curves of MgI_2 etherate in the presence or absence of magnesium metal and therefore no evidence of univalent magnesium by this method.

1. E.C. Ashby, Ann. N.Y. Acad. Sci., 31 (1968).
2. F.W. Walker and E.C. Ashby, J. of Chem. Ed., 45, 10, 655 (1968).

ACKNOWLEDGEMENTS

I am most indebted to my mentor, Professor Bernard Bulkin, for the appearance of this work. Those times that I was privileged to work with him were most appreciated as I was able to witness an aware person. I wish that I had listened to his seemingly off-the-cuff suggestions much more closely as the relentless teacher, time, proved his remarks to be nearly infallible.

Many thanks go to my fellow graduate students at Hunter College who were most generous. Special thanks to June McClean (now Dr. McClean) who loved to explore the unknown and share her thoughts; to Art Noguerola who extricated me numerous times from the snares of the computer and provided the basic programs to interface computer and hardware; to Dr. K. Krishnan, a postdoctoral fellow, who through many discussions, taught many of us the finer points of spectroscopy and group theory; and to Ken Brezinsky who always sees the lighter side.

To the midwife of this work, my wife Judy, who typed this manuscript several times and gave me boundless support, goes my greatest appreciation and love. The inspiration was provided by our child, Athena. To watch her "play" is to see complete enthusiasm and pure curiosity (also an impish attraction to paper and the typewriter).

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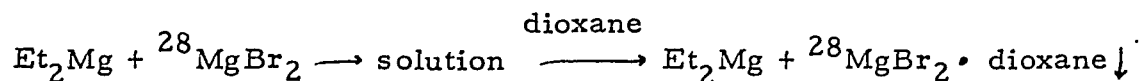
INTRODUCTION

Victor Grignard discovered the Grignard reagent in 1900.¹ It has become an indispensable reagent in the synthesis of organic compounds and is primarily used in adding an alkyl or aryl group to the carbon atom of a ketone. This reaction is normally carried out in ether, usually diethyl ether, because the solvent may be easily removed, having a boiling point of 35°C.

Although Grignard reagents have been used for over 75 years, there is still considerable controversy and confusion regarding the precise structure of the Grignard reagent in ether solution. By X-ray analysis the solid crystal structure of the several Grignards analyzed has shown them to contain four coordinate magnesium, $\text{RMgX} \cdot 2\text{Et}_2\text{O}$. When in diethyl ether, however, the solution structure is not known.

Of the many ideas on the nature of the Grignard reagent, only two differing concepts have been the focus of chemists. The first, offered by Grignard himself,² was that the best representation is RMgX . The second concept, offered by Jolibois,³ was the formula $\text{R}_2\text{Mg} \cdot \text{MgX}_2$. No conclusive experiment differentiating these two structures was carried out until 1957 when Dessy and co-workers⁴ reported no exchange between $^{28}\text{MgBr}_2$ and $(\text{C}_2\text{H}_5)_2\text{Mg}$. At the same time they showed that an equimolar mixture of MgBr_2 and $(\text{C}_2\text{H}_5)_2\text{Mg}$ had the same characteristics as

the classic Grignard reagent prepared by adding $\text{C}_2\text{H}_5\text{Br}$ and Mg . The Dessy experiment was simply:



All the labeled magnesium was recovered with the dioxane which ruled out alkyl exchange and favored the $\text{R}_2\text{Mg} \cdot \text{MgX}_2$ formulation of the Grignard reagent. At the time this conclusion was well accepted. Raos and Zeil⁵, for instance, in 1963 interpret their data by NMR to infer a Grignard structure agreeing with Dessy and co-workers. For EtMgBr and EtMgI in Et_2O and THF the NMR determined structure was:



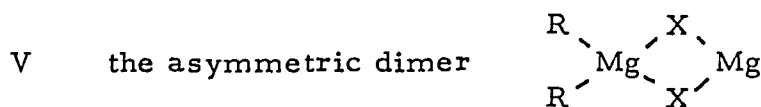
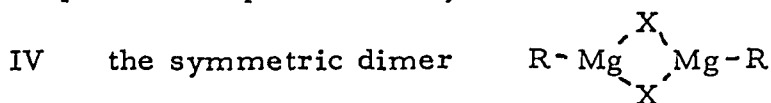
Dessy and Handler⁶ repeated their previous $\text{Et}_2\text{Mg} + {}^{28}\text{MgBr}_2$ experiment but this time with ${}^{25}\text{MgBr}_2$ as a tracer and found complete exchange compared to 6-10% exchange with ${}^{28}\text{MgBr}_2$. Apparently $\text{Et}_2\text{Mg} + {}^{25}\text{MgBr}_2 \rightarrow \text{EtMgBr} + \text{Et}^{25}\text{MgBr} \rightarrow$ possible dimerization. Ashby and Smith⁷ point out that the latter results of Dessy and Handler seemed to be de-emphasized. Dessy rationalized the difference in results to impurities in the ${}^{25}\text{Mg}$ which he postulated catalyzed the exchange while the possibility of an impurity in ${}^{28}\text{Mg}$ that might inhibit exchange was not considered.

Ashby and Smith⁷ lay out the following possibilities and comments on Grignard structure (for simplicity, complexing with ether is not shown although it does occur).

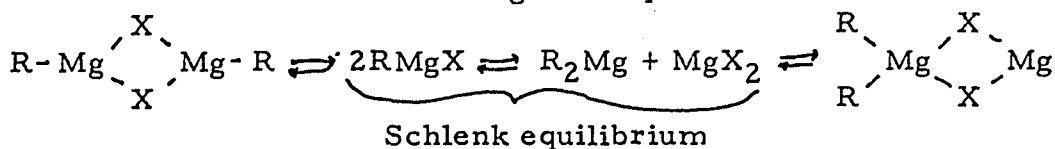
The monomeric species that exist in Grignard solutions are either:

- I RMgX
- II a mixture of R_2Mg and MgX_2
- III equilibrium mixture of I and II

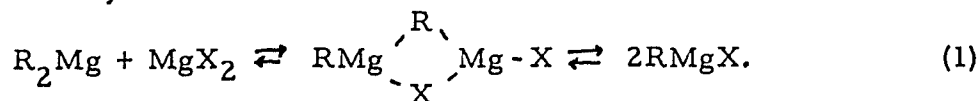
If dimeric species are present, they could include:



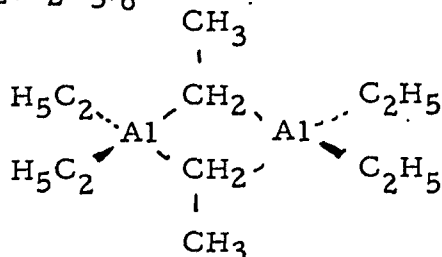
VI both IV and V through the equilibrium



The symmetrical structure has been supported by Ashby and the asymmetric structure by Dessy. Ashby postulates that the asymmetric dimer was probably formed with the $^{28}\text{MgBr}_2$ but that the $^{25}\text{MgBr}_2$ reaction producing the symmetric dimer is the predominant dimer of Grignard solutions. Ashby suggests that the mechanism of alkyl exchange may proceed by



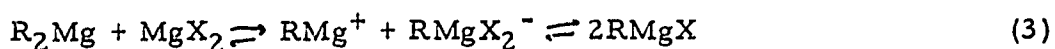
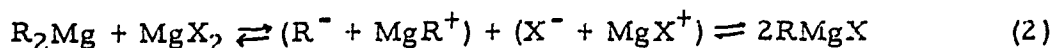
For an R group such as C_2H_5 to be a bridging species may seem unlikely but dilute $\text{Al}_2(\text{C}_2\text{H}_5)_6$ in benzene is dimeric with bridging C_2H_5 as follows:



Evidence will be given subsequently for bridging C_2H_5 with $Mg(C_2H_5)_2$ in diethyl ether. Note that $R_2Mg + MgX_2 \rightleftharpoons 2RMgX$ of the above equation is the Schlenk equilibrium proposed by Schlenk and Schlenk⁸ in 1929.

Vreugdenhil and Blomberg⁹ show that the reaction rate between $(C_2H_5)_2Mg$ and $MgBr_2$ is slow in the concentration range of 10^{-3} to 10^{-2} M. Since the reaction rate is fast at high concentration, the reaction is concentration dependent and, therefore, consistent with mechanism (1).

Other possible mechanisms for alkyl exchange are the two following ionic processes.



Mechanism (2), according to Ashby and Smith, would be expected to be essentially concentration independent and mechanism (3) concentration dependent. Rate evidence showing concentration dependence would tend to rule out mechanism (2). More direct evidence for mechanism (3) is given by Evans and Pearson¹⁰ who reported ionic species in the electrolysis of Grignard reagents. In the electrolysis of nC_4H_9MgBr in diethyl ether, magnesium containing species were found at both anode and cathode. This work was later confirmed by Dessy and Jones¹¹ who concluded that the predominate positive ion in solution is RMg^+ and it appears that the most probable negative ion is $RMgX_2^-$.

Association studies were first reported by Meisenheimer and Schleichenmaier¹² and Terentjev.¹³ But Slough and Ubbelohde,¹⁴ in 1955, cast doubt on previous molecular association data with the finding that

atmospheric oxygen has an effect on the degree of association. They found that compounds varied from monomeric (p-methyloxyphenyl-magnesium) to tetrameric cyclohexylmagnesium bromide.

More recently Ashby and Smith⁷ and also Walker and Ashby¹⁵ have presented ebullioscopic data for Grignard reagents, MgX_2 and R_2Mg compounds (where $\text{R} = \text{Me}, \text{Et}$ and $\text{X} = \text{Cl}, \text{Br} \text{ \& } \text{I}$) over a wide concentration range for diethyl ether and tetrahydrofuran (THF). Molecular weights were determined by boiling point elevation at 740 torr in the latter experiments with a Cottrell boiling point apparatus, surge tank, dry nitrogen and a precision Wallace and Tiernam gauge. The results are reported as a graph of association (i) vs. concentration where i is defined as the molecular weight divided by the formula weight of a single solute species which would give a boiling point equivalent to that observed experimentally. With THF, all compounds studied were monomeric. In diethyl ether all RMgCl compounds were essentially dimers while RMgBr and RMgI associate more with increasing concentration. MgX_2 associates the most, Grignards are intermediate and R_2Mg associates the least (but $(\text{CH}_3)_2\text{Mg}$ associates significantly more than other R_2Mg). (See Fig. 1.)

Apparently in THF solutions the solvent competes so successfully as a ligand that $\text{RMgX} \cdot n\text{THF}$ is isolated as monomers. In diethyl ether, it appears that chloride is such a superior bridging agent that double bridging occurs between two magnesium units through the chlorines

which leave only dimers. As can be seen in Fig. 1, the bromo and iodo Grignards are monomers at low concentrations and tend to association values of two and three, etc.¹⁶

In the Ashby curves of association vs concentration for all RMgBr and RMgI Grignards, as the concentration approaches zero molal, the association becomes exactly 1.0. d^2i/dm^2 is negative as might be expected, however this curvature is so great that di/dm becomes negative at about 2.2m for C_2H_5MgBr and about 0.8m for $n-C_{10}H_{21}MgBr$. In general, the longer the alkyl group, the lower the concentration is when the slope changes from positive to negative. This curvature is the result of large solute-solvent interaction causing a negative deviation from Raoult's law, not surprising when at 2m there are seven solvent molecules per solute molecule. The incontrovertible conclusion that must be reached for iodo and bromo Grignard reagents is that, in dilute solution, there are only monomers and as the concentration increases dimers, trimers, etc form. Compounds may be singly bridged (4) or doubly bridged (5).

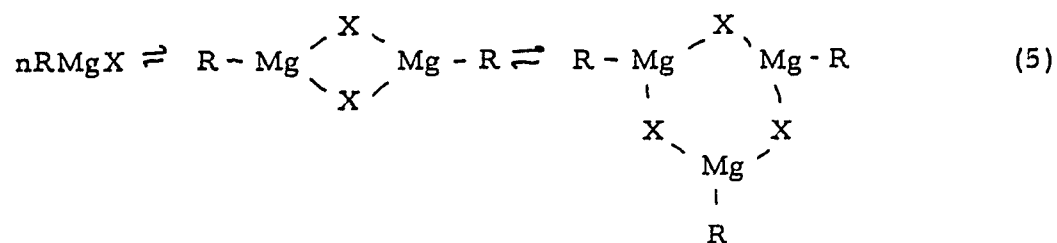
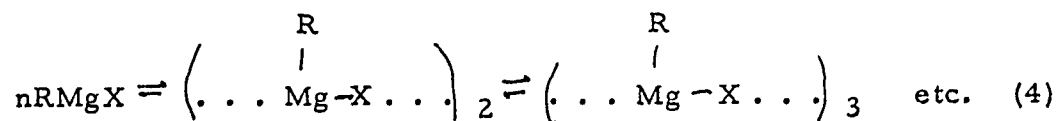


Figure 1

Association vs. concentration: Association is essentially the number of formula weight units per molecule as determined by boiling point elevation, or more precisely, the molecular weight divided by the formula weight of a single solute species that would give a boiling point to that observed experimentally. The concentration is in molality.

This figure is redrawn from Walker and Ashby¹⁵ and Ashby.¹⁶

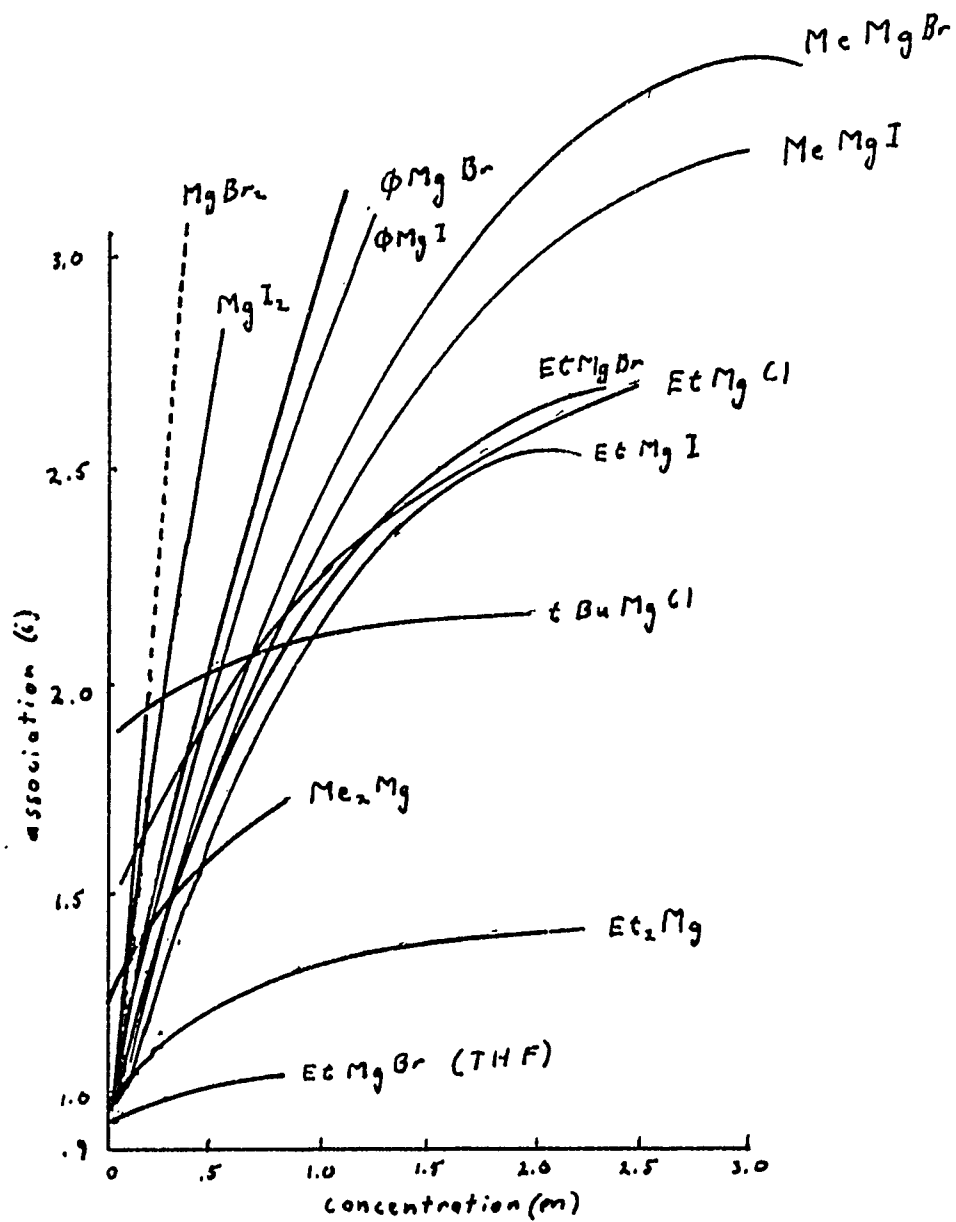


Figure 1

NMR had been disappointing in the analysis of Grignards but has proven to be more effective in recent years. The τ values reported by Evans and Maher¹⁷ for $(\text{CH}_3)_2\text{Mg}$ in diethyl ether show considerable concentration dependence while the dependence for CH_3MgI is slight. The authors attribute the τ change of $(\text{CH}_3)_2\text{Mg}$ to polymer formation. Walker and Ashby¹⁵ confirmed this from ebullioscopic data and also show that the association of MeMgI is even greater. They found that the concentration dependence of MeMgBr is almost identical with MeMgI . The ethyl and n-propyl dialkyls and Grignards are more nearly alike than the methyl compounds. The results are interpreted to indicate that the Grignard species are $\text{R}_2\text{Mg}\cdot\text{MgX}_2$ because of the similarity of R_2Mg to Grignard in contrast with large τ differences observed between R_2Hg and RHgX . House, Latham and Whitesides¹⁸ in NMR work of MeMgBr and Me_2Mg , in diethyl ether at 30°C , determined that MeMgBr is insensitive to concentration and Me_2Mg is sensitive. (See Fig. 2.) This agrees essentially with Evans and Maher.¹⁷ Evans and Fazaherley,¹⁹ using $(3, 5\text{ }^2\text{H})\phi\text{MgX}$ and related substituted aryl Grignards, were able to determine the ratio of $\text{RMgX}/\text{R}_2\text{Mg}$ by NMR.

In THF Ashby and Smith⁷ report little if any difference in $\text{C}_2\text{H}_5\text{MgCl}$ and $(\text{C}_2\text{H}_5)_2\text{Mg}$. Another example of the inability of NMR to distinguish between two different species is the little if any difference found between CH_3MgI and CH_3Li by Fraenkel, Adams, and Williams.²⁰ In 1967 Ashby, Parris and Walker²¹ reported the direct observation of

Figure 2

The sensitivity of chemical shift vs. concentration of Me_2Mg is seen contrasting the insensitivity of the Grignard MeMgBr .

This figure is from House, Latham, and Whitesides.¹⁸

Species	Concentration	Chemical shift in CPS upfield from internal TMS
MeMgBr	2.40 M	92.5
	.70	92.5
	.20	92.3
Me ₂ Mg	.71	83
	.18	85
	.09	87

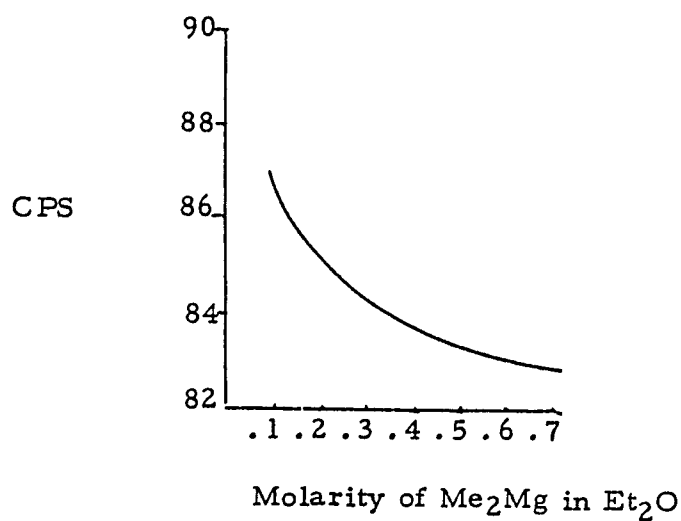


Figure 2

Me_2Mg and MeMgBr in diethyl ether of methyl magnesium bromide at low temperature. At 30°C one peak is observed for Me_2Mg and MeMgBr at 11.40 and 11.60 τ respectively. At -100°C Me_2Mg shows three peaks: at 11.32, 11.69 and 11.74 which correspond to bridging methyl, terminal methyl and monomer respectively. The Grignard methyl peak is observed at 11.60 τ plus a peak for Me_2Mg . At -100°C , this peak grows as MgBr_2 slowly precipitates with time. (No concentrations are reported.)

Previously the possibility of ionic species was discussed. However the concentration of such species cannot be high from the low conductances reported. For instance, Dessy and Jones²² determined the specific conductance of the equimolar mixture of $(\text{C}_2\text{H}_5)_2\text{Mg}$ and MgBr_2 in diethyl ether to be $2.26 \cdot 10^{-4}/\text{ohm cm}$ and $0.61 \cdot 10^{-4}/\text{ohm cm}$ for the equivalent concentrations (1.0 M) of $\text{C}_2\text{H}_5\text{MgBr}$. The discrepancy is most likely due to impurities. (Impurities would no doubt increase the conductance.)

In 1965 Smith and Becker²³ determined the equilibrium of various Grignards by adding R_2Mg to MgX_2 or vice versa. The data were obtained by measuring the incremental heat of reaction when R_2Mg and MgX_2 were mixed. The measurements were made at low concentrations where all species were monomeric. Heats of dilution were found to be insignificant. The heat of reaction is a direct measure of the formation of RMgX from the reactants. The average heat of reaction is -3.6 kcal/mole . The break in the plot slightly before the

Figure 3

The heat of reaction of $\text{Et}_2\text{Mg} + \text{MgBr}_2$ is related to the ratio of $\text{Et}_2\text{Mg}/\text{MgBr}_2$ and demonstrates compound formation at a 1/1 ratio.

This figure is from Smith and Becker.²³

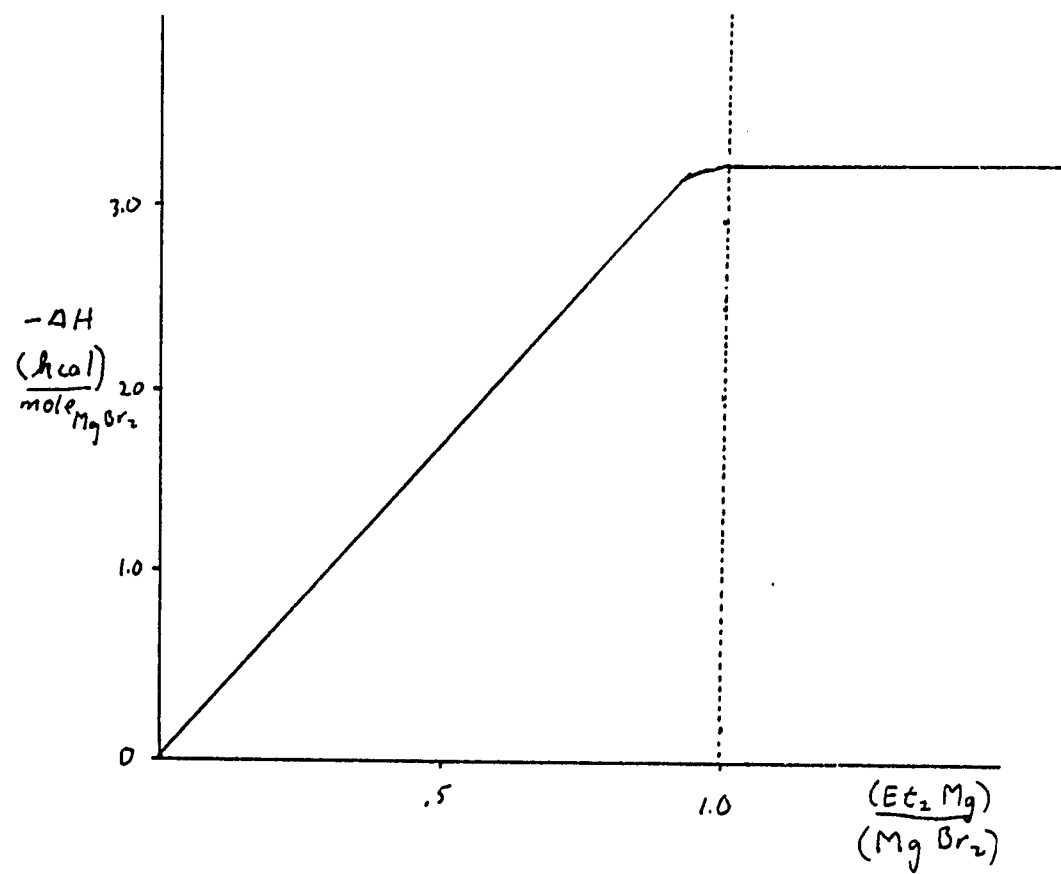


Figure 3

Equilibrium constants for the redistribution of dialkyl and diaryl magnesium compounds with MgBr_2 and MgI_2 , assuming the Schlenk equilibrium $\text{R}_2\text{Mg} + \text{MgX}_2 \rightleftharpoons 2\text{RMgX}$.

$$K = \frac{(\text{RMgX})^2}{(\text{R}_2\text{Mg})(\text{MgX}_2)}$$

R_2Mg	MgX_2	$K(\text{Et}_2\text{O})$	$K(\text{THF})$
Et_2Mg	MgCl_2	-	5.5
Et_2Mg	MgBr_2	480	5.1
Et_2Mg	MgI_2	630	-
$\phi_2\text{Mg}$	MgCl_2	-	1.7
$\phi_2\text{Mg}$	MgBr_2	55	3.8
$\phi_2\text{Mg}$	MgI_2	15	-

This table is from Ashby.¹⁶

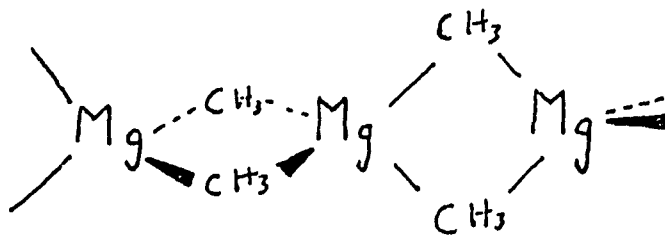
Table 1

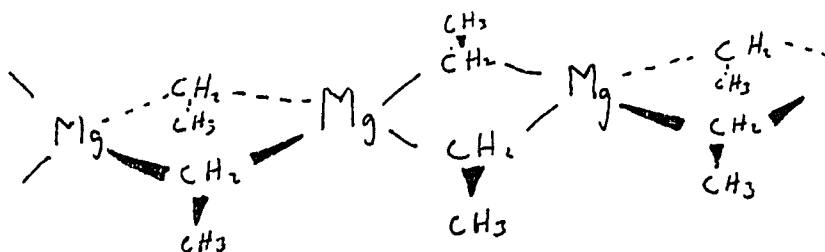
ratio of 1.0 is a reflection of the equilibrium point for the reaction. From data like that of Fig. 3, equilibrium constants were obtained.²⁴ (See Table 1.)

The experimental technique where definitive structure can be obtained is X-ray but, unfortunately, only compounds in the solid state can be studied. However, valuable inferences can be related to species in solution.

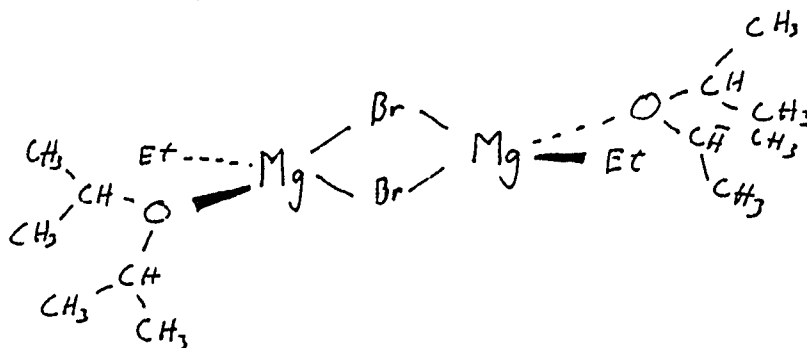
The X-ray structure of phenylmagnesium bromide dietherate was reported by Stucky and Rundle²⁵ in 1963 as tetrahedral. In 1964, Guggenberger and Rundle²⁶ reported the X-ray structure of ethylmagnesium bromide dietherate as a distorted tetrahedron. The bond distances are: $\text{Mg}-\text{Br} = 2.48 \text{ \AA}$, $\text{Mg}(1)-\text{O} = 2.03 \text{ \AA}$, $\text{Mg}(2)-\text{O} = 2.06 \text{ \AA}$, $\text{Mg}-\text{C} = 2.16 \text{ \AA}$. These units are monomers as the next $\text{Mg}-\text{Br}$ distance is $5.81 \text{ \AA}$ which is too long for a chemical bond. This $\text{Mg}-\text{O}$ single bond is the shortest known.

Weiss²⁷ reports the X-ray powder diffraction study of $(\text{CH}_3)_2\text{Mg}$ and $(\text{CH}_3\text{CH}_2)_2\text{Mg}$ as polymeric chains of the following structures:





In 1967 Schibilla and LeBihan²⁸ reported the X-ray crystal structure of $\text{MgBr}_2 \cdot 2(\text{CH}_3\text{-CH}_2)_2\text{O}$ as independent tetrahedral molecules. The X-ray crystal structure of Grignard reagents in diethyl ether has shown them to be monomers. For the first time Spek, Voorberger, Schat, Bloomberg, and Bickelhaupt²⁹ reported a dimeric structure with EtMgBr in diisopropyl ether:



An obvious and natural technique for the study of the structure of Grignard compounds in solution is vibrational spectroscopy, that is, infrared and Raman spectroscopy. A practical experimental technique of infrared spectroscopy was developed first. Hence, it is not surprising that as early as 1937 Plum³⁰ looked at the infrared of two Grignard compounds. The spectrum of ethyl and phenylmagnesium bromide was observed in diethyl ether but no definite assignments could be made.

Zeil³¹ examined the 780 cm^{-1} to $10,000\text{ cm}^{-1}$ region and assigned the 780 cm^{-1} and 900 cm^{-1} bands to Mg-Br stretch. Hamelin and Hayes³² reported these bands to be the C-O-C group of ether. Later work will show a different interpretation.

In 1964 Salinger and Mosher³³ reported in detail the Mg-C stretch region in the infrared on Grignards. They studied the compounds of R_2Mg and RMgX where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ and $\text{X} = \text{Cl}, \text{Br}, \text{I}$ for diethyl ether and THF. For CH_3 and C_2H_5 in THF, the reported C-Mg band varied from 500 cm^{-1} to 535 cm^{-1} while in ether the range was 508 cm^{-1} for EtMgBr , 512 cm^{-1} for Et_2Mg , 520 cm^{-1} for MeMgBr and 525 cm^{-1} for Me_2Mg plus a band at 593 cm^{-1} that was thought to possibly be a dimeric form, as intensity increases with concentration. MeMgCl in Et_2O is not stable as MgCl_2 precipitates. $\phi_2\text{Mg}$ in both THF and Et_2O reportedly absorbs at 381 cm^{-1} while in Et_2O , ϕMgBr and ϕMgI absorb respectively at 378 cm^{-1} and 365 cm^{-1} . The ether bands were compensated by using reference Et_2O . As will be discussed later, the conformation of ether changes with concentration causing the ether spectrum to change which casts some doubt on the results of Salinger and Mosher³³ because the reference ether and solute ether were not the same.

The infrared spectrum of dimethylmagnesium has features in common with $(\text{CH}_3)_2\text{Mg}$. Holm³⁴ reports that coordinated ether bands of Grignard compounds give rise to infrared absorption peaks at 780, 834, 999 and 1035 cm^{-1} . These bands seem to replace the peaks at 793,

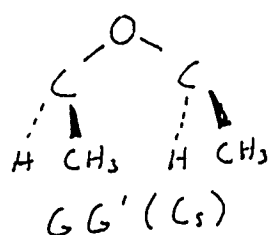
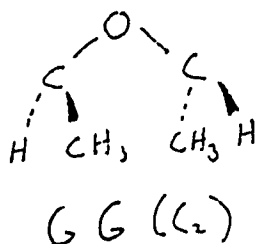
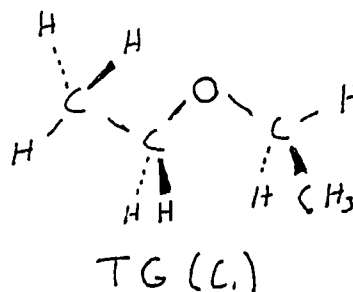
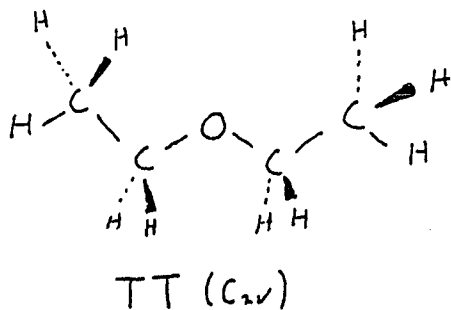
845, 916, 934 and 1120 cm^{-1} in the "undisturbed" ether spectrum.

Spectra of solid CH_3MgCl and CH_3MgBr etherates and MgBr_2 etherate prepared by solvent evaporation or precipitation with petroleum ether showed ether in the "disturbed" form. The spectra were all similar but two bands at 1190 and 1260 cm^{-1} that appear in both CH_3MgCl etherate and CH_3MgBr etherate were also apparently present in ether free $\text{Mg}(\text{CH}_3)_2$. They also become visible in a film of CH_3MgI after removal of some of the bound ether.

Holm³⁴ believes CH_3MgCl and CH_3MgBr represent Grignard reagents and not just a mixture of $(\text{CH}_3)_2\text{Mg}$ and MgX_2 as the Grignards retained ether at two torr at 20°C and $(\text{CH}_3)_2\text{Mg}$ and MgX_2 did not. $(\text{CH}_3)_2\text{Mg}$ showed bands at 440, 590, 1025, 1108, 1206, 2785, 2825 and 2862 cm^{-1} .

Wieser, Laidlaw, Krueger and Fuhrer,³⁵ from a comparison of the high resolution infrared and Raman spectra of diethyl ether and three deuterated analogues $\text{CD}_3\text{CH}_2\text{OCH}_3\text{CD}_3$, $\text{CH}_3\text{CD}_2\text{OCD}_2\text{CH}_3$ and $\text{CD}_3\text{CD}_2\text{-OCD}_2\text{CD}_3$ have made fairly complete vibrational assignments for the trans-trans (TT) and trans-gauche (TG) conformers. A valence force field with a weighted least squares fit was used to match the observed TT conformer. Also a calculated set of frequencies was made for all four species.

The four possible spectroscopically distinguishable conformers of diethyl ether are the following:



The plot of log absorbance of the ratio of the 1297 cm^{-1} band/ 1279 cm^{-1} band of the neat diethyl ether or the 1286 cm^{-1} / 1261 cm^{-1} band of $(\text{CD}_3\text{CH}_2)_2\text{O}$ vs. $1/T$, shows $\Delta H = -1.1\text{ kcal/mole}$, indicating that the TT conformer is slightly more stable than the TG conformer. In general, the higher the concentration of magnesium species, the more TG and possibly GG conformers are observed.

Wieser and Krueger³⁶ report on the infrared ($250 - 4000\text{ cm}^{-1}$) and Raman ($100 - 4000\text{ cm}^{-1}$) of MgBr_2 and MgI_2 and the solid MgI_2 etherate in diethyl ether. Both magnesium halides form two layers, a concentrated lower layer and a less concentrated upper layer.

	Phase	
	Upper	Lower
MgBr ₂	.14 M	2.5 M
MgI ₂	.3 - .4 M	1.4 M

The dilute layer is interpreted as monomeric tetrahedrally coordinated magnesium while the concentrated layer is interpreted as six coordinate polymeric species. The concentrated MgI₂ ethereal solution 147 and 163 cm⁻¹ bands are assigned to Mg-I polymer stretch and 329 cm⁻¹ to Mg-O stretch. A striking feature in the skeletal vibrations of diethyl ether is the intensity enhancement of TG bands over TT bands with increasing concentration of magnesium species showing a shift in equilibrium to TG and possibly GG conformers.

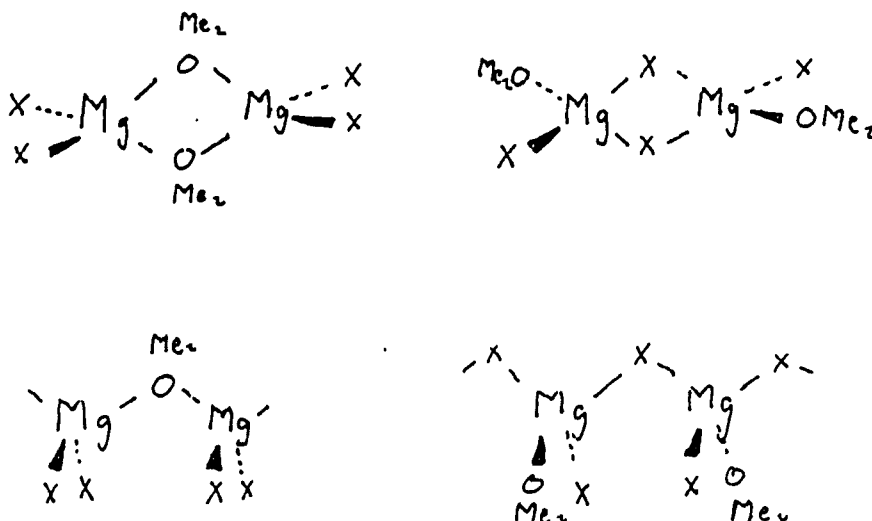
In the Raman the 833/844 cm⁻¹ doublet is the most obvious example of the peak intensities dramatically reversing where the lower TG frequency becomes dominate with higher concentration.

Theophanides, Guillermet and Novak³⁷ report the infrared at 300° K, the Raman at 125° K of CH₃OCH₃ and the infrared and Raman at 300° K of MgBr₂·2CH₃OCH₃ solid and infrared at 90° K. Most bands are assigned, however, the Raman data seems sketchy.

Guillermet and Novak³⁸ report on the modification of the diethyl ether spectrum upon coordination. They interpret the cause of the

change as due to the weakening of the C-O bond in ether. They point out that in the X-ray structure determination carried out by Guggenberger and Rundle³⁹ the ether conformation in $\text{EtMgBr} \cdot 2\text{Et}_2\text{O}$ is GG. From their own previous work Guillermet and Novak looked at the infrared of $\text{MgBr}_2 \cdot 2\text{Et}_2\text{O}$ and pointed out remnants of free ether bands at -180°C .

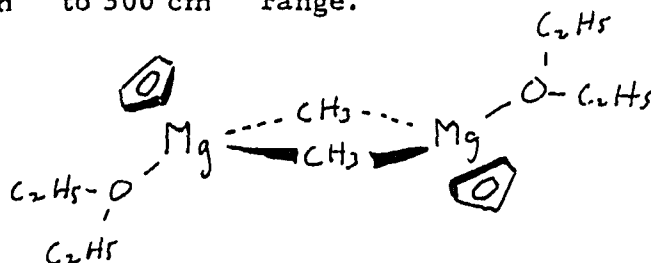
Kress and Guillermet⁴⁰ studied the compounds $\text{MgBr}_2 \cdot 2(\text{CH}_3)_2\text{O}$, $\text{MgBr}_2 \cdot 2(\text{CD}_3)_2\text{O}$, $\text{MgBr}_2(\text{CH}_3)_2\text{O}$, $\text{MgBr}_2(\text{CD}_3)_2\text{O}$ and $\text{MgI}_2(\text{CH}_3)_2\text{O}$ by infrared (40 cm^{-1} to 4000 cm^{-1}) and by Raman of the crystal at -180°C and 25°C . These structures were considered:



The authors claim that the data suggest oxygen bridging. Oxygen bridges are proposed on the basis that a band defined as $\text{Mg}-\text{O}-\text{Mg}$ stretch in the 1-1 complex ($\text{MgBr}_2 \cdot \text{Me}_2\text{O}$) is 30% lower than the $\text{Mg}-\text{O}$ of the 1-2 complex.

Kress and Novak⁴¹ report on the infrared and Raman of the solid $\text{MgBr}_2 \cdot 2\text{Et}_2\text{O}$ as a function of temperature and pressure. Temperatures from 90°K to 300°K and pressures up to 10 kbars were studied. At room temperature or low pressure the GG conformer of ether appears predominate while at low temperature or high pressure there are only TG (or TT) conformers.

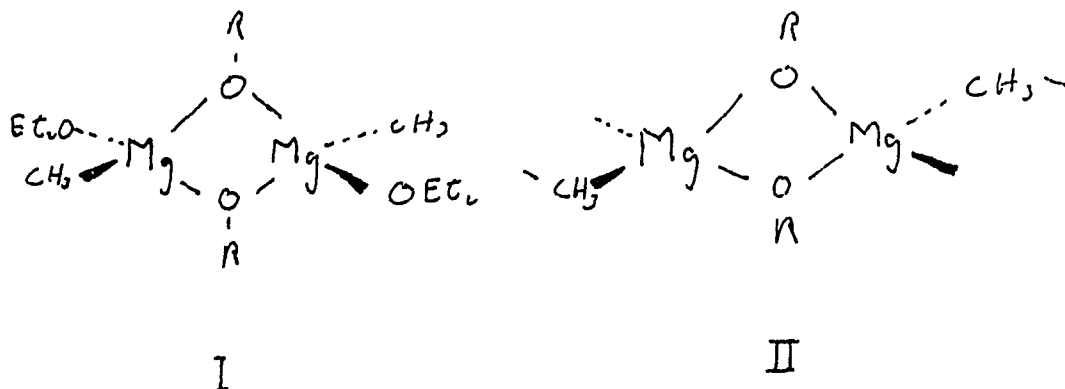
In a continuing series on Grignard compounds by Ashby and co-workers⁴² the structure of cyclopentadienylmethylmagnesium in benzene and ether solvents is discussed, mostly on the basis of infrared work in the 4000 cm^{-1} to 300 cm^{-1} range.



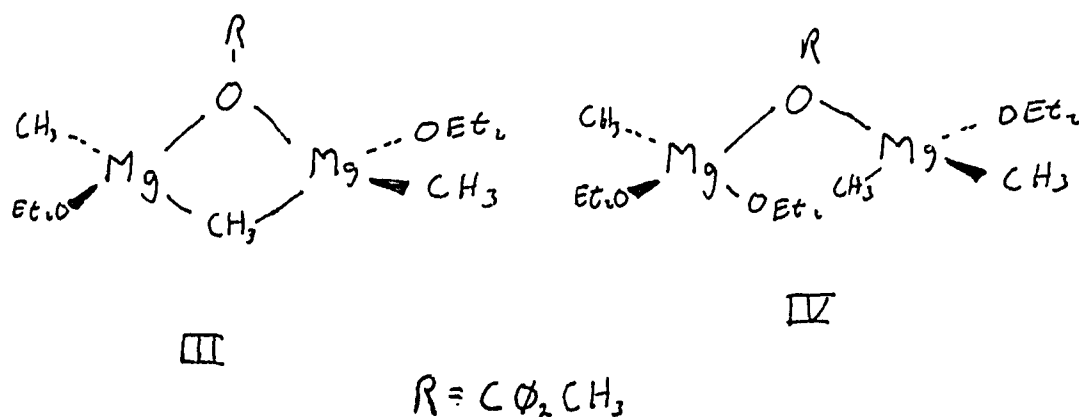
This is the proposed solid state structure of cyclopentadienylmethylmagnesium monoetherate. The cyclopentadienyl fundamentals are most consistent with a D_{5h} ring symmetry.

Ashby, Nackashi and Parris⁴³ report on the NMR, infrared, and molecular association studies of some methylmagnesium alkoxides in diethyl ether, tetrahydrofuran, and benzene where the alkoxides (OR) are $\text{OC}\phi_2\text{CH}_3$, $t\text{-OBu}$, $i\text{-OPr}$, or $n\text{-OPr}$. The geometry of these compounds, the association with concentration, and the manner of bridging are similar to Grignard compounds. A typical reaction is illustrated where $\text{OR} = \text{OC}\phi_2\text{CH}_3$. Addition of one mole equivalent of benzophenone

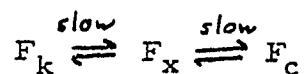
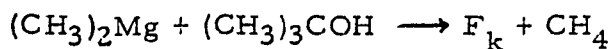
with $(\text{CH}_3)_2\text{Mg}$ in diethyl ether at low temperature produces I. Desolvation of this produces a linear oligomer II as indicated by methyl bridge bands in the infrared spectrum.



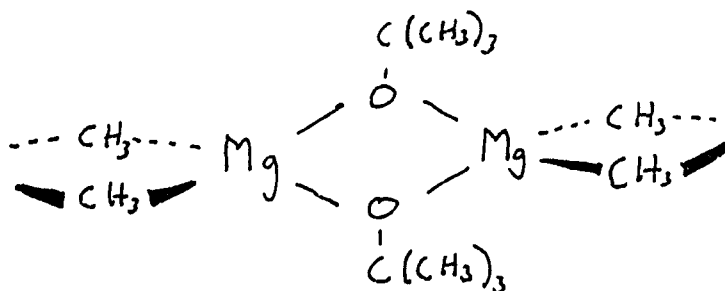
When $(\text{CH}_3)_2\text{Mg}$ is added to I, methyl alkoxy mixed-bridge compound III is the predominate species. However, other species are involved since the ratio of the bridging signal at -80°C ($\tau = 11.24$) to the terminal methyl signal ($\tau = 11.56$) is only 1:49. Structure IV, approximately equimolar in concentration with III, accounts for the results.



When $OR = OC(CH_3)_3$ or smaller, an unusual cubane-like structure is the thermodynamically stable product. Its formation is given as follows:

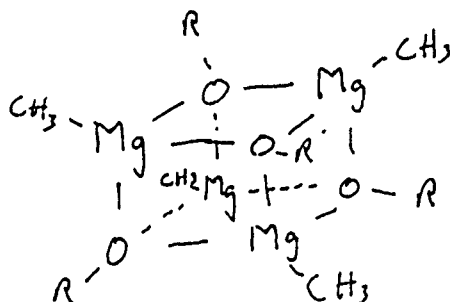


F_k (k indicates kinetic product) is:



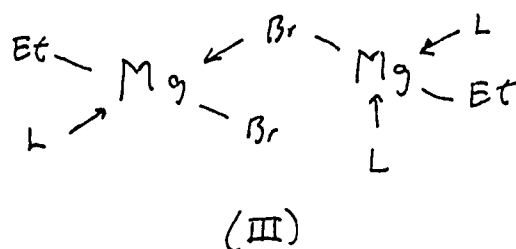
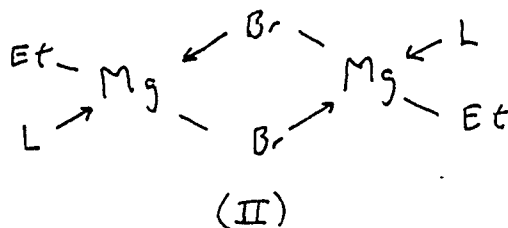
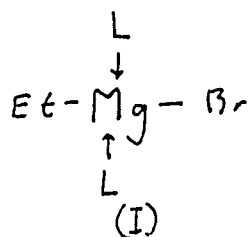
F_x are intermediates that have not been isolated.

F_c is the cubane-like thermodynamically stable product.



In the infrared of structure F_k , says Ashby,⁴³ "The presence of strong, broad bands at 570, 480, and 390 cm^{-1} is consistent with a methyl bridge-bond system with local D_{2h} symmetry." Analysis of this structure does not appear to bear this out. (See Appendix.)

Vink, Bloomberg and Bickelhaupt⁴⁴ have determined the number of ether groups coordinated to various species of EtMgBr. EtMgBr is dissolved in benzene and (+)(S)-1-ethoxy-2-methylbutane [(+)-(S)-L] and the molecular rotation is measured. The principle of the experiment is based on the fact that (+)-(S)-L increases molar rotation with increasing complexation with ether. Assuming the coordination number of magnesium to be four and taking bromine as the bridging atom, the species found were:



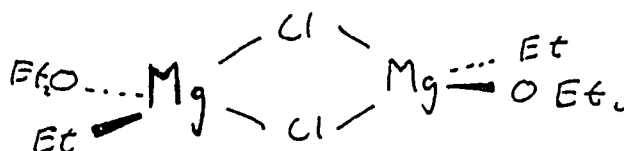
Kress and Novak⁴⁵ reported on the infrared and Raman spectra of $\text{C}_2\text{H}_5\text{MgBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ plus three deuterated derivatives, and $\text{EtMgI} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ at 90°K and $\text{C}_2\text{H}_5\text{MgBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ at 300°K (solution). The structure of $\text{EtMgBr} \cdot 2\text{Et}_2\text{O}$ at 300°K is interpreted to be monomeric even at high concentration. The spectra show that the same bands occur in both infrared and Raman although the intensities differ. In the Raman at 90°C a strong band at 248 cm^{-1} in $\text{EtMgBr} \cdot 2\text{Et}_2\text{O}$ and at 224 cm^{-1} in $\text{EtMgI} \cdot 2\text{Et}_2\text{O}$ is assigned Mg-X. The authors claim that the solution of EtMgBr is easily interpreted as a superposition of dissolved $\text{EtMgBr} \cdot 2\text{Et}_2\text{O}$ and free ether.

The infrared and Raman spectra of $\text{CH}_3\text{MgBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, $\text{CH}_3\text{MgI} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, and $\text{CD}_3\text{MgBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ have been investigated in the 100 cm^{-1} to 4000 cm^{-1} region by Kress and Novak⁴⁶ in the solid state at 90°K and $\text{CH}_3\text{MgBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ in the liquid state at 300°K . The frequencies and intensities of the Raman and infrared bands of coordinated ether of CH_3MgBr , CD_3MgBr , CH_3MgI and even $\text{C}_2\text{H}_5\text{MgBr}$ are very similar. At 90°K , two forms (I and II) of $\text{MeMgBr} \cdot 2\text{Et}_2\text{O}$ are observed. Form I is assigned the GG conformer of ether and form II is assigned the TG or TT conformer.

At 300°K , the spectra of $\text{CH}_3\text{MgBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ is compared at 4 M, 2.3M and 0.5M. At 4M almost all of the ether is complexed. The spectrum at 0.5M is reported to be remarkably similar except for the added bands of free ether. The authors conclude that this indicates

monomer species at all concentrations for $\text{CH}_3\text{MgX} \cdot 2\text{Et}_2\text{O}$, $\text{X} = \text{Br}, \text{I}$. In the Raman at 90°K a strong band at 248 cm^{-1} for $\text{MeMgBr} \cdot 2\text{Et}_2\text{O}$ and 231 cm^{-1} for MeMgI is assigned Mg-X stretch.

Kress and Novak⁴⁷ report on the infrared of the vitreous state at 90°K , Raman of the crystal at 90°K , and Raman of the liquid at 300°K at 1.4M, 3.5M and 6M of $\text{EtMgCl} \cdot \text{Et}_2\text{O}$. The structure of the vitreous solid at 90°K and liquid at 300°K is thought to be a dimer of chlorine bridges of C_{2h} symmetry with the coordinated ether to be of GG conformation.



The spectrum of the crystal at 90°K is interpreted as having chlorine bridges and ethyl bridges between magnesium atoms where dimers and trimers are envisioned.

Kress⁴⁸ studied the Raman spectra of diethylmagnesium in diethyl ether at various temperatures and concentrations. The spectra are interpreted in terms of a monomer-dimer deuilbrium with the dimer having ethyl bridges of formula $(\text{MgEt}_2 \cdot \text{Et}_2\text{O})_2$.

The purpose of the present inquiry is to determine the structure of Grignard reagents in solution. At the beginning of work, in early

1974, on this particular question it was felt that the most recent significant advances on the elucidation of structure were made by Ashby and co-workers. They, for the first time, demonstrated the presence of multimers by determining the association value of magnesium halides, Grignard compounds, and alkyl magnesium compounds as a function of concentration in diethyl ether using ebullioscopic studies. Several structures were proposed as being dimers, trimers, etc.

Having similar experience with an ebullioscopic apparatus like that used by Ashby, it was felt that his conclusions were valid. At the same time, little work had been done on the vibrational spectroscopy of Grignard compounds, which appeared to be the best method of structure determination. Raman spectroscopy, with improved spectrometers and lasers with the ability to easily observe low frequencies, was logical choice in the further investigation of Grignard compounds.

It was felt that the most profitable compounds to study were the simplest, that is, MgI_2 and RMgX where R = methyl, ethyl and X = Br, I in diethyl ether (the chlorides are not stable because the MgCl_2 precipitates). MgI_2 was studied, as it is related to Grignard compounds through the Schlenk equilibrium. It is also a less complicated structure that associates like Grignard compounds. The solvent, diethyl ether, was used because this is the traditional solvent used for Grignard

compounds. In THF only Grignard monomers are observed. A difficulty of working with ether, at first not appreciated, is the different conformers present in solution. The ratio of these conformers changes with magnesium concentration, making interpretation of the Grignard spectra more difficult.

EXPERIMENTAL

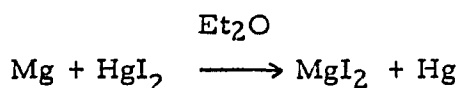
Raman Instrument. Raman spectra were obtained with the Spex Industries Model 1401 spectrometer coupled with the Spectra-Physics Krypton Model 164 or Argon Model 164 laser. The exciting line used with the Krypton laser was 530.9 nm and 514.5 nm for the Argon laser. The laser power before filters ranged from 200 mw to 1000 mw. Entrance and exit slits of 200 microns were used. Some spectra were filtered to remove non-lasing emission lines and other spectra were left unfiltered. In practice, it was found that these lines were not a problem and therefore a filter was not necessary. Using no filter eliminates the very real possibility of filter degradation causing reduced laser intensity to the sample.

The Raman instrument was modified to collect information in a digital form rather than the usual method, using a capacitance technique, to control damping rate. It was programmed thru paper tape instruction via a PDP 8/L digital computer to record intensity point by point. With the spectra reproduced here, the spectrometer was advanced at one cm^{-1} increments. Therefore, a typical scan of 50 cm^{-1} to 1150 cm^{-1} is represented by 1100 separate bits of information. This information is originally printed out on paper tape and then transposed to graph form by the NOVA computer digital plotter associated with the far infrared spectrometer in our laboratory. With the system one can expand spectra,

add or subtract one spectrum from another, etc. A useful plot is to subtract $4/3$ the perpendicular spectrum from the parallel spectrum. In this $// - 4/3 \perp$ plot, a band that is depolarized vanishes, so this plot becomes a measure of the depolarization ratio. An added bonus to the $// - 4/3 \perp$ plot is that bands close to the exciting line which may be difficult to resolve, due to the high background, can often be retrieved. The background, often depolarized in both the parallel and perpendicular spectrum, is cancelled out.

The samples were contained in standard melting point capillaries, 1.6 to 1.8 mm outside diameter. The samples were filled via syringe in a purged drybox. They were then plugged temporarily in an oil base clay, removed from the drybox via the air lock to the lab, placed in dry ice, and sealed with a torch.

Chemicals. Magnesium iodide was made by displacement of Hg in HgI_2 by excess magnesium in diethyl ether under a nitrogen blanket as suggested by Ashby and Arnott.⁴⁹

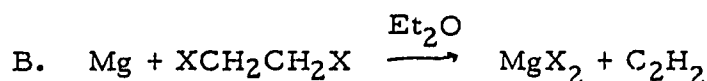
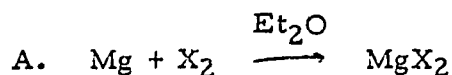


Excess magnesium, about 1.3 Mg/ HgI_2 , was used. Magnesium turnings of Grignard quality and ACS HgI_2 Fisher was used. The diethyl ether was anhydrous diethyl ether dried with freshly formed sodium wire. The magnesium, mercuric iodide and diethyl ether were added to a three necked flask with a stirring bar and condenser. The mixture was heated gently with an ice-water mixture on hand to control the exothermic

reaction. The dry box crystals of MgI_2 etherate were obtained upon cooling. The crystals were redissolved to form the desired solution. These solutions form two phases.

Magnesium iodide etherate solid is light sensitive and extremely hygroscopic. The crystals were kept in a dry box in black plastic. Solutions are best preserved by leaving some magnesium turnings on the bottom.

Most workers have made magnesium halides either by:



Ashby and Arnott⁴⁹ show that at room temperature, A produces "gross" impurities of halogenated ether. The second method, B, did not produce clear solutions. The method used had neither disadvantage and produced pure products with no contaminating mercury salts.

MeMgBr and MeMgI in diethyl ether was purchased from ROC/RIC. EtMgBr and EtMgI were made from certified Fisher EtBr and EtI plus Grignard grade magnesium turnings. For the synthesis of Grignard reagent excess magnesium was used - about 1.2 Mg/EtX . Mg with about half the total ether used plus a stirring bar was added to a three necked flask. The EtX was dissolved in the rest of the ether, and added slowly via a dropping funnel. A condenser was also attached. After all the EtX had been added, the mixture was allowed to reflux over night. The

whole reaction was run under an N_2 blanket, i.e., positive N_2 pressure was fed through the condenser and dropping funnel with an exit through an oil bubbler.

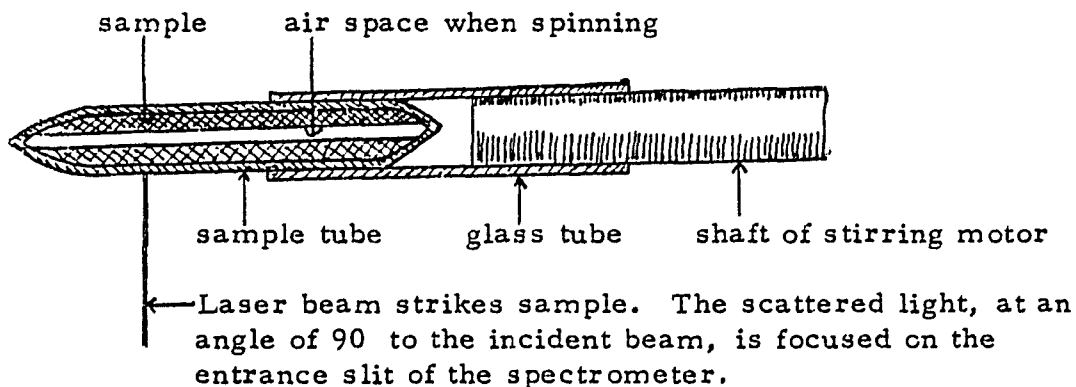
Solutions were analyzed by taking aliquots, hydrolyzing, buffering to pH 10 and then titrating with EDTA with Eriochrome black T as an indicator⁵⁰.

Periodically, fluorescence problems were encountered. The following greases were tested to determine the amount of fluorescence in contact with diethyl ether: Apiezon, Apiezon N, Lubriseal, Norac, and silicon. Silicon grease, which fortunately had been used, showed no fluorescence.

Several attempts were made to obtain the spectrum of concentrated EtMgBr and to improve the spectrum of the bottom layer of MgI_2 . The concentrated EtMgBr had a yellow-green-brown tinge to it. When the EtMgBr was sampled in a capillary, absorption of the incident laser beam produced bubbles which made it impossible to obtain a spectrum. In order to circumvent this problem, the sample was spun by the primary (before reduction) shaft of a stirring motor. The glass tube's inner diameter was originally smaller than the outer diameter of the sample tube. In order to make a tight fit, part of the glass tube was placed in $HF(H_2O)$ until a snug fit was achieved with the sample. The spinning rate of the sample was increased until a non-turbulent air space was achieved and then the spin rate was decreased about 30%,

the air space remaining unchanged. However satisfactory spectra could not be obtained below about 400 cm^{-1} .

Actual size and orientation of sample and sample holder:

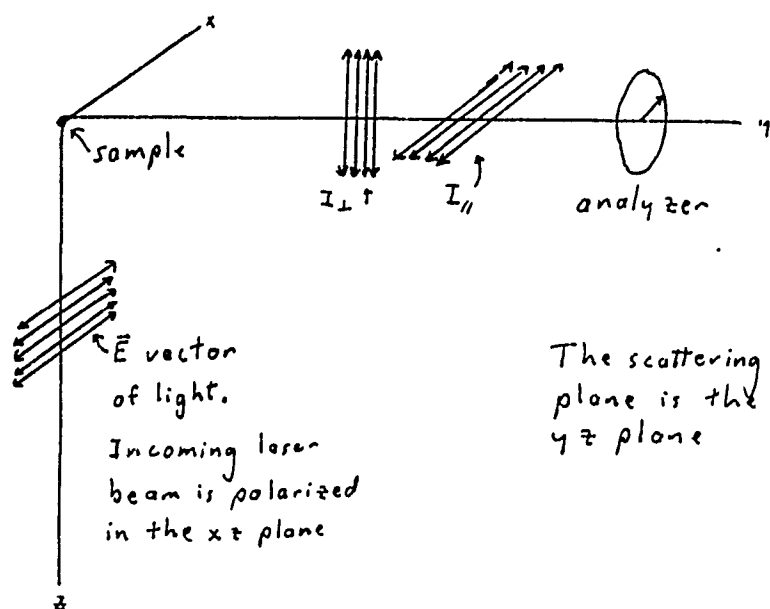


An attempt was also made to remove the color by mixing dry norite with EtMgBr in airless ware and filtering with a sintered glass, but the color remained unchanged. The lower MgI_2 layer was filtered thru sintered glass resulting in a clear solution but with high fluorescence.

RESULTS

In the Raman effect, light scatters differently for the totally symmetric modes, a , a_1 , a_{1g} , than other modes. By observing the depolarization ratio, the scattered intensity perpendicular ($\perp$) to the incoming beam/scattered intensity parallel ($\parallel$) to the incoming beam, inferences can be made as to the symmetry of the mode.

Geometry of the Laser Raman at Hunter College:



The scattered light may be polarized parallel or perpendicular to the incoming electric vector of the laser. The incoming electric vector must be perpendicular to the scattering plane, yz . The analyzer, or polarizer allows either the $I_{\parallel}$ or $I_{\perp}$ to pass thru it into the Raman instrument.

$$I_T = I_{\parallel} + I_{\perp}$$

$$I_T = \frac{16 \pi^4 \gamma^2}{c^2} N I_0 \left(\frac{45 \alpha^2 + 7 \beta^2}{45} \right)$$

$$I_{\parallel} = \frac{16 \pi^4 \gamma^2}{c^2} N I_0 \left(\frac{45 \alpha^2 + 4 \beta^2}{45} \right)$$

only if the incoming beam is polarized perpendicular to the scattering plane.

The depolarization ratio:

$$\rho_e = \frac{I_{\perp}}{I_{\parallel}} = \frac{I_T - I_{\parallel}}{I_{\parallel}}$$

$$= \frac{3 \beta^2}{45 \alpha^2 + 4 \beta^2}$$

α terms are associated with the isotropic or totally symmetric part of the polarizability tensor for a particular mode such as

$$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}.$$

β terms are associated with the anisotropic terms such as

$$(\alpha_{xx} - \alpha_{yy}), \alpha_{yz}, \text{etc.}$$

From the last equation one can see that the depolarization ratio must be less than or equal to 3/4. For the totally symmetric mode, $\rho_e \rightarrow 0$ as $\beta \rightarrow 0$. An example of this case is the symmetric breathing mode of CCl_4 at 459 cm^{-1} where $\rho_e = .005 \pm .002$. This is a completely polarized band. Where $\alpha = 0$ & $\rho_e = \frac{3}{4}$, this is

defined as a depolarized band. An example is the 218 cm^{-1} band of CCl_4 . $\rho_1 < 3/4$ is a polarized band.

Intensity was integrated at a given frequency, usually for two to five seconds, and then the spectrometer was advanced one cm^{-1} and the process was repeated. Dark current in the photomultiplier tube is about six to ten counts/second while a strong band would be in the range of 1000 to 2000 counts/second. The relative recorded peak height for a given band will be the same for all scan rates. However, the signal to noise ratio increases with longer integration times. For example, a scan rate of $1\text{ cm}^{-1}/100\text{ seconds}$ compared to $1\text{ cm}^{-1}/\text{second}$ will increase the signal to noise ratio by $\sqrt{\frac{1\text{ cm}^{-1}/\text{second}}{1\text{ cm}^{-1}/100\text{ seconds}}} = 10\text{ fold}$.

Guide to the Data

For any given solution the $\parallel$, $\perp$ and $\parallel - \frac{1}{3}\perp$ spectra are given. The $\perp$ spectrum is plotted under the $\parallel$ spectrum, while the $\parallel - \frac{1}{3}\perp$ is plotted separately. Since all spectra were in diethyl ether, its spectrum is shown first. Next, magnesium iodide is given and then the Raman of the Grignards: MeMgI, MeMgBr, EtMgI and EtMgBr. Five to six concentrations of each Grignard are presented. The concentrations are labeled - conc., 1/1, 3/4, 1/2, 1/4, 1/8. Conc. means concentrated; that is, the solutions are concentrated by vacuum distillation until no more solvent can be extracted. Then a little diethyl ether is added, if necessary, to obtain a solution. The concentrations listed as 1/1 are that of the Grignard when first produced and are listed as follows along with computed i values from Ashby.²⁴

	<u>i</u>
MeMgBr ₁	= 2.78 M 3.5
MeMgI ₁	= 2.72 M 3.1
EtMgI ₁	= 1.21 M 2.2
EtMgBr ₁	= 1.72 M 2.5

The fractional concentrations, 3/4, 1/2, 1/4, 1/8 are appropriate dilutions of these solutions.

After the spectra are tables of the spectra. The power of the laser in milliwatts (mW) is also given plus the date the spectrum was taken. There are ten columns listed for a specific concentration of a species. The first three columns are of the parallel spectrum. First is the location of the center of the band as observed on the spectrum in cm^{-1} . Second is the intensity of each band. One unit represents 20 counts/second. Third is the relative intensity of a particular band compared to the 833 cm^{-1} band. The 833 cm^{-1} band was used as a reference as it appeared to be a band that least changed in height and also was relatively intense. Columns 4, 5 and 6 relate to the $\perp$ spectrum and are analogous to columns 1, 2 and 3 as are columns 8, 9 and 10 of the $\parallel$ spectrum. The relative intensity of columns 6 and 10 are relative to the same 833 cm^{-1} band. Column 7 is the ratio of column 5/column 2 and is the depolarization ratio.

The first spectrum shown is that of diethyl ether - the solvent used for all of the solutions here. One should keep in mind that neat diethyl ether has two predominant conformers, the trans-trans and the trans-gauche. ΔH for $\text{TG} \rightleftharpoons \text{TT} = -1.1 \text{ kcal/mole}$. If one assumes $\Delta S = 0$, then the ratio of $\frac{\text{TT}}{\text{TG}} = 6.25$. However, from the approximately

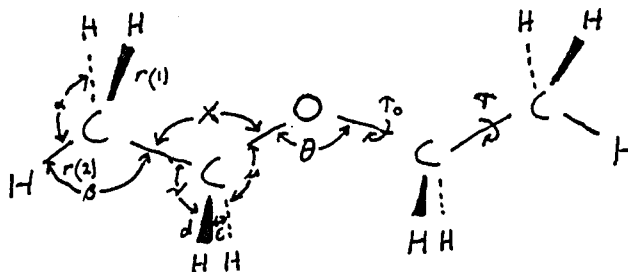
equal band intensities of both species, ΔS would appear to be negative which would be consistent with TG conformer having two minima and the TT having one.

In the table describing the diethyl ether spectrum, the conformation of the band, the band assignment (according to Wieser, Laidlaw, Krueger and Fuhrer³⁵) plus the band symmetry of the TT conformer is given.

Diethyl ether has 39 normal modes. The TT conformer of C_{2v} symmetry has 12 A_1 , 8 A_2 , 11 B_1 , and 8 B_2 modes of which nine (4 A_1 , 1 A_2 , 3 B_1 , and 1 B_2) are vibrations of the skeleton. All 39 modes are Raman active; 31 (A_1 , B_1 , and B_2) are infrared active. The TG conformer belongs to C_1 symmetry, therefore all 39 modes belong to the same symmetry and all should be both Raman and infrared active. The absorption of the "T" ethyl group is essentially the same as the TT conformer, while the "G" ethyl group becomes increasingly different at lower frequency.

At least six bands, possibly eight, were found in the region 50 cm^{-1} to 1550 cm^{-1} not previously reported in the Raman. The six bands do, however, have a counterpart in the infrared region. There are two other bands at 201 cm^{-1} and 1521 cm^{-1} . The 201 cm^{-1} band has not been found in the infrared or Raman but is close to a calculated band of Wieser, Laidlaw, Krueger and Fuhrer,³⁵ while the band at 1521 cm^{-1} does not appear to correspond to a reported or calculated band.

In accord with accepted conventions, the internal coordinates for diethyl ether as defined by Wieser, Laidlaw, Krueger and Fuhrer³⁵ are:



From these internal coordinates, the definition of group and skeletal coordinates are as follows:

Methyl $\text{CH}_3\text{-C}$	α = asymmetric HCH bend U = symmetric HCH bend β = methyl rock τ = methyl torsion
Methylene $\text{C-CH}_2\text{-O}$	δ_o = methylene bend W_o = methylene wag T_o = methylene twist ρ_o = methylene rock Z_o = combination of W_o , T_o , and ρ_o (used only in TG conformations)
Skeleton	R = C-C stretch S = C-O stretch X = O-C-C bend T_o = C-O torsion θ = C-O-C bend

See Table 2 for diethyl ether assignments.

One difficulty that was experienced in reading spectra was the determination of band centers near the exciting line. A glance at the spectrum of MeMgI, for instance, shows bands that appear as shoulders on the exciting line. These bands were resolved by using the Dupont 310 Curve Resolver (courtesy of the Ethicon Corporation in Sommerville,

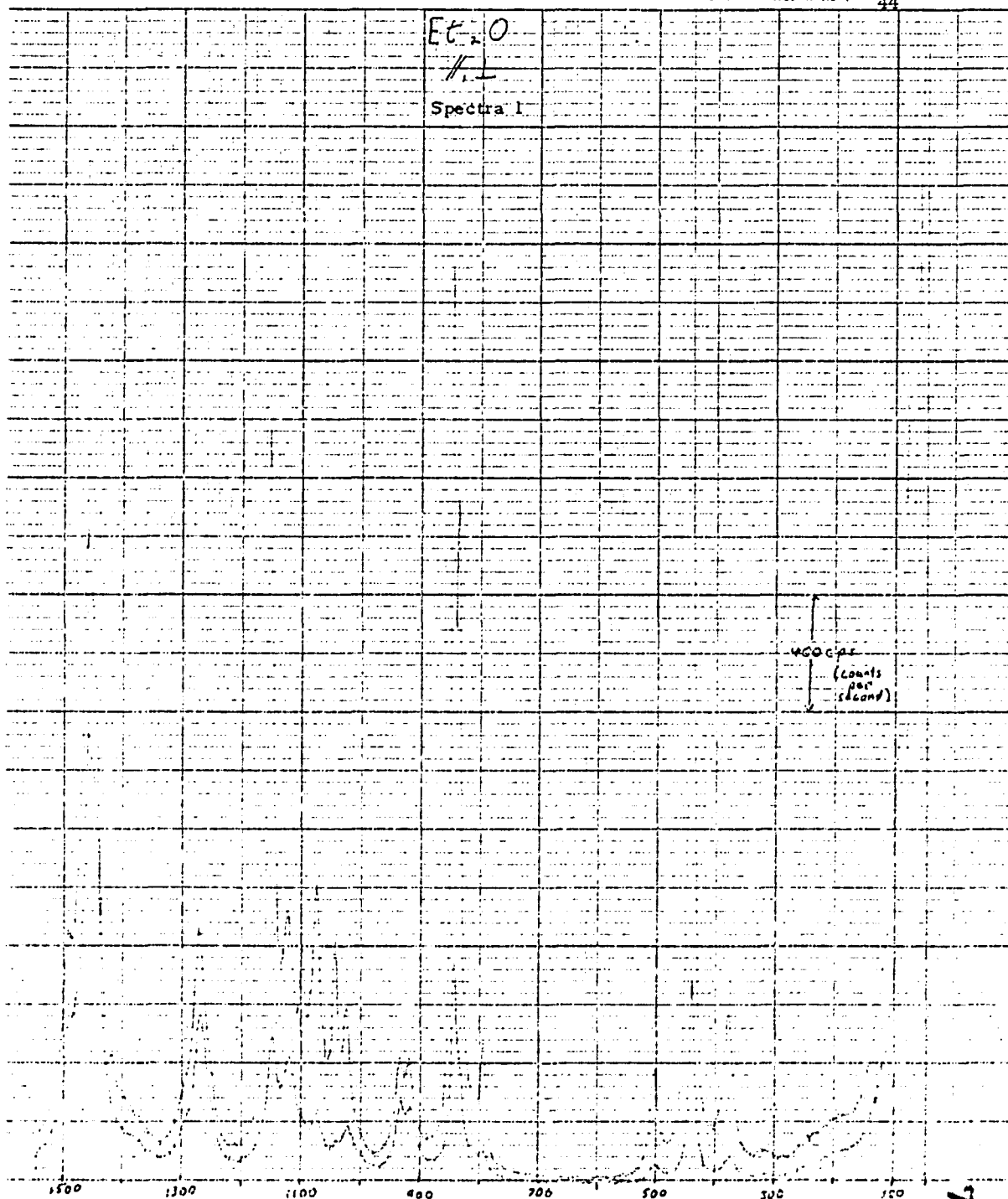
New Jersey). This instrument is basically a cathode ray tube with ten channels to make ten bands. With each band, height, width and shape (usually Gaussian or Lorentzian or intermediate) can be controlled independently.

For resolving the specific spectrum, it was first assumed that the band half width would be the same for bands of the same species. For the MeMgI spectra the band at 225 cm^{-1} was used. The exciting line was approximated as one side of an intense band. By trial and error, the experimental curve was fitted. In the tables listing spectral bands, the bands marked with an * are deduced from using the curve resolver.

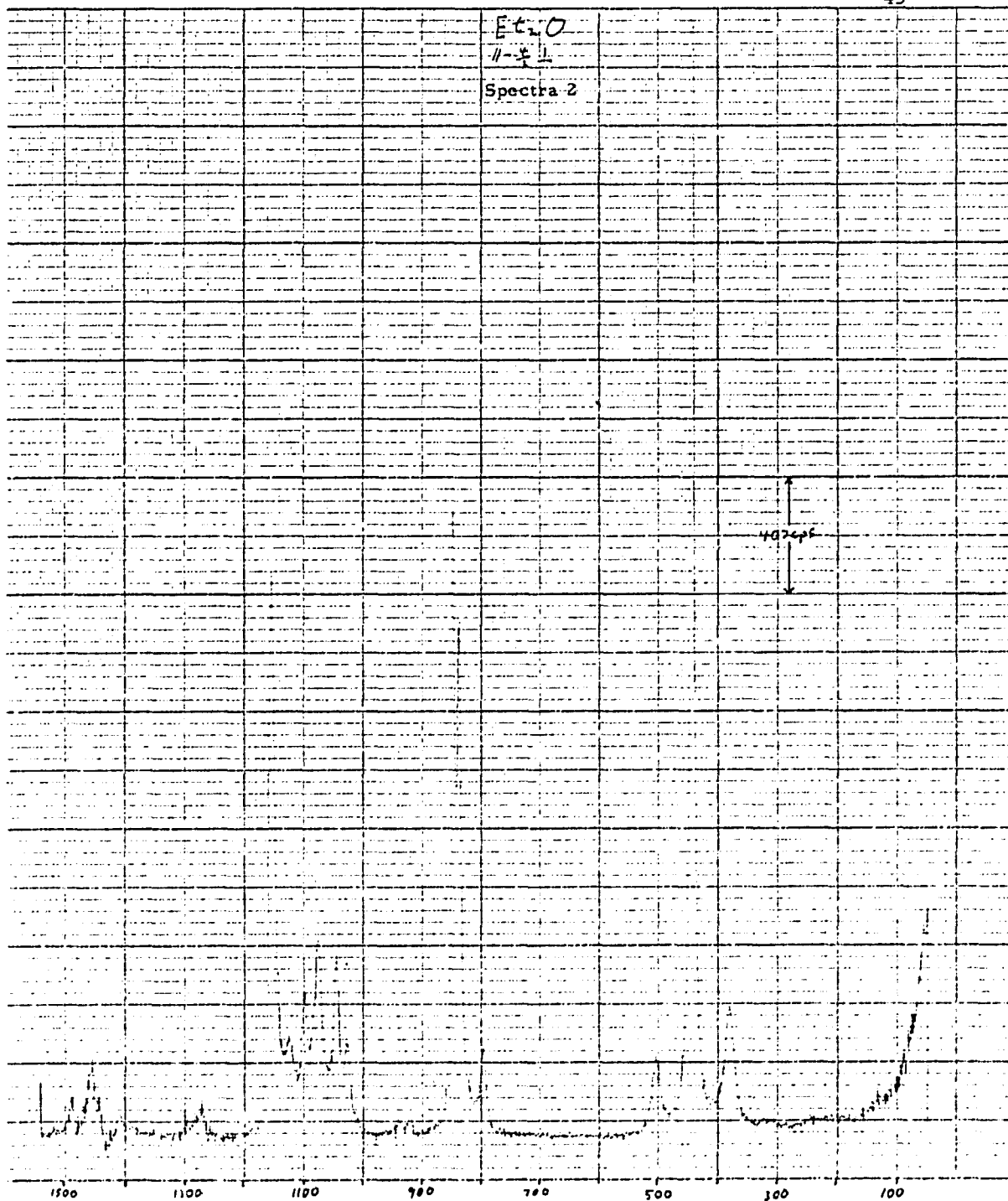
Following the tables of the Grignard spectra, the graphs of relative intensity vs concentration are next presented for a given band in a given Grignard. The 833 cm^{-1} band in these graphs is designated by @ as a reminder that these points are defined to have a relative intensity of 1.0.

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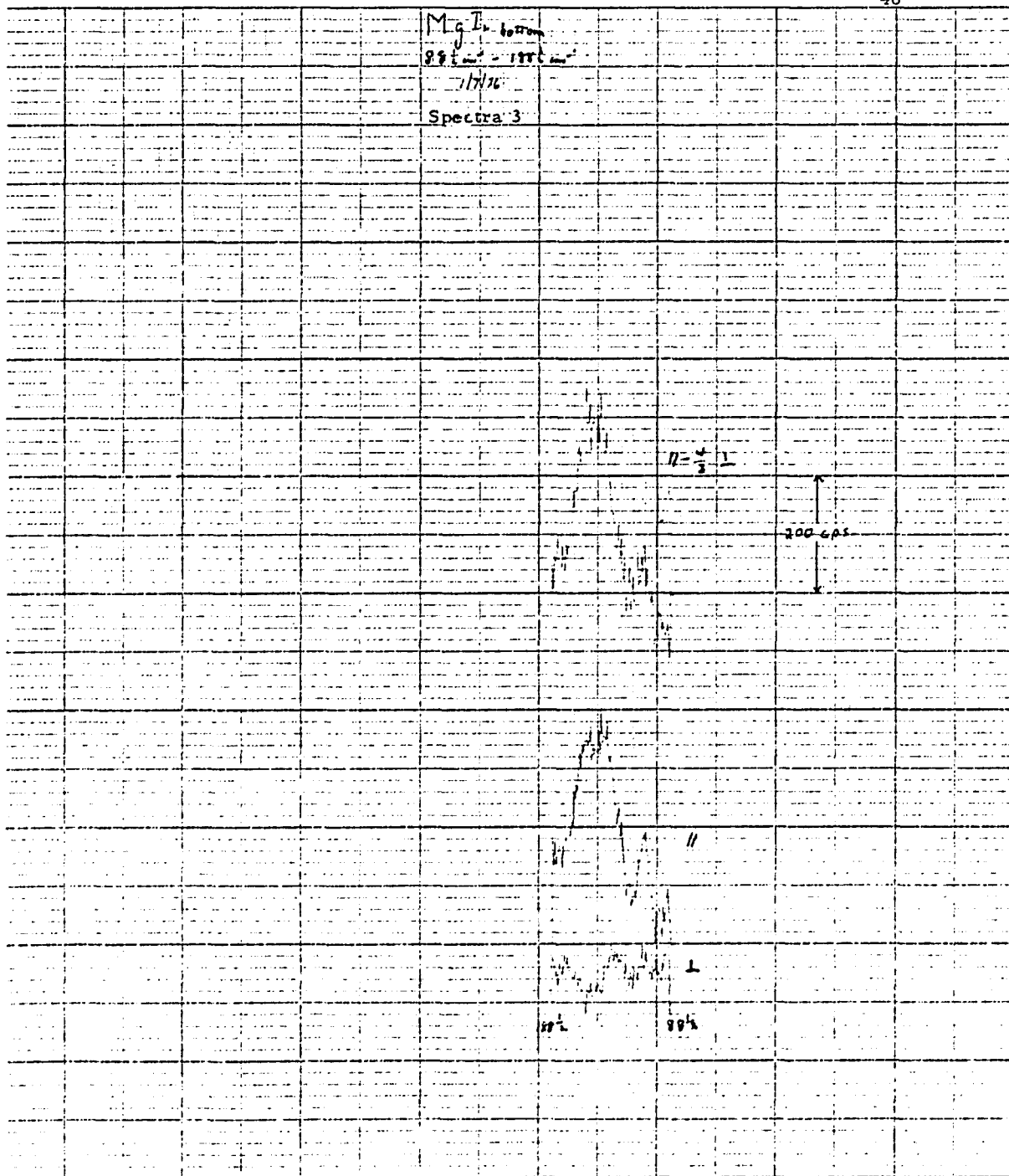


24



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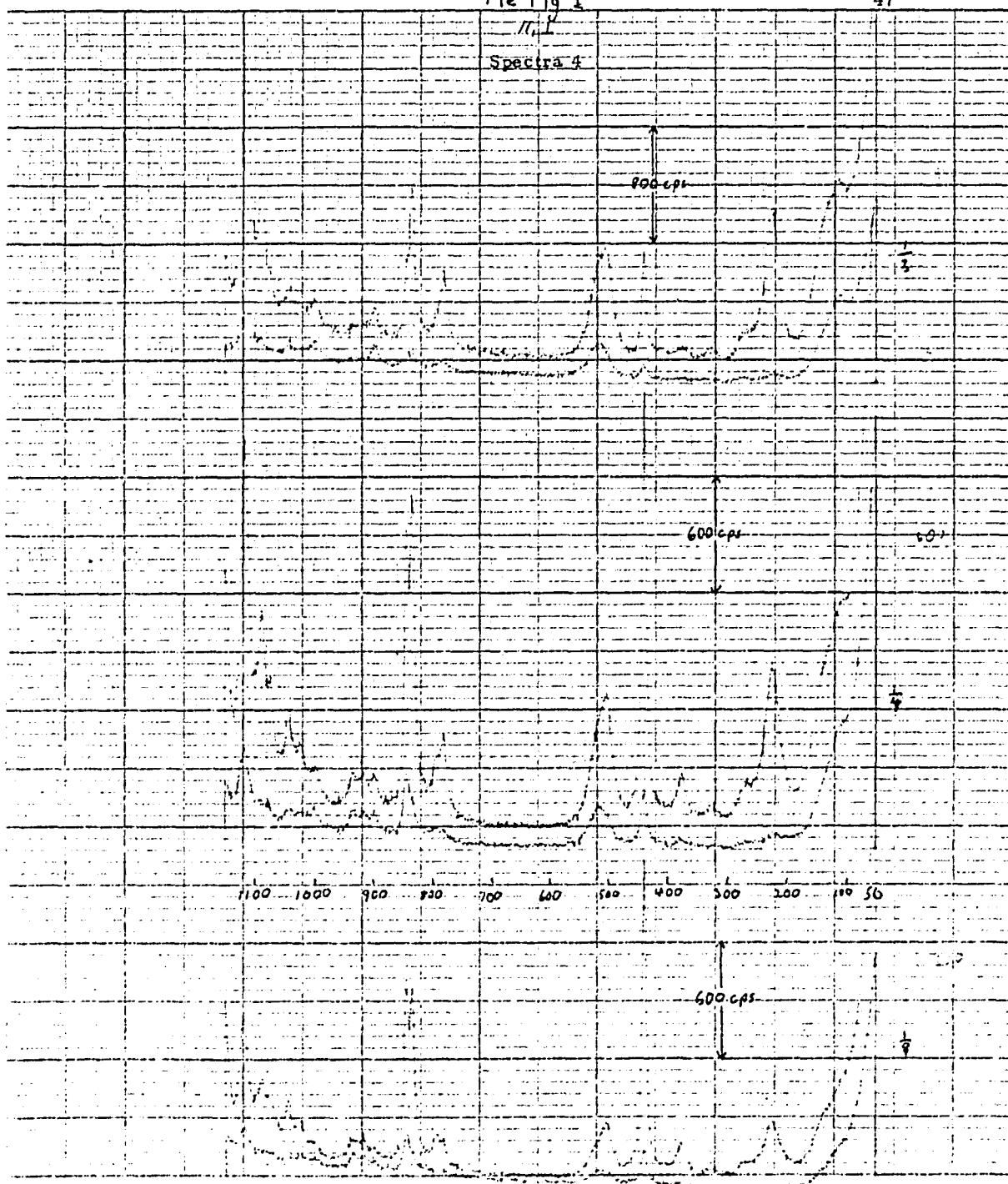
24

Me Mg I

47

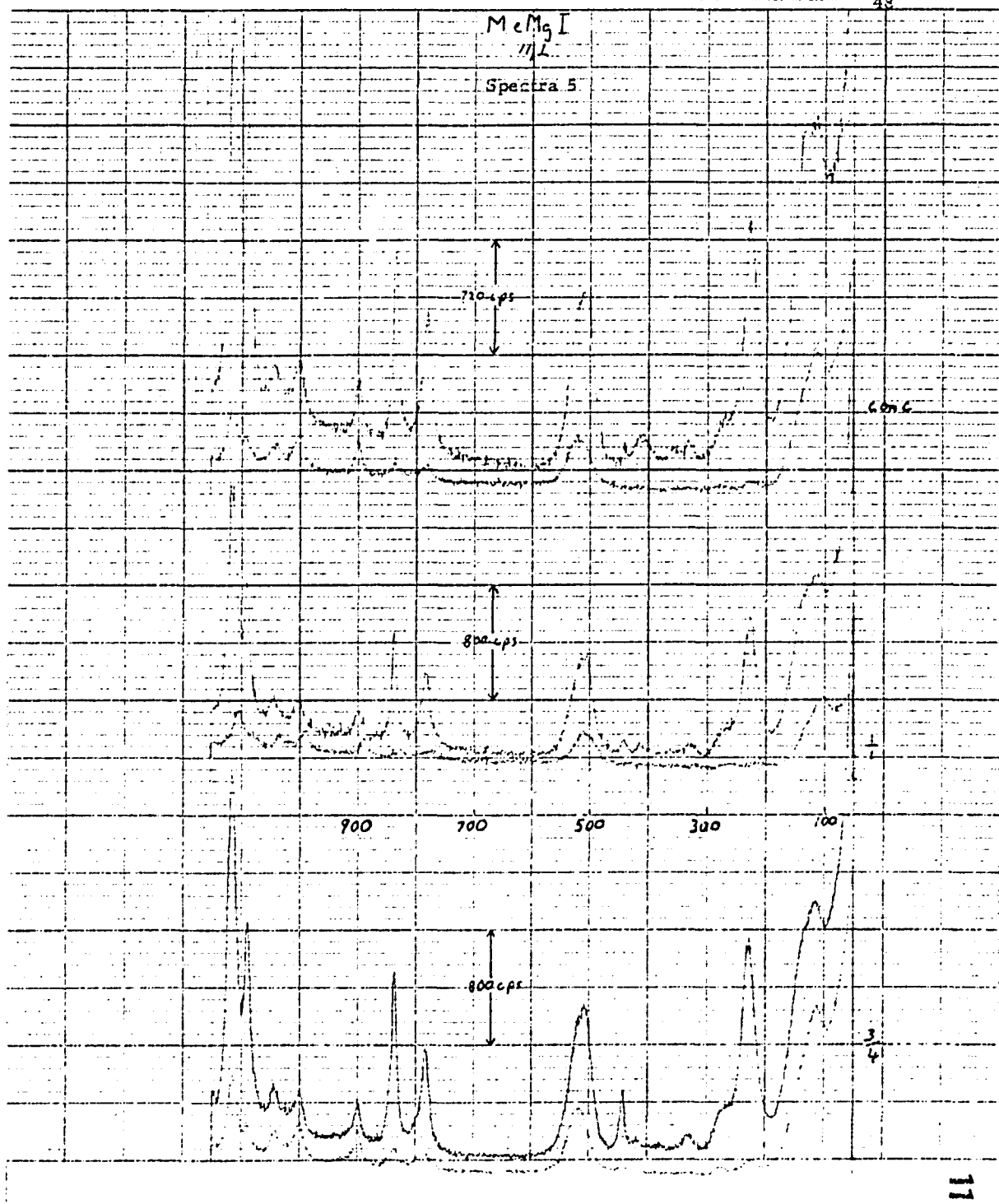
π_1

Spectra 4



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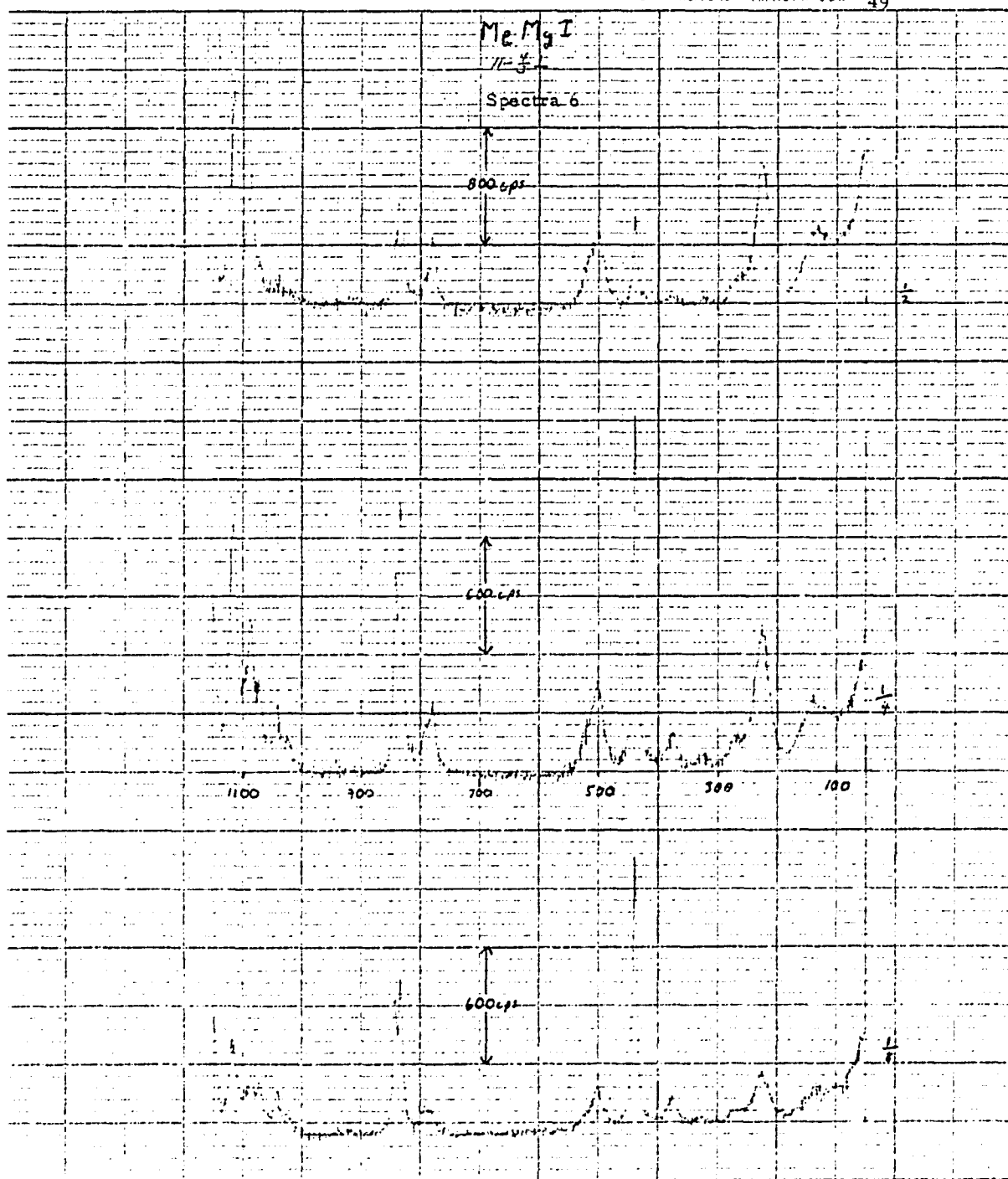
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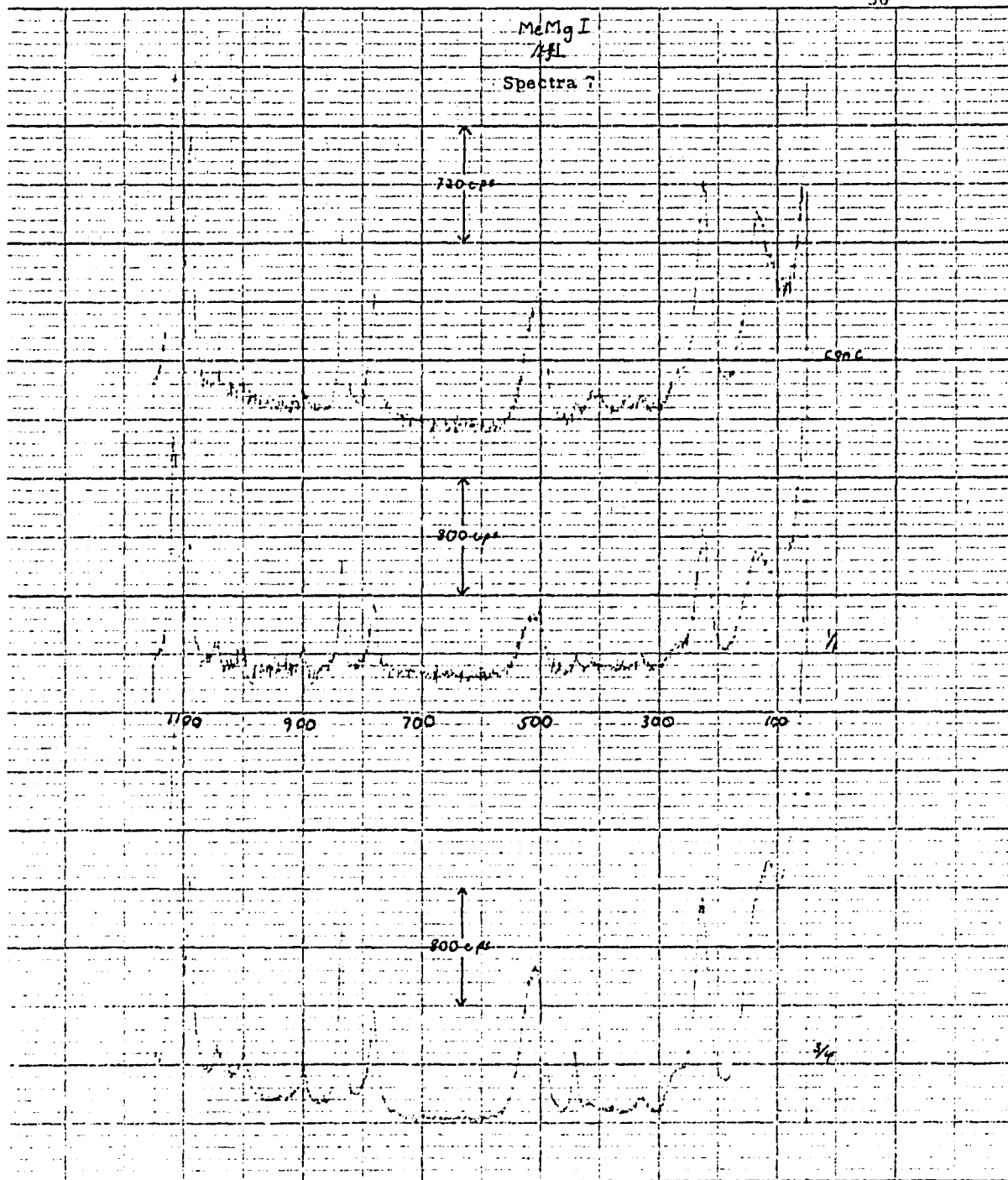
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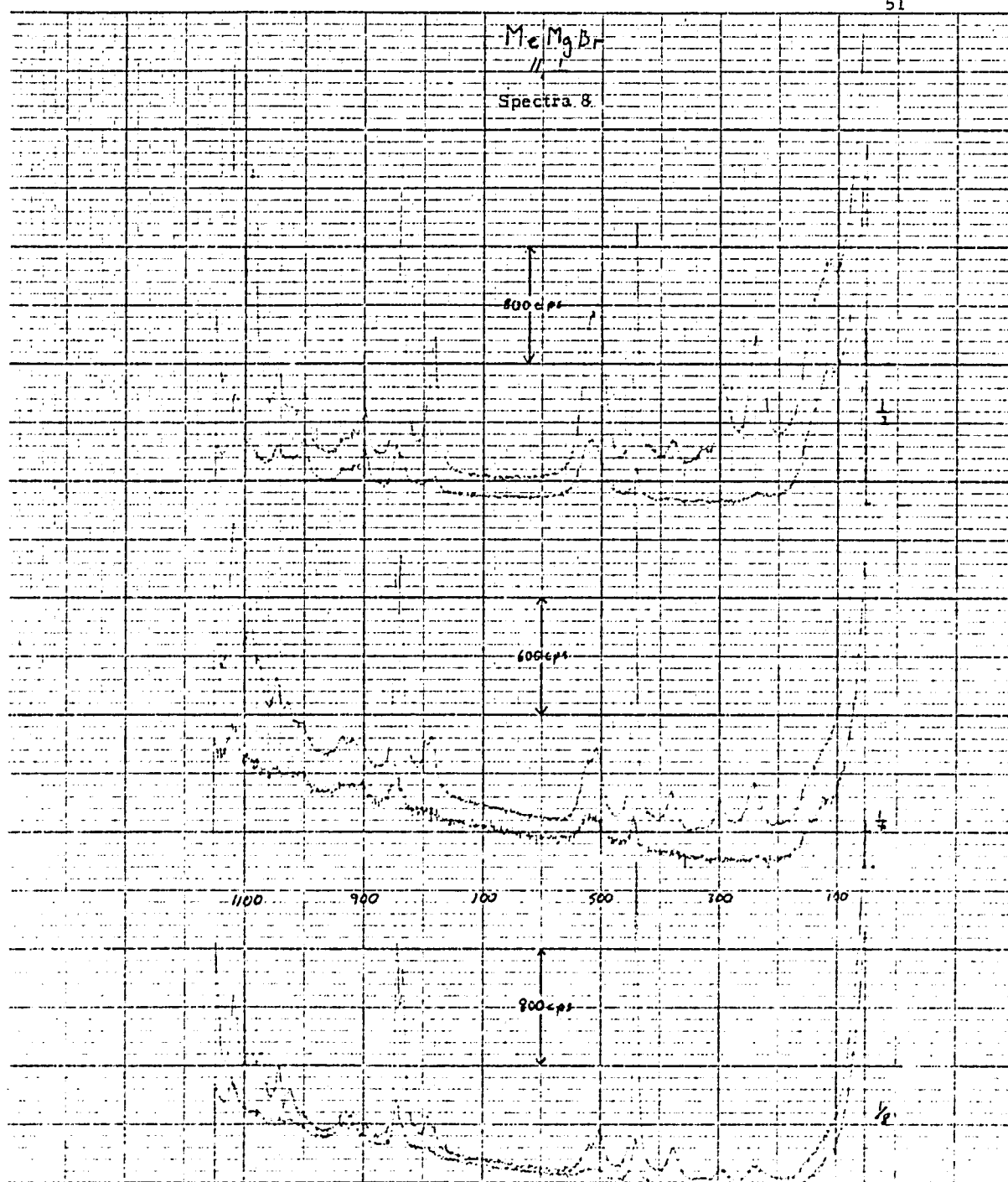
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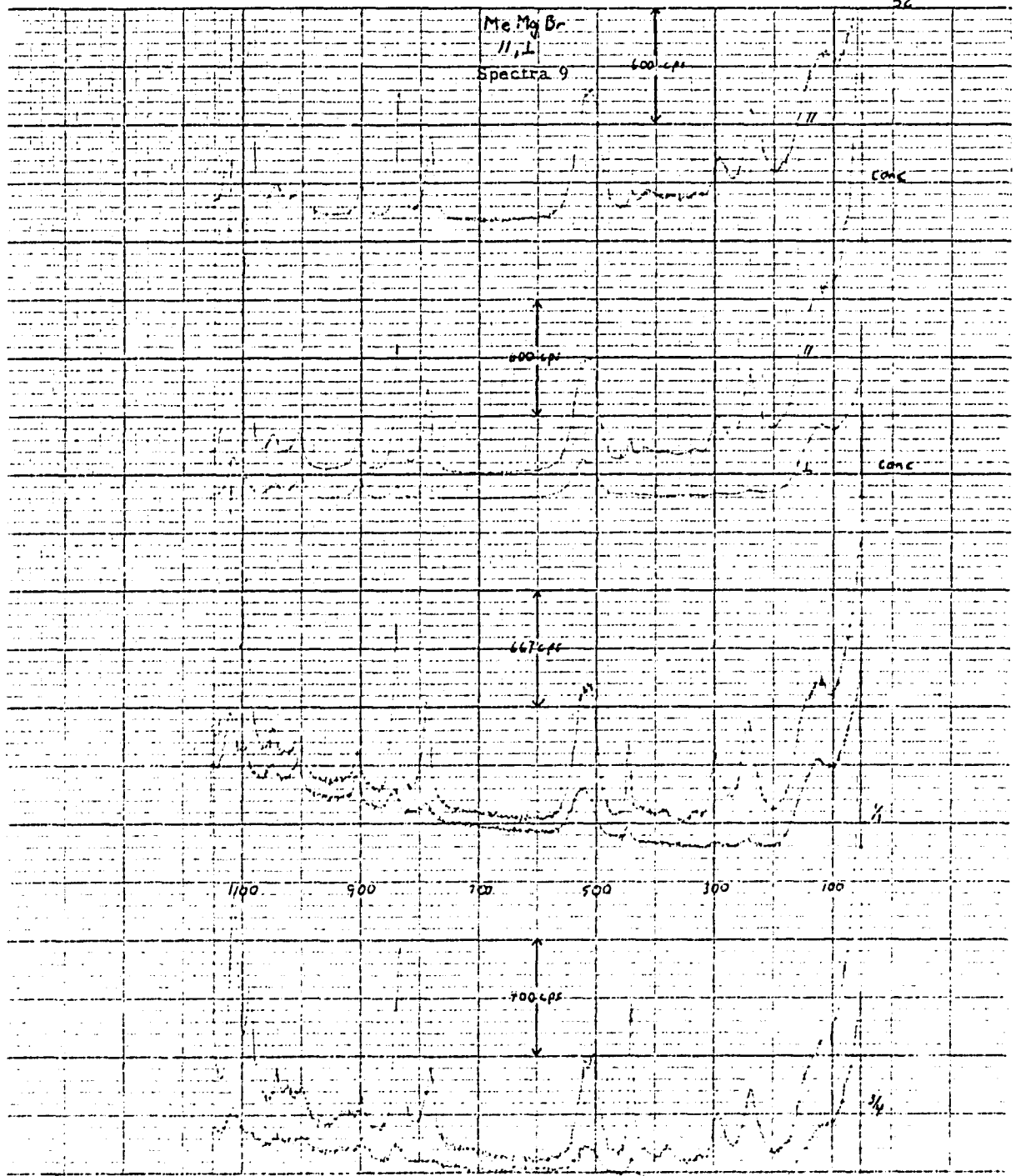


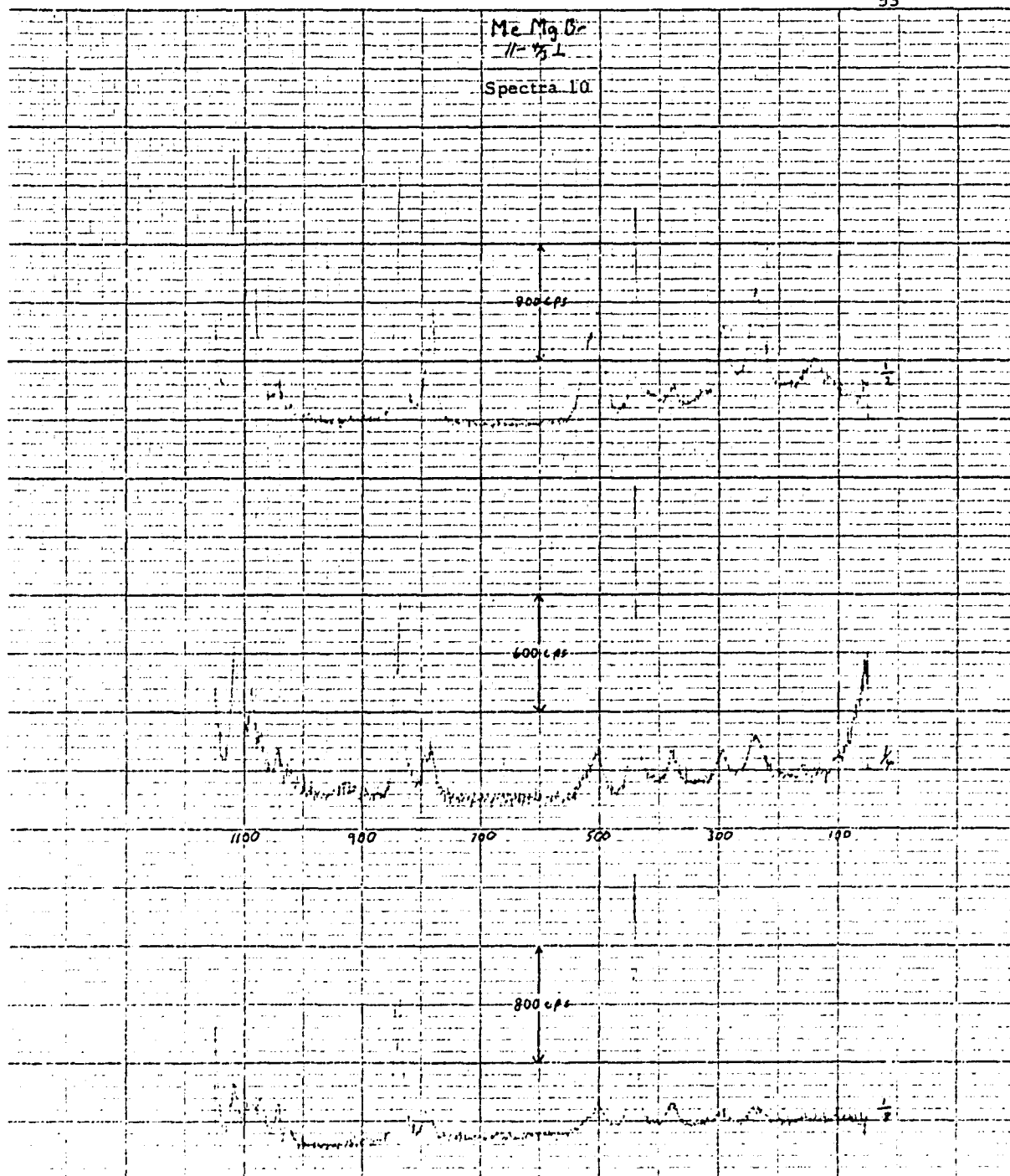
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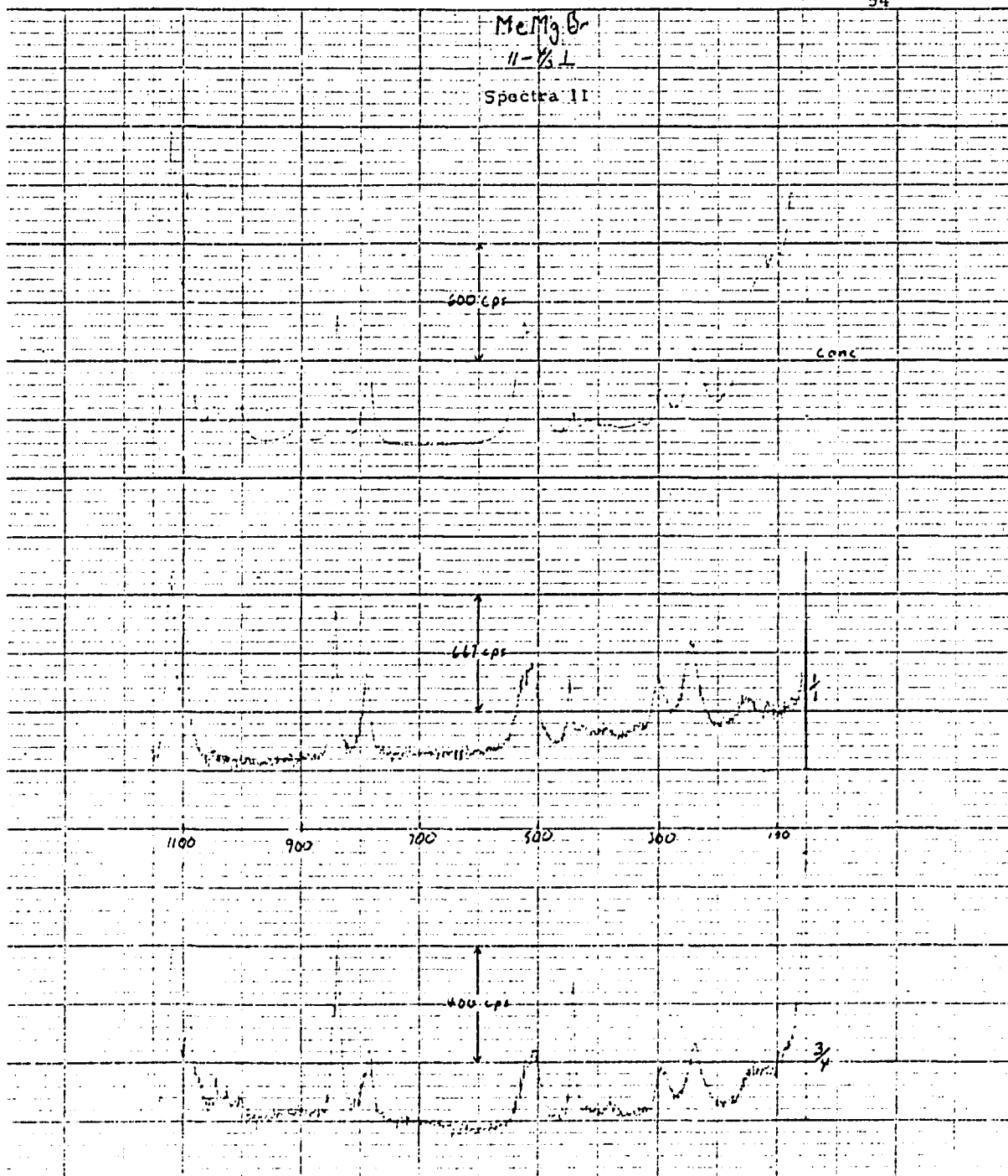
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10

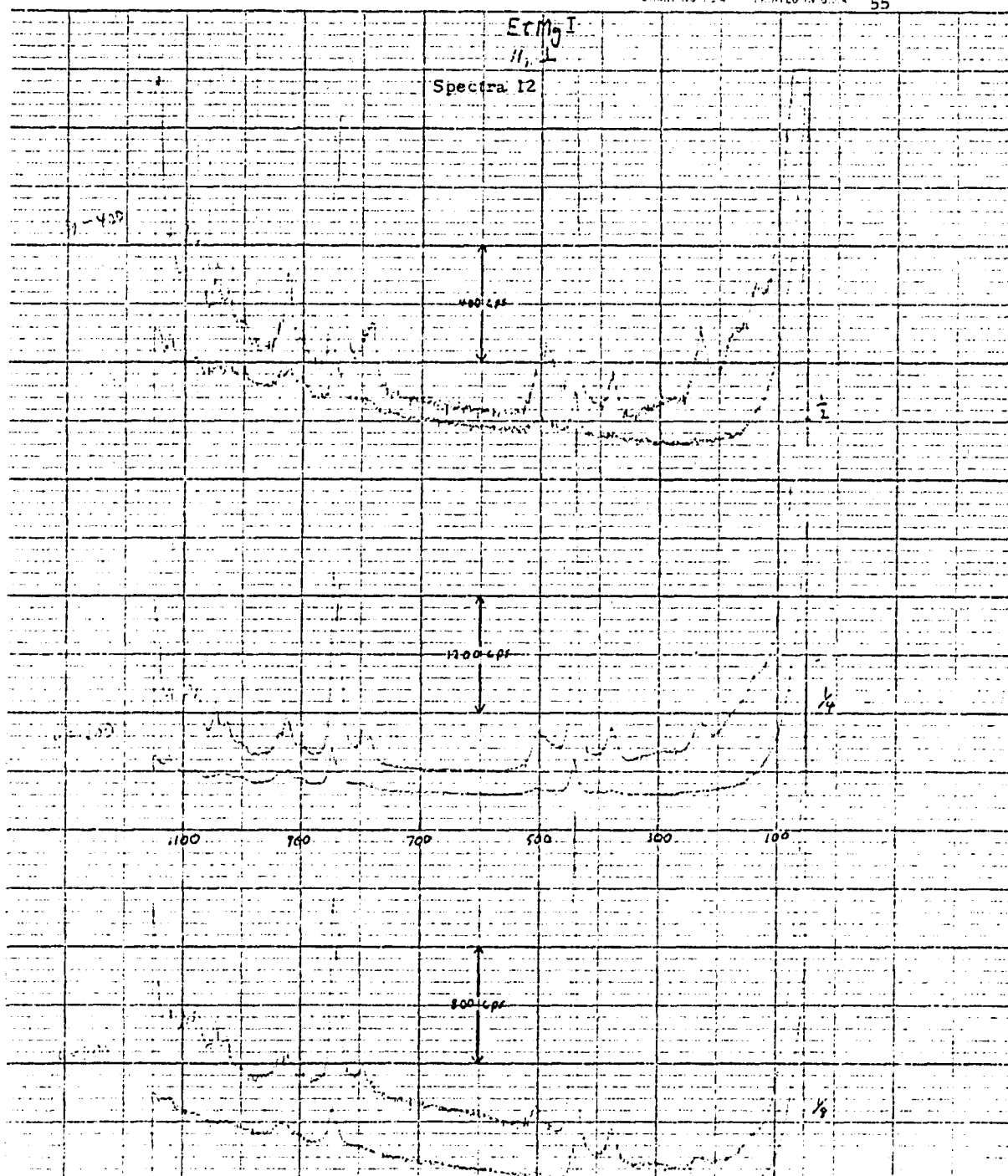






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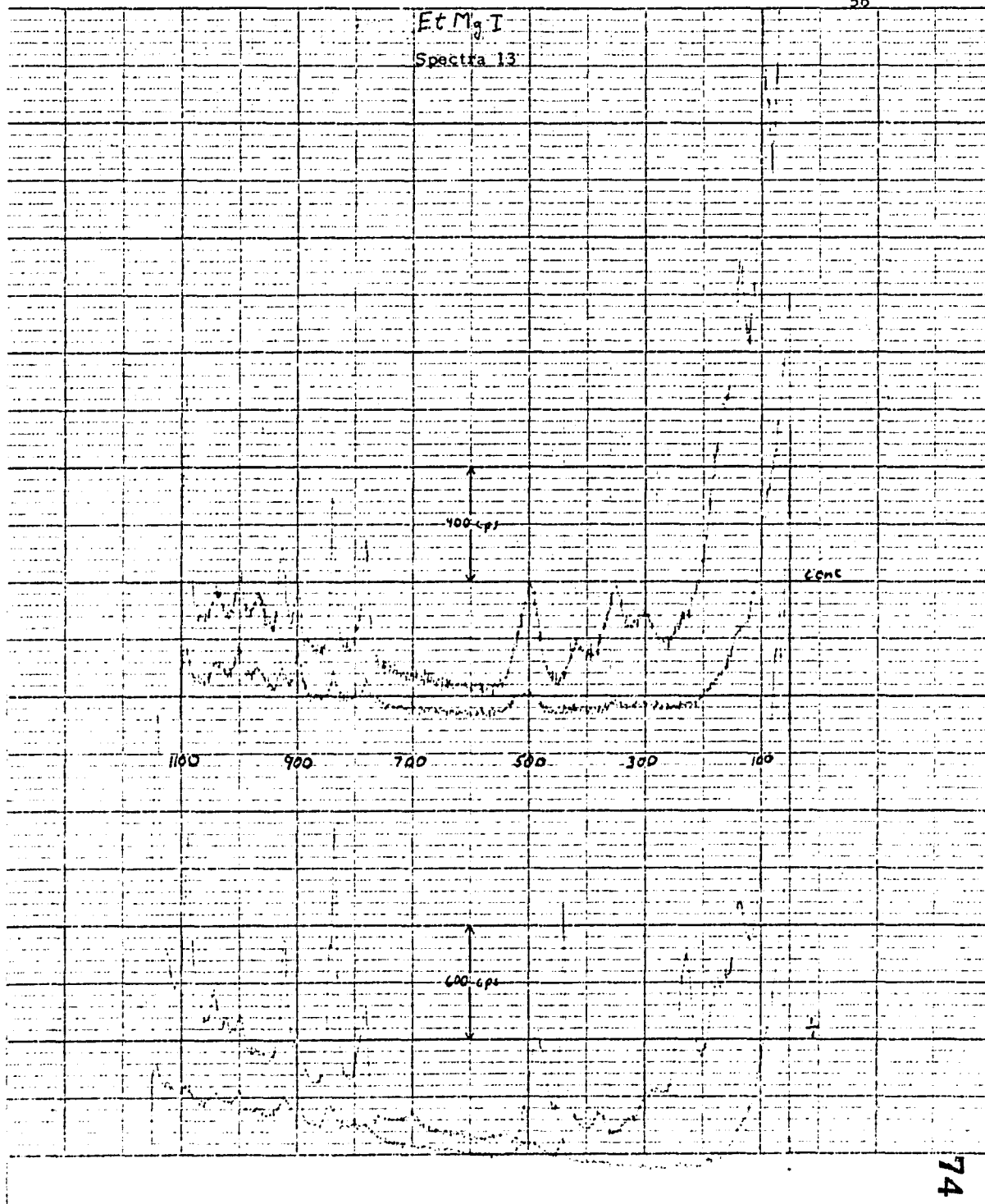
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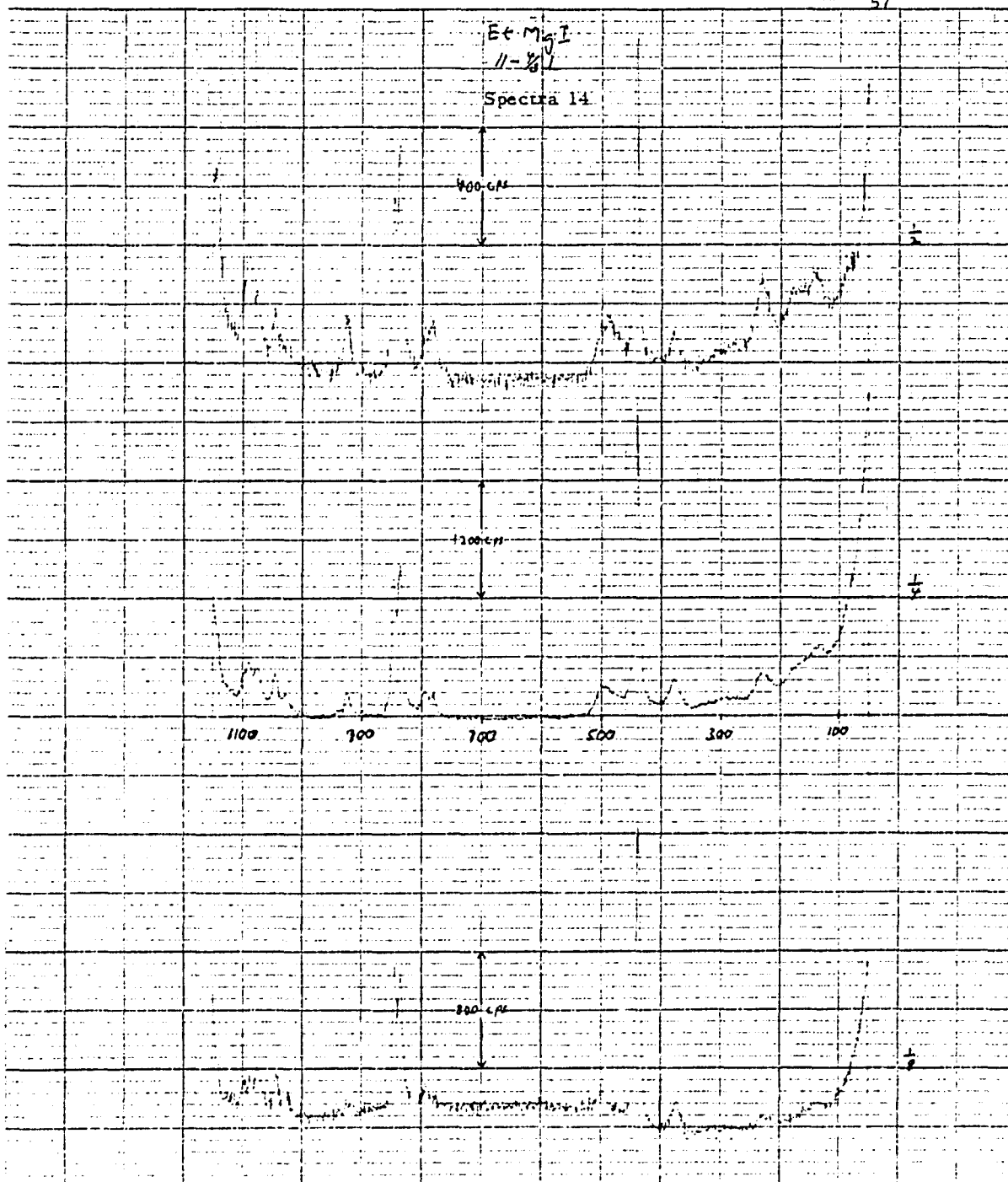
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56

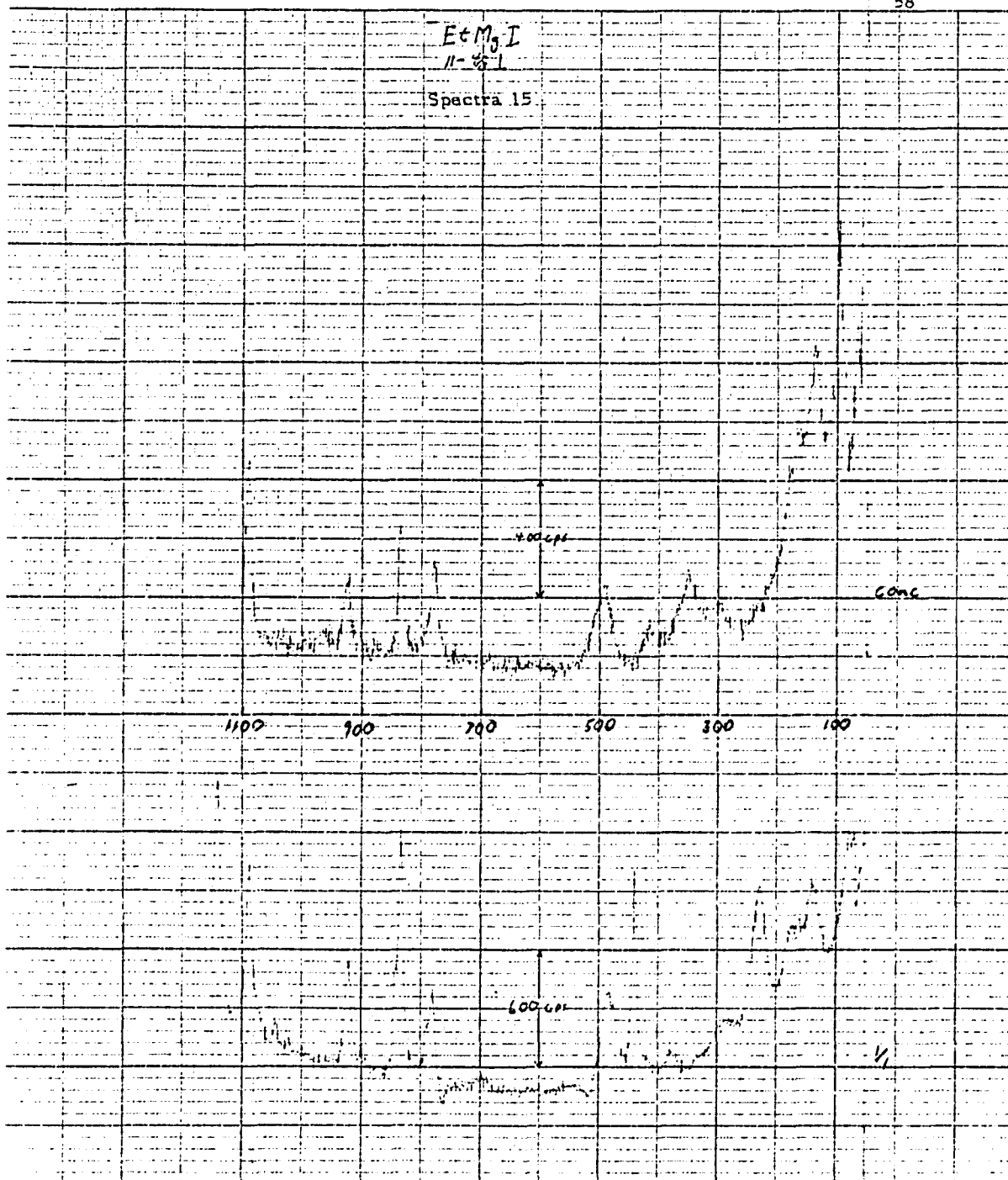


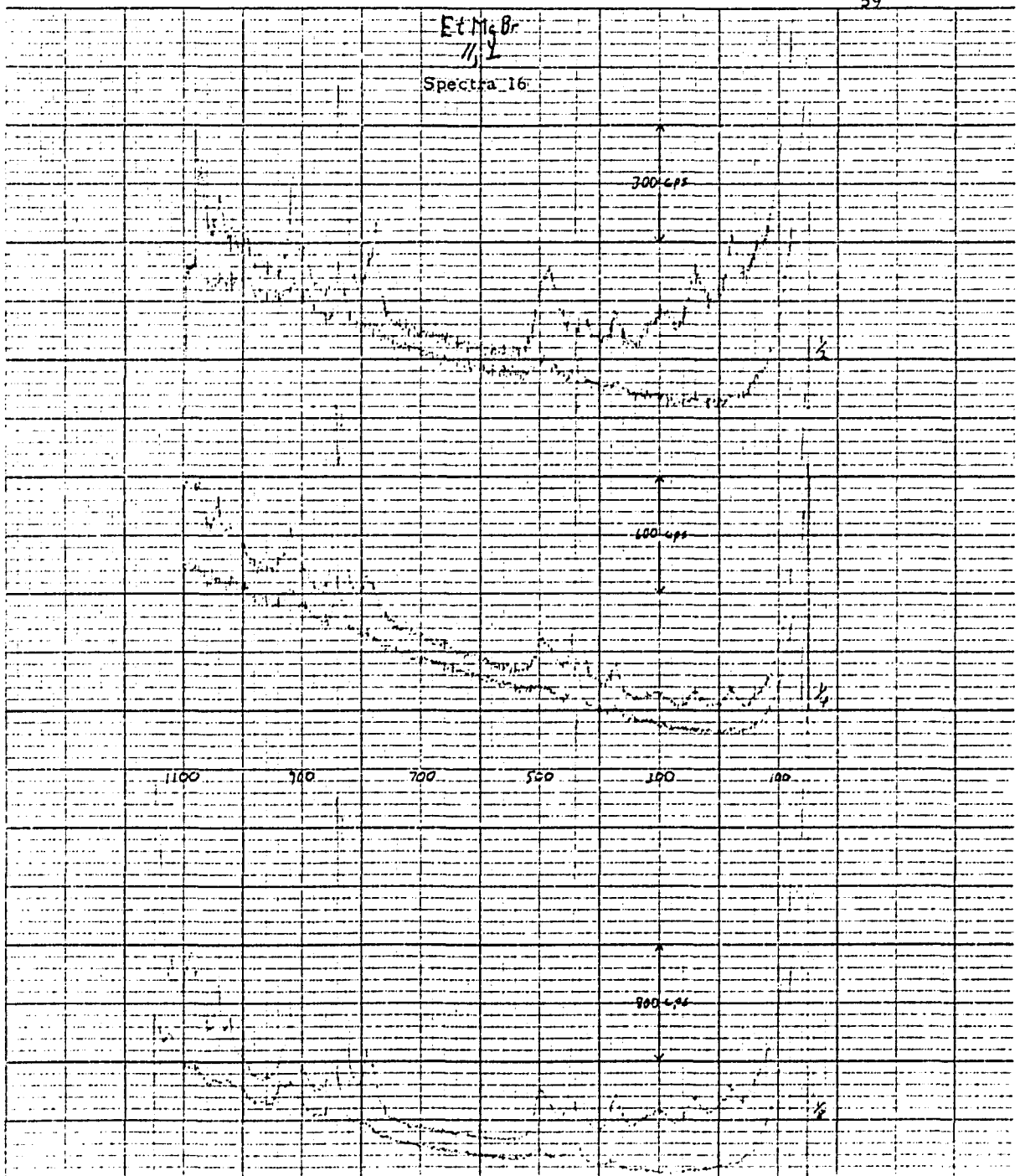
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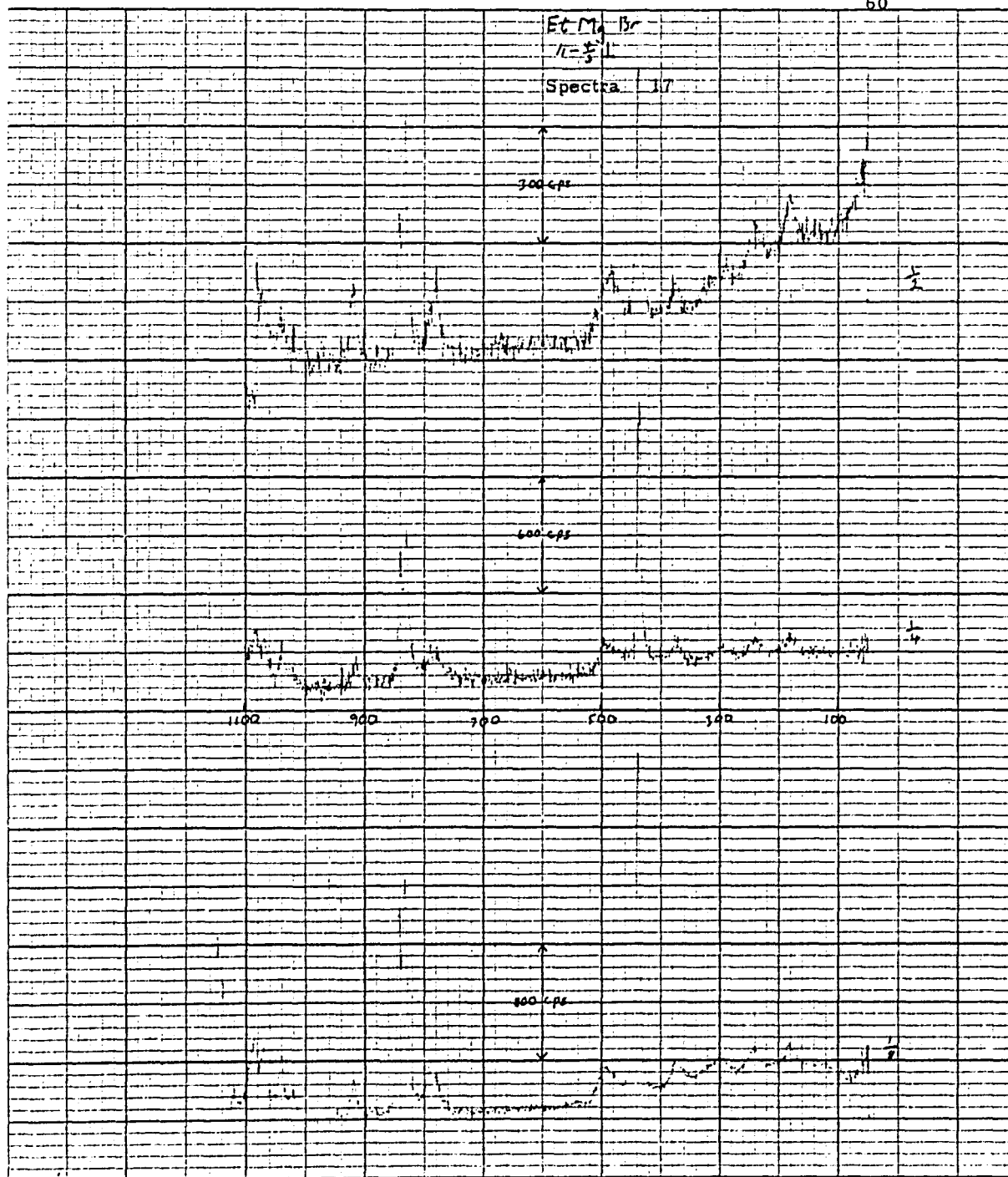
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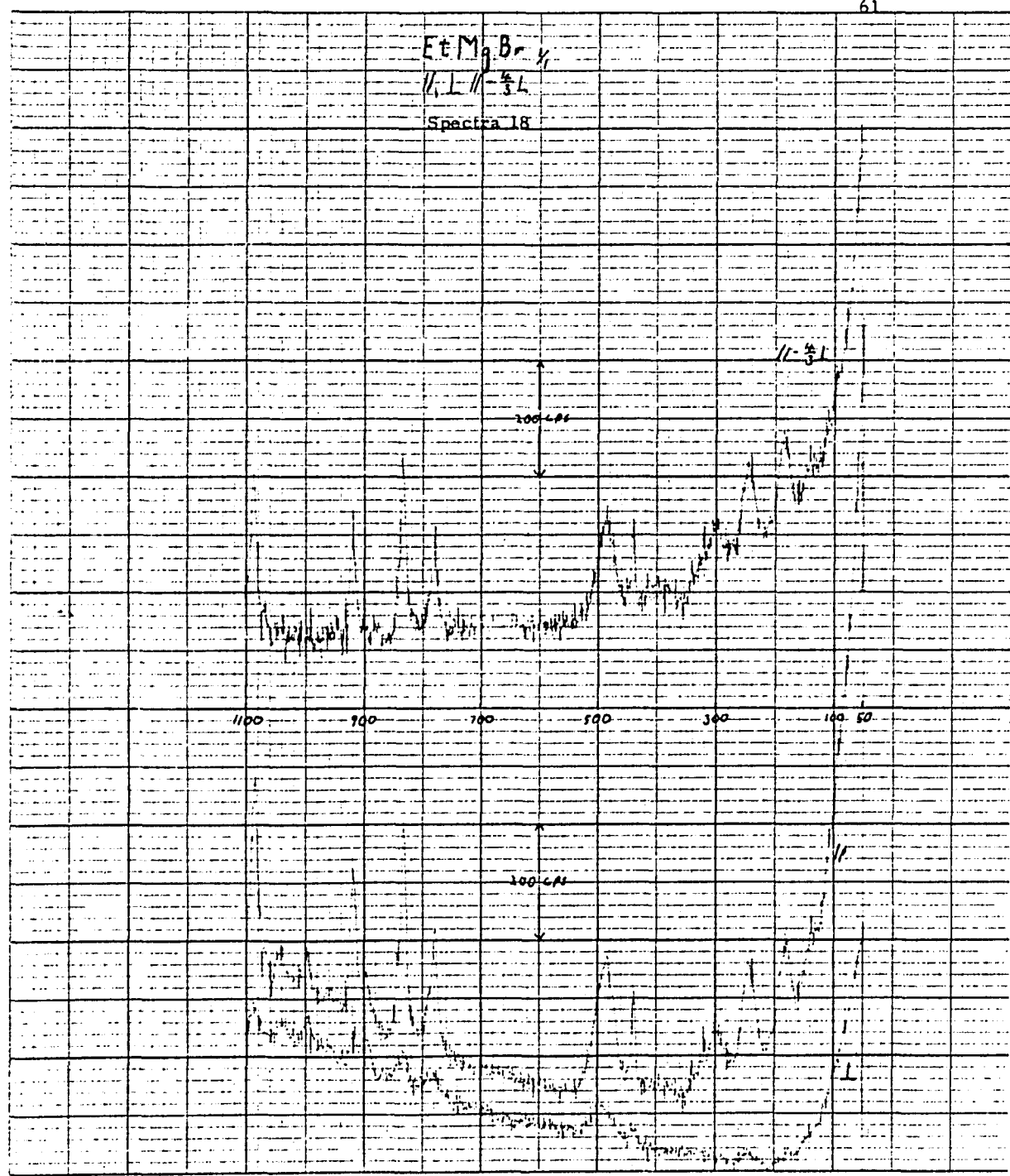


85









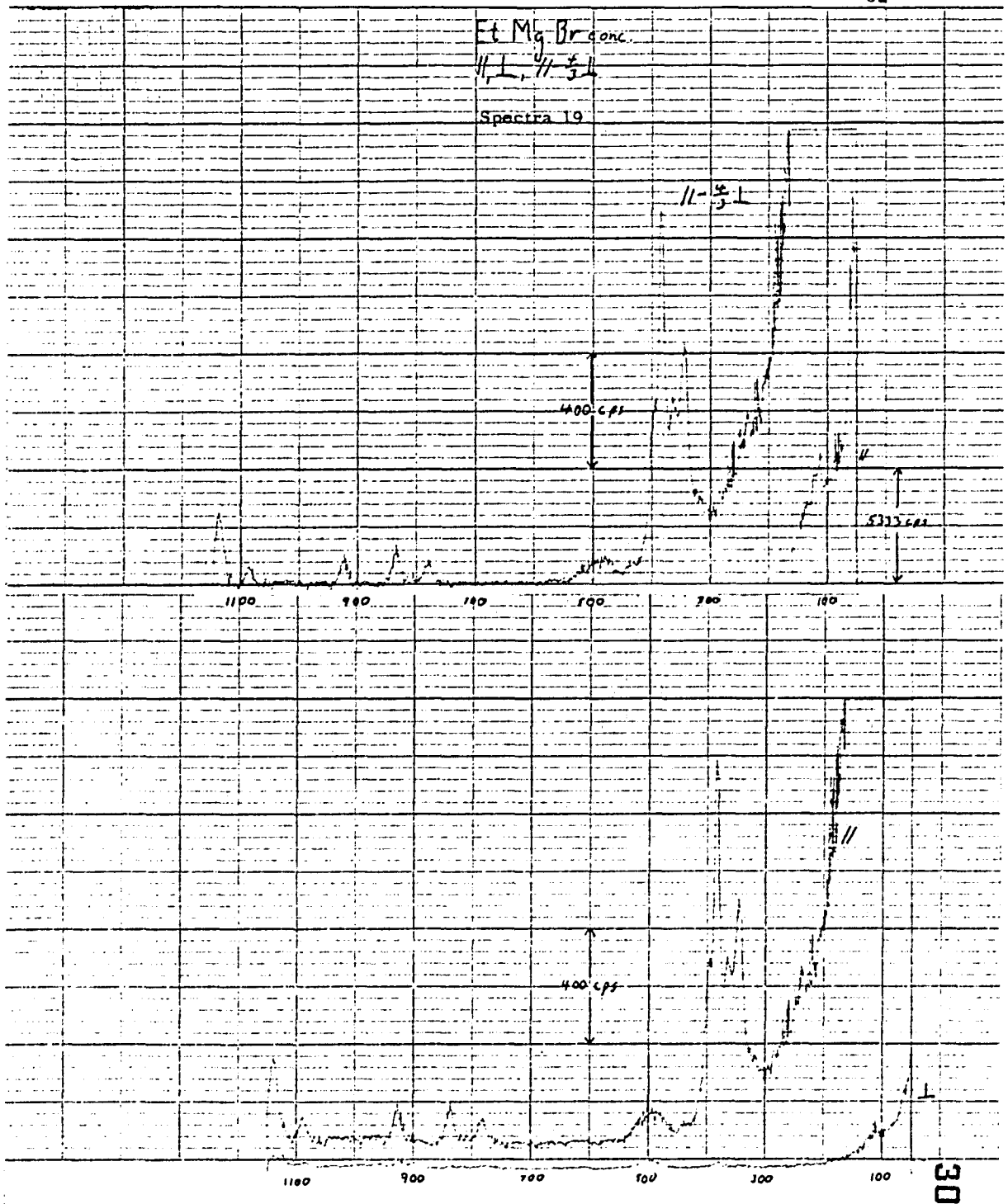
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Table 2

//				⊥				// - 1/2 ⊥				Assignments ³⁵
ν cm ⁻¹	I:	$\frac{I_i}{I_{374}}$		ν cm ⁻¹	I:	$\frac{I_i}{I_{374}}$		ν cm ⁻¹	I:	$\frac{I_i}{I_{374}}$		
201b	3	.026		202b	2	.017	.67	125	2	.017	TT (B ₂) ¹⁰ , f ₀	
224b	3	.026						225b	1	.009	TT (A ₂) ⁷ ; TG ⁷	
242	3	.026									TT (B ₂) ⁷ ; TT (A ₁) ⁷ X, θ	
319	2	.017		320	.5	.004	.25	318	2	.017	TG X, θ	
376	25	.218		375	4	.035	.16	374	21	.183	TG X, R, θ	
439	269	2.34		439	34	.287	.126	439	225	1.95	TT (A ₁) ⁷ θ , R, X	
501	17	.148		500	3	.026	.176	500	13	.113	TG θ , X, R	
792	21	.183		795	4	.035	.19	793	16	.14	TT (A ₂) ¹⁰ , β ; TG f ₀ , β	
834	115	1.00		833sh	20	.174	.174	833	90	.78	TG S, β , ρ , R	
844	153	1.32		843	36	.313	.235	843	99	.86	TT (A ₁) ⁷ S, β	
916	17	.148		917	10	.087	.59	917	3	.026	TG β , S, R	
933	17	.148		933	11	.096	.65				TT (B ₂) ⁷ R, S, δ	
1023	24	.208		1023	6.5	.056	.27	1021	16	.14	TG R	
1042	36	.313		1043	4	.035	.111	1040	31	.27	TT (B ₂) ⁷ β , R, W ₀	
1072	45	.390		1075	8	.070	.138	1071	35	.304	TT (A ₁) ⁷ R, S, β	
1098	35	.304		1100sh	7	.061	.20	1095	25	.218	TG β , W ₀	
1121	41	.356		1121	18	.157	.44	1120	17	.148	TT (B ₂) ⁷ S, R	
1150	126	1.09		1149	21	.183	.167	1149	95	.83	TT (A ₁) ⁷ β , R, X β , S; TG S, β , R	
1182sh	5	.045		1183	2	.017	.40	1179sh	4	.035	TG β , S, $\bar{z}$	
1269	37	.322		1267	25	.217	.68	1269	5	.044	TT (A ₂) ⁷ T ₀	
1296sh	3	.026		1290sh	-			1285	2	.017	TG T ₀	
1369sh	4	.034		1368sh	3	.026	.75				TG U; TG U, W ₀	
1414sh	5	.044		1415	-			1411	5	.044	TT (A ₁) ⁷ W ₀ , δ	
1447sh	93	.81		1447	65	.565	.70	1445	6	.052	TT (A ₂) ⁷ α ; TT (B ₂) ⁷ α ; TG α	
1454	124	1.08		1456	72	.63	.58	1456	9	.078	TT (A ₁) ⁷ α ; TT (B ₂) ⁷ α ; TG α ; TG α	
1488sh	36	.313		1486sh	25	.217	.69	1491	5	.044	TG δ , W ₀ , α	
								1521	2	.017	TG $\bar{z}$	

b = broad

(MeMgI)_{1/8}

10/12/75

Table 3

//			⊥			// - $\frac{4}{3}$ ⊥			
ν cm ⁻¹	I:	$\frac{I_i}{I_{933//}}$	ν cm ⁻¹	I:	$\frac{I_i}{I_{933//}}$	$\frac{I_{\perp}}{I_{//}}$	ν cm ⁻¹	I:	$\frac{I_i}{I_{933//}}$
118*	5	.11	115	3	.065		130	4	.087
137*	8	.173					223	12	.26
223	12	.26	224	.6	.013	.05	268	3	.065
270	2.5	.054					375	7	.152
323	1.5	.033	375	1	.022	.118	439	68	1.48
377	8.5	.185	439	9	.196	.111	502	9	.196
439	81	1.76	498	3	.065	.214	520	3	.065
502	14	.305	516	4	.087		780	6	.13
780	8	.174	780	1.4	.031	.175	793	7	.152
793	9	.196	793	1.4	.031	.155	833	40	.87
833	46	1.0	833	5	.109	.108	843	35	.76
843	47	1.02	843	11	.24	.234			
898	3.5	.076	900	3	.065	.86			
913	6	.13	918	5	.109	.83			
933	5	.109	934	4.5	.98	.9			
1000	1.5	.033	995	1.5	.033	1			
			1002	2.5	.054		1024	4	.087
1022	5.5	.12	1025	3	.065	.546	1041	8	.174
1041	10.5	.229	1041	2.5	.054	.238	1072	10	.218
1072	9	.196					1087	11	.24
1085	10.5	.229	1080	2	.044	.19			
			1098	1.8	.039				
1117	23	.5	1119	6	.13	.26	1117	17	.37

(MeMgI)_{1/4}

11/5/75

Table 4

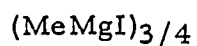
//			⊥			$\frac{I_{\perp}}{I_{\parallel}}$	// - $\frac{4}{3}\perp$		
ν cm ⁻¹	I _i	$\frac{I_i}{I_{833}}$	ν cm ⁻¹	I _i	$\frac{I_i}{I_{833}}$		ν cm ⁻¹	I _i	$\frac{I_i}{I_{833}}$
104	8	.098	105	9	.11	1.125	105	4	.049
							138	9	.11
223	35	.427	225	1.4	.017	.04	222	33	.403
265	6	.073					265	6	.073
325	2.5	.031					325	3	.037
374	11	.134	380	2.4	.029	.218	372	11	.134
439	100	1.22	439	14	.171	.14	438	90	1.1
500	33	.402					500	22	.268
520	24	.293	518	10	.122	.417	520	11	.134
778	21	.256	783	3	.037	.143	780	18	.22
790	17	.209	795	3.2	.039	.188	790	13	.16
807	10	.122							
833	82	1.0	831	11	.134	.134	833	69	.84
843	72	.88	842	16	.195	.222	843	52	.635
898	9	.11	895	6.4	.078	.71			
915	9	.11	915	5.6	.068	.623			
932	8	.098	932	5.8	.071	.725			
1000	6	.073	1000	6	.073	1			
1023	8	.098	1025	3.4	.042	.425	1022	7	.086
1040	14	.171	1045	3	.037	.214	1040	13	.159
1072	18	.22	1076	4	.049	.222	1072	17	.208
1086	33	.402	1088	3	.037	.091	1087	31	.378
1116	74	.9	1117	14	.171	.189	1116	55	.647

(MeMgI)_{1/2}

10/22/75

Table 5

//			⊥				// - $\frac{1}{2}$ ⊥		
γ cm ⁻¹	I:	$\frac{I_i}{I_{933//}}$	γ cm ⁻¹	I:	$\frac{I_i}{I_{933//}}$	$\frac{I_{i\perp}}{I_{i//}}$	γ cm ⁻¹	I:	$\frac{I_i}{I_{933//}}$
115	22	.423	110	10	.19	.045			
117*	12	.23							
137*	10	.19	137sh				132	11	.212
225	46	.89	224	2.5	.48	.054	225	43	.828
265	8	.154	275	1.5	.288	.187	265	8	.154
325	2	.039					323	3	.058
375	3	.058					380	3	.058
438	35	.67	439	6	.115	.171	438	30	.578
503	37	.71					502	25	.48
520	30	.58	515	11	.211	.367			
780	26	.5	780	4.2	.081	.161	780	21	.404
793	12	.23					793	10	.192
833	52	1.0	833	6.5	.125	.125	833	45	.867
843	28	.54	842	6.2	.119	.221	843	22	.423
896	10	.192	895	6	.115	.6			
915	5	.096							
940	3	.058	935	2.5	.48	.833			
998	8	.154	998	6	.115	.75			
1040	8	.154	1040	4	.077	.5	1039	6	.115
1088	43	.83	1088	4	.077	.093	1086	41	.79
1109	81	1.56	1115	12.5	.24	.154	1114	61	1.17



10/13/75

Table 6

//			⊥				// - $\frac{4}{3}$ ⊥		
$\nu \text{ cm}^{-1}$	I:	$\frac{I_i}{I_{933//}}$	$\nu \text{ cm}^{-1}$	I:	$\frac{I_i}{I_{933\perp}}$	$\frac{I_{\perp}}{I_{//}}$	$\nu \text{ cm}^{-1}$	I:	$\frac{I_i}{I_{933//}}$
115	40	.67	110	25	.417	.625	80	4	.067
138	50	.833					138	18	.3
225	65	1.08	222	3	.05	.046	225	63	1.05
275	12	.2	275	2	.033	.167	275	12	.2
330	6	.1					330	5	.835
380	2	.033					375	2	.333
418	4	.067					415	4	.067
441	21	.35	440	4	.067	.19	440	17	.284
503	50	.833	503	17	.283	.34	503	27	.45
520	47	.78	515	22	.367	.47			
783	34	.567	775	5	.083	.147	782	29	.48
			790	4	.067				
835	60	1.00	835	6	.1	.1	836	52	.87
			844	5	.083				
900	14	.233	898	11	.183	.785	900	6	.1
1000	13	.216	996	12	.2	.923			
							1022	3	.105
1045	12	.2	1040	9	.15	.75	1048	5	.835
1090	66	1.1	1089	9	.15	.136	1087	55	.92
1113	116	1.93	1111	25	.417	.216	1112	86	1.42

(MeMgI)_{1/1}

10/12/75

Table 7

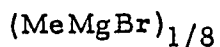
//			⊥			$\frac{I_{\perp}}{I_{\parallel}}$	// - $\frac{4}{3} \perp$		
$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{833}}$	$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{833}}$		$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{833}}$
115	23.4	.63	113	18	.49	.77	125	25	.675
137	28	.76					137	29	.785
225	42	1.13	218	1	.027	.024	225	47	1.23
265	8	.216	270	1.2	.032	.15	270	9	.243
330	5	.135	330	1	.027	.2	330	8	.216
412	4	.108					412	6	.162
439	5	.135	435	1	.027	.2	440	9	.243
502	35	.95					502	24	.65
514	35	.95	508	12	.32	.34	514	24	.65
780	29	.79	780	3.8	.103	.13	780	29	.785
793	10	.27					793	10	.27
834	37	1.0	835	2	.054	.054	833	40	1.08
898	9	.24	896	5	.135	.55	899	12	.322
998	9	.24	998	6.5	.176	.72	1002	12	.322
1043	9	.24	1043	4.2	.114	.467	1044	12	.322
1090	46	1.24	1092	4.5	.122	.098	1089	43	1.16
1115	75	2.03	1113	12.5	.34	.167	1115	75	2.03

(MeMgI)_{conc.}

10/22/75

Table 8

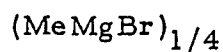
//			⊥			$\frac{I_{\perp}}{I_{//}}$	// - $\frac{4}{3}$ ⊥		
$\nu \text{ cm}^{-1}$	I:	$\frac{I_i}{I_{833//}}$	$\nu \text{ cm}^{-1}$	I:	$\frac{I_i}{I_{833//}}$		$\nu \text{ cm}^{-1}$	I:	$\frac{I_i}{I_{833//}}$
112	38	.633	113	16	.127	.42	110sh	17	.282
114*	53	.88					135	38	.63
125	50	.835							
137*	59	.97							
225	64	1.07	225	2	.033	.031	225	62	1.03
268	10	.167	275	1.2	.02	.12	269	8	.13
330	5	.083	330	.75	.012	.15	330	6	.10
355	4	.067					360	5	.08
408	8	.13					410	9	.15
439	6	.10					439	5	.08
503	54	.90					501	41	.68
515	48	.80	520	15	.25	.31	520	31	.86
780	43	.717	780	4.8	.08	.11	780	37	.62
793	12	.20							
833	60	1.0	833	4.5	.075	.075	833	56	.93
843	10	.167	843	2	.033	.2			
897	16	.267	897	10	.167	.62	901	6	.10
998	18	.30	997	10	.167	.55	1002	5	.08
1042	13	.217	1038	7	.115	.54	1040	7	.12
1088	~80	1.30	1090	8	.133	.10	1086	77	1.3
1113	~130	2.17	1110	16	.26	.12	1112	~100	1.67



12/12/75

Table 9

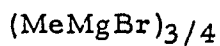
//			⊥				// - $\frac{4}{3}$ ⊥		
$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{233//}}$	$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{233//}}$	$\frac{I_{i\perp}}{I_{i//}}$	$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{233//}}$
225	5	.082	235	1	.016	.2	235	6	.098
295	4	.066					290	5	.082
375	10	.164	375	2.7	.044	.27	374	7	.115
440	108	1.77	439	15.5	.254	.143	439	86	1.41
502	15	.246	500	2.5	.041	.166	500	9	.148
520	9	.148	520	3	.049	.333	518	4	.066
780	9	.148					780	7	.115
793	12	.197					791	10	.164
812	8	.131					810	5	.082
834	61	1.0	833	9	.148	.147	833	48	.787
844	69	1.13	844	18	.295	.261	843	46	.755
898	6	.098							
915	9	.148	917	7	.115	.78			
932	8.5	.139	933	6	.098	.71			
1023	7	.115	1021	4	.066	.57	1025	5	.082
1042	12	.197	1040	3	.049	.25	1040	12	.197
1072	13	.213	1078	3	.049	.23	1070	12	.197
1088	10	.164					1085	21	.345
1098	8	.131							
1120	25	.41	1120	10	.164	.4	1117	15	.246



12/13/75

Table 10

//			⊥				// - $\frac{4}{3}\perp$		
$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{933//}}$	$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{933//}}$	$\frac{I_{i\perp}}{I_{i//}}$	$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{933//}}$
130	2	.527	115	1.5	.039		135	1.2	.032
			135	1.7	.045	.85	160	2	.053
							197	2	.053
235	7.5	.197	230	.7	.018	.094	239	8	.21
294	5	.131					292	5.5	.145
330	.8	.02							
376	5	.131	375	1.5	.04	.3	378	6	.158
412	2	.053							
441	59	1.55	441	6	.158	.102	440	50	1.32
503	13	.342	503	4	.105	.308			
515	10	.264	520	5	.132	.5	520	7	.184
781	9.5	.25					782	8.5	.224
793	8	.184	793	1	.026	.125	793	8	.210
835	38	1.0					834	35	.92
845	35	.92	845	6	.158	.171	844	25	.658
900	4.5	.118	900	4	.105	.89	912	2	.053
916	4.5	.118	918	2.5	.066	.557			
							930	2.5	.066
933	4	.105	940	2	.053	.5	950	1.5	.04
1000	3	.079	1002	3	.079	1.0			
1024	4	.105					1025	2.5	.066
1045	7	.184	1044	2	.053	.286	1042	5.5	.145
1075	7	.184					1071	7	.184
1088	14	.369					1087	14	.27
1117	27	.71	1119	6	.158	.222	1117	20	.527



12/19/75

Table 11

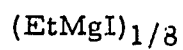
//			⊥			$\frac{I_{\perp}}{I_{//}}$	// - $\frac{\pi}{3}$ ⊥		
$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{833H}}$	$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{833H}}$		$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{833H}}$
82*	12	.35					95	2	.059
111	11	.324	115	5	.147	.455	115	6	.177
118*	16	.47							
135	12	.354	146	6	.177		135	9	.265
146*	12	.35							
236	12	.354	235	1	.029	.083	237	15	.44
290	8.5	.25					290	11	.324
325	1	.029					325	1.2	.035
377	3	.088	372	.75	.025	.25	378	4	.118
415	2.5	.073	420	1.0	.029	.4	415	3	.088
439	27	.795	439	4	.118	.148	440	34	1.0
503	19	.56	503	5	.147	.263	502	21	.62
518	18	.53	518	5.5	.162	.305	520	19	.56
781	13	.383	780	1	.029	.77	780	17	.5
790	9	.265							
833	34	1.0	833	2.5	.074	.074	833	43	1.27
843	23	.677	843	3	.088	.013	843	28	.825
898	6	.177	900	3.2	.094	.533	900	5	.147
915	3	.088					925	5	.147
935	3	.088							
1000	6	.177	998	2.2	.065	.367	1000	5	.147
1022	5	.147	1019	2	.059	.4	1021	7	.206
1041	6	.177	1041	2.2	.067	.367	1040	8	.236
1075	6	.177					1071	7	.206
1088	20	.59	1090	.75	.025	.038	1087	26	.0766
1115	33	.97	1116	5	.147	.15	1113	40	1.18

(MeMgBr)_{conc.}

11/16/75

Table 12

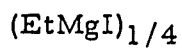
//			⊥			$\frac{I_{\perp}}{I_{\parallel}}$	// - $\frac{4}{3}\perp$		
$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{833\parallel}}$	$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{833\parallel}}$		$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{833\parallel}}$
82*	12	.136							
104	32	.36					100	5	.056
115*	30	.34							
118	50	.57	119	27	.30	.54			
							130	11	.123
144*	22	.25							
							180	2	.022
238	41	.47	239	2	.022	.049	237	39	.44
290	21	.24	290	1	.011	.048	290	21	.235
328	3	.034	330	.8	.009	.27	325	2	.02
374	2.5	.028					372	3	.034
411	8	.091	415	1.8	.020	.225	412	6	.068
439	14	.16	441	3.2	.036	.23	439	11	.123
							503	45	.50
510	72	.82	520	25	.28				
							620	1	.011
782	56	.64	780	7	.078	.125	781	46	.51
836	88	1.0	833	8	.09	.091	835	75	.84
901	21	.24	899	13.5	.15	.64	900	4	.045
							925	1.5	.017
							942	1	.011
1002	22	.25	1000	14	.157	.64	1004	4	.045
1046	18	.205	1043	9	.10	.56	1044	6.5	.073
1090	172	1.96	1090	11	.12	.064	1090	~160	~1.8
1115	206	2.34	1112	25	.28	.12	1115	~180	~2.0



(6/23/75)

Table 13

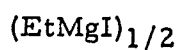
//			⊥			$\frac{I_{\perp\perp}}{I_{\perp//}}$	// - $\frac{4}{3}$ ⊥		
$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{833//}}$	$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{833//}}$		$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{833//}}$
137*	3	.053							
140	3	.053					145	5	.088
173*	3	.053							
232	3	.053					231	4	.07
315	2	.035							
375	11	.19	380	2	.035	.18	374	10	.17
440	121	2.1	440	13	.23	.107	440	90	1.6
503	13	.23	503	3	.053	.23	499	8	.14
793	11	.19	793	3	.053	.27	790	8	.14
835	57	1.0					832	42	.74
845	68	1.2	845	16	.28	.24	842	42	.74
925	11	.19	930	7	.12	.63			
940	8	.14	940	5	.09	.63			
1024	9	.16	1028	3	.053	.33	1025	8	.14
1045	12	.21					1042	13	.23
1075	12	.21	1080	3	.053	.25	1074	14	.25
1100	9	.16	1097	2.5	.043	.28	1100	5	.09
1125	10	.12	1122	8	.14	.80			



6/24/75

Table 14

//			⊥			$\frac{I_{\perp}}{I_{//}}$	// - $\frac{4}{3}$ ⊥		
$\nu \text{ cm}^{-1}$	I:	$\frac{I_i}{I_{833//}}$	$\nu \text{ cm}^{-1}$	I:	$\frac{I_i}{I_{833//}}$		$\nu \text{ cm}^{-1}$	I:	$\frac{I_i}{I_{833//}}$
143*	24	.26					140	11	.12
							167	10	.11
177*	18	.20							
228	12	.13					230	10	.11
300	4	.044					295	4	.044
378	20	.22	376	2	.02	.10	379	17	.187
440	140	1.54	440	18	.20	.13	441	155	1.70
488sh	18	.20	485sh	2	.02	.11	488sh	14	.155
500	20	.22	502	3	.033	.15	501	17	.187
782	14	.15	781	2	.02	.285	782	13	.14
795	17	.187	795	3	.033	.176	794	14	.155
836	91	1.0	836	11	.12	.12	836	78	.86
847	95	1.04	847	20	.20	.21	846	71	.78
898	8	.088	900	4	.044	.50			
922	21	.23	919	8	.088	.38	924	13	.14
935sh	11	.12	935	7	.077	.64			
991	3	.033							
1000	3	.033	1000	2	.02	.67	1001	3	.033
1025	11	.12	1028	3.5	.038	.32	1027	9	.09
1043	17	.187					1045	19	.21
1074	19	.21	1076	3	.033	.16	1075	21	.23
1088	19	.21					1088	21	.23
1123	12	.13	1122	7	.077	.58			



6/18/75

Table 15

//			⊥			$\frac{I_{\perp}}{I_{//}}$	// - $\frac{4}{3}\perp$		
$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{833//}}$	$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{833//}}$		$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{833//}}$
135	4	.091					82	2	.045
145*	9	.20					140	8	.18
178*	7	.16							
180	3	.068					170	7	.16
230	10	.227					230	10	.227
							275	2	.045
300	1	.022					300	2	.045
375	7	.159	375	.5	.011	.07	375	6	.135
439	66	1.5	440	7	.16	.106	440	56	1.26
490	12	.27	490	2	.045	.167	485	11	.25
							500	9	.20
780	11	.25	780	1.5	.034	.136	780	10	.227
							793	9	.25
833	44	1.0	835	6	.135	.136	832	39	.89
843	40	.9	843	9	.20	.225	842	30	.68
897	5	.113	900	2.5	.057	.50	898	1	.02
924	14	.32	920	4	.091	.28	922	10	.227
			932	4	.091				
996	3	.068	995	2	.045	.67			
1025	6	.136	1025	2	.045	.33	1025	3	.068
1042	8	.18	1042	2	.045	.25	1042	7	.16
1074	9	.204	1077	2	.045	.224	1072	9	.20
1088	17	.39	1090	2	.045	.117	1089	17	.39
1122	7	.16	1122	6	.135	.85			
							1143	26	.59

(EtMgI)_{1/1}

6/18/75

Table 16

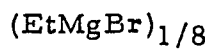
//			⊥			$\frac{I_{\perp}}{I_{\parallel}}$	// - $\frac{4}{3}\perp$		
$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{923\parallel}}$	$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{833\parallel}}$		$\nu_{cm^{-1}}$	I_i	$\frac{I_i}{I_{833\parallel}}$
70	14	.23					70	20	.328
							78	23	.38
136	14	.23	140	.5	.008	.036	140	21	.34
142*	34	.56							
175	11	.18	180	2	.032	.18	170	15	.25
178*	24	.39							
230	31	.51	235	2	.032	.064	230	12	.2
290	4	.066					290	6	.098
327	2	.033							
380	6	.098					380	7	.115
440	61	1.0	440	6	.098	.10	440	55	.9
482	29	.477	485	4	.066	.138	482	26	.43
504	9	.015	504	4	.066	.445			
700	5	.082					700	7	.115
782	29	.477	780	4	.066	.139	782	26	.43
			800	5	.082				
833	61	1.0	835	6	.098	.10	835	66	1.15
843	40	.657	845	8	.131	.20	845	30	.5
901	13	.213	900	7	.115	.538	900	6	.098
923	35	.573	922	6	.098	.16	921	28	.46
			970	2	.033				
1000	8	.131	1000	6	.098	.75			
1020	6	.098					1025	3	.05
1043	11	.18	1045	3	.05	.27	1045	6	.098
1087	47	.77	1090	4	.066	.085	1087	46	.75
			1122	5	.082				
1141	68	1.11	1140	8	.13	.118	1140	66	1.1

(EtMgI)_{conc.}

1/24/75

Table 17

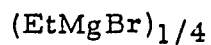
//			⊥			$\frac{I_{\perp}}{I_{//}}$	// - $\frac{2}{3}$ ⊥		
ν cm ⁻¹	I _i	$\frac{I_i}{I_{938}}$	ν cm ⁻¹	I _i	$\frac{I_i}{I_{938}}$		ν cm ⁻¹	I _i	$\frac{I_i}{I_{938}}$
65	13	.48					68	13	.48
95*	50	1.85							
98	53	1.96					98	44	1.63
134	24	.89					138	31	1.15
137*	48	1.77							
165	9	.33					165	20	.74
168*	28	1.04							
230	2	.074					230	2	.074
300	7	.26	290	1.5	.055	.214	305	8	.296
349	15	.56	350	2.5	.925	.167	350	13	.48
387	3	.11					390	5	.185
417	6	.22	417	1.5	.055	.25	418	6	.22
495	17	.63	503	5	.185	.294	493	14	.52
583	2	.074	579	1	.037	.5			
780	21	.777	778	5.5	.198	.262	780	18	.67
838	27	1.00	837	7	.26	.259	839	23	.85
897	12	.443	897	10	.37	.83			
925	17	.63	925	6	.22	.353	922	14	.52
965	8	.296	969	5	.185	.625			
996	10	.37	1000	9	.33	.9			
1045	7	.26	1040	6	.22	.857			
1090	39	1.44	1091	8	.296	.205	1089	32	1.18



5/16/75

Table 18

//			⊥			$\frac{I_{\perp}}{I_{\parallel}}$	// - $\frac{\pi}{2}$ ⊥		
$\nu_{\text{cm}^{-1}}$	I_i	$\frac{I_i}{I_{835}}$	$\nu_{\text{cm}^{-1}}$	I_i	$\frac{I_i}{I_{835}}$		$\nu_{\text{cm}^{-1}}$	I_i	$\frac{I_i}{I_{835}}$
182	7	.074	180	.5	.005	.071	182	9	.095
240	7	.074	230	.5	.005	.071	240	8	.084
300	5	.053					300	7	.074
372	22	.23	375	2	.021	.091	372	23	.24
439	154	1.63	439	22	.23	.143	439	120	1.26
498	16	.17	500	4	.042	.25	500	10	.105
784	17	.18	782	4	.042	.23	782	13	.137
792	19	.20	790	4	.042	.21	792	15	.158
835	95	1.00					832	77	.81
843	110	1.16	842	25	.26	.23	843	72	.76
900	10	.105	900	6	.063	.60	892	2	.021
920	25	.26	918	10	.105	.40	920	13	.137
935	12	.126	935	9	.095	.75			
1022	11	.105	1022	4	.042	.36	1021	10	.105
1042	19	.20	1045	3	.031	.16	1042	20	.21
1075	22	.023 ¹¹	1075	3	.031	.137	1072	22	.23
1088	20	.21					1088	23	.24
1121	11	.105	1120	6	.062	.54	1121	0.5	.005



3/26/75

Table 19

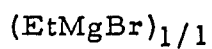
//			⊥			$\frac{I_{\perp}}{I_{//}}$	// - $\frac{4}{3} \perp$		
$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{932 //}}$	$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{932 //}}$		$\nu \text{ cm}^{-1}$	I_i	$\frac{I_i}{I_{932 //}}$
140	2	.041					140	2	.041
182	5	.102					180	6	.12
240	4	.082					240	5	.102
310	3	.061					300	3	.061
375	7	.14	375	3	.061	.43	375	7	.14
439	84	1.7	439	12	.25	.14	439	68	1.4
495	10	.202	500	3	.061	.3			
							598	9	.18
780	9	.18					780	7	.18
791	10	.202					791	9	.18
832	49	1.0	832	8	.16	.16	832	40	.82
842	50	1.02	842	12	.26	.26	843	35	.71
898	6	.12							
918	13	.26	920	6	.12	.46	917	8	.16
			997	4	.082				
1025	5	.102	1020	3	.061	.6			
1040	9	.18					1040	13	.26
1070	11	.22					1070	13	.26
1085	12	.25					1085	15	.305

(EtMgBr)_{1/2}

3/25/75

Table 20

//			⊥			// - $\frac{y}{J}$ ⊥			
$\nu_{cm^{-1}}$	I _i	$\frac{I_i}{I_{931} //}$	$\nu_{cm^{-1}}$	I _i	$\frac{I_i}{I_{931} //}$	$\frac{I_{\perp}}{I_i //}$	$\nu_{cm^{-1}}$	I _i	$\frac{I_i}{I_{931} //}$
143	2	.058							
180	6	.17	185	.5	.014	.083	180	8	.23
240	6	.17					245	7	.20
300	3	.086					300	5	.14
375	4	.115					380	5	.14
437	43	1.23	438	8	.23	.19	438	35	1.00
485	10	.29					482	8	.23
495	9	.26	500	2	.058	.22	495	7	.20
777	12	.34					778	12	.34
788	8	.23	790	2	.058	.25			
831	35	1.00	831	6	.17	.17	832	31	.88
841	28	.80	841	8	.23	.285	842	8	.23
900	5	.14	895	4	.115	.8			
917	14	.40	920	4	.115	.28	918	9	.26
995	5	.086	1000	4	.115	.8			
1018	5	.115					1020	5	.14
1040	6	.17	1040	2	.058	.3	1040	7	.20
			1085	3	.086		1075	10	.285



3/11/75

Table 21

//			⊥			// - $\frac{4}{3}$ ⊥			
νcm^{-1}	I_i	$\frac{I_i}{I_{932} //}$	νcm^{-1}	I_i	$\frac{I_i}{I_{932} //}$	$\frac{I_{\perp}}{I_{//}}$	νcm^{-1}	I_i	$\frac{I_i}{I_{932} //}$
105	2	.105					107	2	.105
136	3	.158					137	3	.158
180	6	.316					180	7	.37
245	8	.42	245	1	.05	.12	245	7	.37
295	4	.21					293	5	.26
318	4	.21					318	5	.26
439	9	.47	439	1.5	.079	.167	437	8	.42
481	12	.63	490	3	.158	.25	480	10	.05
778	10	.52	775	2	.105	.20	778	9	.47
790	5	.26							
832	19	1.0	830	3	.158	.158	833	15	.079
842	7	.37					843	5	.26
898	4	.21	898	3	.158	.75			
918	13	.68	916	3	.158	.23	917	11	.58
955	2	.10	955	1	.05	.50			
995	5	.26	995	3	.158	.6			
1040	4	.21	1040	2	.105	.5			
1083	18	.95	1085	2	.105	.11	1085	15	.79

(EtMgBr)_{conc.}

9/4/76

Table 22

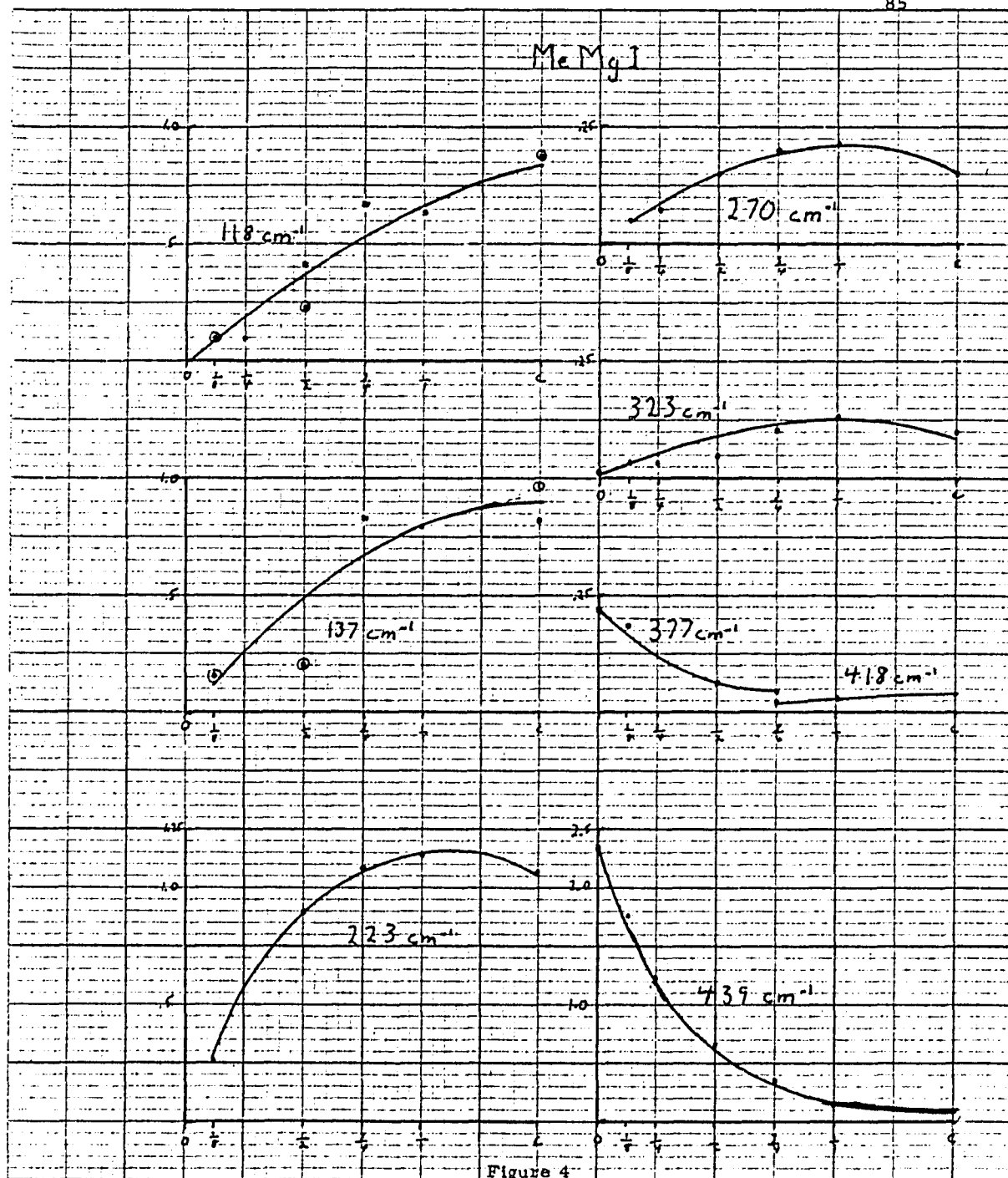
			⊥				- $\frac{\pi}{2}$ ⊥		
ν cm ⁻¹	I _i	$\frac{I_i}{I_{937 }}$	ν cm ⁻¹	I _i	$\frac{I_i}{I_{937 }}$	$\frac{I_{i\perp}}{I_{i }}$	ν cm ⁻¹	I _i	$\frac{I_i}{I_{937 }}$
111	190	27	112	4.4	.064	.023	112	203	29
124	159	23					124	165	23
137	95	13.5					137	115	16
238	9	1.3					238	9	1.3
343	37	5.3	345	.6	.085	.016	345	35	5
363	28	4					365	27	3.9
382	63	9	380	1.0	.14	.016	384	61	8.6
395	30	4.3					395	28	4
440	3	.43					439	2	.19
482sh	6	.86					480	4	.57
495	6	.86	495	1.4	.20	.23	495	4	.57
780	4	.57	778	.8	.129	.20	782	4	.57
837	7	1.0	835	.6	.085	.086	838	6	.86
			901	1.2	.17				
925	7	1.0	925	1.4	.20	.2	925	6	.86
1089	4	.57	1088	1.0	.14	.25	1089	4	.57
1140	14	2.0	1138	2	.28	.14	1140	30	4.3

Figures 4 through 16

Relative Intensity vs. Concentration
of the Following Raman Bands.

For each spectrum, the 833 cm^{-1} band is used as a reference. The relative intensities of this band are defined as 1.0 and are denoted by $\odot$ as a reminder. For each band, the relative intensity $\frac{I_i}{I_{833}}$ is given which is simply a ratio of the band height in question relative to the 833 cm^{-1} band. For a particular Grignard reagent the relative intensity vs concentration plots are generally smooth. For different Grignard reagents, bands assigned the same vibration have plots of similar shape.

Those intensities that were determined by use of the curve resolver are denoted by $\odot$.



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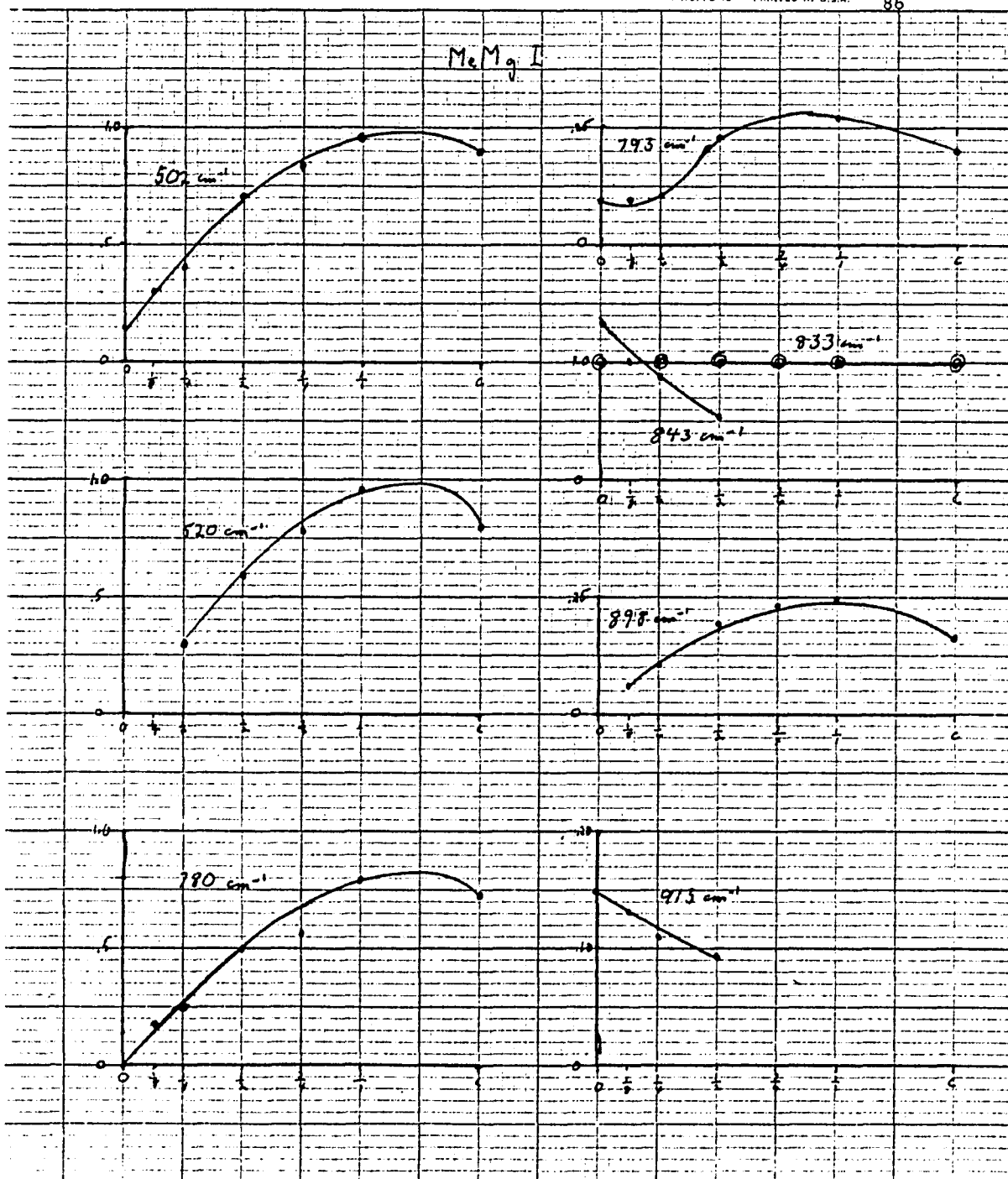
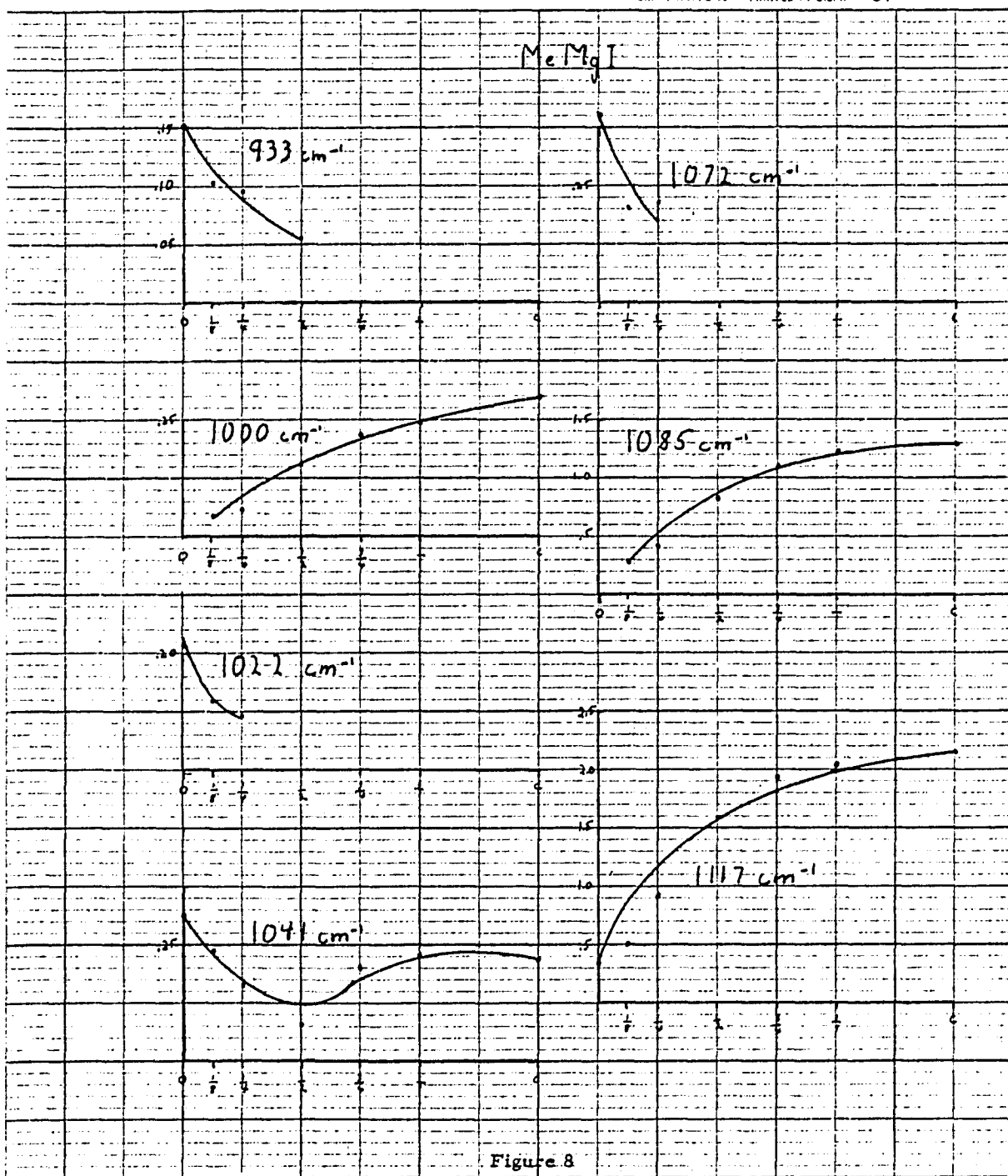


Figure 5

75



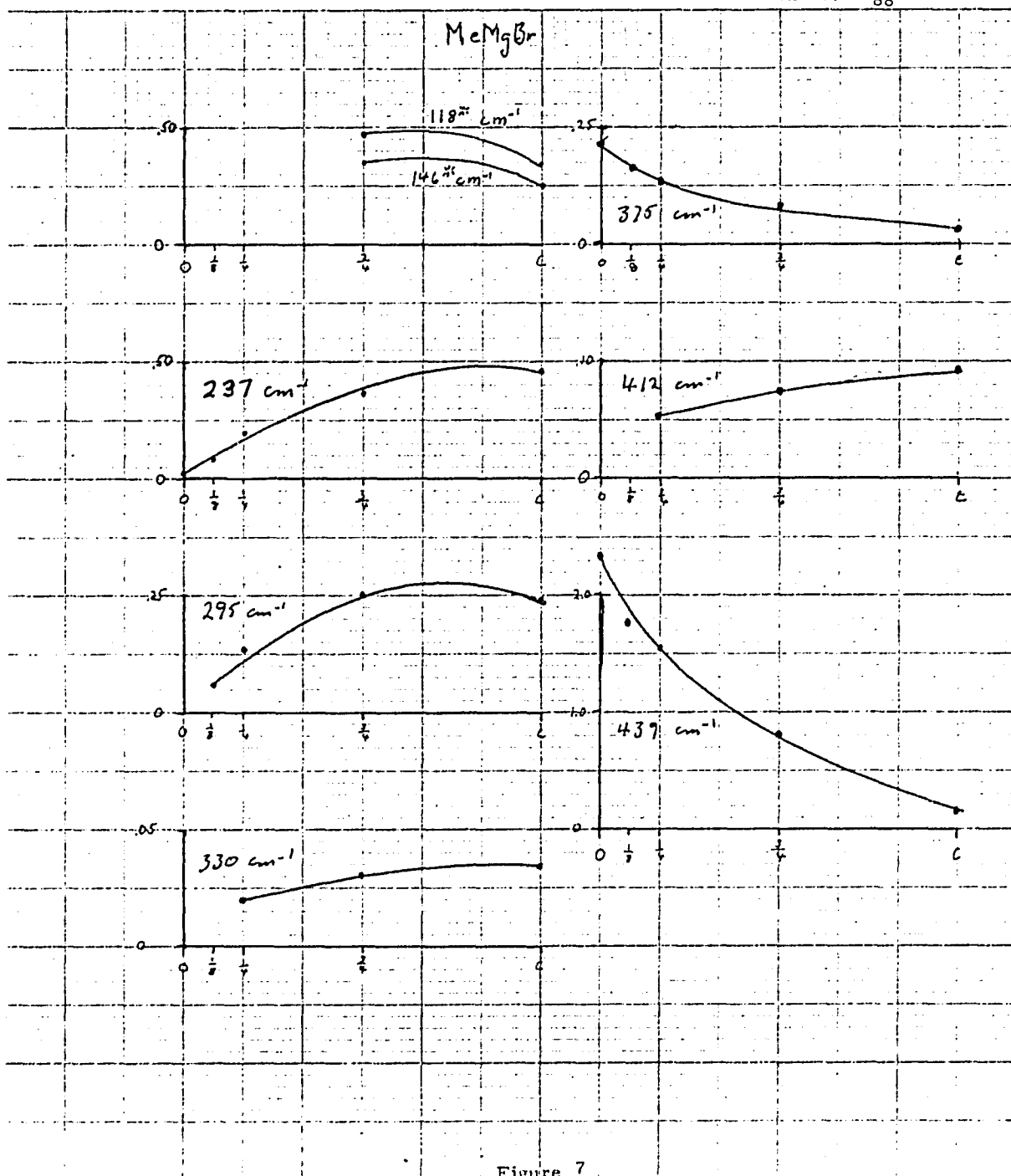


Figure 7

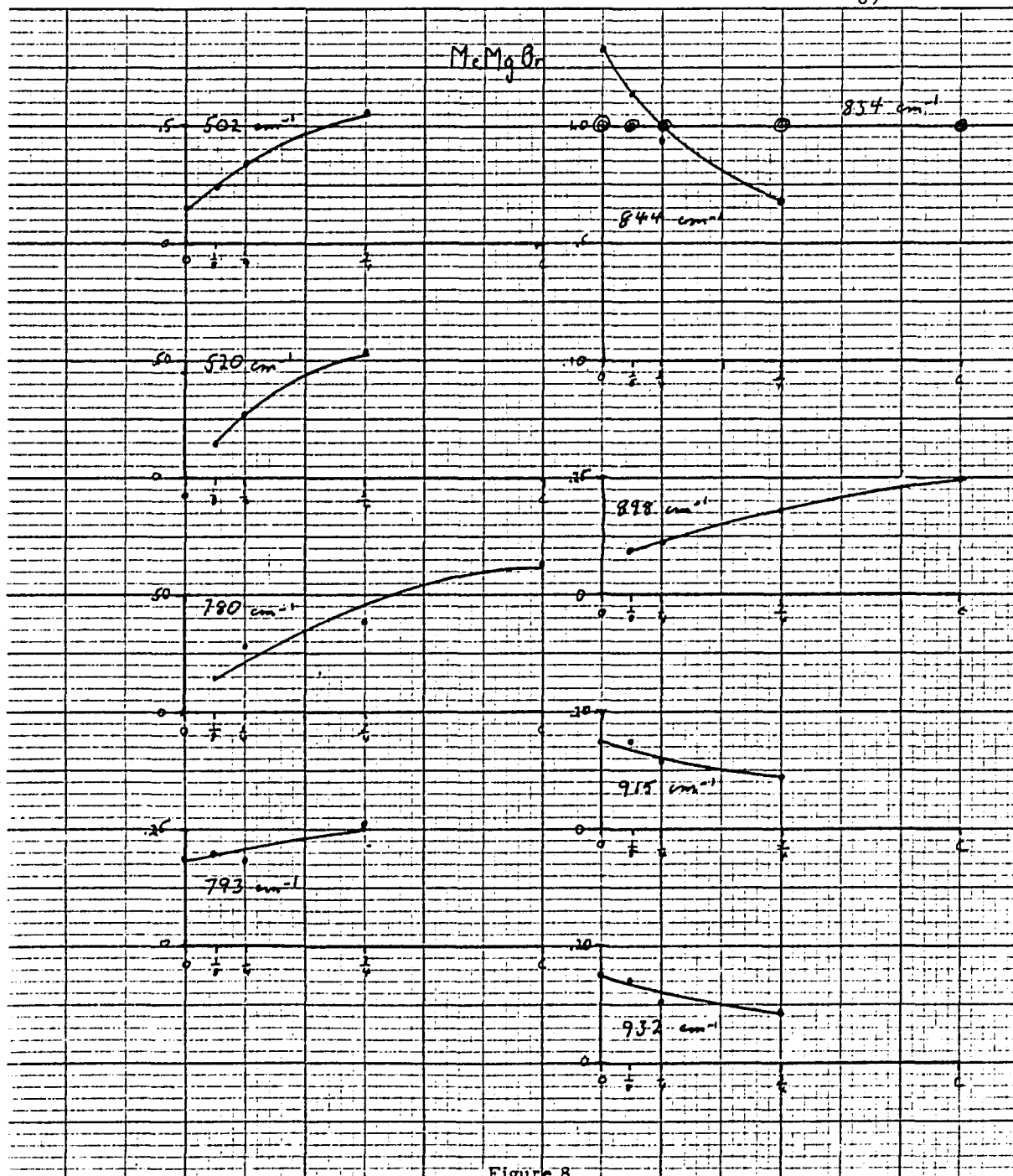
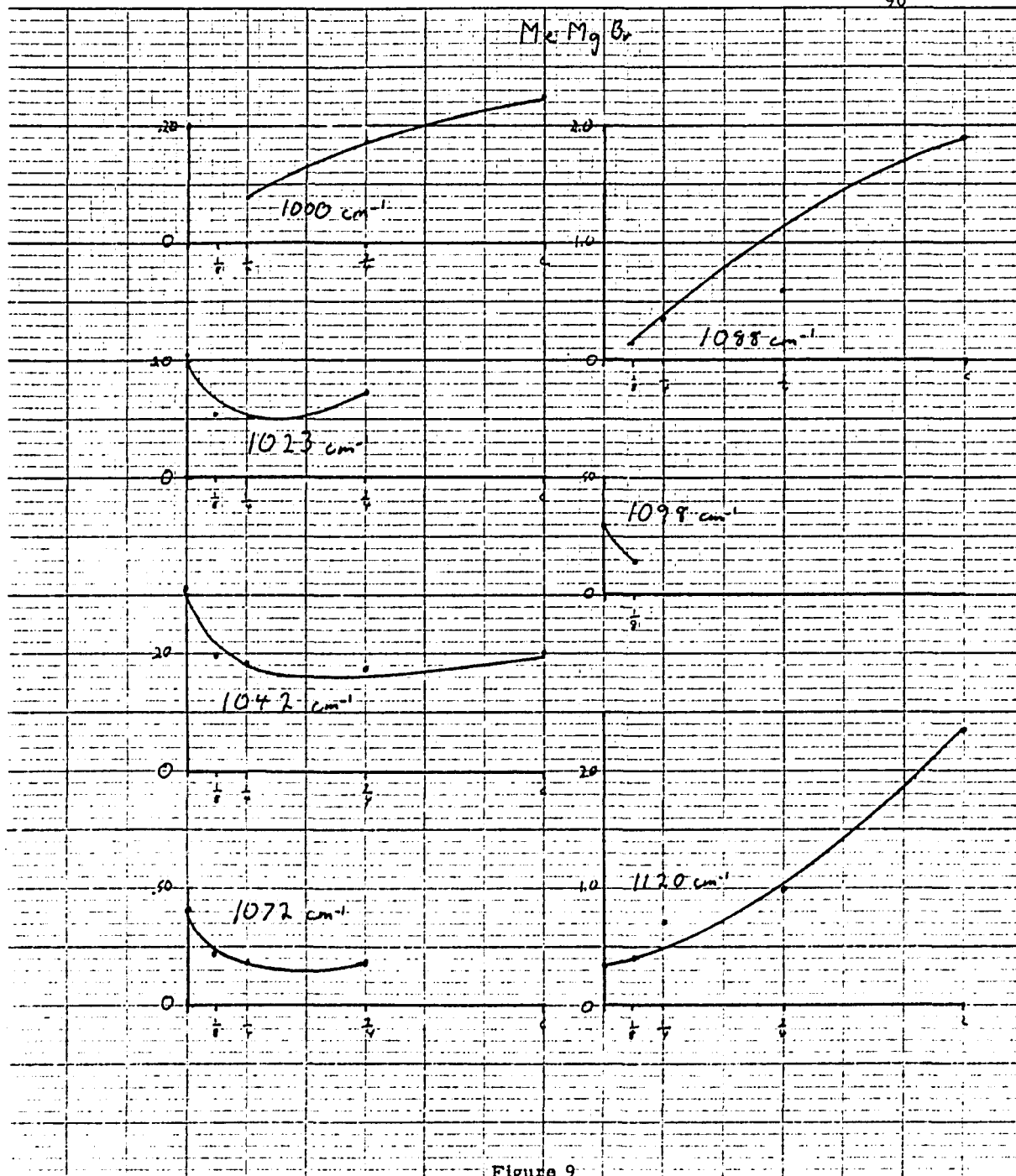


Figure 8

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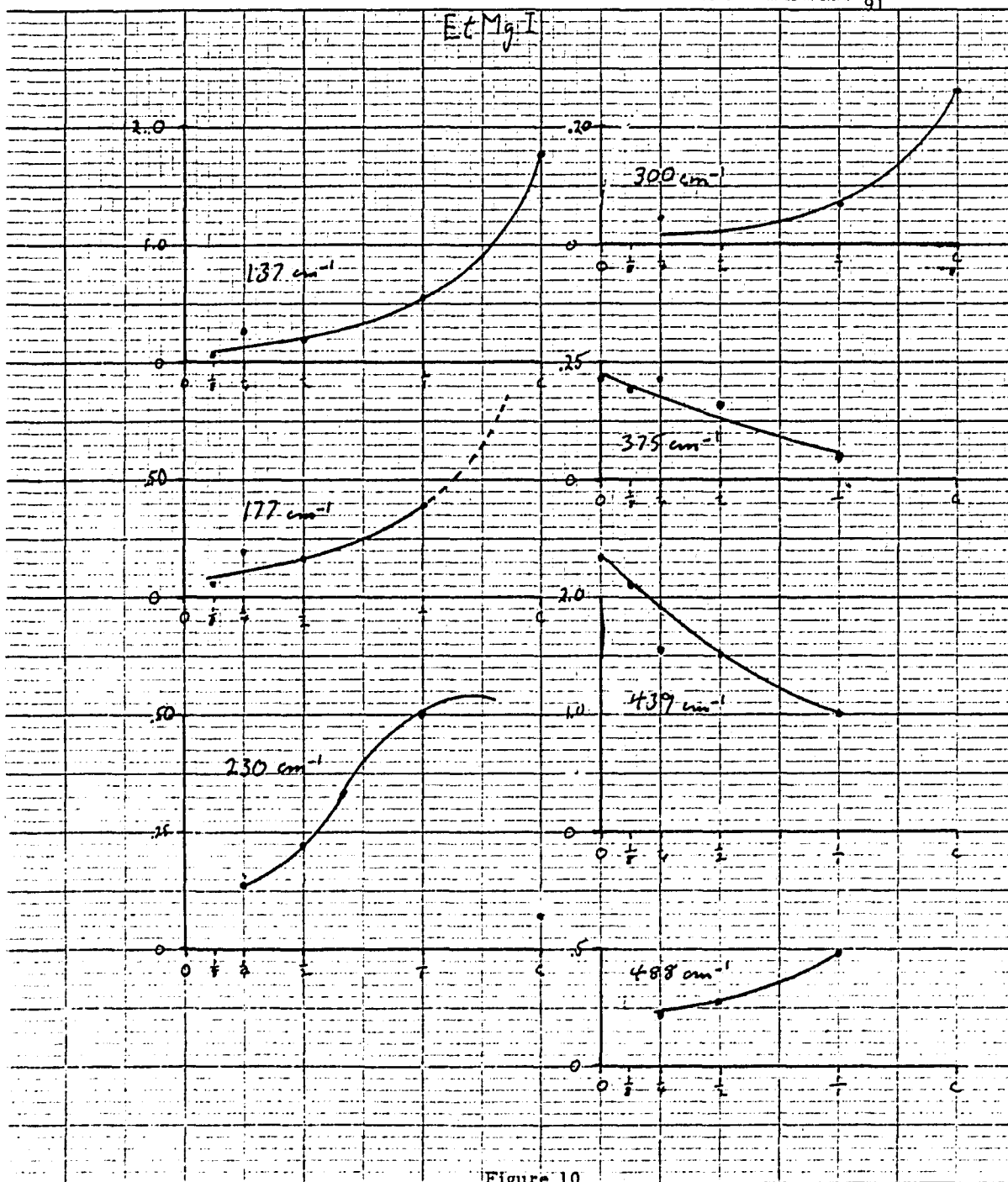
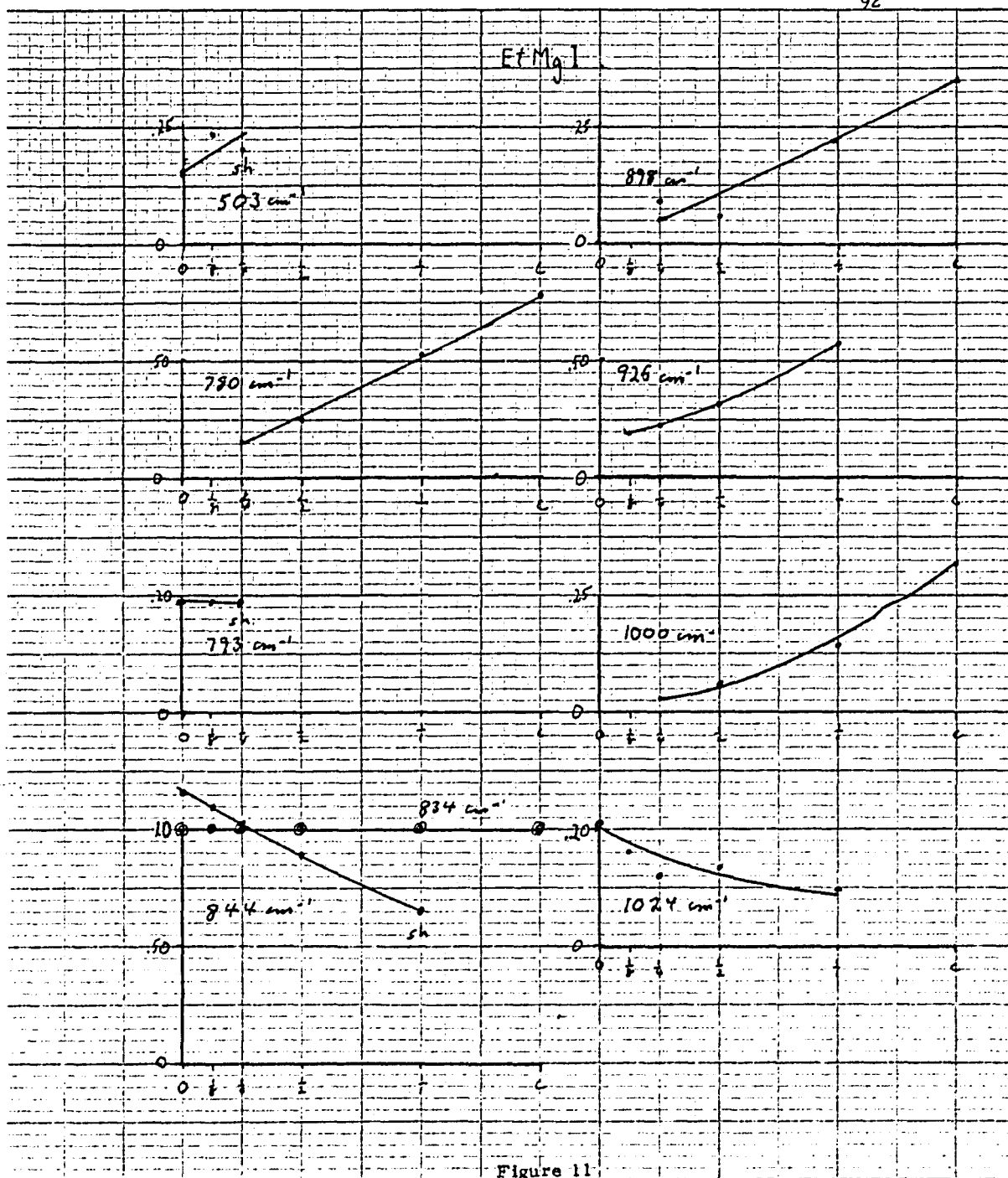
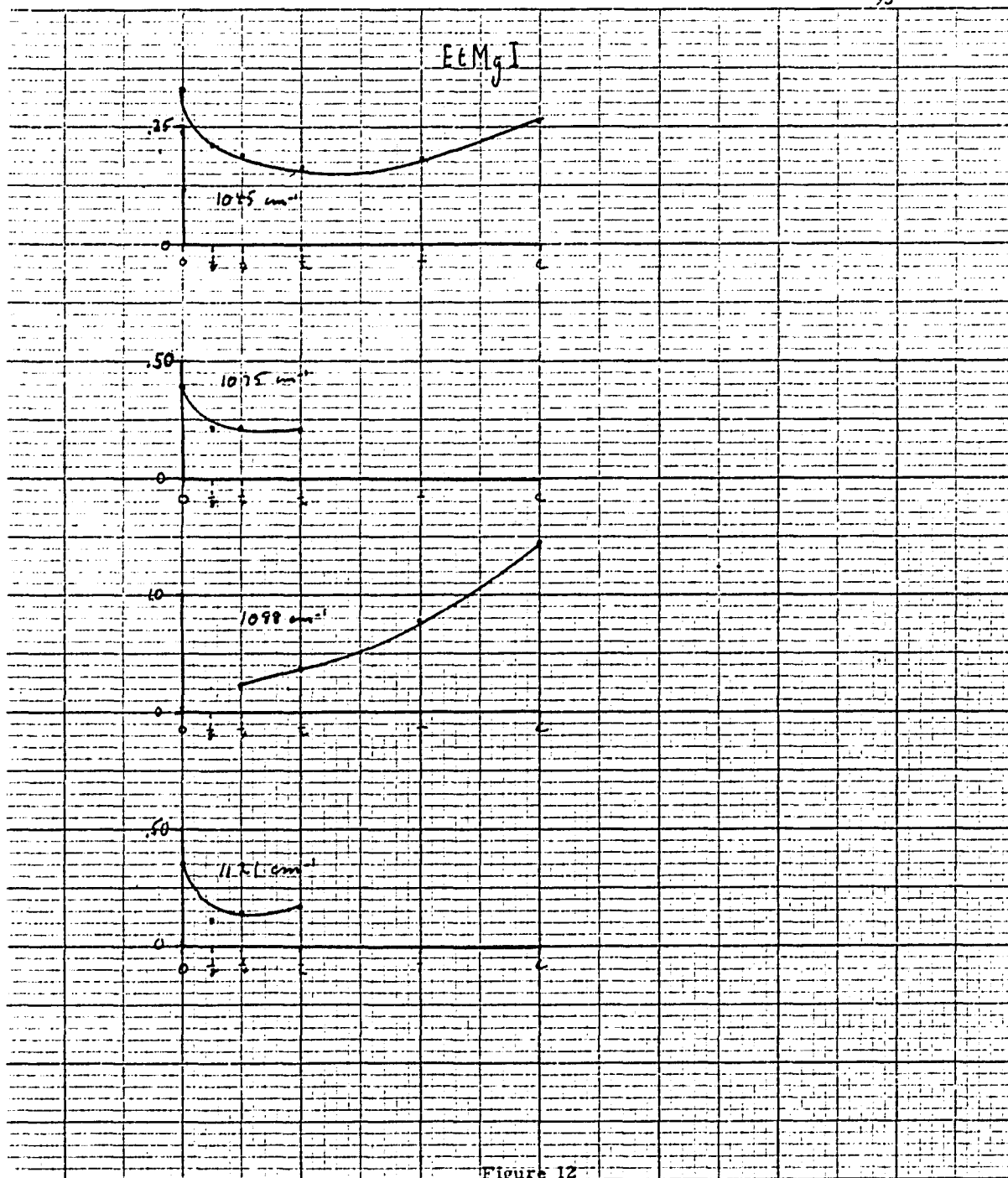


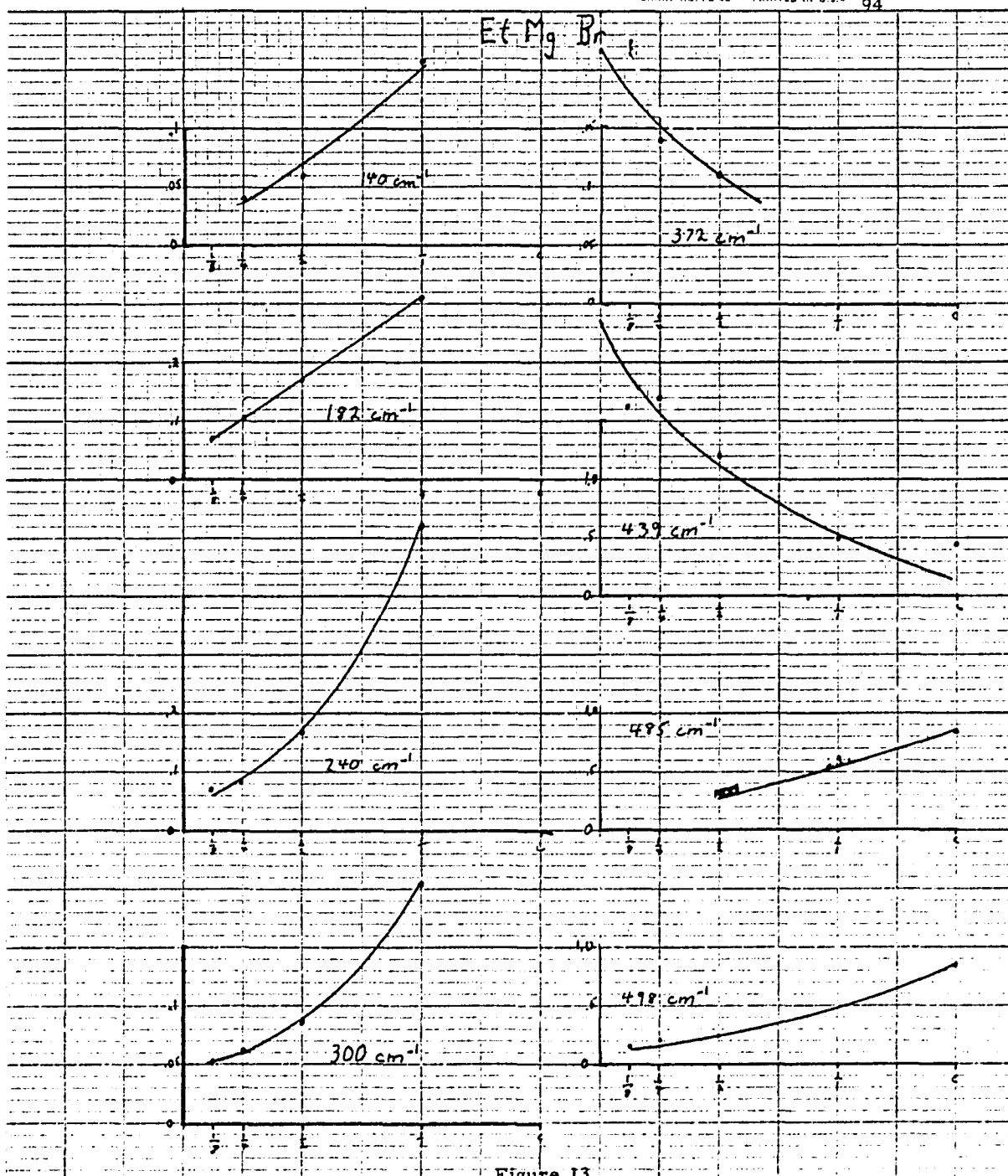
Figure 10





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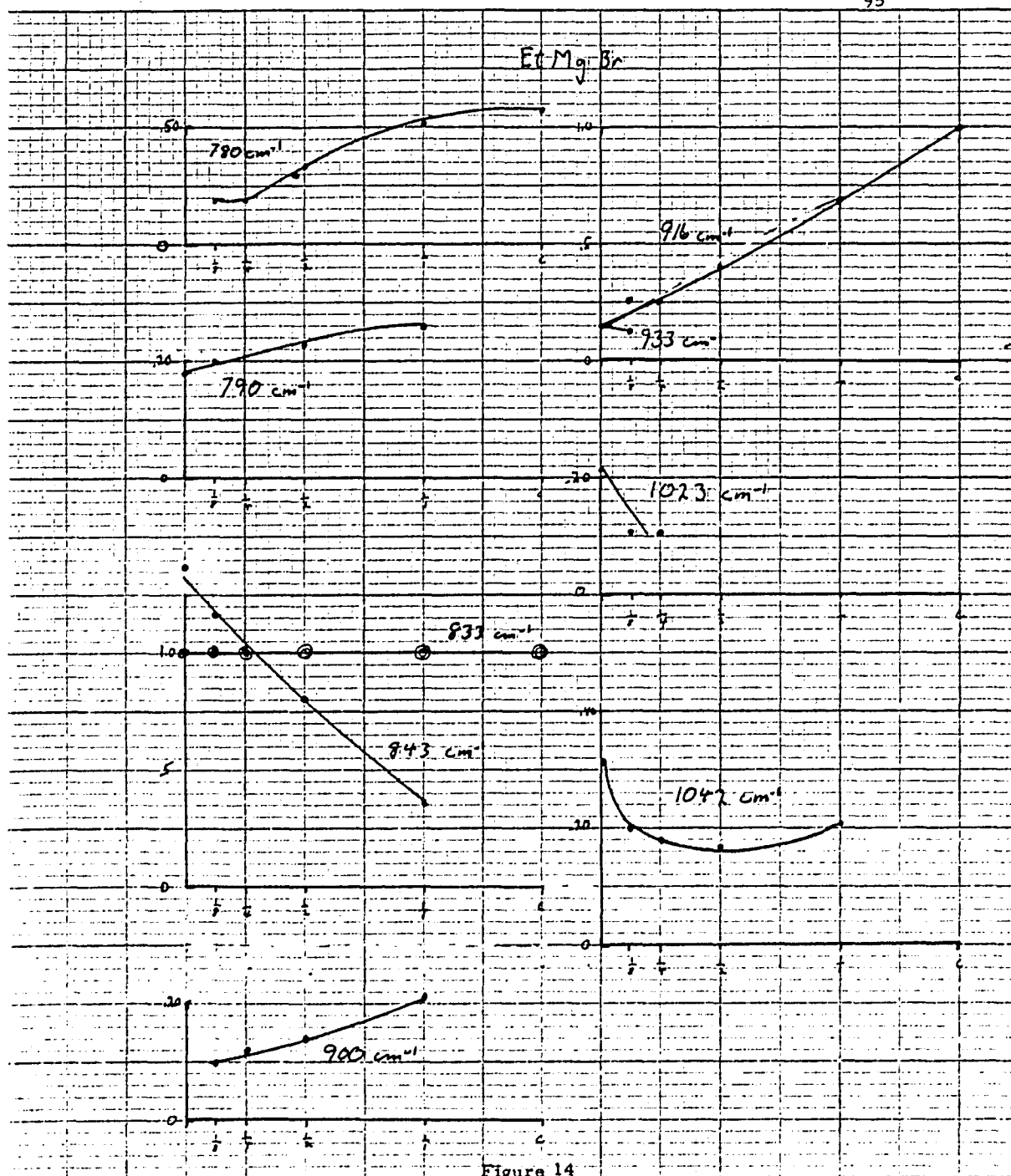
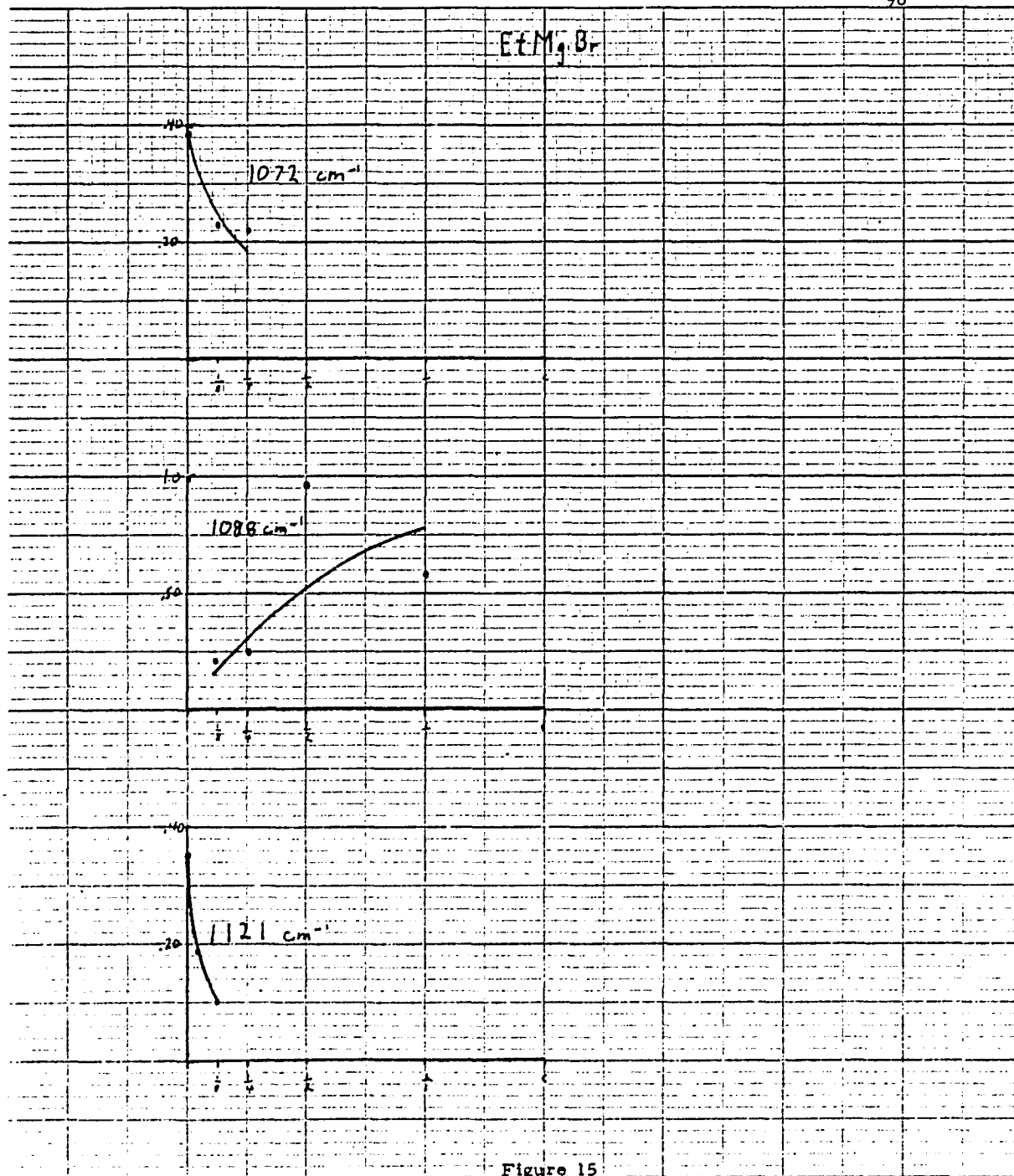


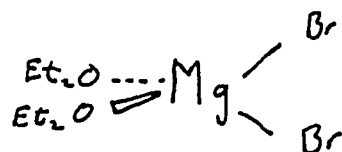
Figure 14



DISCUSSION

An appropriate beginning to a discussion of the structure of Grignard reagents is a look at the structure of MgBr_2 etherate and MgI_2 etherate because of the relation between MgX_2 and the Grignard reagent via the Schlenk equilibrium. The relatively small values of the equilibrium constant for the Schlenk equilibrium (see Table 1) and similarity of structures of reactants would suggest that the coordination number of the reactants is similar to that of the products. It is generally agreed that the coordination number of dialkyl and diaryl magnesium is four (see Introduction). Evidence will be presented to show that MgI_2 etherate and MgBr_2 etherate upper (dilute) and lower (concentrated) solutions are four coordinate and the spectra of Grignards are consistent with a coordination number of four for magnesium.

An X-ray diffraction study²⁸ has shown crystalline $\text{MgBr}_2 \cdot 2\text{Et}_2\text{O}$ to be tetrahedral magnesium and monomeric.

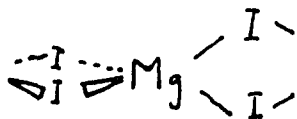


The same is likely to be true of MgI_2 . Both crystallize at room temperature to a $\text{MgX}_2/\text{Et}_2\text{O}$ ratio of 1/2.

Wieser and Krueger,³⁶ in a Raman and infrared study, interpret the spectra of the upper phase MgI_2 solution to indicate four coordinate tetrahedral magnesium and hexacoordinate D_{2h} polymer MgI_4O_2 for the concentrated layer of the lower phase. The Raman data below 305 cm^{-1} for MgI_2 in the lower and upper phase and $\text{MgI}_2 \cdot 2\text{Et}_2\text{O}$ crystal of Wieser and Krueger are presented in Table 23. Also included are our Raman data of the lower phase.

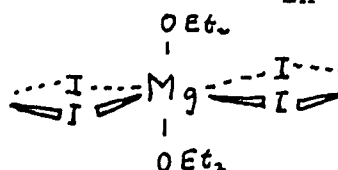
It is generally agreed that the two symmetries under consideration for the multimer structures of the two phases are the following:

Four Coordinate C_{2v}



Expected: Four Mg-X stretch
($2A_1 + B_1 + B_2$).
All are Raman active.

Six Coordinate D_{2h}



Skeleton with planar bridges.
Expected: Four Mg-I stretch
($A_g + B_{1g} + B_{2u} + B_{3u}$).

A_g and B_{1g} are Raman active.

The upper phase was considered to be four coordinate by Wieser and Krueger as more than two Mg-I stretching frequencies were observed. The concentrated solution was considered six coordinate as only two bands were observed, consistent with the A_{1g} and B_{1g} bands expected. According to Le Chatelier's principle, if a change in

Table 23

Raman MgI_2 Etherate at 300° K

Our Work Lower Phase	Upper Phase*	Lower Phase*	Crystal*	Assignments*
111s				
	112m		111s	Mg-I bend monomer
140m dp				
	143	147s		
146m p				Mg-I stretch polymer
	163	163s		
163m p				
	183w		183w	Mg-I stretch monomer
183w dp				

*From Wieser and Kreger.³⁶

coordination number were to occur, the opposite would be expected. That is, in the dilute solution with a higher ratio of ether to solute, the equilibrium would favor the species having more coordinated ether.

Wieser and Krueger did not report the depolarization ratios of the bands. Such studies are important in assigning the vibrations and are reported in this thesis. Of the five bands found in the lower phase at low frequency, three bands were polarized and two were depolarized. If one considers just the higher four frequencies, at $140\text{ cm}^{-1}(\text{s}, \text{p})$, $146\text{ cm}^{-1}(\text{m}, \text{p})$, $163\text{ cm}^{-1}(\text{m}, \text{dp})$ and $183\text{ cm}^{-1}(\text{w}, \text{dp})$, to be Mg-I stretches, this is consistent with the expected four coordinate C_{2v} structure with the two A_1 bands expected to be polarized and the B_1 and B_2 each to be depolarized. However, it will be argued that the $111\text{ cm}^{-1}(\text{s}, \text{p})$ band in the lower phase may be a normal coordinate containing the symmetric Mg-I stretch and not an Mg-I bend as assigned by Wieser and Krueger. With the addition of association data of Walker and Ashby,¹⁵ (see Figure 1) doubt is cast on the two bands assigned as monomer by Wieser and Krueger. With the data available to Wieser and Krueger the monomer assignments were reasonable. The X-ray crystal data showed the crystal to be monomeric and to contain four coordinate magnesium. There was, and still is, reasonably good evidence that the crystal was a monomer. Two bands in the upper phase appeared at the same frequency as the crystal and seemed to disappear in the concentrated phase, hence the monomeric assignment. Our data show that these

same bands appear in the lower phase.

Walker and Ashby¹⁵ show that MgI_2 in Et_2O has an i (association or number of magnesium units per molecule) value of 2.5 for 0.5m. Assuming the i value to increase linearly, the concentration of the lower 1.4M MgI_2 would have an i value of $1 + 1.5/.5 (1.4) = 5.2$. (This is a conservative estimate as an exponential increase would be expected at high concentrations because, in this case, association is expected to be a function of solute/solvent ratio.) At this i value one would expect the concentration of monomer to be too small to show a significant intensity.

If the 111 cm^{-1} band were a stretching mode, how could one account for five bands instead of the expected four? The C_{2v} skeleton is approximate, the basic structure being a pentamer with the ends of the chain coordinated to the oxygen of diethyl ether. For this structure (an) extra band(s) would be expected, either the polarized 146 cm^{-1} or 163 cm^{-1} band being the best candidate. There are two reasons for this: First, polarized bands are more intense and are therefore more likely to be observed; second, the end of the chain probably has lower symmetry, causing vibrations at the end of the chain to be totally symmetric, hence polarized. This assignment would leave the polarized 111 cm^{-1} band for the lowest frequency and the depolarized 183 cm^{-1} band as the highest frequency, which is consistent with the lower frequency expected to be of A_1 symmetry (where the iodines

alone vibrate against a motionless magnesium atom) relative to the higher expected frequency of an asymmetric B_1 or B_2 band.

The coincidence in frequencies of the 111 cm^{-1} and 183 cm^{-1} bands in a solution containing multimers and in supposedly monomeric crystal is difficult to resolve. Since the structures of the two species are so different there seems to be no reason why the coincidence is observed, however two possible reasons come to mind. One is that it is an accident and the other is that the crystal of MgI_2 etherate may not be a monomer. The solid may crystallize in different forms depending on the method of crystallization. The same problem exists for Grignard compounds; the solution multimer spectra have similar bands to the "monomeric" crystal. Guggenburger and Rundle,²⁶ who did the X-ray structure of $\text{EtMgBr} \cdot 2\text{Et}_2\text{O}$, point out, in a discussion of crystal growth, that different methods of forming crystals "may indeed be significant."

The large difference in frequency between the 111 cm^{-1} band and the 183 cm^{-1} band in the lower (solution) phase of MgI_2 etherate, where the bands are assigned symmetric and asymmetric stretches respectively of the C_{2v} multimer, may appear surprising until the literature is more closely examined. The easiest compounds to compare are $T_d\text{MX}_4$ compounds where ν_1 and ν_3 are A_{1g} symmetric and asymmetric stretches respectively. ν_2 and ν_4 are bending modes (see Table 24). All compounds of MI_4 from Ross⁵¹ are listed, having

Table 24
Selected Frequencies of ML_4^n Species

		$\nu_1 A_1$	$\nu_2 E$	$\nu_3 F_2$	$\nu_4 F_2$	$\nu_3 - \nu_1$	$\frac{\nu_3 - \nu_1}{\nu_3}$	100%
gases	CH_4	2917	1534	3019	1306	102	3.38	
	CD_4	2109	1092	2259	996	150	6.64	
	SiH_4	2187	975	2190	914	3	.14	
	GeH_4	2106	931	2114	914	8	.38	
	GeD_4	1504	665	1522	596	18	1.18	
IR R solid	$(Et_4N)_2MnI_4$	108	-	193	56	85	44	
R solid	Cs_2ZnI_4	130	60	172	70	42	24	
R sol'n H_2O	CdI_4	117	45	147	37	30	22	
R sol'n H_2O	HgI_4	126	35	140	41	14	10	
R sol'n	GaI_4^-	145	52	222	73	77	34.6	
R sol'n	InI_4^-	139	42	185	58	46	24.8	
IR R solid	Cl_4	178	90	555	123	377	68	
R liquid	SiI_4	168	63	168	94	0?	0?	
R sol'n CS_2	GeI_4	159	60	264	80	105	40	
R sol'n CCl_4	SnI_4	149	47	216	63	67	31	

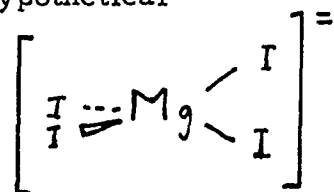
ν_1 = symmetric stretch

ν_3 = asymmetric stretch

ν_2 and ν_4 = bending modes

Columns $\nu_1 A_1$, $\nu_2 E$, $\nu_3 F_2$, and $\nu_4 F_2$ from Ross.⁵¹

been abstracted unselectively. Columns showing $\nu_3 - \nu_1$ and $(\nu_3 - \nu_1/\nu_3) 100\%$ were added from these data. The data show that large atomic weight cations and small atomic weight anions result in a small $\nu_3 - \nu_1/\nu_3$. Note how much smaller $\nu_3 - \nu_1/\nu_3$ is for GeH_4 and SiH_4 compared to CH_4 and how the deuterated compounds in each case have larger values. Looking at the MI_4 compounds we notice the same trend within metals in the same column: Mn, Zn, Cd, Hg; Ga, In; and C, Ge, Sn. SiI_4 is the only compound that does not fit, and there appears to be an error in assignment of bands here. In general, taking all compounds together, the data appear to fit this model (see Figure 4). With the hypothetical



the predicted value of $\nu_3 - \nu_1/\nu_3 = 0.60$. If $\nu_3 = 183 \text{ cm}^{-1}$ (Mg-I assigned asymmetric stretch for the MgI_2 etherate lower phase), $\nu_1 = 73 \text{ cm}^{-1}$ predicted from all compounds. Using the divalent series Mn, Zn, Cd and Hg, $\nu_3 - \nu_1/\nu_3 = 0.46$, and for $\nu_3 = 183 \text{ cm}^{-1}$, the predicted $\nu_1 = 99 \text{ cm}^{-1}$.

In a qualitative sense the reason for the observed trend is easy to understand. In a compound like Cl_4 , the carbon atom doesn't move in the symmetric stretch and the frequency is a function solely of the mass of the iodine atom and the C-I stretch force constant. In the asymmetric stretch, where the mass ratio of four iodine to one carbon

Figure 16

$$\frac{\nu_3 - \nu_1}{\nu_3} \cdot 100\% \quad \text{vs. atomic mass of the metal atom.}$$

ν_3 = asymmetric frequency

ν_1 = symmetric frequency

□ = tetra valent MI_4 compounds

○ = trivalent MI_4 species

● = divalent MI_4 species

} T_d symmetry

_____ = average for all species (except SiI_4)

----- = average for divalent species

The graph shows that the relative difference between symmetric and asymmetric frequencies increases with smaller atomic mass for all MI_4^{n-} species of T_d symmetry.

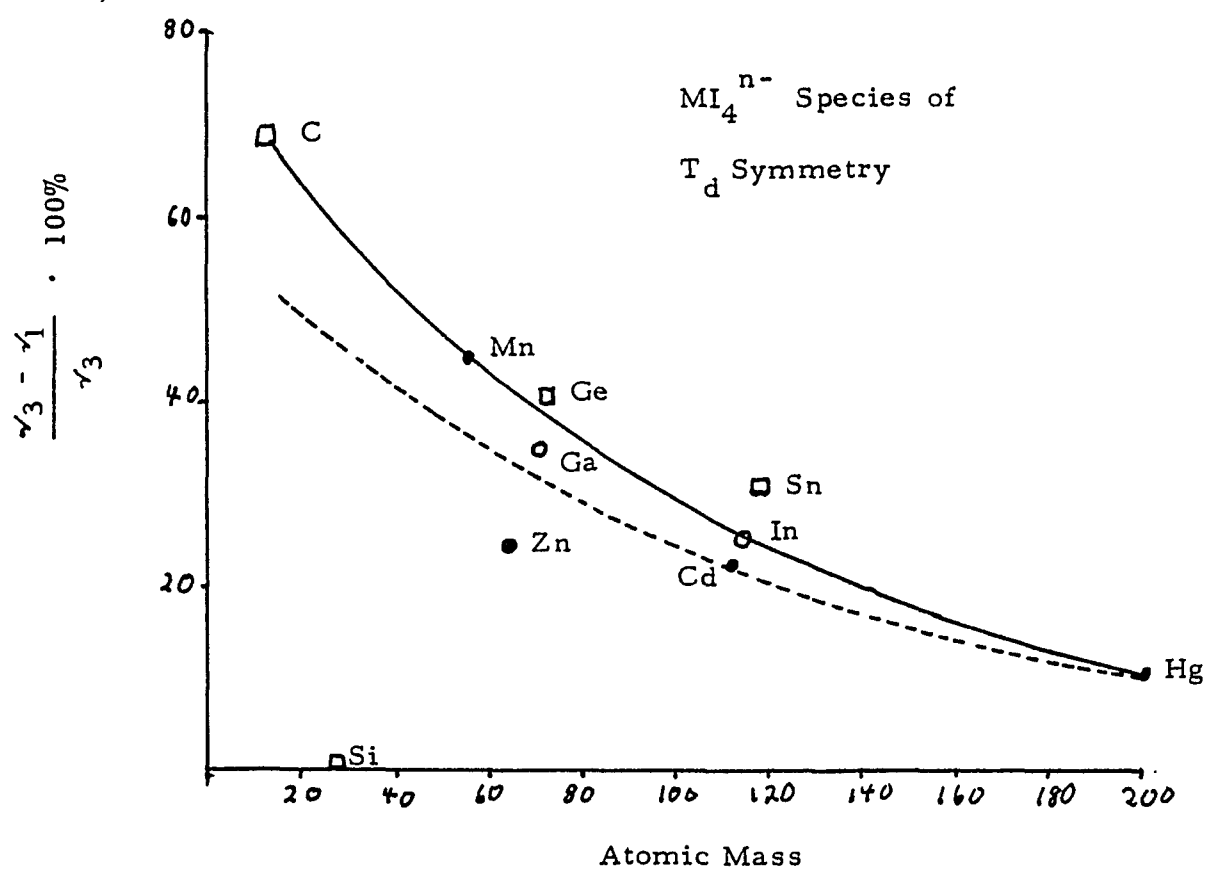
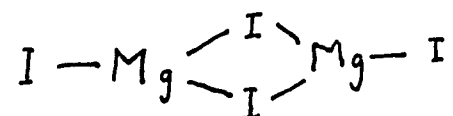


Figure 16

is forty-two to one, the iodine atoms are essentially motionless and only the carbon atom moves. For hypothetically fixed iodine atoms, in the asymmetric mode, the ratio of symmetric frequency/asymmetric frequency = $\sqrt{\frac{\text{atomic mass iodine}}{\text{atomic mass carbon}}} = \sqrt{\frac{126}{12}} = 3.24$, while the actual ratio is $\frac{555 \text{ cm}^{-1}}{178 \text{ cm}^{-1}} = 3.14$.

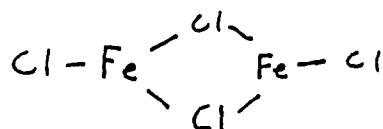
It is recognized that the T_d symmetry of the compounds presented and the C_{2v} MgI_2 etherate multimer are different but the working principle should be the same. For MgI_2 etherate multimer, if one takes into account the 2I/1Mg ratio, then the effective mass of magnesium is twice as much when comparing data from Table 24. For atomic mass = 48 ($2 \cdot 24$), $\sqrt[3]{3} - \sqrt[3]{1} / \sqrt[3]{3} \cdot 100\% = 38$ (see Figure 16) and the predicted $\nu_1 = 113 \text{ cm}^{-1}$. This result seems surprisingly close to the observed frequency, especially with the observed scatter of data in Figure 4 and the possible perturbation caused by bridging iodine. Thus, the reported value of 111 cm^{-1} is quite consistent with the expected value for Mg-I symmetric stretch.

The A_{1g} symmetric stretching and bending modes of MgI_2 etherate solution may also be estimated from matrix isolation studies of Mg_2I_4 , found to have the bridged structure below of D_{2h} symmetry.



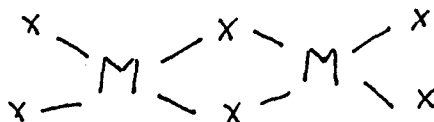
The A_{1g} ν_2 ring stretch is found at 110 cm^{-1} , remarkably close to the 111 cm^{-1} band found in solution. The ring bend is not found,

however, a rough estimate can be made. Frey, Werder, and Günthard⁵² have calculated the twelve vibrations expected for Fe_2Cl_4 .



The calculations seem to be good, at least for three infrared bands where the precise frequency was predicted. The calculated $A_{1g} \nu_3$ ring bend was 103 cm^{-1} and the calculated $A_{1g} \nu_2$ ring stretch was 250 cm^{-1} . Thus $\nu_3/\nu_2 = 0.4$ for Fe_2Cl_4 . By comparison, the $A_{1g} \nu_3$ ring bend is predicted to be approximately 45 cm^{-1} , agreeing with an estimate of between 30 and 60 cm^{-1} from Table 24.

Before we go on to evaluate the spectra of the Grignard reagents, it will be useful to abstract some known information about bridged structures. Adams and Churchill⁵³ report on the vibrational spectra of Au_2Cl_6 , Al_2Br_6 , Al_2I_6 and In_2I_6 . The compounds have the general structure



The Au compound is planar and the Al and In compounds have a T_d symmetry around the metal. In a force constant calculation, Adams and Churchill show Au-Cl terminal (t) stretch force constant (f. k.) = $2.384 \text{ mdynes/\AA}$ and AuCl bridge (b) stretch f. k. = $1.740 \text{ mdynes/\AA}$. b stretch f. k. / t stretch f. k. = 0.73. Calculations on Al_2Cl_6 and Ga_2Cl_6 , both with T_d metal geometries show b stretch f. k. / t stretch

f.k. = 0.50. They suggest that the sharing of an edge between two square planes produces little distortion but the same sharing for two tetrahedra allows the metal atoms to interact producing electrostatic repulsion causing the bridge bonds to be longer. Pauling's rule is quoted, "The presence of shared edges . . . in a coordinated structure decreases its stability; this effect is large for cations with large valency and small ligancy."⁵⁴ Adams and Churchill state that the result, $k_b = k_t/2$, is generally true for halogen bridges between tetrahedrally coordinated metal atoms. In the Al_2X_6 compounds where the normal coordinates are much less mixed in contrast to Au_2Cl_6 , the ratio of the force constants for the $Al-X_t$ stretch/ $Al-X_b$ stretch more closely parallels the ratio of the ν_1/ν_2 frequencies. An observed frequency results from a mixture of normal coordinates. The mixing, of course, can only occur among normal coordinates of the same symmetry. It is useful to remember that greater mixing is expected when frequencies of the same symmetry are found close together.

For Al_2Br_6 , in the Raman, the $A_{1g}\nu_2$ bridge stretch/ $A_{1g}\nu_1$ terminal stretch = $212\text{ cm}^{-1}/410\text{ cm}^{-1} = 0.52$ and in the infrared, the $B_{3u}\nu_{17}$ bridge stretch/ ν_{16} terminal bridge stretch is $198\text{ cm}^{-1}/373\text{ cm}^{-1} = 0.53$ while in Al_2I_6 , the same B_{3u} ratio is $143\text{ cm}^{-1}/334\text{ cm}^{-1} = 0.43$ and for In_2I_6 , it is $125\text{ cm}^{-1}/178\text{ cm}^{-1} = 0.70$.⁵¹

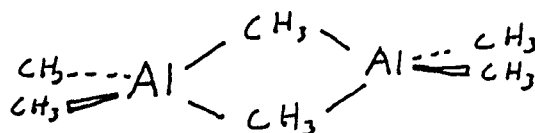
A ratio of about the same value is observed for the bending modes. Adams and Churchill⁵³ report, in the Raman spectra of Al_2Br_6 , the

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$A_{1g} \gamma_4$ ring deformation (bridge bend)/ $A_{1g} \gamma_3$ terminal MX_2 deformation
 $= 70p \text{ cm}^{-1} / 142p \text{ cm}^{-1} = 0.49$. Corresponding ratios in the infrared
 cannot be determined because the $B_{1u} \gamma_{10}$ ring deformation (bridge
 bend) was reported as not observed for Al_2Br_6 , Al_2I_6 and In_2I_6 , how-
 ever, the corresponding B_{3u} terminal MX_2 deformation (terminal bend)
 is 110 cm^{-1} , 66 cm^{-1} and 59 cm^{-1} . Beattie, Gilson and Ozin⁵⁵ report
 the following results:

γ_1	γ_2	γ_3	γ_4		$\frac{\gamma_2}{\gamma_3}$
348 cm^{-1}	148 cm^{-1}	95 cm^{-1}	56 cm^{-1}	Al_2I_6	.59
291 cm^{-1}	204 cm^{-1}	119 cm^{-1}	64 cm^{-1}	Ga_2Br_6	.54
229 cm^{-1}	143 cm^{-1}	85 cm^{-1}	50 cm^{-1}	Ga_2I_6	.59
187 cm^{-1}	134 cm^{-1}	69 cm^{-1}	40 cm^{-1}	In_2I_6	.58

Methyl bridging, which will be proposed in the structure of
 Grignard compounds is a well characterized phenomenon, as shown
 in the following example:



$Al_2(CH_3)_6$ has an identical skeleton symmetry to Al_2X_6 compounds,
 Gray⁵⁶ lists $\gamma_2 = 453 \text{ cm}^{-1}$ and $\gamma_1 = 592 \text{ cm}^{-1}$: $\gamma_2 / \gamma_1 = 0.767$.

Before we discuss the spectra in detail, it is useful to note some
 general information relating to the structure of Grignard compounds.

Halogen bridging is generally accepted to occur in diethyl ether solutions. Phenyl and alkyl groups may also form bridges. Among alkyl groups, Ashby¹⁵ has shown, from ebullioscopic studies, that methyl is a significantly better moiety for bridging than ethyl and longer alkyl groups. In Grignard solutions that are not dilute, one would expect varying values of multimers to be in equilibrium, and the more concentrated the solution, the longer the average chain length. Also, for a multimer of a given length, several species are likely to be present.

In the subsequent discussion of Grignard compounds there are included data from the articles of Kress and Novak^{40, 41, 45, 46, 47} who have, as mentioned in the Introduction, reported Raman and infrared spectra of various Grignards, both solid and solution, plus MgBr_2 etherate and diethyl magnesium. Most of the Raman and infrared bands are found to be coincident, and as noted previously, the solution spectra of Grignards were observed to be quite similar to the solid. Principally, on that basis, RMgX , where $\text{R} = \text{Me, Et}$ and $\text{X} = \text{Br, I}$, Grignards in solution were assigned as monomers. We will demonstrate that Grignard spectra are consistent with multimer formation showing increased association with increasing concentration. At the same time it is difficult to reconcile the similarity of solution and solid, for a monomeric solid and a multimeric solution would appear to require significantly different spectra. A possible explanation is that the crystals used for spectroscopy may have been formed differently than those used for X-ray crystallography.

TABLE 25

Bands Below 550 cm^{-1} of $\text{C}_2\text{H}_5\text{Cl} \cdot (\text{C}_2\text{H}_5)_2\text{O}$

Assignment	IR 90°K vitreous	Raman 300°K liquid	Raman 90°K crystal
			543vw
rock (CH_2) (terminal & bridge) and $\delta(\text{COC})$	510vs	502m	525w 505m 491m
$\nu(\text{MgC})$ terminal	486sh	498vs, p	479m
$\delta(\text{CCO})$	464w		461sh 417vw
	410w	409w, p	409vw
	385vw		393vw
$\nu(\text{MgCMg})$ bridge			364vs
$\delta(\text{CCO})$	338sh	322w, p	339sh
$\nu(\text{MgO})$			330m
	322sh		314vw
$\nu\text{Mg}_2\text{Cl}_2$	$\begin{cases} 288\text{vs} \\ 278\text{vs} \end{cases}$		304vw
$\nu\text{Mg}_2\text{Cl}_2$		$\begin{cases} 263\text{sh, p} \\ 241\text{m, p} \end{cases}$	
$\delta(\text{MgCMg})$ bridge			289sh
$\delta(\text{MgCMg})$ bridge			274m 248w
	228vw		
$\nu(\text{MgClMg})$ bridge			225m
$\delta(\text{CCMg})$ terminal bridge		188m, p	187sh

This table is reproduced from Kress and Novak.⁴⁷

Parenthetically, it should be mentioned that many of the crystalline bands appear to be multiplets due to magnesium and chlorine isotopes. For instance, in the infrared spectrum, the ν_3 vibration of linear MgBr_2 , obtained by matrix isolation,⁵⁷ has the following assignment:

$^{24}\text{MgBr}_2$	497.1 cm^{-1}	} ν_3
$^{25}\text{MgBr}_2$	488.4 cm^{-1}	
$^{26}\text{MgBr}_2$	480.4 cm^{-1}	

The intensities are consistent with an 80% - 10% - 10% ratio of ^{24}Mg - ^{25}Mg - ^{26}Mg isotopes. In a bridged Grignard the observed isotope induced multiplet would be expected to be considerably more complicated than MgBr_2 .

Table 26 shows Raman frequencies obtained for the lower phase of MgI_2 and MgBr_2 plus the Grignards RMgX , where $\text{R} = \text{Me}$, Et and $\text{X} = \text{Br}$, I , up to 512 cm^{-1} , as well as the relative intensity data. This frequency range is most useful as this shows skeletal vibrations. Higher vibrations belong mostly to diethyl ether plus alkyl vibrations. The concentrated and 1/1 bands are compared here because, in general, the solutions from 1/8 to 1/1 show progressive enhancement of Grignard bands and progressive changes in the ether spectra. In contrast, the concentrated solution shows bands sometimes not found at all in the more dilute solutions and perhaps just emerging in the 1/1 solutions. Since the peaks between 111 cm^{-1} and 190 cm^{-1} , especially in MeMgBr

Low Frequency Lower Phase MgX_2 and Grignard Frequencies plus Relative Intensities.

(The intensities are relative to the 833 cm^{-1} band of each spectrum.)

MgI_2	MgBr_2	$\text{MeMgI}_\uparrow$	$\text{MeMgI}_{\text{low}}$	$\text{MeMgBr}_\uparrow$	$\text{MeMgBr}_{\text{low}}$	$\text{EtMgI}_\uparrow$	$\text{EtMgI}_{\text{low}}$	$\text{EtMgBr}_\uparrow$	$\text{EtMgBr}_{\text{low}}^{**}$
				82 .35	82 .36	70 .23	65 .48 98 1.96		
111s		115 .63	114 .88	118 .47	115 .34			105 .105	111 27
140m dp		137 .76	137 .97	146 .35	144 .25	142 .56	134 .89	136 .158	124 23
147m									137 13.5
167m							165 .33		
183m dp	187s*					178 .39		180 .316	
		225 1.13	225 1.07	236 .354	238 .47	230 .51	230 .074	245 .42	238 5.3
		265 .216	268 .167						
306*				290 .25	290 .24	290 .066	300 .26	295 .21	
	317w*							318 .21	
329*		330 .135	330 .083	325 .029	328 .034	327 .033			
			355 .067				349 .56		343 5.3
									363 4
380*	383vw*			377 .088	374 .028	380 .094	387 .11		382 9
									395 4.3
	417vw*	412 .108	408 .13	415 .074	411 .091		417 .22		
445*	446m*	439 .135	439 .10	439 .795	439 .16	440 1.0		439 .47	440 .43
						482 .48	(482)~.50	481 .63	482sh .86
	503vw*	502 .95	503 .90	503 .56	(503)~.7		(503)~.50		495 .86
		514 .95	515 .80	518 .53	(518)~.7				
590*							583 .074		

* Values from Wieser and Krueger³⁶.

() Two sets of () in a column indicate that a peak halfway between was composed of the two shown.

EtMgBr^{**} The unusually high intensity at low frequency may be due to a resonance Raman effect resulting from interaction with a colored impurity in the sample.

Table 26

and MeMgI solutions, are deconvoluted from one broad asymmetrical peak, the frequencies in this range are not as precise as higher frequencies.

In a previous article Kress and Novak⁴⁶ report on the spectra of $\text{CH}_3\text{MgBr}\cdot 2\text{Et}_2\text{O}$ of the solid at 90°K and the solution at 300°K , plus $\text{CD}_3\text{MgBr}\cdot 2\text{Et}_2\text{O}$ and $\text{CH}_3\text{MgI}\cdot 2\text{Et}_2\text{O}$ at 90°K (see Table 27). In both MeMgI and MeMgBr a band at about 115 cm^{-1} is observed. Both $(\text{MeMgBr})_{1/8}$ and $(\text{MeMgI})_{1/8}$ have an i value of 1.6 which means that about 60% dimer and 40% monomer exist in solution. Bands that belong to monomer species are expected to increase in intensity with concentration and then to decrease as multimer formation dominates. This would be manifested by either a band that disappears with increasing concentration or an apparent frequency shift in a band. The latter is not observed while the former is clearly a result of TT ether bands that have an appreciable intensity in neat ether. Hence, this band, and all others (not associated with ether) belong to multimer species. The band at 118 cm^{-1} (this work) is described as the Kress and Novak⁴⁶ 115 cm^{-1} $\delta(\text{CMgX})$ band consistent with a decrease in frequency to 103 cm^{-1} for $\text{CD}_3\text{MgBr}\cdot 2\text{Et}_2\text{O}$ at 300°K . This band is first observed as a small shoulder on the large background near the exciting line. Hence, as the band grows, it is difficult to measure the depolarization ratio accurately, however it is between 0.3 and 0.5 (the largest depolarization ratio observed for skeletal bands below 450 cm^{-1}) and is relatively intense. When the spectrum of the solution phase of MgI_2 etherate is

TABLE 27

Bands Below 550 cm^{-1} of $\text{CH}_3\text{MgX} \cdot 2\text{Et}_2\text{O}$, X = Br, I

Assignments	$\text{CH}_3\text{MgBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$				$\text{CH}_3\text{MgI} \cdot 2\text{Et}_2\text{O}$	
	IR 90°K	Ram 90°K I	Ram 90°K II	Ram 300°K	IR 90°K	Ram 90°K
(CH ₃)(lig)			532s			
not assigned	518vs	515sh	514sh	516s	520vs	524vs
coupled w/ δCOC		508vs	499vs	506s, p	510vs	515sh
$\nu(\text{MgC})$						
$\delta(\text{COC})$	491m	488w	507w		488m	487m
$\delta(\text{CCO})$	464m		407m		462s	
$\nu(\text{CCO})$	326w	332w	355w	329vw	325s	331m
$\nu_{\text{asy}}(\text{MgO}_2)$	304s	303w	294m	293m, p	295sh	
$\nu_{\text{sym}}(\text{MgO}_2)$	289s	288vw			287vs	286w
νMgX	246w	248s	249s	238m, p	229m	231s
δMgO_2			144s	145sh, p		140s
$\delta(\text{CMgX})$			114s	115s		113m

Bands Below 550 cm^{-1} of $\text{CD}_3\text{MgBr} \cdot 2\text{Et}_2\text{O}$
Does Not Include $(\text{C}_2\text{H}_5)_2\text{O}$ Bands

Assignments	IR 90°K	Ram 90°K I	Ram 90°K II	Ram 300°K
$\nu(\text{CH}_3)$			420s	
not assigned	408vs	410s	402s	409m
$\nu(\text{MgC})$	478s	482s	481s	486s, p
$\nu_{\text{asy}}(\text{MgO}_2)$	293s	292m	290m	285m, p
$\nu_{\text{sym}}(\text{MgO}_2)$	280m			
$\nu(\text{MgX})$	239vw	240s	247s	234m, p
$\delta(\text{MgO}_2)$				150sh
$\delta(\text{CMgX})$				103s

Form I is GG conformer of ether.

Form II is either TG or TT conformer of ether.

This table is reproduced from Kress and Novak.⁴⁶

viewed next to the methyl Grignard reagents, it is difficult not to see the similarity of these two bands in frequency and intensity. Kress and Novak⁴¹ report a band in the same region in $\text{MgBr}_2 \cdot 2\text{Et}_2\text{O}$ in the Raman at 117 cm^{-1} (vs) at -180°C , although they assign it to δMgBr_2 (see Table 28). The assignment of the MgI_2 etherate band is a ring stretch of $\text{Mg} \begin{smallmatrix} \text{X} \\ \diagup \quad \diagdown \\ \text{X} \end{smallmatrix} \text{Mg}$. As will be developed in later pages, methyl Grignard reagents are also expected to have this basic structure and it is tempting to assign the same vibration to both bands. In EtMgX etherate ($\text{X} = \text{Br}, \text{I}$) solution, however, the 118 cm^{-1} band vanishes and a new band at 183 cm^{-1} is found. A band at about 180 cm^{-1} is clearly observed in EtMgBr and EtMgI . In MeMgBr and MeMgI there may be a small band at this frequency but it is not clearly resolved. Kress and Novak⁴⁵ assign this band in EtMgI and EtMgBr to $\delta\text{Mg-C-C}$ on the basis that the frequency of this band shifts from 183 cm^{-1} for $\text{C}_2\text{H}_5\text{MgBr} \cdot 2\text{Et}_2\text{O}$ to 173 cm^{-1} for $\text{CD}_3\text{CH}_2\text{MgBr} \cdot 2\text{Et}_2\text{O}$ and $\text{C}_2\text{D}_5\text{MgBr} \cdot 2\text{Et}_2\text{O}$ of solid at 90°K . (See Table 29.) There is evidence (see the last part of the Discussion) that for long multimers the methyl Grignard reagents have the alternate bridge system of Structure IX while the EtMgI appears to tend toward the mixed bridge of Structure VIII. This suggests that the 118 cm^{-1} band is associated with two internal coordinates; the $\text{Mg} \begin{smallmatrix} \text{X} \\ \diagup \quad \diagdown \\ \text{X} \end{smallmatrix} \text{Mg}$ (ring stretch mixed with the $\delta\text{C-Mg-X}$). Likewise, the 183 cm^{-1} band is associated with $\text{Mg} \begin{smallmatrix} \text{R} \\ \diagup \quad \diagdown \\ \text{X} \end{smallmatrix} \text{Mg}$ (ring stretch) mixed with $\delta\text{C-C-Mg}$.

The band at 146 cm^{-1} for MeMgBr and 137 cm^{-1} for MeMgI is

TABLE 28
Bands Below 550 cm^{-1} of $\text{MgBr}_2 \cdot 2\text{Et}_2\text{O}$

25° C		-180° C		Assignment	
IR	Raman	IR	Raman		
		512 s	517 m		II
				δCOC	I
512 m	515 w				I
461 w		467 vw			I
				δCCO	II
395 w	396 vw	396 s	398 s		II
355 sh		364 s	364 w		II
				δCCO	I
	332 vw		341 vw		I
320 vs	313 vw				I
				$\nu_4\text{MgO}_2$	II
		315 vs	320 w		II
286 sh		290 s	298 vw	$\nu_1\text{MgO}_2$	I + II
	282 vw		278 m	$\nu_1\text{CH}_3$	II
		268 sh	269 w		II
204 vs		213 vvs	226 w	$\nu_4\text{MgBr}_2$	I + II
162 m	159 vvs	161 m	163 vvs	$\nu_1\text{MgBr}_2$	I + II
115 w		118 w	117 vs	δMgBr_2	I + II
86 vw		91 w		—	
39 vw		45 w		—	

This table is reproduced from Kress and Novak.⁴¹

TABLE 29

EtMgBr·2Et₂O & EtMgI·2Et₂O
 Bands Below 550 cm⁻¹ All at 90°K
 (Plus Last Two Assignments at 300°K)

C ₂ H ₅ MgBr·2(C ₂ H ₅) ₂ O			C ₂ H ₅ MgBr·2(C ₂ D ₅) ₂ O		C ₂ H ₅ MgI·2(C ₂ H ₅) ₂ O	
Assignment	IR	Raman	IR	Raman	IR	Raman
r(CH ₂)(lig)*	521vs	519s	520s	519m	508vs	518s
δ(COC) coupled to (Mg-C)	508vs	508m	429m	426m	508vs	508m
ν(MgC)	485s	485s	500vs	504s	481s	481m
δ(CCO)	466m	465w	410m	410w	464m	465vw
δ(CCO)	326sh	335m	283sh	288m	328s	331m
ν _{asy} (MgO ₂)	317s	314vw	306s	305w	314vs	311vw
ν _{sym} (MgO ₂)	301s	299vw	293s	-	295s	293vs
ν(MgX)	253w	248s	247w	249s	233w	224s
δ(MgCC)300°K		183m		179m		179sh
δ(MgO ₂)300°K		141s				145sh

CD ₃ CH ₃ MgBr·2Et ₂ O		CH ₃ CD ₂ MgBr·2Et ₂ O		C ₂ D ₅ MgBr·2Et ₂ O	
IR	Raman	IR	Raman	IR	Raman
503vs	501m	419s	415w	407s	406s
480s	479s	469s	471m	466vs	468m
315s	311vw	317s	312vw	313s	312vw
299s	299vw	295m	290vw	289m	282vw
247w	244s	245vw	241s	239vw	239s
	173m		182m		173w
	139m		146w		142w

This table is reproduced from Kress and Novak.⁴⁵

*r(CH₂) = rock

assigned $\delta(\text{MgO}_2)$ of the monomer by Kress and Kovak.⁴⁶ This assignment is more difficult to establish. A band in this range occurs in all the Grignard species. Also, since the frequency of a bending mode is expected to be about half the frequency of the stretching mode, and the Mg-O stretch mode is generally accepted to be about 300 cm^{-1} , the δMgO_2 assignment does not seem unreasonable for a monomeric structure but is not tenable for a doubly bridged dimer. This band is likely to be a $\nu\text{Mg-X}$.

The next band, at 225 cm^{-1} for MeMgI and 236 cm^{-1} for MeMgBr, is assigned to a $\nu\text{Mg-X}$ stretch by Kress and Novak.⁴⁶ Again the difference in frequency, about 5%, is surprisingly small as it was with the supposed $\delta\text{C-Mg-X}$. Assuming equal force constants, the expected difference in frequency would be in the range of $\left(\sqrt{\frac{\text{atomic weight iodine}}{\text{atomic weight bromine}}} - 1 \right) 100\% = 26\%$. The data do not warrant this assumption. From a cursory examination of a few low frequency bands which could possibly be Mg-X stretch, as listed below, the bands in the same line have similar intensities and intensity vs. concentration profiles suggesting that they arise from the same vibrations.

<u>MeMgI</u>	<u>MeMgBr</u>
<u>cm^{-1}</u>	<u>cm^{-1}</u>
115m	118m
137m	136m
225s	236s
265w	290w

Mg-X stretch bands would not be expected at higher frequencies. This

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same lack of dependence on halide is observed with EtMgI and EtMgBr, where bands are found at 230 cm^{-1} and 245 cm^{-1} respectively. For the four Grignard reagents each band in this region has a low depolarization ratio and is assigned to a νMgX , in agreement with Kress and Novak.^{45, 46}

The next bands considered are the 265 cm^{-1} of MeMgI, the 290 cm^{-1} of MeMgBr, and the 295 to 300 cm^{-1} of EtMgI and EtMgBr. Other workers, namely Kress and Novak,^{45, 46} assign two bands in this range to MgO_2 stretch. See Tables 27 and 29. Reproduced below are selected frequencies from Kress and Novak.⁴⁶

	$\text{CH}_3\text{MgBr}\cdot 2(\text{C}_2\text{H}_5)_2\text{O}$				$\text{CD}_3\text{MgBr}\cdot 2(\text{C}_2\text{H}_5)_2\text{O}$				$\text{CH}_3\text{MgI}\cdot 2(\text{C}_2\text{H}_5)_2\text{O}$	
	IR 90°K	Ram. 90°KI	Ram. 90°KII	Ram. 300°K	IR 90°K	Ram. 90°KI	Ram. 90°KII	Ram. 300°K	IR 90°K	Ram. 90°K
asym νMgO_2	304s	303w	294m	293m, p	293s	292m	290m	285m, p	295sh	
sym νMgO_2	289s	288vw			280m				287vs	286w
Mg-X	246w	248s	249s	238m, p	239vw	240s	247s	234m, p	229m	

It would appear that the data of Kress and Novak are not consistent with the usual intensity changes associated with infrared and Raman bands, nor with the relative intensities expected for bands of differing polarizabilities. Usually, in the Raman, symmetric bands are more intense than asymmetric bands. The reverse is observed with the

above methyl magnesium bromide etherate bands of Kress and Novak. In addition, the Raman intensities of the assigned ν Mg-O and ν Mg-I bands are comparable in intensity in several cases, which is not expected. The intensity of Raman bands is proportional to the polarizability of the band in question. Since the Mg-O bond is considerably less covalent than Mg-I, and hence less polarizable, it is expected to be significantly less intense. These observations, in addition to other evidence, place doubt on the Kress and Novak assignments.

From our data there is no evidence for Mg-O stretches. As the concentration of the Grignard reagent increases along with multimer formation, the number of Mg-O bonds/RMgX unit will decrease as ether coordination is expected only at the ends of the predicted doubly bridged multimer unit. Since the number of Mg-X stretches is proportional to the number of RMgX units, a plot of the relative intensity of a suspected $\frac{\text{Mg-O band}}{\text{Mg-X band}}$ vs. concentration would decrease. The bands at about 225 cm^{-1} and 240 cm^{-1} for the iodo and bromo Grignard reagents respectively are accepted by most workers, including us, to be Mg-X stretches and are therefore used as a reference. This reference however, may be questionable for some Grignard reagents as there is evidence (see end of Discussion) that this band ($225 - 240\text{ cm}^{-1}$) is associated with the doubly bridged halogen $\text{Mg} \begin{smallmatrix} \text{X} \\ \diagup \quad \diagdown \\ \text{X} \end{smallmatrix} \text{Mg}$. For long multimers, especially, this structure seems

to predominate for MeMgI and probably for MeMgBr, but the mixed bridge ($\text{Mg} \begin{smallmatrix} \text{R} \diagup \\ \text{X} \diagdown \end{smallmatrix} \text{Mg}$) seems to become increasingly important for EtMgI and possibly EtMgBr.

The only bands that could possibly be considered Mg-O stretches are the bands between 270 and 300 cm^{-1} , of which one Raman band is found in the solution spectrum of each Grignard reagent. The next lower band is the $\nu\text{Mg-I}$ reference while the 323, 377, and 439 cm^{-1} bands belong to ether. A band found at about 415 cm^{-1} is discussed in succeeding pages.

If a band were an Mg-O stretching mode, the ratio of $\frac{I''_{\text{Mg-O}}}{I_{\text{Mg-X}}}$ would be expected to decrease in inverse proportion to the number of RMgX units/multimer, i. e., for a multimer of eight units for the concentrated solution, $\frac{I''_{\text{Mg-O}}}{I_{\text{Mg-X}}}$ would be expected to be 1/8 the value of the extrapolated ratio at zero concentration. The plots are found to average a slight negative slope but do not indicate bands belonging to νMgO_2 . (See Fig. 17.)

The next higher frequency, at about 330 cm^{-1} , seems to be a $\delta(\text{CCO})$ TG band that is shifted, due to magnesium complexation, from its neat Et_2O position. The very weak Raman band at 319 cm^{-1} in neat Et_2O was found in this work, but was not observed in the Raman by Wieser, Laidlaw, Krueger and Fuhrer³⁵ although they did observe a 318 cm^{-1} band in the infrared. In this work, the Raman band at about 330 cm^{-1} for MeMgI and 325 cm^{-1} for MeMgBr is observed to increase with

Figure 17

Ratio of $\frac{I \text{ "Mg-O" }}{I \text{ Mg-X}}$ vs. Concentration

The low percent change in slope indicates that there are no Raman Mg-O stretching vibrations in solution.

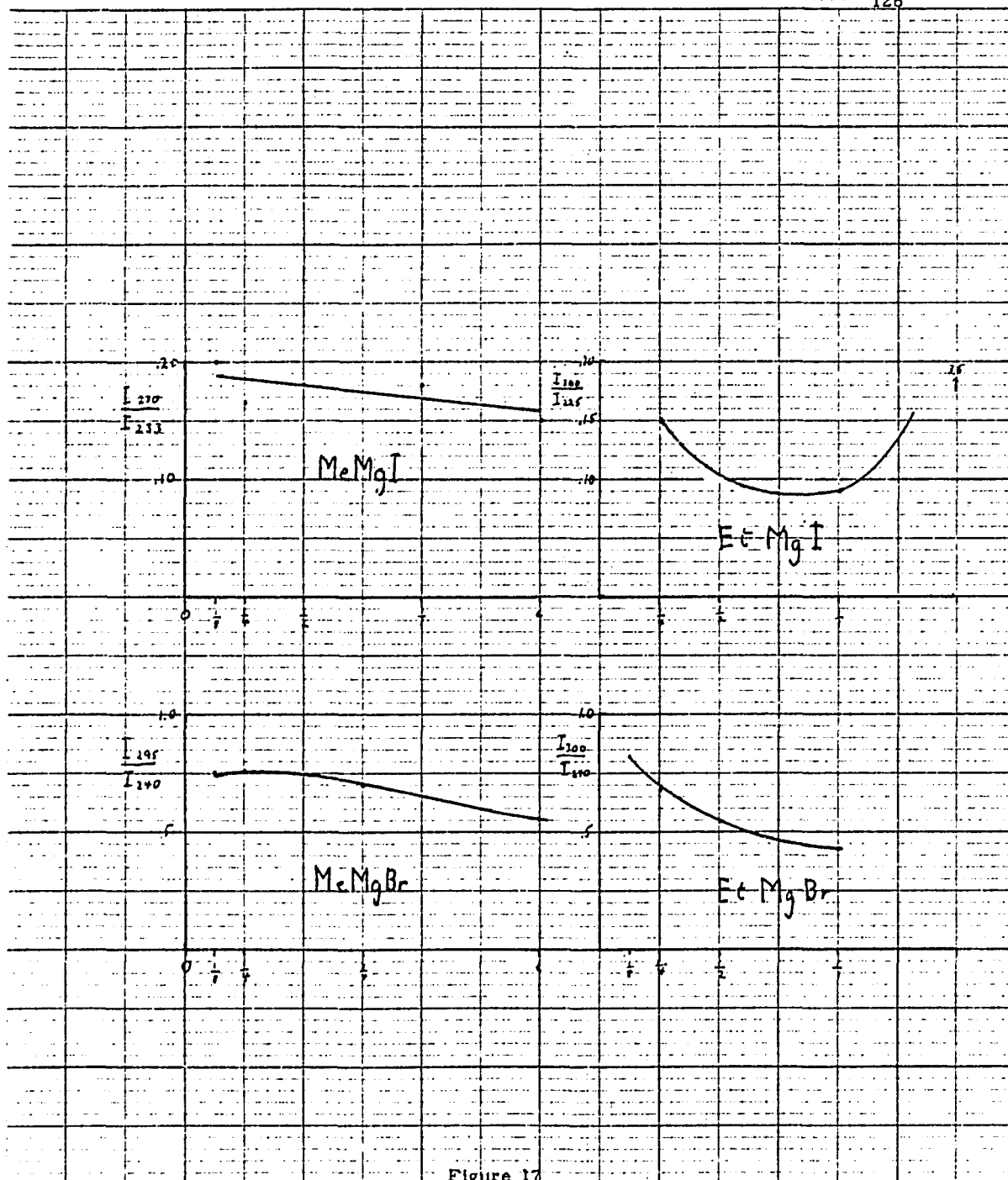
COMPLØT³OMNIGRAPHIC³HOUSTON INSTRUMENT
DIVISION OF FALCON INDUSTRIES
TEXAS
CHART NO. FC-40 PRINTED IN U.S.A. 126

Figure 17

27

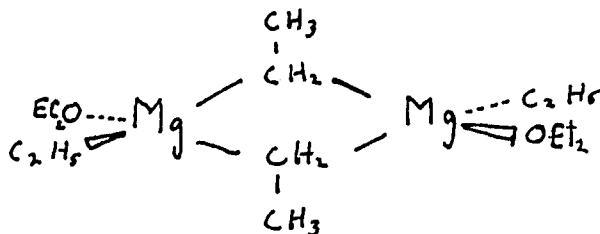
increasing concentration, consistent with the assignment of TG for this band. The next higher frequency band observed in the four Grignard reagents is at about 377 cm^{-1} which decreases in intensity with increasing concentration. This is not consistent with the TG assignment of Wieser, Laidlaw, Krueger and Fuhrer.³⁵

For the moment we pass by intervening bands and look next at the most prominent band in the low frequency end of diethyl ether bands at 439 cm^{-1} . In all Grignard reagents it decreases in intensity with increasing concentration, consistent with a TT ether conformation. The next band, at about 500 cm^{-1} , has a depolarization ratio of between 0.3 and 0.5 and is also an ether band assigned TG θ , X, R, consistent with increased intensity with increasing magnesium concentration. The next band is seen at about 514 cm^{-1} for MeMgI and about 518 cm^{-1} for MeMgBr and is the Mg-C stretch. This band increases in intensity with the same concentration dependence as the 500 cm^{-1} TG ether band. These bands are so close together that they appear to merge together as one band. In EtMgX the $\nu\text{Mg-C}$ band occurs at about 480 cm^{-1} which also merges with the ether TG θ , X, R band.

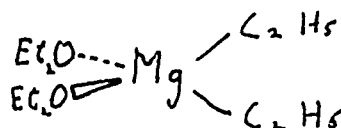
Now returning to the 412 cm^{-1} band, we see a weak band in MeMgX, appearing at high concentration. A similar band in EtMgI is observed at 417 cm^{-1} . Wieser and Krueger³⁶ report a Raman band in the lower phase of MgBr_2 at 417 cm^{-1} (vw) but leave it unassigned. Kress,⁴⁸ in a Raman study of diethylmagnesium in diethyl ether at 300°K , reported on the range from 300 cm^{-1} to 570 cm^{-1} . Three of the bands with their

assignments are listed below with a discussion:

360 cm^{-1} : Mg_2C_2 . No structures are described but presumably this structure is:



410 cm^{-1} : MgC_2 (monomer). This must be:



This band grows and then becomes smaller which seems to be good evidence for an assignment of monomer because the monomer-multimer equilibrium is shifted to multimer with increasing concentration. Unfortunately, lower frequencies are not given as the band or bands of νMgO_2 should also reflect the change from monomer to dimer.

500 cm^{-1} : Superposition of bands of pure ether, and of ether bands in monomeric and dimeric species.

Also in the spectrum of Et_2Mg in ether are the ether bands at 325 cm^{-1} and 380 cm^{-1} plus remnants of the 439 cm^{-1} band.

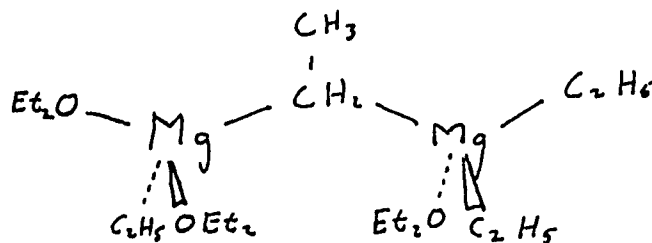
This worker offers the following interpretation of the spectrum that seems to be simpler and also compatible with the present study

on Grignard species. In the region from 450 to 550 cm^{-1} two bands are observed, one at 480 cm^{-1} and one at 505 cm^{-1} . The positions of these two bands are identical to those observed in EtMgBr and EtMgI in ether at 300° K and are therefore given the same assignment:

$$\begin{aligned} 480\text{ cm}^{-1} &= \nu\text{Mg-C} \\ 505\text{ cm}^{-1} &= \text{TG } \theta, \text{X, R}^{35} \end{aligned}$$

In MeMgBr and MeMgI the ether band remains at the same frequency and the Mg-C stretch increases to about 515 cm^{-1} .

The band at 410 cm^{-1} in Et_2Mg is ascribed to one ethyl group as a bridge as follows:

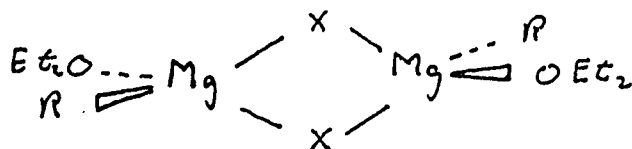


This species would be expected to have the same intensity profile with changes in concentration as would a monomer. The frequency at 410 cm^{-1} is intermediate between monomer and doubly bridged dimer as expected. The band at about 410 cm^{-1} in Grignard solutions may have the same or a similar species containing a bridging halogen.

The band assignment at 360 cm^{-1} seems quite plausible. The bands at 355 cm^{-1} for MeMgI and at 349 cm^{-1} for EtMgI appear to be the same $\nu\text{Mg} \begin{smallmatrix} \text{C} \\ \diagup \quad \diagdown \end{smallmatrix} \text{Mg}$ skeleton. This is discussed further in succeeding pages.

Given that the evidence presented so far predicts that in multimer

formation of Grignards, one would predict dihalide bridging, then the structure expected for a dimer is:



With this geometry it is difficult to predict the frequency of the various modes. One approach is to choose another chemical system that is similar and to use it as a model. Of course, the first problem is to choose a good model. One possible model reproduces the basic rhomboid structure of the central ring $\text{Mg} \begin{smallmatrix} \text{X} \\ \text{X} \end{smallmatrix} \text{Mg}$. Since this four atom structure is discussed several times and in different contexts it may be useful to provide a description of the normal coordinates (see Figure 17).

Dimers of alkali halides (M_2X_2) are reported to have the bridged structure $\text{M} \begin{smallmatrix} \text{X} \\ \text{X} \end{smallmatrix} \text{M}$. Trugman and Gordon⁵⁸ calculate the potential energy surface from an electron gas model and predict the binding energies, equilibrium geometries and vibrational frequencies for M_2X_2 alkali halide molecules. See Table 29.

It is interesting to note that in all cases, the A_{1g} symmetric breathing mode is the highest Raman frequency. This is in contrast to the usual observation where the asymmetric stretch is higher in frequency than the symmetric stretch. The A_{1g} is also the highest calculated frequency for infrared and Raman active bands.

Figure 18

Normal Modes of M_2X_2 Bridged Dimers

Redrawn from Lesieki and Nibler.⁵⁹

Normal Modes of M_2X_2 Bridged Dimer

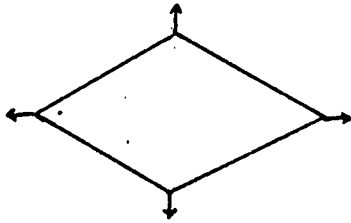
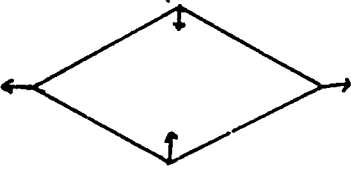
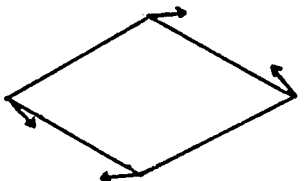
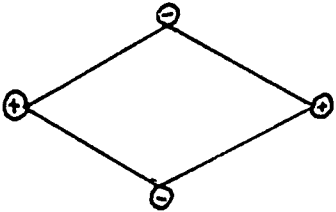
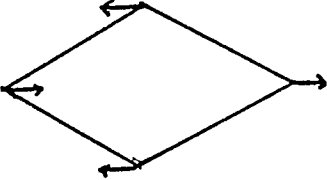
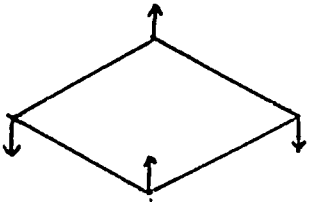
	<u>Normal Modes</u>	<u>Approximate Description</u>
A_g		Symmetric breathing mode (stretch).
A_g		Symmetric ring bending mode.
B_{1g}		Ring deformation (stretch).
B_{1u}		Ring pucker (out-of-plane bend)
B_{2u}		Ring vibration (stretch).
B_{3u}		Ring vibration (stretch).

FIGURE 18

TABLE 30

Vibrational Frequencies of Alkali-Halide Dimers (cm^{-1})

Dimer		$\frac{B_{1u}}{B_{2u}}$ **	B_{3u}	B_{2u}	B_{1u}	A_g	$A_{g'}$	B_{1g}
LiF	Experimental	.527	655*	570*	300*	560*	260*	490*
	Calculated	.59	644	690	360	713	424	522
LiCl	Experimental	.54	460	335	180			
	Calculated	.58	403	391	226	471	218	331
LiBr	Experiment	.527	413	295	155			
	Calculated	.55	356	349	191	427	134	300
NaF	Experimental	.54	380	363	190	320	287	293
	Calculated	.48	373	368	178	400	225	326
NaCl	Calculated	.47	235	235	111	252	139	207
KF	Calculated	.43	305	305	131	329	153	275
KCl	Calculated	.407	207	209	85	218	106	190
RbF	Calculated	.376	283	285	107	309	103	263
RbCl	Calculated	.42	156	158	67	170	74	143

This table is reproduced from Trugman and Gordon.⁵⁸

* B_{3u} , B_{2u} , and B_{1u} are observed bands from the infrared data of A. Snelson, J. Chem. Phys. 46, 3652 (1967). The A_g , $A_{g'}$, and B_{1g} are calculated frequencies from the observed B_{3u} , B_{2u} , and B_{1u} bands.

** B_{1u}/B_{2u} is calculated from the data reproduced from this table. (Appendix, page 155, refers to this ratio.)

In the Grignard reagents, where double bridging is expected, the bands at 225 cm^{-1} for RMgI and 240 cm^{-1} for RMgBr seem particularly high when compared to MgX_2 compounds in Et_2O . When interpreted with the alkali halides as a model, however, these bands seem more reasonable as ring stretches. Credibility is lent to the 225 cm^{-1} and 240 cm^{-1} assignments by their high intensity and low depolarization ratios.

Other models, also taken from matrix isolation studies, are MgX_2 dimers. Lesiecki and Nibler⁵⁷ report on the infrared and Raman of MgX_2 (where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) of monomers and dimers. The dimer structure is thought to be the D_{2h} structure $\text{X}-\text{Mg}\begin{smallmatrix} \text{X} \\ \diagup \quad \diagdown \\ \text{X} \end{smallmatrix}\text{Mg}-\text{X}$. Such a model would have six infrared (2B_{1u} , 2B_{2u} , 2B_{3u}) and six Raman (3A_g , 2B_{1g} , B_{2g}) active fundamentals. This model has the advantage of having the same ring atoms but the terminal halogen atoms and the dissimilar terminal geometry may radically change frequencies. The assignments, observed frequencies, and calculated frequencies are given in Table 31.

Especially interesting is the 274 cm^{-1} band for Mg_2I_4 and the 312 cm^{-1} band for Mg_2Br_4 in the infrared assigned to the B_{2u} ν_9 ring stretch. Since the Grignard species are of low symmetry, all modes become infrared and Raman active (actually observed). The bands at 265 cm^{-1} and 290 cm^{-1} of MeMgI and MeMgBr respectively may be analogous to the 274 cm^{-1} and 312 cm^{-1} bands. In EtMgBr and EtMgI , however,

Calculated* and observed frequencies (cm^{-1}) for M_2X_4 species (argon matrix).

Assignment	Symmetry	Mg_2F_4	Mg_2Cl_4	Mg_2Br_4	Mg_2I_4	$\text{Fe}_2\text{Cl}_4^{**}$
Raman						
ν_1 terminal M-X stretch	A_g	585 (771)	(550)	284? (456)	(413)	(429)
ν_2 ring stretch	A_g	353 (425)	286 (253)	155 (153)	110 (113)	(250)
ν_3 ring bend	A_g					(103)
ν_4 ring stretch	B_{1g}	(508)	(350)	180 (253)	(247)	(306)
ν_5 terminal M-X bend	B_{1g}					(130)
ν_6 terminal M-X bend						(87)
Infrared						
ν_7 terminal M-X bend	B_{1u}	240	140	108	92	(134)
ν_8 ring pucker	B_{1u}					(34)
ν_9 ring stretch	B_{2u}	487 (508)	372 (350)	312 (278)	274 (247)	325 (325)
ν_{10} terminal M-X bend	B_{2u}					(84)
ν_{11} terminal M-X stretch	B_{3u}	747 (771)	514 (550)	425 (456)	387 (413)	438 (438)
ν_{12} ring stretch	B_{3u}	450 (425)	260 (253)	210 (153)	(113)	249 (249)

This table is from Leseicki and Nibler.⁵⁷

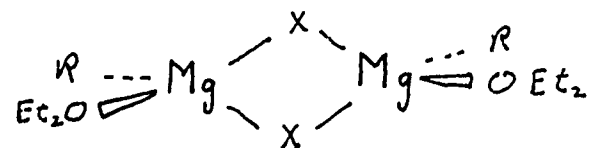
*Values in parentheses are calculated.

**R.A. Frey, R.D. Werder, and Hs.H Gunthard, J. Mol. Spectros. 35, 260 (1970).

Table 31

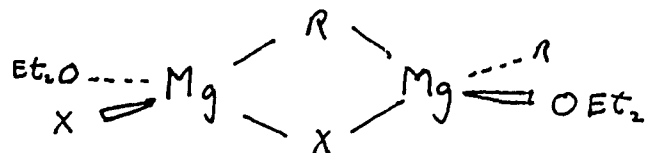
only one band, at about 295 cm^{-1} , is seen in this region.

As we have seen, the double bridged halide dimer appears to be the structure of favor for the dimer.

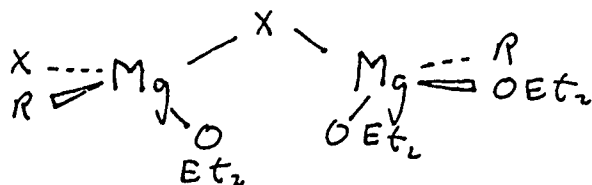


Structure I

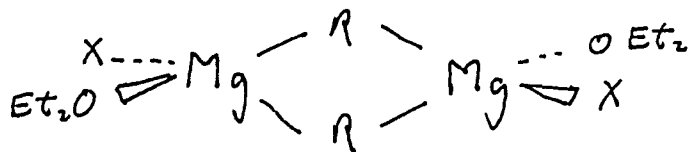
Structures II through V are seen to be progressively less likely as the halogen bridge band is more likely than an alkyl bridge band.



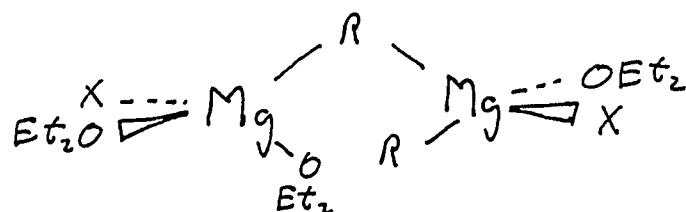
Structure II



Structure III



Structure IV



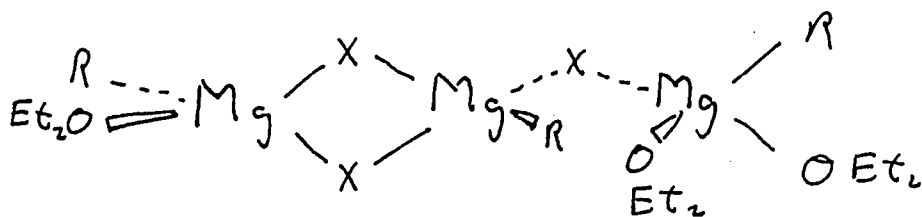
Structure V

However, it is not unreasonable that these structures are present in small concentration. In these dimer structures and others presented there is no implication of a specific configuration such as trans or cis ether groups.

As the Grignard solution becomes more concentrated and the ratio of Grignard to Et_2O increases, double bridging becomes more likely. The following trimers, VI and VII, are considered most likely, with structure VI favored at higher concentrations.

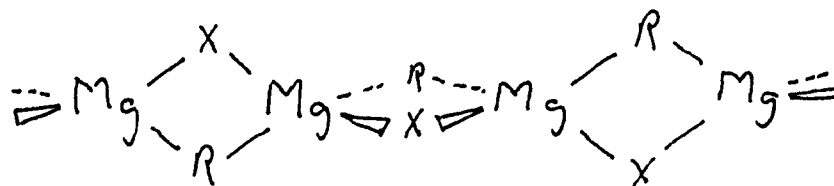


Structure VI

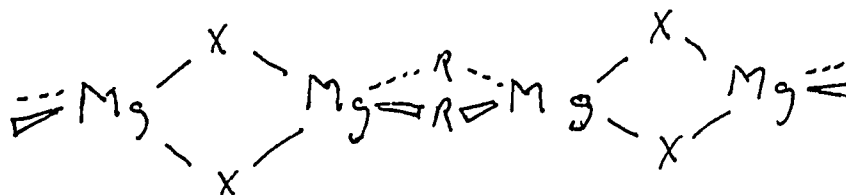


Structure VII

As one considers longer multimers a question arises whether the tendency is towards mixed bridge VIII or alternate bridge IX.



Structure VIII



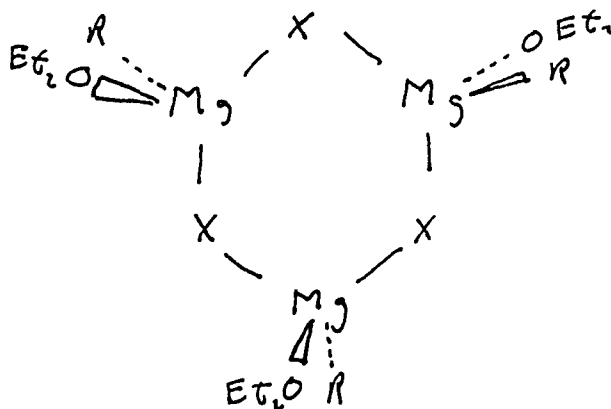
Structure IX

The evidence seems to reveal that both forms are present in solution. In $\text{MeMgI}_{\text{conc.}}$, the band at 355 cm^{-1} is half the intensity of the 408 cm^{-1} band. These bands are thought to be an indication of the relative amount of single alkyl bridge to dialkyl bridge. A single alkyl bridge implies structure VIII. The presence of the dialkyl bridge in a long multimer implies a dihalide bridge and therefore structure VIII. The presence of both bands implies a mixture of structures VIII and IX. Whether these two structures occur within the same molecule or are separate is not known. $\text{EtMgI}_{\text{conc.}}$ also has these two bands, but with the lower frequency more than twice the intensity of the upper frequency. At the

same time the band at 230 cm^{-1} , associated with the dihalide bridge, is weak. This is good evidence for predominance of the mixed bridge of structure VIII. Consistent with this conclusion is evidence from the very low frequency region at 65 cm^{-1} and 98 cm^{-1} . Bands that occur in this region are suspect, especially those with high intensity. However, taken at face value, the band at 98 cm^{-1} may be the $\delta\text{Mg}-\text{I}-\text{Mg}$ of the mixed bridge $\text{Mg} \begin{smallmatrix} \text{Et} \\ \text{I} \end{smallmatrix} \text{Mg}$ and the less intense band at 65 cm^{-1} , which is a shoulder, may be the $\delta\text{Mg} \begin{smallmatrix} \text{I} \\ \text{I} \end{smallmatrix} \text{Mg}$.

In MeMgBr and EtMgBr , the evidence is not as conclusive. In MeMgBr , however the band at 236 cm^{-1} increases in relative intensity from the 1/1 to the conc. solution. This may be indicative of a tendency toward structure IX. The spectrum of EtMgBr is not good enough to make a speculation.

The possibility of cyclic structures has been raised by Ashby.¹⁵ Excluding the dimer, the trimer, if at all, would appear to be the most likely structure, where the bond angles of such a structure would seem plausible.



Larger cyclic structures would seem unreasonable for two main reasons. Unfavorable bond angles would have to be formed and the linking of the end of a long chain would cause a decrease in entropy with a resulting increase in free energy (the absolute value of the free energy would decrease).

The evidence against cyclic trimer formation is that double bridging is established in Grignard solutions and that thermodynamically, double bridging, having the lowest free energy, would seem to be favored. On the other hand, there is no hard evidence to rule out small concentrations of cyclic trimers.

DISCUSSION OF ETHER BANDS

The spectra of Grignard reagents in diethyl ether above 520 cm^{-1} are mostly due to the bands of diethyl ether. The consensus is that two conformers, TT and TG, are predominant in solution. Wieser, Fuhrer, Krueger and Laidlaw³⁵ made assignments of particular bands by temperature dependence studies. In neat ether, the TT conformer is $1.1 \frac{\text{kcal}}{\text{mole}}$ more stable than the TG conformer; the TT bands become more intense relative to TG bands as the temperature is lowered.

It has also been observed that when the concentration is increased in Grignard compounds and magnesium halides in diethyl ether, some ether bands grow more intense and others less intense. It is generally agreed that the TG conformer is favored with increasing magnesium concentration. This is clearly observed for some predominant ether bands. Some band concentration profiles show an initial decrease, such as the 1041 cm^{-1} band, and then an increase. This occurs in all four Grignards for this case and may indicate both TT and TG bands at the same frequency. In Table 32, the ether bands below 550 cm^{-1} are listed plus all other bands found above 550 cm^{-1} . The conformer assignments of Wieser, Fuhrer, Kureger and Laidlaw are given plus agreement or disagreement with the band concentration profiles. The conformers predicted by the two methods are mostly in agreement with a few exceptions.

The band concentration profiles are all relative to the 833 cm^{-1} band in each spectrum which is a TG band and therefore this band intensity vs concentration gives a straight line with a relative intensity of 1.0 for all concentrations by definition and therefore a slope of zero. One might expect that other TG bands would also have an approximate slope of zero while the TT bands have a negative slope. One observes, however, that TG bands have a positive slope with a change in relative intensity of at least four. TT bands have a negative slope as expected.

TABLE 32

Diethyl Ether Conformation of Bands

Band cm ⁻¹	Assignment of Wieser, Laidlaw, Krüeger and Fuhrer 35	Agreement of Band Concentration Profile
323	TG	Yes
376	TG	No
439	TT	Yes
500	TG	Yes
780	-	
793	TT & TG	Yes
833	TG	Yes
843	TT	Yes
899	-	-
915	TG	?
933	TT	Yes
1000	-	-
1022	TG	No
1041	TT	Yes
1072	TT	Yes
1088	-	-
1098	TG	No
1117	TT	Yes

Comments on Table 32

- 323 cm^{-1} : This band is present only in the methyl Grignards. It is probably present in ethyl Grignards but is weak.
- 780 cm^{-1} : This band behaves like a classic TG band but is not found in neat ether.
- 793 cm^{-1} : Since a positive slope is observed, either the TG component is greater than the TT component or the band is pure TG.
- 898 cm^{-1} : This band appears to be a TG band but is not found in neat ether.
- 915 cm^{-1} : The methyl Grignards appear to be TT bands. The EtMgI band is found at 923 cm^{-1} and the EtMgBr band averages 918 cm^{-1} . The latter two bands seem to be strongly TG. It would appear that the 915 cm^{-1} band in MeMgX is TT while the EtMgX band is from the ethyl group bonded to magnesium.
- 1000 cm^{-1} : The band concentration profile is like TG. This band is not present in neat ether.
- 1022 cm^{-1} : Three Grignards show clear TT patterns but MeMgBr is not clear having a slight U shape.
- 1041 cm^{-1} : Discussed in text.

- 1072 cm^{-1} : The band concentration profiles of MeMgI and EtMgBr are clearly TT but MeMgBr and EtMgI have the U shape of the 1041 cm^{-1} band. The latter two Grignards may have TG contributions like the 1041 cm^{-1} band.
- 1088 cm^{-1} : The profiles are clearly TG in shape. This band appears to be the reported band at 1098 cm^{-1} of neat ether that has shifted. This band is labeled TG θ, w_4 .
- 1098 cm^{-1} : This band is observed only in MeMgBr and is of TT profile.
- 1117 cm^{-1} : The methyl Grignards are clearly TG in shape and are very intense while the EtMgI band is U shaped and the EtMgBr band indicates TT. Both of the latter bands are weak. The methyl Grignards are polarized and the ethyl Grignards have a high depolarization ratio and are consistently higher in frequency by about 5 cm^{-1} . All this is good evidence that the ethyl Grignards have the TT band at this frequency and the methyl Grignard band has a different origin.

TABLE 33

Band Assignments (cm^{-1})

MeMgI	MeMgBr	EtMgI	EtMgBr	Assignments
	82m	65m		Ring bend $\text{Mg} \begin{smallmatrix} \text{X} \\ \text{X} \end{smallmatrix} \text{Mg}$
		98vs	105w	Bend $\text{Mg}-\text{X}-\text{Mg}$
115s	116m			$\text{Mg}-\text{X}$ stretch of ring $\text{Mg} \begin{smallmatrix} \text{X} \\ \text{X} \end{smallmatrix} \text{Mg}$ and bend $\text{C}-\text{Mg}-\text{X}$
137s	145m	138s	136w	$\text{Mg}-\text{X}$ stretch of ring $\text{Mg} \begin{smallmatrix} \text{X} \\ \text{X} \end{smallmatrix} \text{Mg}$
		171m	180m	$\text{Mg}-\text{X}$ stretch of ring $\text{Mg} \begin{smallmatrix} \text{X} \\ \text{X} \end{smallmatrix} \text{Mg}$ and bend $\text{Mg}-\text{C}-\text{C}$
225vs	237m	230m	245m	$\text{Mg}-\text{X}$ stretch of ring $\text{Mg} \begin{smallmatrix} \text{X} \\ \text{X} \end{smallmatrix} \text{Mg}$
266w	290w	295w	295w	$\text{Mg}-\text{X}$ stretch of ring $\text{Mg} \begin{smallmatrix} \text{X} \\ \text{X} \end{smallmatrix} \text{Mg}$
330w	327w	327w	318w	Ether TG χ, θ
355w		349m		Ring stretch $\text{Mg} \begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix} \text{Mg}$
376w	376w	388w		Ether TT
412w	413w	417w		Stretch $\text{Mg} \backslash \text{R} / \text{Mg}$
439w	439w	439w	439w	Ether TT (A_1) θ, R, χ
515s	518s	482m	482m	$\text{Mg}-\text{C}$ stretch
508s	503s	503m	503m	Ether TG θ, χ, R
780s	780m	780s	780m	Probably ether TG
793m	793w	793w	790m	Ether TG ρ, β
833s	834s	834s	833m	Ether TG δ, β, ρ, R

Band Assignments (cm^{-1})

Continued

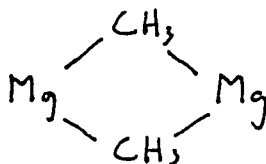
MeMgI	MeMgBr	EtMgI	EtMgBr	Assignments
843w	844m	844m	843m	Ether TT (A_1) S, β
899w	898w	989m	900w	Probably ether TG
913w	915w			Probably ether TT
		925w	916s	Ether TG β, S, R
933w	932w		933w	Ether TT (B_1) R, S, β
1000w	1000w	1000w		Probably ether TG
1022w	1023w	1024w	1023w	Ether TG
1041w	1042w	1045w	1042w	Ether TT (B_1) β, R, W (low conc.) probably ether TG (high conc.)
1072w	1072w	1075w	1072w	Ether TT (A_1) R, S, β
1085vs	1088vs	1088s	1088s	Ether TG
	1098w			Ether TT
		1121w	1121w	Ether TT (B_1)
1117vs	1120vs			Probably ether TG

APPENDIX

Group Theoretical Analysis of the Dimethyl Bridged Skeletal System

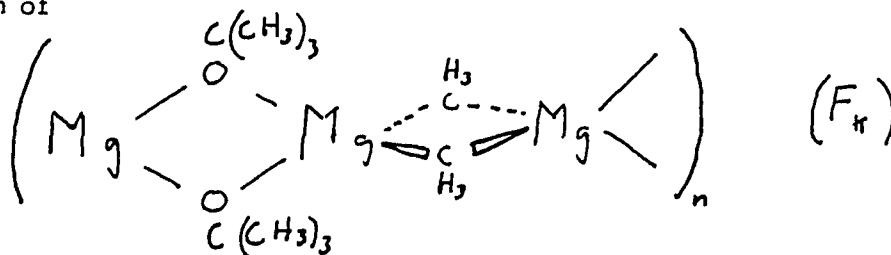
(Refer to Page 25)

In a discussion of the kinetic (F_k) product of the reactants $(\text{CH}_3)_2\text{Mg} + (\text{CH}_3)_3\text{COH}$ (see page 25) Ashby⁴³ says, "The presence of strong, broad bands at 570, 480, and 390 cm^{-1} in the infrared spectrum is consistent with a methyl bridge-bond system with local D_{2h} symmetry." Via a footnote, he refers to an article by Parris and Ashby⁴² wherein they report, "when the bridged system (1) is treated as a group with D_{2h} local symmetry, vibrations belonging to the B_{1u} , B_{2u} , and B_{3u} irreducible representation are expected to be infrared active."



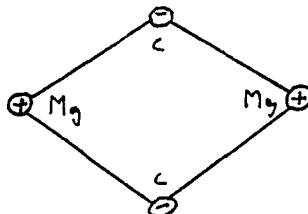
Structure 1

The implication here is that the three bands described in the infrared spectrum of



belong to B_{1u} , B_{2u} , and B_{3u} which arise from the skeletal bonds of structure (1).

The B_{1u} , B_{2u} , and B_{3u} vibrations are expected. As the analysis shows, however, the B_{2u} and B_{3u} are stretching modes while the B_{1u} is an out of plane ring bend or ring pucker which would be expected



to be of significantly lower frequency than the lowest frequency B_{2u} or B_{3u} band, and therefore lower than 390 cm^{-1} .

The following is a group theoretical analysis of structure (1) which demonstrates the kind of vibrations that are associated with the six irreducible representations expected for the skeleton (see page 126 for diagrams of approximate normal coordinates). A discussion is also included for the expected frequency of the B_{1u} vibration.

The total number of modes for the D_{2h} skeleton are $2A_g + B_{1g} + B_{1u} + B_{2u} + B_{3u}$. This is determined from the four atoms of the skeleton as follows:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Number of atoms unshifted	4	0	2	2	0	4	2	2
Character per unshifted atom	3	-1	-1	-1	-3	1	1	1
Product	12	0	-2	-2	0	4	2	2

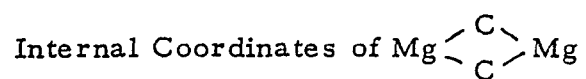
From this reducible representation we find the irreducible representations:

D _{2h}	E	C ₂ (z)	C ₂ (y)	C ₂ (x)	i	σ(xy)	σ(xz)	σ(yz)	Total	r _i & R	Net
A _g	= 1/8(12	+0	-2	-2	+0	+4	+2	+2)	= 2A _g		2
B _{1g}	= 1/8 (12	+0	+2	+2	+0	+4	-2	-2)	= 2B _{1g}	R _z	1
B _{2g}	= 1/8(12	+0	-2	+2	+0	-4	+2	-2)	= B _{2g}	R _y	0
B _{3g}	= 1/8(12	+0	+2	-2	+0	-4	-2	+2)	= B _{3g}	R _x	0
A _u	= 1/8(12	+0	-2	-2	+0	-4	-2	-2)	= 0A _u		0
B _{1u}	= 1/8(12	+0	+2	+2	+0	-4	+2	+2)	= 2B _{1u}	z	1
B _{2u}	= 1/8(12	+0	-2	+2	+0	+4	-2	+2)	= 2B _{2u}	y	1
B _{3u}	= 1/8(12	+0	+2	-2	+0	+4	+2	-2)	= 2B _{3u}	x	1
									$\overline{12}$	$\overline{6}$	

The total number of modes of a molecule are $3n$, where n = number of atoms. This becomes 12 for the bridged system considered. After subtracting the three rotations (R_x , R_y and R_z) and three translations (x , y and z), six normal coordinates remain: $2A_g + B_{1g} + B_{1u} + B_{2u} + B_{3u}$.

In order to relate the physical vibrating skeleton to the six normal coordinates determined, we can describe the skeleton by internal coordinates. Ideally, one would prefer to assign the same number of internal coordinates as normal modes, however, for this skeleton, it is easier to consider twelve internal coordinates. The first four considered are interatomic bond coordinates r_1 , r_2 , r_3 and r_4 which are actually all equivalent. Then four in-plane angles are defined; θ_1 , θ_2 , θ_3 , and θ_4 . Lastly, the four out of plane bend angles are defined; γ_{x_1} , γ_{x_2} , γ_y , and γ_{y_2} . When operations are performed on the

FIGURE 19



Twelve internal coordinates are given for the bridged structure (1).

r_1, r_2, r_3, r_4 are interatomic coordinates.

$\theta_1, \theta_2, \theta_3, \theta_4$ are in-plane bend coordinates.

$\gamma_{x1}, \gamma_{x2}, \gamma_{y1}, \gamma_{y2}$ are out-of-plane bend coordinates.

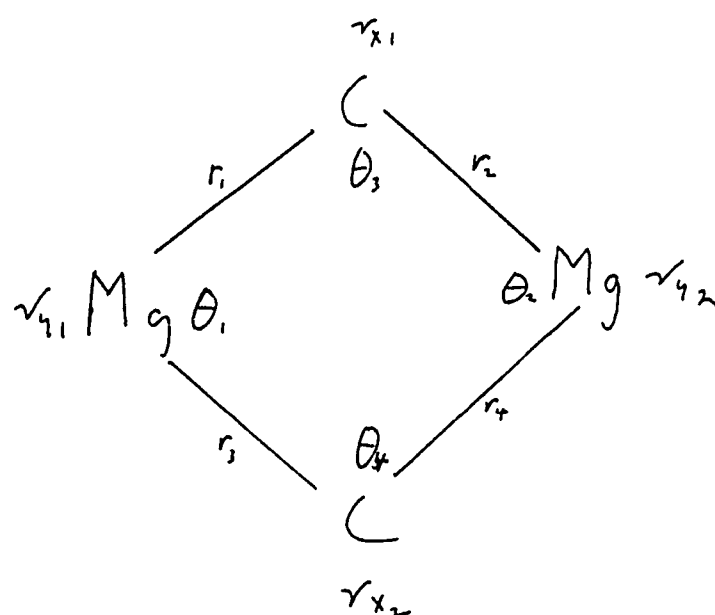


Figure 18

✓ coordinate, it is conveniently considered as an arrow pointing out of the paper.

To determine the vibrational modes of r_1 , r_2 , r_3 , and r_4 the number of unshifted coordinates per symmetry operation is noted as follows and then reduced to determine the irreducible representation, ie. the symmetry species represented.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
r_i unshifted per operation	4	0	0	0	4	0	0
A_g	$= 1/8(4 \cdot 1 \cdot 1) + 0 + 0 + 0 + 4 \cdot 1 \cdot 1 + 0 + 0) = 1A_g$						
B_{1g}	$= \text{etc.}$						

In this case, by inspection, we see that the reducible representation transforms as the symmetry species in the row where +1 is found for $\sigma(xy)$ in the character table for D_{2h} . This becomes $A_g + B_{1g} + B_{2u} + B_{3u}$. A_g and B_{1g} are Raman active and the B_{2u} and B_{3u} are infrared active (they must transform as the coordinate x, y or z; B_{2u} transforms as z and B_{3u} as x). Hence, 2Mg-C stretch modes are predicted for the infrared.

Accounting for the four Mg-C in plane internal coordinates, $A_g + B_{1u}$ are left. The four in plane bending coordinates transform in a similar manner as above, as $2A_g + B_{2u} + B_{3u}$ of which three ($A_g + B_{2u} + B_{3u}$) are equivalent to some linear combination of Mg-C stretch, leaving an A_g as the in plane ring bending mode. The irreducible representation

for the four out of plane bending (ν) for which four angles are defined are $2B_{1u} + B_{2g} + B_{3g}$.

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
Reducible ν_x	2	0	0	2	0	-2	2	0	$= B_{1u} + B_{2g}$
Reducible ν_y	2	0	-2	0	0	-2	0	2	$= B_{1u} + B_{3g}$

The B_{2g} and B_{3g} are cast out as redundant as they are not D_{2h} skeletal modes. This leaves the B_{1u} as the ring pucker.

Then to summarize:

- A_g = breathing mode
- A_g = ring bending
- B_{1g} = ring vibration (stretching)
- B_{1u} = ring pucker (out-of-plane bend)
- B_{2u} = ring vibration (stretch)
- B_{3u} = ring vibration (stretch)

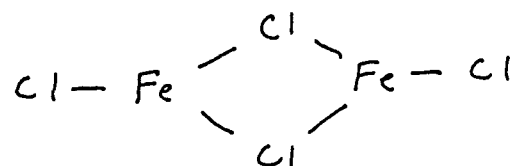
The Mg-C stretch is recognized to be about 500 cm^{-1} for alkyl Grignards.

The three bands reported by Ashby are in the range expected for Mg-C stretch of a bridged system, but only two (B_{2u} and B_{3u}) bands may be due to Mg-C stretching. The third infrared active band (B_{1u}) must, as we have seen, be the ring pucker. From data compiled by Ross,⁵¹ the $B_{1u} \nu_{10}$ frequency is 15% to 20% of the $A_g \nu_1$ frequency for the bridged ring of B_2H_6 and Ga_2X_6 ($X = Cl, Br, I$). (The A_{1g} frequency of the Ashby compound is probably the 570 cm^{-1} band.)

Of the three bands described by Ashby, the ratio of the lowest two

is $390/480 = 81.3\%$. For alkyl halide dimers (see Table 29) the ratio of $B_{1u}/B_{2u} = 53\% \pm 1\%$ ($B_{2u} \leq B_{3u}$ in frequency), for Li_2F_2 , Li_2Cl_2 , Li_2Br_2 and Na_2F_2 . Experimental data is not available for the halides of potassium and rubidium, however the calculated ratio ranges from 38% to 43%. For Tl_2F_2 ,⁵⁹ $\nu_4(B_{1u}) = 81 \text{ cm}^{-1}$, $\nu_5(B_{2u}) = 316.0 \text{ cm}^{-1}$ and $\nu_6(B_{3u}) = 257.5 \text{ cm}^{-1}$: $B_{1u}/B_{3u} = 31.5\%$.

For Fe_2Cl_4 (see Table 31)



the calculated values for the B_{1u} frequency = 34 cm^{-1} . The lowest B_{2u} or B_{3u} frequency is the B_{3u} ring stretch at 249 cm^{-1} . $B_{1u}/B_{3u} = 13.7\%$. A trend observed is that the B_{1u}/B_{2u} ratio tends to be lower where the ring structure is one part of a longer molecule like the bridged structure in question. From available data, it would appear that the 390 cm^{-1} band is too high in frequency to be a ring pucker.

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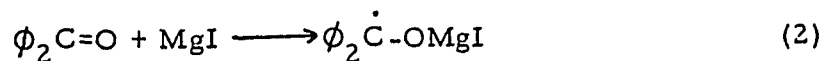
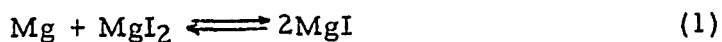
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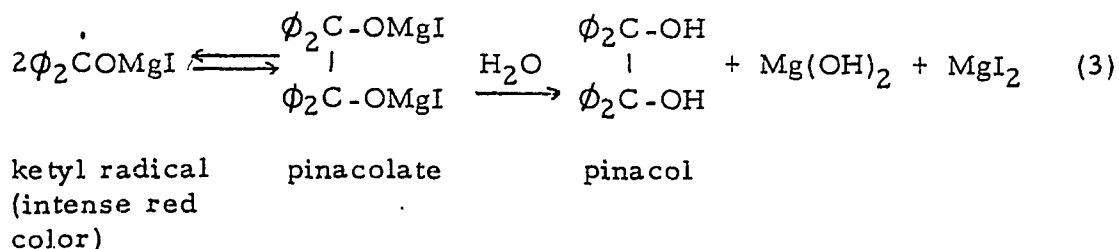
THE SEARCH FOR UNIVALENT MAGNESIUM PLUS THE
DESIGN AND OPERATION OF A SENSITIVE EBULLIOSCOPIC
APPARATUS FOR AIR AND WATER SENSITIVE COMPOUNDS

INTRODUCTION

Alkaline earth metals have been reduced from the usual +2 oxidation state to the univalent species by fusion at 800 - 1200° C in a mixture of the halide salt and metal, or by electrolysis of the anhydrous salt at high temperatures.¹ There is also flame spectroscopic evidence for univalent magnesium. However, the search for univalent magnesium at ordinary temperatures is at present still inconclusive.

Gomberg and Bachman,² in 1927, reported on the reducing action of a mixture of magnesium iodide (or bromide) and magnesium in diethyl ether and benzene on aromatic ketones, aldehydes, etc., and in general of compounds with the C=O group. Since magnesium metal alone was not observed to have reducing properties, univalent magnesium species were postulated to form which would further oxidize and simultaneously reduce the organic compound. The following reaction sequence was proposed for the reduction of benzophenone.

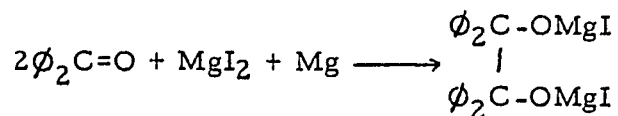




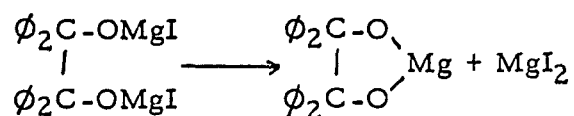
The authors state that only a "minute" amount of MgI is expected from equation (1) as the equilibrium is assumed to be to the left in that equation. They reported that analysis indicated no weighable amount of MgI. The method of analysis was not indicated. Presumably, no loss of magnesium was found when the metal was added to MgI_2 in an ether-benzene mixture. MgI_2 was made by reacting magnesium with I_2 . The product does not form in benzene, however, only 1% diethyl ether is enough to cause reaction. The reduction, usually carried out in an ether/benzene mixture, also takes place in benzene alone, with Mg and I_2 added.

Gomberg and Bachman found that, in general, ketones react with MgI_2 in ether/benzene to form $[(\text{R}_2\text{C=O})_2\text{O}(\text{C}_2\text{H}_5)_2\text{MgI}] \text{I}$ where the coordination number of magnesium is four. Benzophenone reacts with MgI_2 to form $[(\text{R}_2\text{C=O})_3\text{MgI}] \text{I}$, which is slightly soluble. Absolutely no reduction occurs when the mole ratio of $\phi_2\text{C=O}$ to MgI_2 is greater than three to one in the presence of magnesium. This is consistent with the postulate that no "magnesiumous" iodide can be formed without free "magnesiumic" iodide. Complete reduction, as determined by the isolation of benzopinacol, occurs when this ratio is only slightly

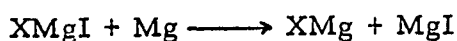
less, even though the number of gram atoms of iodine (in the form of MgI_2) per mole of $\phi_2\text{C}=\text{O}$ is 0.7 instead of the theoretical 1.0.



It is assumed, therefore, that iodomagnesium pinacolate is partially converted to magnesium pinacolate by splitting off a molecule of magnesium iodide; the latter can thus form more "MgI" by reacting with magnesium which can further reduce ketone.



Gomberg and Bachman also postulate that univalent magnesium is involved in forming the Grignard reagent. Adding I_2 or MgI_2 equally activates magnesium for Grignard formation. Grignard³ believed that a little MgI_2 etherate was formed which was continuously used and regenerated, while Gomberg and Bachman proposed the following reactions for Grignard formation:



There are solutions that have reducing properties other than

Mg + I₂. Mg + Br₂ produces 84 to 92% pinacol but with impurities as Br₂ reacts with benzene to produce bromobenzene which further reacts with $\phi_2\text{C}=\text{O}$ to give $\phi_3\text{COH}$. MgBr₂ produced by the reaction of Mg + HgBr₂ gives 90 to 95% benzopinacol. ZnBr₂ and CdBr₂ plus Mg also form MgBr₂. Likewise, HgI₂, ZnI₂, CdI₂ and AlI₃ plus Mg form MgI₂. BeI₂ + Be was found to give up to 50% pinacol.

Other binary systems were found to give negative results in ether/benzene. No reduction of benzophenone was found with Zn-ZnI₂; Zn-ZnBr₂; Zn-ZnCl₂; Cd-CdI₂; Cd-CdBr₂; Al-AlI₃; nor with the mixed systems Ag-MgI₂; Zn-HgI₂; Zn-MgBr₂; Zn-HgCl₂; Zn-MgI₂.

Bachman⁴ did further work on ketals in 1933. One puzzling aspect of the reaction was that univalent magnesium and sodium metal were expected to react similarly. The reactions were found to be different as the Na + R₂C=O adduct, upon hydrolysis, formed R₂C=O + R₂CHOH (i. e., no pinacol). Bachman discovered that small amounts of alkali decompose the pinacol so when the sodium adduct was hydrolyzed with dilute acetic acid, 95% pinacol was produced.

Bachman was also successful in reducing benzophenone with magnesium amalgam. The amalgam was prepared from 0.24 gm of magnesium ribbon and 36 gm of mercury heated under toluene. An 80% yield of pinacol was observed after two days of shaking. Earlier failures of amalgams to reduce were ascribed to the solid amalgams

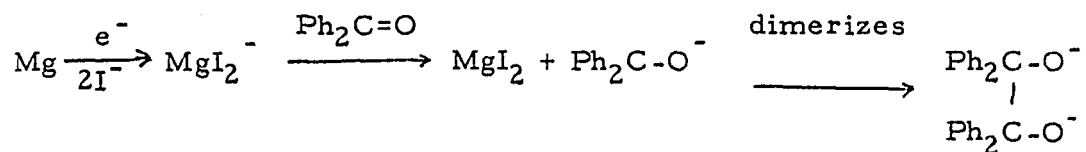
used, where fresh surfaces of magnesium could not be obtained.

Reductions have also been observed at the magnesium anode of aqueous and nonaqueous solutions. Rausch, McEwen and Kleinberg,⁵ in a review article on "Reductions Involving Unipositive Magnesium," report that there have been numerous observations of H_2 evolved at the anode when aqueous NaCl solutions are electrolyzed between magnesium anodes. There is the suggestion that univalent magnesium is responsible, i. e., that $2Mg^+ + 2H^+ \longrightarrow 2Mg^{+2} + H_2$. The initial mean valence number, $V_i = \frac{\text{Mass Cu deposited in coulometer} \cdot 24.32}{\text{Mass Mg lost from anode} \cdot 31.77}$ (24.32 = atomic mass of magnesium and $2(31.77)$ = atomic mass of copper). Values in the range of 1.3 were found to be independent of current density, temperature, concentration, and composition of electrolyte. In the electrolysis of aqueous Na_2SO_4 between magnesium electrodes in a divided cell, MnO_4^- was reduced to MgO_2 and Ag^+ was reduced to Ag under conditions which did not permit the oxidizing agent to come into contact with the anode. In the absence of electrical current, magnesium is not attacked by any of the solutions employed.

To eliminate problems where the solvent is reduced, an aprotic solvent, such as pyridine, can be used. With sodium iodide, $V_i = 2$. When a substance such as benzophenone is added, V_i is "significantly" less than two.

Gould⁶ believes that, in this case, "the reducing agent is certainly unipositive magnesium formed by oxidation of the magnesium anode, for

the ketone is not reduced by oxidation at the electrode in the absence of electric current." He writes the following reaction:



The possibility of reduction occurring by magnesium metal is still not ruled out. One wonders what the results would be if a divided cell was used with the pyridine solutions. It is also useful to remember that the oxidation potential of magnesium is high; $\text{Mg} + \text{Mg}^{+2} + 2\text{e}^- \dots + 2.375\text{V}$. ($\text{Na} = \text{Na}^+ + \text{e}^- \dots + 2.7132\text{V}$.)⁷ Magnesium that has a fresh metal surface (excess from Grignard reaction or formation of MgI_2) will react vigorously with water ($\text{Mg} + 2\text{H}_2\text{O} \longrightarrow \text{Mg}(\text{OH})_2 + \text{H}_2$). This observation may implicate H_2 as the reducing agent in aqueous systems. It is possible that nonelectrolytic attack of magnesium metal occurs only during electrolysis because under these conditions fresh magnesium surfaces are exposed.

In the search for univalent magnesium we wanted to find experimental conditions that would be unambiguous in their interpretation. We reasoned that such an experiment might be to measure the difference in boiling point elevation of a solution of MgI_2 and $\text{Mg} + \text{MgI}_2$ in diethyl ether.

Walker and Ashby⁸ have studied the association of MgI_2 , MgBr_2 and several Grignard reagents in diethyl ether. They also describe

the ebullioscopic apparatus that is used in their work.⁹ It is a basic design to handle air and moisture sensitive compounds. A schematic diagram of the apparatus used by them is shown in Fig. 20.

In the following section we describe an alternative apparatus for ebullioscopic measurements and apply this system to Mg/MgI_2 solutions. In the Walker and Ashby apparatus, the boiling point of the solution is measured directly. The boiling point has a substantial dependence on pressure; hence the pressure must be measured very accurately. In our design, the boiling point of solution minus the boiling point of pure solvent is measured. Because the solution and solvent have almost identical pressure dependencies, ΔT has a negligible dependence on pressure. This substantially reduces the cost of the apparatus, simplifies the operation, while maintaining precision.

Figure 20

Apparatus for Molecular Weight Determinations of Air Sensitive
Compounds by Walker and Ashby⁹

The limiting factor for accuracy in measuring boiling point elevation with this system is a precision manometer as the boiling point is a direct function of pressure.

Redrawn from Walker and Ashby.⁹

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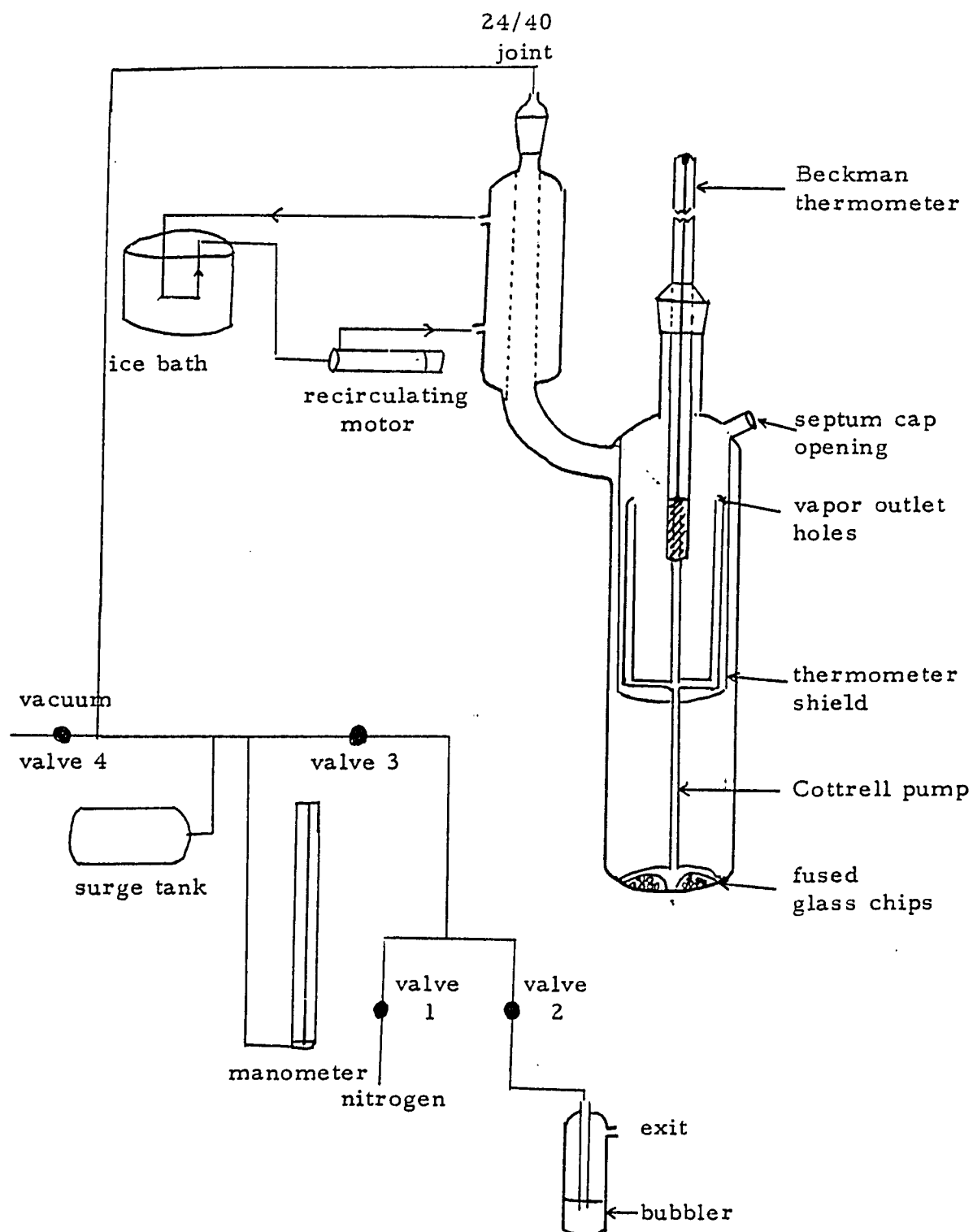


Figure 20

EXPERIMENTAL

Chemicals.

Magnesium - Mackay 99.99% magnesium in ribbon form.

Mercuric iodide - Baker, reagent grade.

Benzophenone ($\phi_2\text{C}=\text{O}$) Fisher Scientific, certified (used for calibration of the ebullioscopic apparatus).

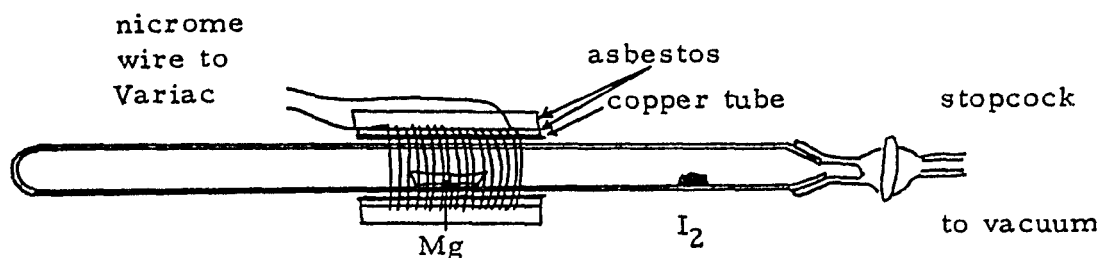
Ether - Baker anhydrous and Fisher anhydrous. The ether is dried over freshly formed sodium wire, degassed, sometimes vacuum distilled, then saturated with nitrogen.

Magnesium iodide etherate was made by reacting magnesium with HgI_2 in diethyl ether as described in the Experimental section of "Structure of Grignard Reagents." Magnesium iodide etherate was collected as a precipitate in a dry box by cooling and was recrystallized from ether. White fluffy crystals were obtained which were dried under vacuum.

Magnesium iodide etherate was analyzed by adding water (carefully because the reaction is very exothermic) to a weighted amount of sample and heating in a porcelain crucible until constant mass of MgO was obtained.

The first attempt at making MgI_2 failed. I_2 was passed over

magnesium metal at a high temperature.¹⁰ This was carried out in the absence of air in a vycor tube. The center of the tube containing the magnesium was heated to about 600°C while the I_2 was sublimed over the magnesium several times. The temperature was monitored by a Pt/Pt + 13% Rh thermocouple and calibrated by the melting point of NaCN. A small amount of white powder was obtained that did not dissolve in Et_2O .



For the remaining part of the Experimental section we will discuss the ebullioscopic apparatus we built. The schematic of this apparatus is given in Fig. 21. With this system one boiling chamber (A) always has pure solvent while the other (B) has solution. The accuracy with which pressure must be measured is easily obtained with mercury in a U tube. This can be read to 1 torr. Since the effect of $\partial T / \partial P$ is about the same for both boiling chambers, the direct difference of the thermometers is a measure (discussed further below) of the boiling point elevation. The molal boiling-point elevation constant K_b of the solution is a function of pressure, but only changes

Figure 21

A Unique Apparatus for Molecular Weight Determination of Air
Sensitive Compounds

This system measures the temperature difference between solution and pure solvent. Thus, a simple U tube manometer is sufficient to measure pressure. The method of reading is simplified while precision is maintained.

V = valve.

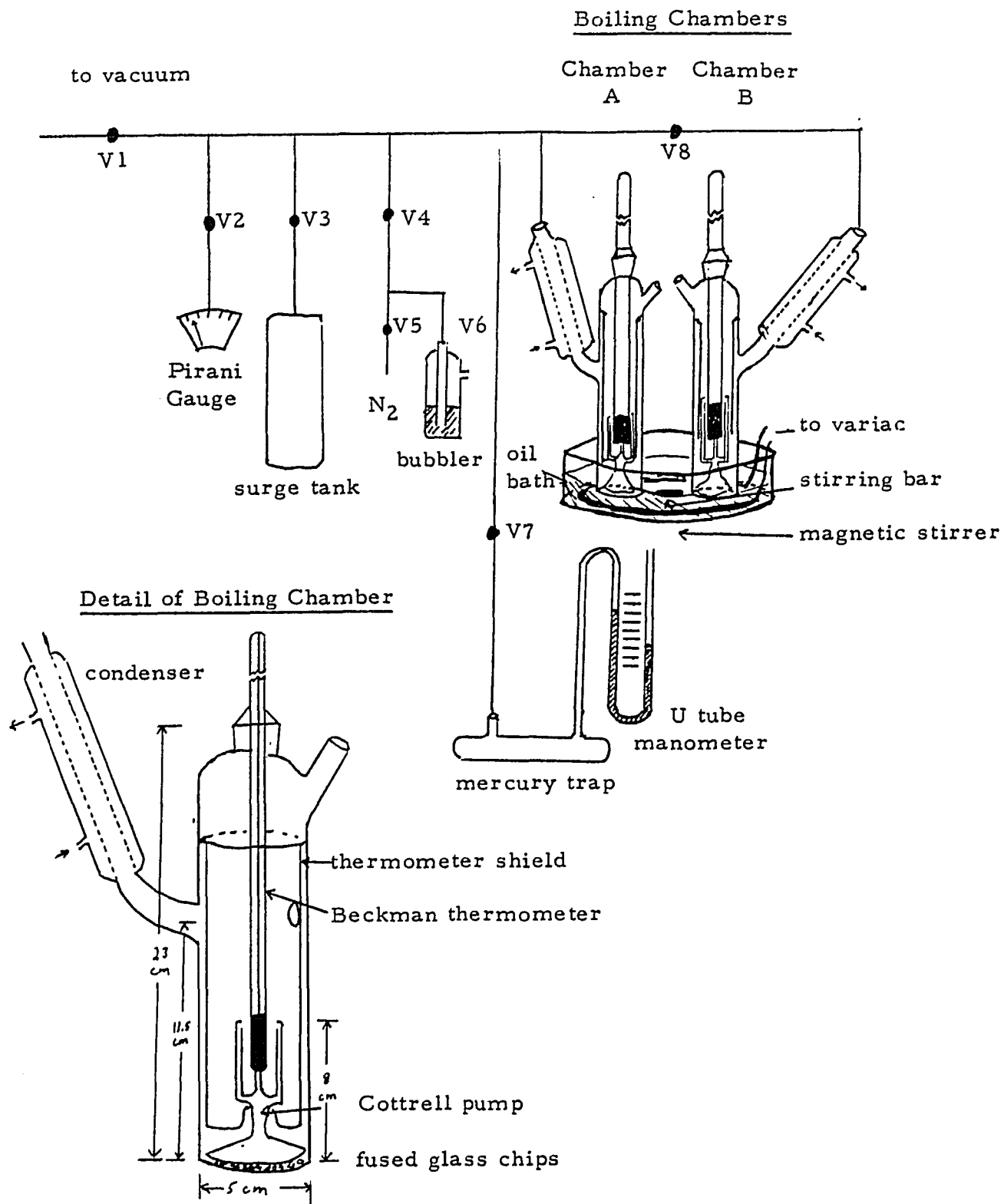


Figure 21

1% for a change in pressure of 40 mm Hg or 0.025%/torr for diethyl ether.

In the usual ebullioscopic apparatus the boiling-point of elevation is a first order function of pressure. Therefore the pressure must be monitored very accurately. Walker and Ashby discuss the rather involved procedure for taking measurements with their apparatus under conditions above and below atmospheric pressure. For operation below atmospheric pressure, for instance 740 mm Hg, "... valve 4 is opened to the vacuum line and valve 3 is closed. After reaching the desired pressure, valves 1 and 2 are opened to obtain a rapid flow of nitrogen past the system. Finally, valve 3 is adjusted so as to maintain a constant pressure in the system by slowly leaking nitrogen thru the system to the partially closed valve 4 which remains under vacuum."⁸

The net difference between the systems of Figures 20 and 21 is that with two boiling chambers instead of one a more sensitive apparatus can be built without the cost of a precise manometer, with greater ease in reading.

To insure uniform heating of the boiling chambers, they are both heated in the same oil bath. While the apparatus is operating and the bath is being heated, the oil in the bath is stirred via a stirring bar and magnetic stirrer. The bath is heated by resistance wire via a Variac. Walker and Ashby⁸ recommend that the condenser be cooled

by ice water, but that does not appear to be necessary in our case. Apparently our laboratory water is cold enough so that there is no measured loss of solvent. A surge tank is necessary to keep pressure fluctuations to a minimum. A convenient surge tank is a spent nitrogen tank. The lines from the surge tank are copper with an epoxy copper-glass junction. The apparatus is very sensitive to drafts and radiation, consequently it is necessary to insulate the apparatus, especially the boiling chambers. This cannot be over emphasized. We carried out our work at 740 mm Hg, the same pressure that Walker and Ashby used in their work. It is recommended that operation of the apparatus be either below or above ambient pressure so that if there is a leak, it will become apparent by an observed pressure change.

Each boiling chamber and its condenser is a single unit to minimize joints. Initially, we built a chamber that could come apart to facilitate cleaning. This had two major drawbacks; (1) Solvent could interact with the vacuum grease in the joint; (2) Two more large ground glass joints had to be sealed.

The boiling chambers are patterned after the Walker and Ashby chamber and are designed to operate with about 60 to 75 ml of solvent. Sharp glass chips are fused to the bottom of the chambers to insure a minimum of superheating by facilitating the boiling process. In each chamber a Cottrell pump directs the boiling liquid and vapor over the bulb of the Beckman thermometer. A Cottrell pump is necessary in

order to measure the temperature at which the liquid is in equilibrium with the vapor. The Cottrell pump is free to move within the boiling chamber. Each pump has three arms, the inside diameters of which are 2 mm. We found that ordinary Cottrell pumps designed for aqueous use did not work properly when used for diethyl ether. It appears that the small surface tension of diethyl ether necessitates the smaller diameter tubing. The thermometer shield prevents cold condensate from cooling the Beckman thermometer.

The Beckman thermometer may be read directly to 0.01°C but may be interpolated to 0.001°C with the aid of a magnifying glass. Since the range of the Beckman thermometer is only a few degrees, it is worth while spending the time to adjust the mercury level in the thermometers to operate in the middle of the range.

The top of the boiling chamber has an arm in which a serum stopper is inserted where aliquots of sample may be inserted via a syringe or wire needle without air contamination. We found ultra high vacuum stopcocks to work well with silicone grease as a lubricant.

The operation of the apparatus is described as follows: With all valves open except 4 and 7, the complete system is evacuated, using a roughing pump combined with a diffusion pump, to a pressure of less than 1 millitorr, as measured by a calibrated Pirani gauge. If this pressure cannot be achieved a leak may be the cause. A Tesla coil is an invaluable aid in locating leaks in a glass apparatus such

as this one.

To fill the system with N_2 , close valves 1 and 2, open valves 5 and 6, allow N_2 to flow thru the bubbler to eliminate any residual air, and then monitor valve 4 carefully until atmospheric pressure is achieved. Valve 8 is always left open except under two conditions: (1) To isolate leaks. (2) To isolate the chambers so as to prevent possible distillation when the apparatus is allowed to boil for long periods of time. Next a measured mass of solvent is injected into each chamber (60 ml is the best initial volume for diethyl ether). To facilitate boiling the solvent usually must have a gas dissolved in it (nitrogen is the most convenient), otherwise it will only bump.

After good boiling and pumping is achieved (we found a temperature of $57^\circ C$ for the oil bath to be optimal), the final desired pressure is regulated according to the barometric pressure.

Barometric pressure = system pressure + monometer pressure.

When the system reaches equilibrium, the difference in readings of the Beckman thermometers will remain constant. When three consecutive difference readings agree to within $0.001^\circ C$, the difference reading (ΔT) may be taken as final. Now the sample may be added to chamber B. The change from the original ΔT ($\Delta \Delta T$) is the boiling point elevation. There are a number of ways to introduce the sample. Most convenient for us was to add crystalline $MgI_2 \cdot 2Et_2O$ to a pre-weighed sample chamber in a dry box, then the sample

Figure 22

Sample Chamber and Transfer Process

With careful technique the sample may be transferred from the sample chamber into the boiling chamber with no air contamination.

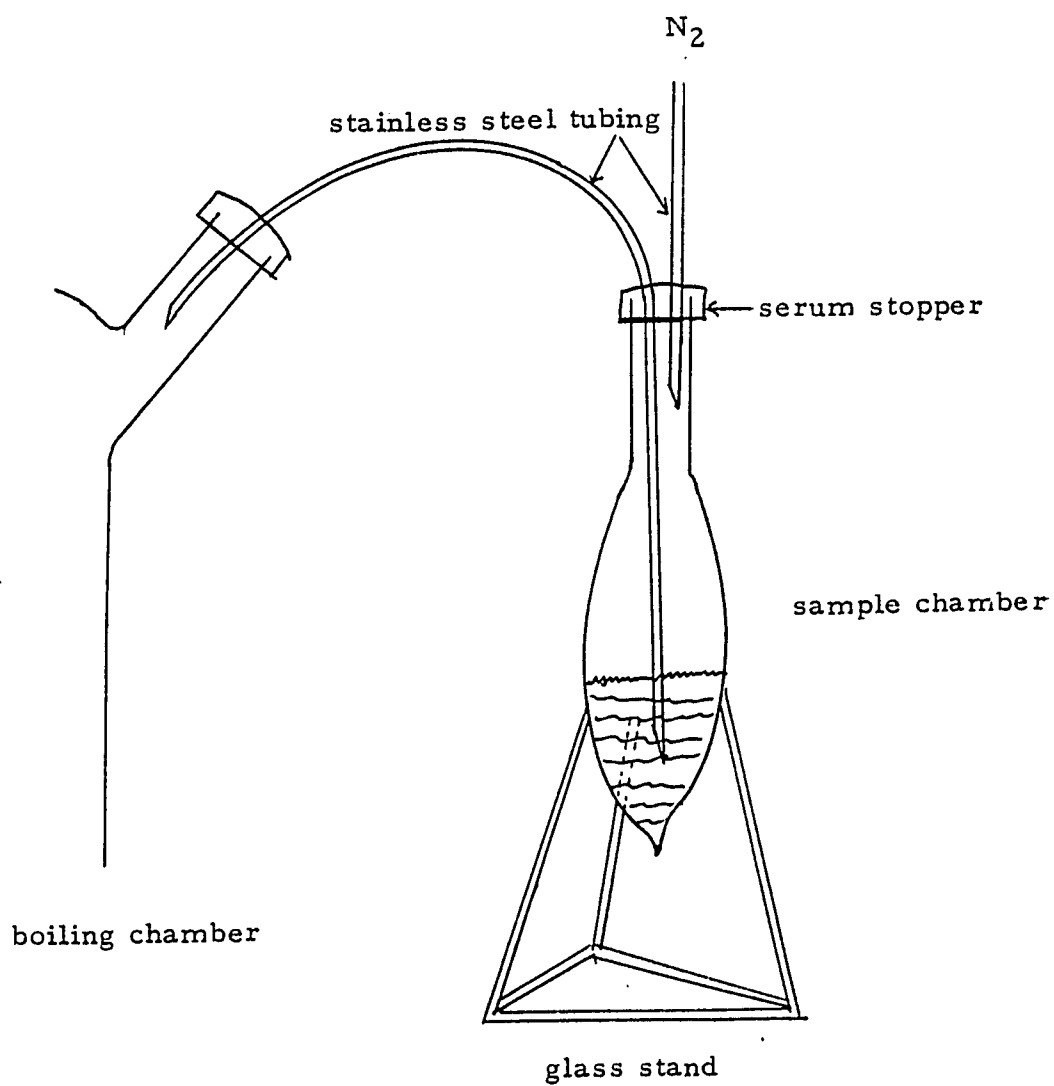


Figure 22

chamber was reweighed. A known volume of diethyl ether was added via a syringe. The sample was then introduced into a boiling chamber via a double ended needle under N_2 pressure. (See Fig. 22.)

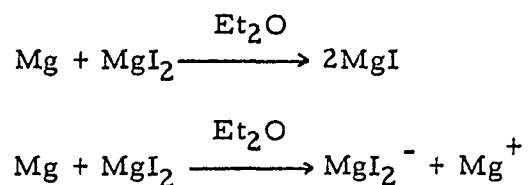
We made a sample chamber with a cone shaped bottom so that a double ended needle would match the bottom, allowing almost all the solution to be transferred. The sample chamber may then be rinsed with a small amount of solvent, say 1/2 cc, to transfer all the sample. With careful technique, there will be no air contamination. Several additions of sample are usually desirable.

Various compounds require different lengths of time for ΔT to remain stable. Benzophenone is rapid while MgI_2 etherate may require one and one half hours, especially at higher concentrations. With MgI_2 etherate, $\Delta \Delta T$ is generally observed to decrease while the system is approaching equilibrium.

The standard equation that relates boiling point elevation to molality is used: $\Delta \Delta T = K_b m$. K_b , the molal boiling point elevation constant, is 2.01 for diethyl ether at 740 torr.⁸ It is important to remember for the calculations of molecular mass that the solvent in each fraction must be added to the mass of the initial solvent.

RESULTS

We compared the association of MgI_2 etherate in diethyl ether with and without magnesium. The association (i) is the molecular mass observed/formula mass. If univalent magnesium was formed with $\text{Mg} + \text{MgI}_2$, one might expect reactions such as



If either or both of these reactions were to occur, one would expect the association to be less than with pure MgI_2 etherate. Calibration of the ebullioscopic apparatus was accomplished with benzophenone. In Fig. 23 the % deviation from the expected boiling point elevation and observed boiling point elevation is given. One can observe that the precision in an individual run and between runs is good. From this data the molal boiling-point elevation constant ($^{\circ}\text{C}/\text{mole per } 1000 \text{ gm Et}_2\text{O}$) for diethyl ether, as the concentration approaches zero molal at 740 torr, is 2.06. A summary of the association experiments, with and without added Mg to MgI_2 etherate, is given in Fig. 24. No difference was observed. Also, no significant

Figure 23

Calibration Curve of Ebullioscopic Apparatus

Plot of the $\frac{\text{Actual } \Delta T - \text{Calculated } \Delta T}{\text{Calculated } T} \cdot 100\%$ (% deviation of the molal boiling point constant for diethyl ether of 2.01 degree/mole per 1000 gm diethyl ether at 740 torr) vs. molality of benzophenone. As can be observed, the consistency is good between runs and within individual runs.

This graph shows two runs, one marked with a • and the other with an x.

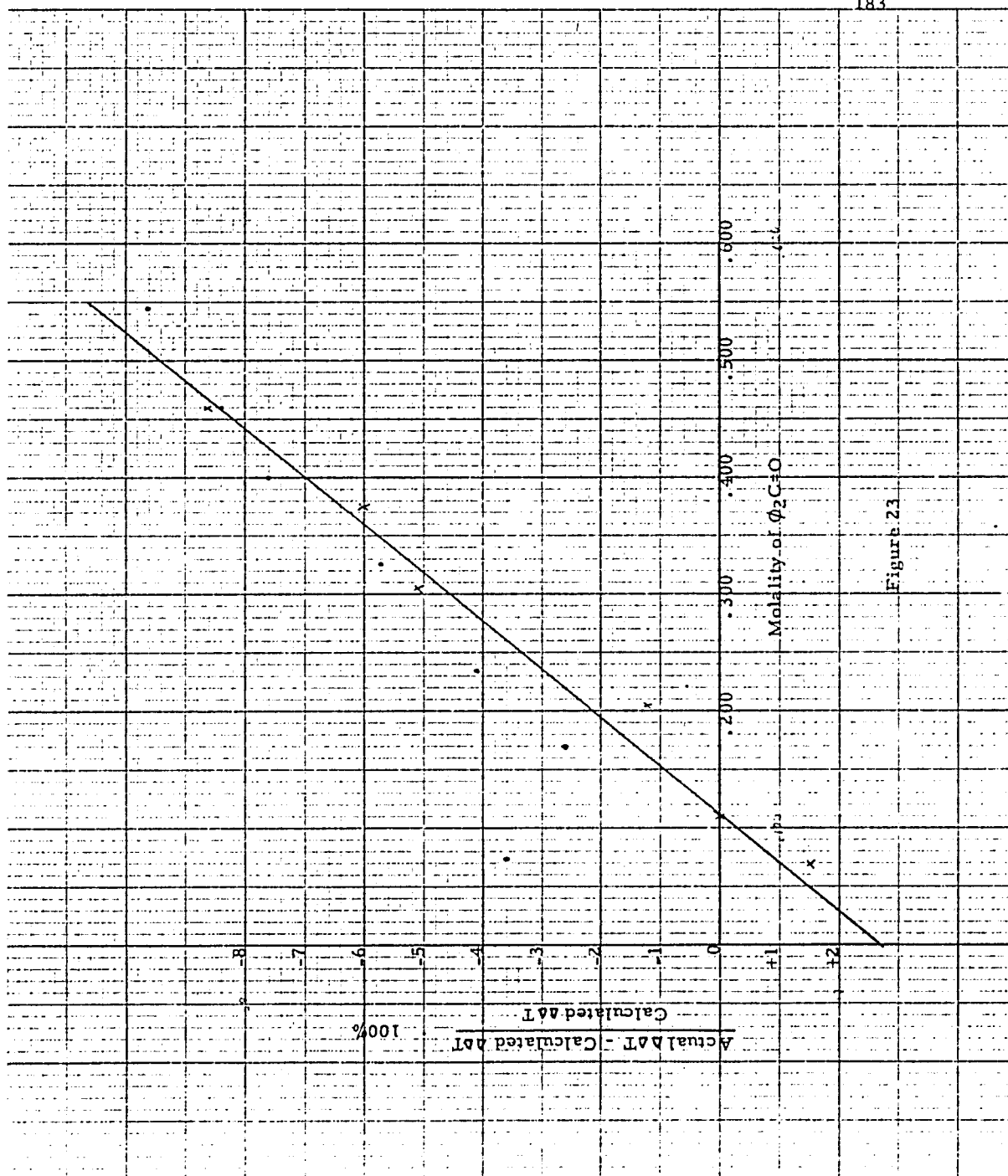
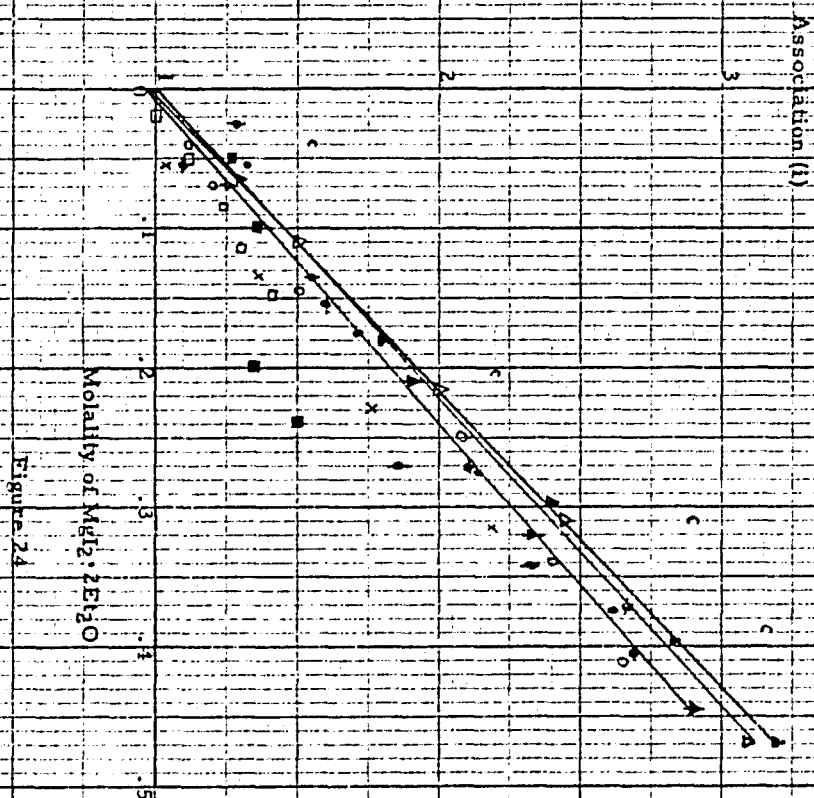


Figure 23

Figure 24

Association vs. Molality of $\text{MgI}_2 \cdot 2\text{Et}_2\text{O}$ in the Presence
and Absence of Magnesium Metal

A particular shaped mark represents the same run. Solid marks such as $\blacktriangle$, $\blacktriangleup$, $\blacktriangleright$, $\blacksquare$ and $\blacklozenge$ are runs with magnesium metal and open marks such as $\triangle$, $\triangleright$, $\lozenge$ and $\times$ are runs with no magnesium added to $\text{MgI}_2 \cdot 2\text{Et}_2\text{O}$. The mark c is a run that was contaminated (there was a leak). The runs indicated by $\blacktriangle$, $\blacktriangleup$ and $\triangle$ used degassed diethyl ether that was saturated with nitrogen and the plots show the best straight line for each of these runs. As can be seen, these three plots are the most consistent, and show no difference between $\text{MgI}_2 \cdot 2\text{Et}_2\text{O}$ solutions with and without magnesium metal. For these plots it was assumed that the ratio of MgI_2 to Et_2O for MgI_2 etherate was one to two while Walker and Ashby⁸ used a ratio of one to one. This only slightly changes the position of the plots as a whole but doesn't change their relative positions.



mass change of magnesium was observed before and after the experiment. Sometimes a slight mass increase was observed (on the order of 0.0010 gm per gram of Mg). This was attributed to slight oxidation during weighing.

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