

Infrared Absorption Spectra of Four Grignard Solutions

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8/3 hydrate the maxima are, respectively, $\Delta\bar{\nu}$ 3346 and 3424 with a great disparity in intensities of the two shifts. The influence of the configuration of the crystals is evidently reflected in a change in force constant between the hydrogen and oxygen atoms.

The accuracy of determining the maxima of the extremely broad O \leftrightarrow H oscillations does not permit too much weight to be placed on reasonable variations in the magnitude of these shifts. This may be said also of the lowest frequencies. In the case of ice, however, there is a genuine displacement of the maxima, and the change in the magnitude of $\Delta\bar{\nu}$ 2170 between hot and cold water is likewise real.

SUMMARY

The Raman shifts obtained from water, ice and some solutions have been investigated particularly from the point of view of the low frequency oscillations. These could not be present

in the spectrum of a simple unhindered triatomic molecule and their existence is explicable only as a result of intermolecular interaction regardless of the precise mechanism of such interaction. The greatly enhanced intensities of these lines in ice as compared with water furnish reasonably conclusive evidence that the assignment of these frequencies to intermolecular coupling is proper. Moreover their alteration in intensity in the liquid phase with temperature variations is consistent with the concept of structural changes in the liquid as a function of temperature. In solution, however, the results are not in entire agreement with the lowering of the structural temperature of the solutions by ions of small radii or with an equivalent elevation in temperature by ions of large radii. New frequencies are reported for ice and the existence of a shift at $\Delta\bar{\nu}$ 2170 for water has been found to be genuine. Other low frequencies noted by a few observers have been confirmed.

Infrared Absorption Spectra of Four Grignard Solutions*

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(Received May 18, 1936)

Absorption spectra are reported for twelve liquids: four typical Grignard solutions, and eight related substances, for the range 1.0 to 13 μ . Absorption frequencies at 784, 910, 4250 and possibly 1950 cm^{-1} appear to be associated with compounds which contain magnesium. Possible origins of these frequencies are discussed.

INTRODUCTION

THE infrared absorption spectra of twelve compounds, including four typical Grignard solutions, are reported in this paper, for the range from 1 μ to 13 μ . The primary purpose of the work was to determine the wave-lengths at which selective absorption occurs, in several Grignard compounds. This work is part of a broad study of a number of the physical properties of such compounds, which has been carried on under the leadership of Professor R. T. Dufford; it is

hoped that eventually it may prove to be possible to correlate these properties with the very interesting photovoltaic effects which have been shown¹ to exist in solutions of Grignard compounds.

Grignard compounds are prepared in anhydrous ethyl ether solution, by the action of magnesium metal on various organic halides.

TABLE I.

Region	Wave-lengths	Cell Thickness	Slit Width
1.	1.0- 1.9 μ	1.00 cm	0.025 cm
2.	1.9- 4.5 μ	0.032 cm	0.030 cm
3.	4.5- 9.0 μ	0.026 cm	0.035 cm
4.	9.0-13.0 μ	0.016 cm	0.065 cm

* Abstracted from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Missouri.

While some of these compounds can be crystallized out, into crystals containing ether of crystallization, most of the work done on them is done with ether solutions. In any case, they are so readily attacked by oxygen and by water that they must be carefully shielded from contact with the atmosphere; this condition multiplies the difficulties of studying them. It is true that absorption spectra of vapors may be more instructive, generally; but in the case of compounds such as these, which are not known to exist in the vapor state, it seems necessary to be satisfied with spectra obtained from their solutions. The photovoltaic properties mentioned above are, of course, also properties of the solutions.

EXPERIMENTAL

A Wadsworth type of prism-mirror spectrometer, equipped with a 60° rocksalt prism, was used. The instrument was designed by Professor Dufford, and was built by Mr. Gus Tornsjo, instrument maker at the University of Missouri. A great advantage of such an instrument is that, since all the focusing is done by mirrors, the spectrometer can be adjusted by means of visible light, such as the green mercury line; it will then be in adjustment for all wave-lengths.

A street lamp with a linear tungsten filament was used as a source of light for the region 1.0 to 4μ . For longer wave-lengths, which would be cut off by glass, a Nernst glow lamp was used. The sensitive element of the outfit was a vacuum linear thermopile built by Dr. W. W. Coblentz, of the National Bureau of Standards. A Leeds and Northrup type HS galvanometer was used with this thermopile. The galvanometer deflections, and also the prism settings, were read by lamp and scale. A calibration table similar to that made by Cross² was made and used. The calibration was checked frequently.

After preliminary trials, it was found desirable to take the readings for each spectrum in four parts, each of which required about four hours of observing time for completion. Numerous check runs were made, every spectrum being observed at least twice. Actually, several spectra would be studied in a given range before going on to the next, to avoid frequent resetting of slits, etc. The wave-lengths covered in each part, together with

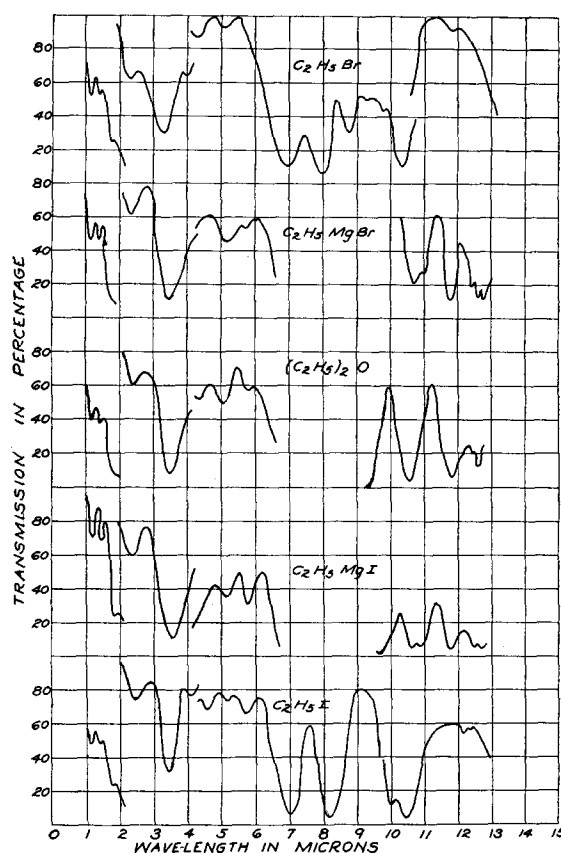


FIG. 1.

the slit widths and cell thicknesses used, are given in Table I.

The increased slit widths which were made necessary at longer wave-lengths by the decreasing energy of the source in this part of the spectrum, are about balanced by the increased dispersion; so that the slit widths used correspond approximately to a range of from 0.001 to 0.003μ . The rear slit was set at approximately the same width as the entrance slit. The thinner cells had rocksalt windows separated by wire spacers; it would be very difficult to work with much thinner layers of liquid. In taking readings, the energy transmitted was compared with that transmitted by a similar dummy cell, so that any possible absorption by the windows would be eliminated. With an empty dummy cell, this method introduces a slight error due to the fact that the reflection losses in each cell are not quite equal. This error varies continuously with the wave-length; and a slight further error might enter on

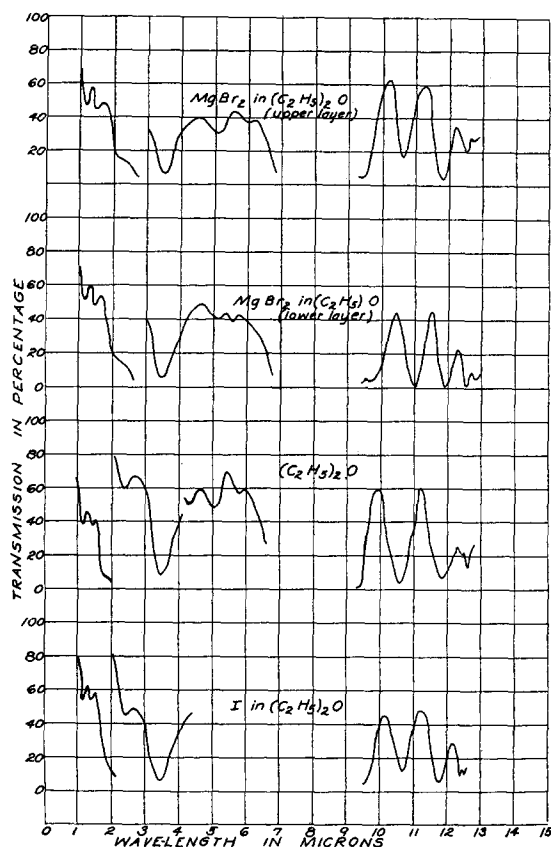


FIG. 2.

account of the fact that the light passing through the cells was not quite parallel. Hence extinction coefficients computed from these data might be in error by two or three percent. Since the amount of time needed to determine these corrections accurately for all wave-lengths for each compound would be prohibitive, and since they are not necessary for the purpose of locating wave-lengths of selective absorption, these small corrections were neglected. Curves were plotted showing the percentage transmission of the cell as compared with the dummy cell, and the intensity of the absorption bands was then expressed qualitatively on a scale of 0 (barely perceptible) to 3 (very intense).

RESULTS

In the following paragraphs, the results for individual compounds are given first; then the results for the Grignard compounds are discussed collectively.

Ethyl ether, $(C_2H_5)_2O$

Results for this substance are stated first, since it is the solvent for all the Grignard solutions. Absorption bands were found with the points of most intense absorption at the following wave numbers; the relative intensities are given in parentheses: 8680 (1), 7190 (1), 5850 (0), 4330 (2), 2896 (3), 2255 (0), 1978 (1), 1720 (1), 1032 (3), 843 (3), 802 (1), 796 (2). The four highest frequencies are pretty certainly combination or overtone bands. The intense band centered at 2896 cm^{-1} is known¹⁹ to be a fundamental associated with the C—H linkage. The absorption here is so intense that the ether is practically opaque; even with a cell of only 0.016 cm thickness, and with wide slits, no transmission above 10 percent was obtained in the region from 6.8 to $9.5\text{ }\mu$. While the necessity for leaving this gap in the spectra of ether and the ether solutions is regretted, the lack is less serious than at first appears; for it is known from the Raman effect¹⁹ that the frequencies which characterize ether in this region are at 2980, 2930, and 2870 cm^{-1} , and there is small reason to expect anything else in this region except possibly unimportant combination bands. The identification of the remaining bands is not essential for present purposes.

Ethyl bromide, C_2H_5Br

This substance might be present in ethyl magnesium bromide solution as an impurity, if the reaction which formed the Grignard compound did not go to completion. It is therefore necessary to have its spectrum for comparison. Absorption bands were found at the following wave numbers: 8880 (1), 7300 (1), 5840 (0), 4410 (1), 2910 (3), 2520 (1), 2300 (1), 1980 (0), 1920 (0), 1740 (0), 1430 (3), 1257 (3), 1123 (2), 1065 (1), 1018 (0), 967 (3), 844 (1). Cross and Daniels⁴ have reported an additional band at 1385 cm^{-1} , which was not observed in the present work.

While this compound contained no ether, the similarity of its spectrum to that of ether is striking, the same frequencies frequently occurring in both spectra. This is just what should be expected; for the hydrocarbon part of both molecules is the same. The differences between the spectra should be due to the substitution of the C—Br bond for the C—O bonds of the ether.

Similar remarks apply in the case of the following compounds also.

Ethyl iodide, C_2H_5I

This substance might be present in ethyl magnesium iodide solution as an impurity, if the reaction which formed the Grignard compound did not go to completion. It is therefore desirable to have its spectrum for comparison. Absorption bands were found at 8850 (1), 7140 (1), 5720 (0), 4205 (2), 2940 (3), 2430 (1), 2196 (1), 1960 (1), 1727 (2), 1428 (3), 1211 (3), 1010 (1), 961 (3), 855 (0), 840 (0), 825 (1), and 806 (0). An additional band at 1380 cm^{-1} , reported by Cross and Daniels,⁴ was not observed in this work. This spectrum is strikingly like that of ether and that of ethyl bromide, for the reasons suggested in the preceding paragraph.

Ethyl magnesium bromide, C_2H_5MgBr , in ether solution

This is one of the typical Grignard solutions studied. Structurally, the compound differs from ethyl bromide, discussed above, by the insertion of the magnesium atom between the bromine atom and the ethyl radical. This solution, like all the other Grignard solutions discussed, had a concentration of approximately one mole per liter. Absorption bands were found as follows: 8550 (1), 7030 (1), 4250 (2), 2870 (3), 1990 (0), 1955 (2), 1740 (1), 1665 (0), 932 (3), 908 (3), 843 (3), 802 (1), 796 (2), and 784 (2). Of course, this spectrum shows the frequencies of the solvent ether; but many of these should be equally characteristic of the Grignard compound also, as they were of the other compounds discussed above. It is of course impossible to state to what extent any of these is to be attributed to the Grignard compound. However, the bands at 784, 908, 4250, and possibly 1955, did not appear in any of the preceding spectra, and hence appear to belong definitely to the Grignard compound, and to be there because of the introduction of the magnesium atom into the molecule. They will be discussed later on, in connection with the results from the other Grignard compounds.

Ethyl magnesium iodide, C_2H_5MgI , in ether solution

This is another typical Grignard solution, differing from the last only in that it contains

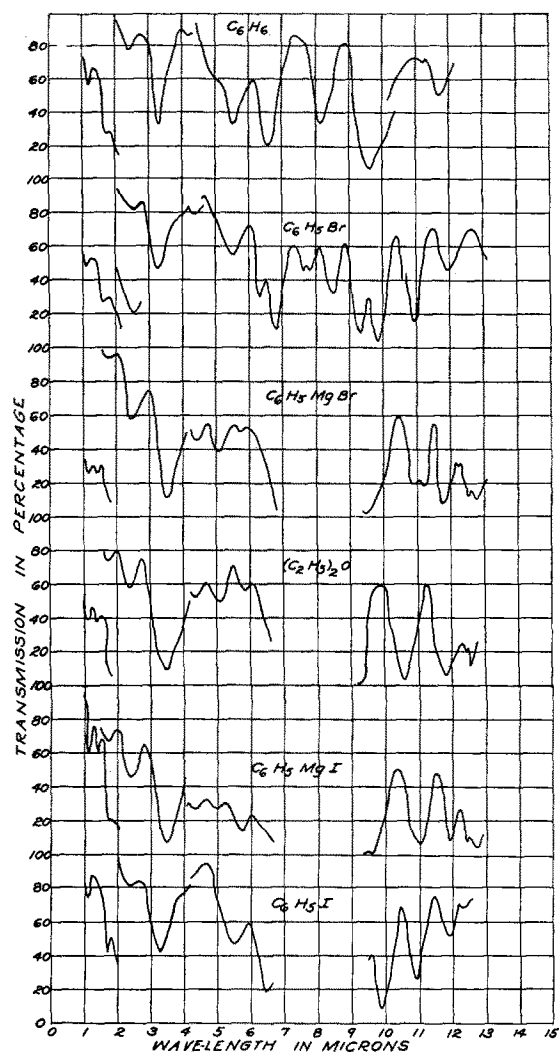
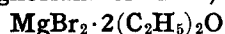


FIG. 3.

iodine instead of bromine. Absorption bands were found at 8550 (1), 6890 (1), 5410 (0), 4255 (2), 2870 (3), 1970 (1), 1715 (2), 1033 (3), 938 (3), 914 (3), 844 (3), 798 (0), and 783 (1). As with the preceding compound, many of the frequencies that are certainly due in part to the solvent ether are probably also partly due to the Grignard compound too. But, just as in the preceding case, there are frequencies at 783, 914, 4255, and possibly 1970, which appear to belong to the Grignard compound, and not to any of the related compounds previously discussed. The band at 1950 cm^{-1} is close to a weak ether band, so that its exact location and identification are somewhat uncertain.

Magnesium bromide, in ether solution;

This substance is a possible impurity in certain of the Grignard solutions, as the result of possible side reactions. For the present work, it was prepared by the action of magnesium on "ethylene bromide" (dibromoethane), in ether solution. The solution separates into two layers, the upper layer being clear and colorless, the lower dark brown and nearly opaque. The lower layer contains about twenty times as high a concentration of MgBr_2 as the upper; the MgBr_2 crystallizes easily from the lower layer, forming transparent colorless crystals which contain ether of crystallization. Both the crystals and the solution react vigorously with water, which apparently replaces the ether associated with the MgBr_2 molecules. For the lower layer, bands were found at 8620 (1), 7040 (1), 2900 (3), 1930 (2), 1790 (1), 1027 (3), 907 (3), 840 (2), 793 (2), and 778 (1). All of these are ether bands except those at 778 and 907 cm^{-1} , which are the same as the lowest frequencies that appeared to belong to the Grignard compounds discussed above. These will be discussed further later on. The results from the upper layer are the same, except that the non-ether bands are weaker.

Iodine, in ether solution

This is another possible impurity in certain Grignard solutions. While the iodine solutions

are somewhat more opaque in the infrared than pure ether, they do not show any new bands; no bands were found that did not clearly belong to the solvent ether. Coblenz⁶ has shown that bromine solutions behave similarly. Hence it seems permissible to conclude that neither of these substances, if present, would give rise to any bands which could mistakenly be attributed to the Grignard compounds, in the region studied here.

Benzene, C_6H_6

The results on this compound are not new; they are quoted partly because of the interest in comparing benzene itself with the derivatives discussed below, and partly because they will enable the reader to judge as to the accuracy of the present work by comparing these results with those of other observers. The absorption bands found were at 9050 (1), 5780 (0), 4130 (1), 3030 (3), 2410 (0), 1802 (2), 1500 (3), 1233 (3), 1042 (3), 897 (1), 857 (2), 806 (1) cm^{-1} . It is interesting to point out how, when the symmetry of the benzene molecule is destroyed by substituting a halogen for one of the hydrogen atoms, certain bands which are single in benzene become double in the spectra of the derivatives. Thus, the 1042, 1233, and 1500 cm^{-1} bands of benzene are replaced by doublets in the two following derivatives.

Bromobenzene, $\text{C}_6\text{H}_5\text{Br}$

This compound might be present as an impurity in certain Grignard solutions if the reac-

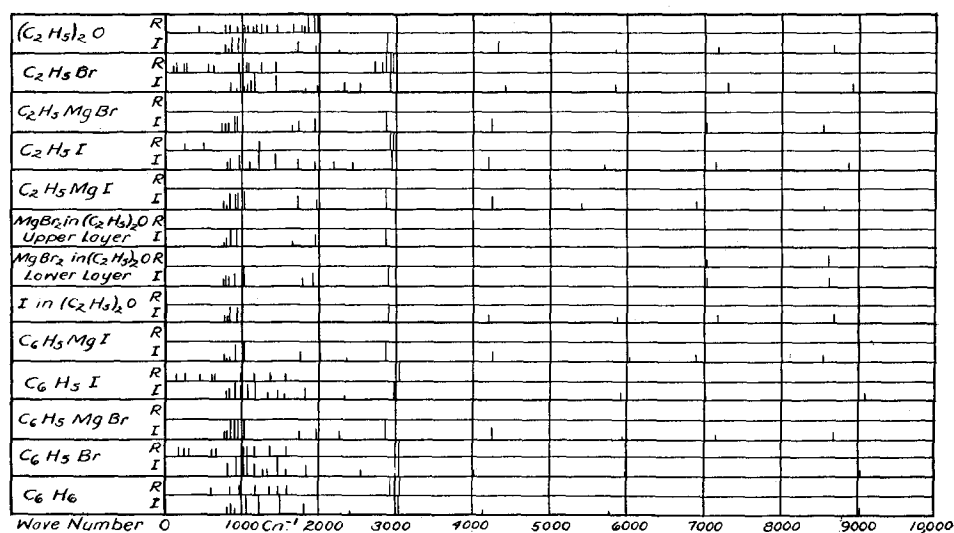


FIG. 4.

tion failed to go to completion. Its spectrum is therefore given for comparison. Its absorption bands were found at 9020 (1), 5980 (0), 4000 (1), 3060 (3), 2545 (1), 1833 (1), 1577 (1), 1473 (3), 1315 (1), 1280 (1), 1170 (2), 1075 (3), 1015 (3), 914 (3), 837 (2), and 793 (0). In this compound, the 1042 cm^{-1} band of benzene is replaced by bands at 1015 and 1075; the 1233 band by bands at 1170 and 1280; and the 1500 band by bands at 1473 and 1577 cm^{-1} .

Iodobenzene, $\text{C}_6\text{H}_5\text{I}$

Since this compound is one that might be present as an impurity in certain Grignard solutions, its spectrum is given for comparison. Absorption bands were found at 9090 (1), 7030 (0), 5920 (1), 4000 (1), 2990 (3), 2330 (0), 1823 (2), 1563 (1), 1470 (2), 1340 (1), 1265 (0), 1177 (2), 1069 (3), 1010 (3), 913 (3), 837 (2), 789 (1). In this compound, the 1042 cm^{-1} band of benzene is replaced by bands at 1010 and 1069; the 1233 band by bands at 1177 and 1265; and the 1500 band by bands at 1470 and 1563 cm^{-1} , just as was found in bromobenzene above. While some of these bands are fairly intense, no one of them was found in the spectra of the corresponding Grignard solutions; hence it seems possible to conclude that the Grignard solutions were not badly contaminated by unreacted bromobenzene or iodobenzene, respectively.

Phenyl magnesium bromide, $\text{C}_6\text{H}_5\text{MgBr}$, in ether solution

This is one of the typical aromatic Grignard solutions studied. Absorption bands were found at 8680 (1), 7140 (1), 5950 (0), 4255 (2), 2870 (3), 2270 (1), 1980 (2), 1740 (1), 1040 (3), 913 (3), 890 (3), 843 (3), 820 (0), 798 (1), 784 (1). Most of these bands coincide with bands due to the solvent ether or with bands due to the parent bromobenzene (which could not have been present in large quantity); but probably most of these bands are just as characteristic of the Grignard compound as of the other compounds, on account of the similarity of structure. There are three bands, at 784, 913 and 4255 cm^{-1} , which do not appear in the spectra of the related compounds, and which therefore appear to belong to the Grignard compound. They agree with the bands found in the spectra of the aliphatic Grignard compounds already discussed.

Phenyl magnesium iodide, $\text{C}_6\text{H}_5\text{MgI}$, in ether solution

This is another typical aromatic Grignard compound in solution. Absorption bands were found at 8550 (1), 6890 (1), 6020 (0), 4250 (2), 2870 (3), 2360 (0), 2020 (1), 1765 (2), 1032 (3), 907 (3), 841 (2), 798 (0), and 784 (1). As in the preceding compound, there are bands at 784, 907, and 4250 cm^{-1} which appear to belong to the Grignard compound.

In order to make possible a further check on the results presented in this article, curves showing the experimental results on the aliphatic Grignard compounds and their related substances are included in Fig. 1; Fig. 2 are the curves for the substances magnesium bromide and iodine that are related to both groups of Grignard compounds. Fig. 3 shows the curves for the aromatic Grignard compounds and their related substances. Fig. 4 shows how the observed infrared frequencies compare with those found by various workers for the same substances, in the Raman effect. The check is close for the aliphatic compounds, but less so for the aromatic compounds.

To summarize the results for the Grignard compounds: it is probable that the group of frequencies that persist through ether, ethyl bromide, etc., or through benzene, bromobenzene, etc., being associated with the hydrocarbon part of the molecules, are equally characteristic of the Grignard compounds also; but the present method of attack does not lend itself readily to proof of this. Outside of these, there remain the bands at approximately 784, 910, 4250, and possibly 1955 cm^{-1} to be explained. One suggestion is that they are ether bands which have been shifted because of the material in solution. If so, the unmodified ether bands appear along with them. The 4250 band appeared in all the spectra of Grignard solutions, and nowhere else. It is no doubt a combination band of some sort, but further statements appear unjustified at present. The 1955 band, which is also no doubt some kind of combination band, is more doubtful; it appeared only in the spectra of the aliphatic Grignard solutions, and it may possibly be an ether band. The bands at 784 and 910 require further attention. In addition to the possibility pointed out above, there are at least two other explana-

tions which seem not to be ruled out by the present evidence. It may be pointed out that they are not associated with the C—Mg linkage, since they appear in the spectra of the MgBr_2 solutions. They might be associated with motion along the Mg—Br linkage (according to the view of Dadiou and Kohlrausch¹⁹), since this linkage exists in all the compounds which gave these bands. Against this explanation are the arguments that the frequencies are higher than would be expected from such motion, unless these are overtone or combination bands, and that the frequencies are so nearly alike in bromine and iodine-bearing compounds. There is some evidence for this explanation, however, from the Raman effect in similar compounds.³ Another possible hypothesis is that they are associated with the etheration structure which chemists believe is common to all the compounds studied which gave these bands. On this view, the correct formulas for the compounds would be $\text{C}_2\text{H}_5\text{MgBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, $\text{C}_2\text{H}_5\text{MgI} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, $\text{C}_6\text{H}_5\text{MgBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, etc. Again the frequencies seem higher than would be expected from such a structure. Until the spectra can be explored further into the infrared, so that possible lower frequencies can be investigated, it seems best to leave open the question as to the origin of these bands.

The author wishes to acknowledge the assistance received from the members of the department of physics of the University of Missouri where this work was done, and to make special

acknowledgment of the help and guidance received throughout the work from Professor R. T. Dufford, who suggested the problem and directed the work.

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Note on the Spectra of the Disubstituted Acetylenes and of the Mustard Oils

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(Received December 22, 1936)

IT has been observed that in the Raman spectra of many disubstituted acetylenes the line corresponding to the so-called $\text{C}\equiv\text{C}$ frequency is split into two components of not greatly different intensity,¹ though this is not the case in the monosubstituted compounds. In the mustard oils the $\text{C}\equiv\text{N}$ Raman line is double,² and in allyl

¹ For references see J. H. Hibben, *Chem. Rev.* **18**, 1 (1936).

² For references see K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Springer, Berlin, 1931).

mustard oil,³ the one substance which appears to have been studied with sufficient dispersion, the corresponding infrared band shows definite indications of splitting into two components. This doubling is not observed in the organic thiocyanates. These facts have caused some speculation but so far appear never to have received a satisfactory explanation. The presence of two funda-

³ W. W. Coblenz, *Investigations of Infra-Red Spectra* (Carnegie Institution, 1905).