

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 MgBr₂ 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 C₂H₅MgBr·2(C₂H₅)₂O, C₂H₅MgI·2(C₂H₅)₂O, C₆H₅MgBr·2(C₂H₅)₂O, 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 C≡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 C≡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).

mentals in the 2200 cm^{-1} region appears quite impossible for most of the molecules showing the doubling, and on the other hand the coexistence of two forms of molecule with slightly different frequencies appears unlikely, especially in the case of the acetylenes. Consequently the author proposes an explanation involving a Fermi resonance interaction between the $\text{C}\equiv\text{C}$ or $\text{C}\equiv\text{N}$ fundamental, as the case may be, and the overtone of a certain other vibration of approximately one-half or one-third the frequency.

The situation appears especially clear in the case of the acetylenes. When in acetylene one of the hydrogen atoms is replaced by a heavier atom the $\text{C}\equiv\text{C}$ frequency will be considerably increased, even though the triple bond force constant is unaffected. The replacement of the second hydrogen will produce a further increase of about the same amount. A similar situation is to be expected if replacement is by alkyl radicals. Owing to the zigzag structure of these (bond angles around $109^\circ 28'$) and the absence of disturbing frequencies the $\text{C}-\text{C}\equiv\text{C}-\text{H}$ or $\text{C}-\text{C}\equiv\text{C}-\text{C}$ groups are able to perform the 2200 cm^{-1} oscillation with very little interaction with the remainder of the molecule. In going from acetylene to the monosubstituted compounds the shift in $\text{C}\equiv\text{C}$ frequency is about 160 cm^{-1} . Disubstitution produces a further increase of 150 cm^{-1} , if we measure to the *mean* of the doublet, apparently bringing the frequency close to a multiple of that of another vibration. The shifts observed are not greatly different from those calculated for free $\text{C}-\text{C}\equiv\text{C}-\text{H}$ and $\text{C}-\text{C}\equiv\text{C}-\text{C}$ groups on the assumption of reasonable force constants.

We are now concerned with the identification of the vibration which in a harmonic is capable of interacting with the fundamental of the $\text{C}\equiv\text{C}$ oscillation of the disubstituted acetylenes. It must be a vibration which persists, little modified in type and frequency, through all these compounds, beginning with dimethyl acetylene. It must involve the $\text{C}-\text{C}\equiv\text{C}-\text{C}$ group to a very considerable extent, and its frequency must be approximately equal to some submultiple of 2271 cm^{-1} , which is approximately that to be expected for the $\text{C}\equiv\text{C}$ fundamental in the absence of the interaction under consideration. There appear to be three possibilities. Two of

these are vibrations within the $\text{C}-\text{C}\equiv\text{C}-\text{C}$ group itself which might be designated as $\text{C}-\text{C}$ oscillations, since they mainly involve the stretching and compression of carbon, carbon single bonds. In the symmetrical motion the frequency should be much lower than that of the $\text{C}-\text{C}$ vibration in ethane. A rough estimate indicates that it should be around 700 cm^{-1} , and it may be noted that a Raman line occurs at 773 cm^{-1} in dimethyl acetylene. In the unsymmetrical motion, in which the two central atoms of the group move in one direction and the two extreme ones in the opposite direction, the frequency should be well above 1000 cm^{-1} , owing to the very considerable interaction between first and third, and second and fourth atoms in the chain. This vibration should be inactive in the Raman effect but would probably appear strongly in the infrared.

The two vibrations mentioned meet the symmetry requirements and would appear to have roughly the right frequencies for interaction with the 2271 cm^{-1} fundamental in their second and first overtones, respectively. An infrared investigation would settle most simply the question as to which is really the one involved, by establishing the frequency of the latter one. However, it should be noted that in some cases of substitution by other than alkyl radicals the $\text{C}\equiv\text{C}$ Raman line appears with three components, suggesting that in some compounds both may play some part. The resonance interaction phenomenon is of course a rather delicate affair, depending as it does upon nearly exact integral ratios between frequencies, and it is rather remarkable that conditions may be satisfied through the considerable series of acetylenes which has been studied.

A third but somewhat less likely possibility should be mentioned, namely a vibration involving a swinging of the hydrogens attached to the extreme carbon atoms of the $\text{C}-\text{C}\equiv\text{C}-\text{C}$ group. In dimethyl acetylene there is one such vibration which would nearly meet the requirements. It is degenerate, inactive in the infrared, and should have a frequency a little above 1000 cm^{-1} . It is one which might roughly be described as a tilting of the two methyl groups away from the symmetry axis, in opposite directions. However, in all other members of the disubstituted acetylene series this oscillation is greatly modified, not

only in nature but presumably also in frequency.

Now in the mustard oils there appears to be a characteristic frequency around 1070 cm^{-1} , about half of the $\text{C}\equiv\text{N}$ frequency which in this case is approximately 2150 cm^{-1} . This appears as a strong Raman line in the ethyl and isobutyl compounds and as an intense infrared band in the methyl and ethyl derivatives. The Raman line was not reported for allyl mustard oil but the spectrum appears to have been very weak and incompletely developed. Unfortunately infrared data on this region are also lacking. The Raman

line was also apparently missing in phenyl and *p*-tolyl mustard oils but in the former a strong infrared band was found at about 1070 cm^{-1} and in the latter no data are available. In methyl and ethyl thiocyanate, which show no splitting of the $\text{C}\equiv\text{N}$ line, the 1070 cm^{-1} Raman line is missing.

It seems rather probable that this frequency which is characteristic of the mustard oils is to be attributed to a C-N vibration. Owing to the asymmetry of the C-N \equiv C-S group it is permitted to appear in both infrared and Raman spectra.

The Dissociation Pressure of a Solid Under Inert Gas Pressure¹

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(Received November 30, 1936)

The mole fraction of ammonia in equilibrium with barium chloride octamine at 32°C and at various pressures of helium, argon and nitrogen has been determined. At every pressure, the mole fraction is greater than that expected by a simple application of the Poynting relation. An equation has been derived for the chemical potential of a component of a gaseous mixture in terms of the total pressure, the mole fraction, and the second virial

coefficients. This equation has been tested and shown to give fair agreement between calculated and observed values. One advantage is the fact that it can be used to calculate the mole fraction of the component of a gas mixture which arises from the dissociation of a solid with which the mixture is in equilibrium. It is also shown how these measurements might be used to calculate the second virial coefficients of gaseous mixtures.

INTRODUCTION

FOR the calculation of equilibria in systems containing one component in two phases, that is, in both the gaseous and solid states, it is necessary to know the vapor pressure of that component over the solid. The way in which the vapor pressure changes with the total pressure is also of great importance. It is well known that increasing the pressure on a solid increases its vapor pressure and that from thermodynamic formulae we may get a quantitative measure of this increase.

At constant temperature, the change of the Gibbs free energy of a system with a change in pressure is given by the relation

$$(\partial G/\partial P)_T = V. \quad (1)$$

¹This article is based upon the dissertation submitted to the Faculty of Philosophy of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

When mixtures are to be discussed it is much more convenient to use the chemical potential or partial molal free energy as a measure of the state of any component. The chemical potential of the component *i* is defined as

$$\mu_i = (\partial F/\partial n_i)_{T, V, n_k} = (\partial G/\partial n_i)_{T, P, n_k} \quad (2)$$

and the change of u_i with pressure is given by

$$(\partial \mu_i/\partial P)_T = \bar{v}_i, \quad (3)$$

where \bar{v}_i is the partial molal volume of the component *i*. The condition that the same substance be in equilibrium between two phases at the same temperature but at different pressures is

$$d\mu_i^1 = d\mu_i^2, \quad \text{or} \quad \bar{v}_i^1 dP^1 = \bar{v}_i^2 dP^2, \quad (4)$$

where superscripts refer to the phase and subscripts refer to the component. This relation was first derived by Poynting² for the case of a pure substance in two phases, in which case the

²Poynting, *Phil. Mag.* (5) **12**, 32 (1881).