Vibration Potential Function and Structure of NH3 and AsH3 Molecules

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Energy Differences in Liquid Dichloro- and Dibromoethane Rotational Isomerism VI*

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RECENTLY a number of papers have appeared on the subject of rotational isomerism in dichloro- and dibromoethane.[1-3] Previously Gerding and Meerman[4] had made measurements on the energy difference of the rotational isomers in the liquid state by means of the Raman effect. The above authors[4] have found that $\Delta H \sim 0$ for liquid dichloroethane. Bernstein[2] working with the infra-red spectrum of the gas has shown that $\Delta H = 1325 \pm 50$ cal. per mole. Mizushima *et al.*[3] have reported results which agree with those of Bernstein[2] on gaseous dichloroethane. The above authors[3] also obtain a result of similar magnitude for gaseous dibromoethane, which result surprisingly agrees with the value of ΔH found by Gerding and Meerman[4] for liquid dibromoethane. The results obtained by the above mentioned authors[1,3] yield a value of ΔH for both gaseous dichloro- and dibromoethane which is substantially the same, and in agreement with the value obtained from dielectric constant measurements of the gas.

As stated previously, the value Gerding and Meerman obtained for liquid dichloroethane was $\Delta H \sim 0$. Mizushima *et al.*[3] report a small but definite value for ΔH from their measurements on liquid dichloroethane.

The surprising situation exists that these two very similar molecules behave so differently with regard to variation of relative intensity of line pairs with temperature in the liquid state, while in the gaseous state the behavior of the two molecules is identical.

Making use of direct photoelectric measurement of intensities, we have repeated the measurements on the Raman spectra of liquid dichloro- and dibromoethane. From a large amount of previous work in this laboratory it is well known that the precision of intensity measurements on Raman lines is very much greater with the photoelectric spectrograph than can be obtained by the methods of photographic photometry used by authors given in references 3 and 4.

Dichloroethane. We have made measurements on the relative intensity of the line pair $\Delta \nu = 653$ and 753 cm^{-1}, which is the same line pair as used in both previous investigations[3,4] on dichloroethane. Measurements were made at 278° and 369°K. At 278°K we obtain $[I(653)/I(753)] = 0.813$ with a mean deviation over ten determinations of ± 0.004 and a maximum deviation of 0.013. At 369°K we have obtained the above mentioned intensity ratio, the mean of ten determinations to be 0.780 with a mean deviation of ± 0.007 and a maximum deviation of 0.012. To all intents and purposes these measurements seem to show no variation of intensity ratio of this line pair with temperature, in agreement both qualitatively and quantitatively with the result obtained by Gerding and Meerman.[4] (The mean value obtained by Gerding and Meerman was 0.78. Mizushima *et al.*[3] have quoted the intensity ratio of this line pair at 298°K to be 0.56 and at 423°K to be 0.50. These last mentioned results do not agree with our results or those of Gerding and Meerman and also do not agree with the general frequency and intensity Table I of reference 3.)

The result of our measurements is to show, in agreement with Gerding and Meerman, that ΔH in the liquid for dichloroethane ~ 0.

Dibromoethane. In the case of this molecule the line pair used by Gerding and Meerman[4] ($\Delta \nu = 552$ and 660 cm^{-1}) is less favorable for photographic photometry than the previous case of the dichloro compound, as $[I(552)/I(660)] \sim 0.10$. We have obtained as the mean of ten determinations at 293°K, $[I(552)/I(660)] = 0.128$ with a mean deviation of ± 0.001 and maximum deviation of 0.003. At 371°K we have found the intensity ratio of this line pair to be 0.167 as the mean result of ten determinations with a mean deviation of ± 0.002 and a maximum deviation of 0.005. Making use of the mean deviation, we obtain $\Delta H = 740 \pm 80$ cal. per mole.

If we use the maximum deviation the error will be ± 120 cal. per mole. In any event, it is impossible to reconcile our value with the value of 1385 cal. per mole obtained by Gerding and Meerman[4] which was in substantial agreement with the values obtained by Mizushima *et al.*[3] from infra-red measurements made on the vapor.

Dilution of the dibromoethane with a solvent would be expected to bring its behavior closer to that of the gas. However, in dealing with the Raman effect the manageable degree of dilution obtainable consistent with accurate intensity measurement would be small. We have repeated our intensity measurements on the line pair mentioned above with a solution of one part by volume dibromoethane in 3 parts of CCl$_4$. The result of this experiment was that the ΔH obtained was 580 ± 100 cal. per mole which is in substantial agreement with the value we have obtained for the pure material. It seems that this degree of dilution is insufficient to bring about a marked difference in behavior from that of the pure liquid.

It should be noted that extremely high accuracy in determining ΔH by the above mentioned method is not easy since the intensity ratio of the line pair used is approximately 10 to 1. However, it seems beyond the realm of doubt that our experiments with both liquid dibromoethane and dichloroethane show that behavior in the liquid state does not furnish a reliable measure of the energy difference of the rotational isomers. The influence of change of state of aggregation on the value obtained for ΔH for dibromoethane while not as great as for the dichloro compound, is different only in magnitude and not in kind.

In addition, it should be remarked that in the dilute solution $[I(552)/I(660)]$ at 288°K was measured to be 0.085, while in the pure material this quantity had a value of 0.128. The reason for the apparent change in population of the rotational isomers in solution must await further investigations concerning the influence of solvent solute interaction on the molecular polarizabilities.

Our experiments on diluted dibromoethane largely were the outcome of private discussion (Axford) with Dr. H. J. Bernstein who has recently carried out extensive investigations in the infra-red on the influence of dilution on energy differences between rotational isomers.

[1] H. J. Bernstein, J. Chem. Phys. **17**, 258 (1949).
[2] H. J. Bernstein, J. Chem. Phys. **17**, 262 (1949).
[3] Mizushima, Morino, Watanabe, Simanouti, and Yamaguchi, J. Chem. Phys. **17**, 591 and 663 (1949).
[4] H. Gerding and P. G. Meerman, Rec. Trav. Chim. **61**, 523 (1942).

Vibration Potential Function and Structure of NH₃ and AsH₃ Molecules

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IN a recent letter to the Editor of this Journal, one of us with A. Monfils[1] has suggested that the length-length cross term is always negative when the bonds to which it refers are adjacent and contain at least one hydrogen atom. Essentially the same idea has just been put forward by Linnett and Hoare.[2] The purpose of this note is, in particular, to carry further in a more precise form our previous suggestions taking into account the results of the study of appropriate molecules (NH₃ and AsH₃).

The vibration spectra of the NH₃ and AsH₃ molecules and of their fully deuterated derivatives have been completely analysed recently.[3] Not only is the assignment of the fundamental frequencies well known, but it has also been possible to determine the zeroth-order frequencies. These data provide the possibility of computing the most general potential function describing the molecular movements. We have chosen a force field the expression

of which is given in terms of valency-deformation and interaction forces. If l_i and θ_i are the bond lengths and angles, it may be written

$$2U = f_1 \sum \langle \Delta l_i{}^2 \rangle_{Av} + f_2 \sum \Delta l_i \Delta l_j + g_2 l^2 \sum \langle \Delta \theta_{ij}{}^2 \rangle_{Av} + g_4 l^2 \sum \Delta \theta_{ij} \Delta \theta_{ik} + g_5 l \sum \Delta l_i \Delta \theta_{jk} + g_6 l \sum [\Delta \theta_{ij} + \Delta \theta_{ik}] \Delta l_i.$$

Δl_i and $\Delta \theta_{ij}$ are respectively the changes of the NH and AsH bond lengths and of the H—N—H and H—As—H angles from their equilibrium position. The determinantal equation corresponding to that potential gives relations which have been computed by de Hemptinne and Delfosse.[4] On the assumption that the potential is the same in the hydrogenated and deuterated compounds, the force constants in the potential can be calculated with the harmonic frequencies. From these, if we use for the dimensions of the molecules the values given by Dennison[3] and McConaghie and Nielsen,[3] we obtain $f_1 = 7.171$; $f_2 = 0.074$; $g_2 = 0.612$; $g_4 = -0.087$; $g_5 = 0.291$; $g_6 = 0.436$ for NH$_3$ and $f_1 = 2.878$; $f_2 = -0.032$; $g_2 = 0.301$; $g_4 = -0.018$; $g_5 = -0.276$; $g_6 = 0.305$ for AsH$_3$. Every constant is expressed in units 10 dynes/cm.

Both series of figures show some striking features. The magnitude of the cross terms is not at all negligible as compared with valency forces, in spite of the fact that we are dealing with hydrogenated bonds. Among these forces, however, the length-length cross term f_2 is small, whereas the length-angle cross term g_6 is rather large. It may be worth while noticing that the relative smallness of f_2 seems a general property of hydrogenated bonds (CH$_4$, C$_2$H$_4$, H$_2$O, NH$_3$, AsH$_3$). As the cross terms measure the influence on one bond of a change in another bond or angle, they certainly arise from the hydrogen-hydrogen interactions and from the changes of hybridization at the central atom.[5] One of the main points is concerned with the change of the sign of f_2 in NH$_3$(+) and AsH$_3$(−). This fact presumably depends upon the influence of hybridization which plays a greater part in the former than in the latter. So the positive contribution of hybridization to f_2 would offset the negative contribution due to the H—H interactions in NH$_3$. Moreover, we have new evidence that the repulsive atom-atom interaction, which is the main factor in AsH$_3$, gives rise to a negative sign. Consequently, for molecules without resonance[5] and especially in case of hydrogenated bonds, the length-length cross term is expected to be negative (H$_2$O, H$_2$S, HCN, C$_2$H$_2$, AsH$_3$). It may however occur that the cross term becomes positive either by an offsetting due to hybridization of the central atom in favorable conditions (NH$_3$) or because the representative point of the atom-atom interaction is at the bottom of the atom-atom potential curve. The type of potential recently proposed by Duchesne and Monfils[1] is strongly supported by these results. A full account of this work will appear elsewhere.

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Molecular Structure of Methylbromosilanes

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MONOMETHYLTRIBROMOSILANE and dimethyldibromosilane were prepared by passing methyl bromide over heated silicon containing copper at 350°C.[1] Trimethylmono-bromosilane was prepared by passing a mixture of methyl bromide and dimethyldibromosilane over heated aluminum at 350°C.[2]

The molecular structures of these compounds revealed by electron diffraction experiments at 20–30°C are summarized in Table I. Assumptions made at the calculation are (1) C—H distance 1.09A, (2) angle HCSi 109° 28′ and (3) staggered relative position of Br and H in CH$_3$.

TABLE I.*

Compound	Number of rings observed	Si—Br	Si—C	BrSiBr	CSiBr
SiBr$_4$[a]	—	2.15±0.02A	—	109° 28′	—
CH$_3$SiBr$_3$	12	2.17±0.02	x	109° 28′	x
(CH$_3$)$_2$SiBr$_2$	11	2.21±0.03	1.92±0.06A	109° 28′	x
(CH$_3$)$_3$SiBr	9	2.21±0.03	1.86±0.05	—	105° ±4°

* x means undetermined.
[a] Spitzer, Howell, and Schomaker, J. Am. Chem. Soc. 64, 62 (1942).

The Si—Br distance is shorter than the sum of the covalent radii of Si and Br, that is 2.31A.[3] The observed Si—Br distance increases with the substitution of Br by CH$_3$ and this means the decrease of double bond character of Si—Br bond. The same phenomena were observed in the case of silicon tetrachloride and methylchlorosilanes where the following Si—Cl distances were observed: SiCl$_4$[4] 2.01±0.02A, CH$_3$SiCl$_3$[5] 2.01±0.02A, (CH$_3$)$_2$SiCl$_2$[5] 1.99±0.03A, (CH$_3$)$_3$SiCl[6] 2.09±0.03A.

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[5] L. O. Brockway and R. L. Livingston, J. Am. Chem. Soc. 66, 94 (1944).
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The Effect of an Electric Field on the Thermal Conductivity of Glass

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WE have recently observed a phenomenon which is apparently little known and which may be of both theoretical and experimental interest. The effect observed is an increase in the thermal conductivity of glass when a high potential gradient is applied across it.

The experimental setup was made as follows: A pyrex insulator ring $\frac{3}{16}''$ long, $\frac{3}{4}''$ O.D., and with $\frac{1}{16}''$ wall thickness was clamped between two blocks of metal. The ends of the ring were highly polished as were the mating metal surfaces. One block of metal was maintained approximately at room temperature, while the other was heated to approximately 250°C by a tungsten heater. The assembly was operated in a vacuum of about 10^{-6} mm Hg. Roughly $\frac{3}{4}$ of the heat supplied to the heated block was conducted through the glass ring, the remainder being lost by radiation and by conduction through the electrical leads. The temperature of the heated block was measured with a thermocouple.

With constant heater power, the following effects were observed:

(1) Application of 3000 volts d.c. between the two blocks, with the heated block positive, caused a reduction in temperature of about 10°C, corresponding to a 4 percent increase in thermal conductivity.

(2) With reversed polarity, i.e., the heated block negative, no effect was observed.

(3) Using fused quartz in place of Pyrex, no effect was observed.