The AngleAngle Interaction in the Vibration Potential Function of Pyramidal Molecules

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value, therefore, the molar absorption coefficient is between 0.1 and 0.01. Since in this region the intensity of the $V \leftarrow N$ transition is at least 10 times greater than this we cannot hope to observe this maximum.

The author is indebted to Dr. M. Kasha, Dr. R. S. Mulliken, and Dr. G. Herzberg for illuminating discussions of this problem.

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[6] G. N. Lewis and M. Kasha, J. Am. Chem. Soc. **66**, 2100 (1944).
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Ultrasonic Absorption in the Critical Temperature Region

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IN the course of an investigation of the behavior of the sound velocity in the critical temperature region, a high acoustic absorption has been observed which is believed to be characteristic of this region. Figure 1 shows a plot of both the sound velocity curve and the absorption curve for sulfur hexafluoride in the neighborhood of the critical point. The absorption coefficient plotted is the absorption coefficient per wave-length defined by

$$A = A_0 e^{-\alpha \chi / \lambda},$$

where A_0 is the initial amplitude and A the amplitude at a distance χ measured in wave-lengths. The critical temperature, T_c, is the temperature of meniscus disappearance. At this temperature the sound velocity curve has a minimum, and the absorption coefficient reaches a maximum value. It is noteworthy that the region of anomalous absorption extends over a temperature interval of roughly one degree, and begins approximately 0.3° below the temperature of meniscus disappearance.

The velocity curve below the critical temperature is that for the liquid phase and the measurements were made at a point at least 2 cm below the meniscus. All measurements were made with a single filling of the interferometer, the filling corresponding to the critical density. The meniscus disappeared at the center, i.e., halfway up the tube in which the measurements were made. Each measurement was made only after thermostatting at a given temperature to within ±0.002°C for at least 12 hr. Taking readings in this manner at successively higher temperatures gave the points indicated by the upright triangles on the absorption curve. After the highest temperature above T_c was reached, the temperature was then lowered in steps, and at each temperature readings were
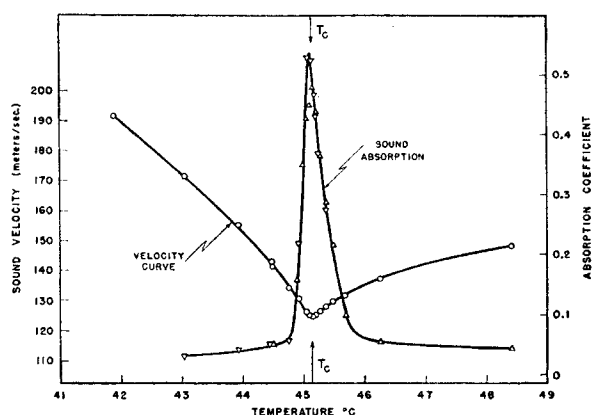

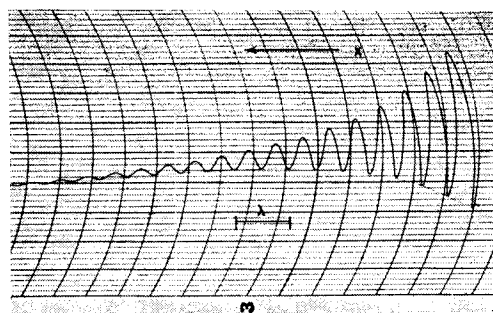FIG. 1. Plot of sound velocity and sound absorption as functions of temperature.

FIG. 2. Resonance peaks close to T_c.

taken only after thermostatting 24 hr. These points are indicated by the upside-down triangles. Accordingly, the absorption measurements carried out in this manner appear to be reversible with respect to temperature. The temperature of reappearance of the meniscus was approximately 0.02° lower than the temperature of meniscus disappearance.

The measurements were carried out with a double crystal acoustic interferometer at a frequency of 600 kc. The acoustic chamber consisted of a heavy walled glass cylinder to permit observations of the meniscus and the positions of the transmitting and receiving crystals. The receiving crystal was moved along the chamber by means of a synchronous motor drive and the voltage on the receiving crystal was amplified and automatically recorded by a pen and paper recorder. Figure 2 shows a record of the resonance peaks obtained at a point very close to T_c.

Several interpretations are possible for the absorption curve shown in Fig. 1. These will be discussed in a forthcoming publication.

The Angle-Angle Interaction in the Vibration Potential Function of Pyramidal Molecules

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RECENTLY Duchesne and Ottelet[1] computed with accuracy the most general valence-force potential function controlling the fundamental vibrations of the NH_3 and AsH_3 pyramidal molecules. It was shown, in particular, that the constant g_4 for the angle-angle interaction is negative and very small. However, in contrast to the various studies devoted to the length-length and length-angle interactions,[2] very little attention has in fact been devoted to g_4. We therefore considered it of interest to extend the former analysis to include such structurally related molecules as PF_3 and AsF_3, with the main aim of studying the changes appearing in g_4 when fluorine is substituted for hydrogen.

In the present investigation, however, no isotopic frequencies are available which would provide additional data from which all the interaction constants might be determined. Thus, the four frequencies at our disposal[3] are not sufficient to evaluate the six parameters of the potential function[1]

$$2U = f_1 \sum_i \langle \Delta l_i{}^2 \rangle_{Av} + f_2 \sum_{i<j} \Delta l_i \Delta l_j + g_2 l^2 \sum_{i,j} \langle \Delta \theta_{ij}{}^2 \rangle_{Av}$$

$$+ g_4 l^2 \sum_{i,j,k} \Delta \theta_{ij} \Delta \theta_{ik} + g_5 l \sum_{j \text{ and } k \neq i} \Delta l_i \Delta \theta_{jk}$$

$$+ g_6 l \sum_{\substack{i,j,k \\ j<k}} [\Delta \theta_{ij} + \Delta \theta_{ik}] \Delta l_i.$$

Δl_i and $\Delta \theta_{ij}$ are respectively the changes of the PF and AsF bond lengths and of the FPF and FAsF angles from their equilibrium position.

TABLE I.

	f_1	f_2	g_2	g_4	g_5	g_6
PF$_3$	6.0	+0 91	0.86	+0.22	−1	+1
AsF$_3$	4.3	+0 70	0 41	+0.15	−0 69	+0.79

In order to overcome the difficulty, we have selected solutions for f_1, f_2, g_2, and g_4 corresponding to a range of values adopted for the g_5 and g_6 constants, the limits of which are taken to be −1.5 to +1.5×10⁵ dynes/cm. This is a method which has been found very successful in other cases [4] This analysis shows clearly that the constant for the angle-angle interaction is positive in both molecules. It is to be noted that the interaction constants are fairly sensitive to the value adopted for the angles. For FPF and FAsF we have chosen respectively 104° and 100° which should not be considered as very accurate.[5] This dependence of the potential function upon the molecular dimensions does not, however, invalidate our general conclusions.

It is now well established that a difference in sign for g_4 may be caused by substitution (AsH$_3$→AsF$_3$). A similar fact has already been observed and explained for other types of cross-terms in some molecules[6] (HCN→ClCN and C$_2$H$_4$→C$_2$Cl$_4$). However, it is to be noticed that Torkington[7] has recently shown the existence of alternative solutions for C$_2$Cl$_4$ in terms of which the sign of these cross-terms remains unaffected on passing from C$_2$H$_4$ to C$_2$Cl$_4$. Consequently, in this particular case, some indetermination remains. However, the present analysis as well as recent theoretical considerations[2] seem to reinforce the validity of the earlier view.

In the case of PF$_3$ and AsF$_3$, g_4 presumably depends, to a large extent, on the interactions between the non-bonded atoms, which should give a positive sign. On the other hand, for the corresponding hydrogenated compounds, changes of hybridization at the P and As atoms during the vibrations are probably the decisive factor, and this may be shown to be a possible explanation of the negative sign. Of course, the H−H interactions have also to be considered as contributing to g_4, but by analogy with the well-known behavior of the length-length cross-terms,[1,2] it is to be expected that a negative sign might also occur.

As far as the exact magnitude of g_4 is concerned, no definite value can yet be put forward. This arises from the fact that variations of g_5 and g_6 within reasonable limits appreciably modify g_4. The very small values* which Howard and Wilson[8] have calculated for a set of pyramidal molecules are based on a limiting potential function and cannot therefore be accepted as entirely conclusive. Even the detailed study of Meister, Rosser, and Cleveland[9] on some tribromomethanes rests on assumptions which might affect considerably the values proposed for the same type of cross-term in the CBr$_3$ group. The only statement at present possible is that g_4 should have the essential property of being small with respect to other types of cross-terms.

A final decision for the other constants of PF$_3$ and AsF$_3$ must be left until further data are available. However, as regards f_2 and g_6, a positive sign can be considered as practically certain. Table I gives tentative solutions expressed in 10⁶ dynes/cm units which show how the force constants may be associated

A detailed account of this work will be published elsewhere.

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General Form of the Force Constant Matrix for Harmonic Vibrations*

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IN the normal coordinate treatment of the vibrations of a molecule one is confronted with the problem of finding a set of force constants consistent with the mass or kinetic energy matrix of the molecule and with the observed frequencies of vibration. In general this problem is indeterminate unless assumptions are made which reduce the number of force constants, or additional data, such as the frequencies of isotopic or related molecules, are available For this reason there is some value in considering the general forms which the solution may assume. Torkington[1] has given a general treatment of the secular equation of second degree, and Glockler and Tung[2] have considered the third degree equation. In the present note it is pointed out that there exists an explicit expression for the most general force constant matrix consistent with a given mass matrix and a given set of frequencies. In principle this expression enables one to obtain all possible sets of force constants satisfying the conditions of the problem *without solving the secular equation.*

Denote by G the reciprocal mass or kinetic energy matrix of Wilson,[3] and by Λ the diagonal matrix whose elements are $\lambda_i = (2\pi\nu_i)^2$, where the $\nu_i (i=1, 2, \cdots, n)$ are the observed frequencies. There exists a real orthogonal matrix A, unique except for the ordering and sign of its columns, which reduces the real symmetric matrix G to diagonal form,

$$A'GA = \Gamma, \qquad (1)$$

where A' is the transpose of A. The elements, γ_i, of the diagonal matrix Γ are the latent roots of G, and are positive, since G is positive definite. The matrices A and Γ may be obtained by solving the secular equation,

$$|G - \gamma I| = 0. \qquad (2)$$

From Eq. (1) one easily obtains,

$$\Gamma^{\frac{1}{2}} A' G^{-1} A \Gamma^{\frac{1}{2}} = I, \qquad (3)$$

where I is the unit matrix of order n. The elements of $\Gamma^{\frac{1}{2}}$ are $\gamma_i^{\frac{1}{2}}$.

Now consider the form the force constant or potential energy matrix, F, must have in order that the secular equation,

$$|F - \lambda G^{-1}| = 0, \qquad (4)$$

have the required roots, λ_i. In view of Eq. (3), Eq. (4) is equivalent to,

$$|\Gamma^{\frac{1}{2}} A' F A \Gamma^{\frac{1}{2}} - \lambda I| = 0, \qquad (5)$$

and there must therefore exist a real orthogonal matrix, B, such that

$$B' \Gamma^{\frac{1}{2}} A' F A \Gamma^{\frac{1}{2}} B = \Lambda. \qquad (6)$$

Equation (6) may be solved for F, and the result put in the form,

$$F = K \Lambda K', \qquad (7)$$

where

$$K = A \Gamma^{-\frac{1}{2}} B. \qquad (8)$$

The matrix $A\Gamma^{-\frac{1}{2}}$ is a constant matrix for any given problem, and need be computed only once. The columns of the matrix K are the normal coordinates. It should be noted that K is not orthogonal.

Equations (7) and (8) show that in order to determine the force constants and normal coordinates it is sufficient to specify the real orthogonal matrix B.[4] Actually it is not necessary to specify B completely, since F is unaffected by a change in sign of any column of B, and the normal coordinates are merely changed in sign. It is easy to show that $n(n-1)/2$ parameters are sufficient to specify the general orthogonal matrix of order n, if the signs of its columns are left indeterminate. This is consistent with the fact that F has $n(n+1)/2$ distinct elements while n frequencies