

VIBRATIONAL SPECTRUM OF $(\text{SiH}_3)_2\text{O}$ -INFLUENCE OF THE LARGE AMPLITUDE VIBRATION*, **

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Equations have been developed to study the coupling between large amplitude vibration (LAV) and the remaining harmonic vibrations in a polyatomic molecule. The method has been used to interpret the vibrational spectrum of disilyl ether where the potential of the SiOSi bending mode has two symmetric minima and the assumed barrier to inversion is 125 cm^{-1} .

1. Introduction

The vibrational spectrum of disilyl ether has been a subject of interest for a long time [1-5]. The most comprehensive study dealing with this problem has been performed by McKean in 1970 [6]. With all these investigations there are still fragments of the spectrum which have not been interpreted.

Hitherto, the vibrational analysis of the spectrum of disilyl ether has been carried out with the use of the standard methods of the theory of normal vibrations neglecting the interactions between the modes of different frequencies. The influence of the SiOSi bending vibration on the other vibrations of a molecule, suggested by Thorson and Nakagawa [7], has not yet been studied systematically.

Our earlier studies of the influence of the large amplitude vibration (further called LAV) on the remaining harmonic modes of a molecular system have shown that the interactions causing the specific anharmonicity appeared [8], which is seen in the spectrum as a shift and splitting of the absorption bands.

The purpose of the present paper is to find the approximate potential describing the skeletal bending mode of disilyl ether giving the spectrum in the far infrared which agrees with the experimental one, and next to analyse the other bands in the i. r. spectrum of $(\text{SiH}_3)_2\text{O}$, which permits one to calculate the interaction constants between LAV and the remaining vibrations. This treatment allows us to interpret uniformly many fragments of the spectrum which are not clear up to now.

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2. Theoretical

The interactions between different vibrations in a molecule have been discussed using the following assumptions:

(i) there is only one vibration of the LAV type in the molecular system being considered (a more detailed discussion of this problem has been given in [8]).

(ii) the LAV frequency is lower than those of the harmonic vibrations, hence the adiabatic approximation can be used to study the influence of the LAV on the harmonic vibrations.

The vibrational Hamiltonian has the form

$$T(Q_i) + T(z) + V(z) + \frac{1}{2} K_i(z) (Q_i - Q_i(z))^2, \quad (1)$$

where z , Q_i describe the LAV and the harmonic vibrations, respectively, T is the kinetic energy operator, $V(z)$ — the LAV potential having two symmetric minima, K_i , Q_i^0 — the force constant and the equilibrium position of the i -th normal vibration, both depending on z , respectively.

In the crude adiabatic approximation the wave function of the Hamiltonian given by Eq. (1) may be written in the form

$$\Psi(Q_i, z) = \frac{1}{\sqrt{2}} (\alpha_{A,p}(z) \Psi_A(Q_i) + \alpha_{B,p}(z) \Psi_B(Q_i)), \quad (2)$$

where $\alpha_{A,p}(z)$, $\alpha_{B,p}(z)$ are the wave functions of LAV localized near the minima at the point $+z^0$ and $-z^0$, respectively, p is a quantum number of the LAV, $\Psi_K(Q_i)$ is a wave function of a normal vibration which exists in two forms for a molecule described by $\Psi(K = A, B)$.

Now, the case in which potential $V(z)$ is symmetric function of z will be discussed. The solution of the Schrödinger equation with a symmetric potential is well known and may be written in the form [9]

$$[T(z) + V(z)]\alpha_{p+}(z) = E_{p+}\alpha_{p+}(z), \quad [T(z) + V(z)]\alpha_{p-}(z) = E_{p-}\alpha_{p-}(z), \quad (3)$$

where E_{p+} is the eigenenergy of a symmetric eigenstate, E_{p-} is the eigenenergy of an anti-symmetric eigenstate.

In Eq. (2) $\alpha_A(z)$ is the function localised near $+z_0$; using the properties of $\alpha_{p-}(z)$ and $\alpha_{p+}(z)$ (cf. [9]) one can get [10]

$$\alpha_{A,p}(z) = \frac{1}{\sqrt{2}} (\alpha_{p+}(z) + \alpha_{p-}(z)). \quad (4)$$

The function $\alpha_B(z)$ localized near $-z_0$ can be expressed likewise

$$\alpha_{B,p}(z) = \frac{1}{\sqrt{2}} (\alpha_{p+}(z) - \alpha_{p-}(z)). \quad (5)$$

The multiplication of the Schrödinger equation with the Hamiltonian given by Eq. (1)

and the wave function from Eq. (2) by $\alpha_{p^+}(z)$ and another multiplication by the $\alpha_{p^-}(z)$ and further integration over z leads to the following set of equations:

$$[T(Q_i) + U_{p^+,p^+}(Q_i)]\Phi^+(Q_i) + U_{p^+,p^-}(Q_i)\Phi^-(Q_i) = E\Phi^+(Q_i), \quad (6a)$$

$$[T(Q_i) + U_{p^-,p^-}(Q_i)]\Phi^-(Q_i) + U_{p^-,p^+}(Q_i)\Phi^+(Q_i) = E\Phi^-(Q_i), \quad (6b)$$

where

$$\Phi^+(Q_i) = \frac{1}{\sqrt{2}}(\Psi_A(Q_i) + \Psi_B(Q_i)), \quad (7a)$$

$$\Phi^-(Q_i) = \frac{1}{\sqrt{2}}(\Psi_A(Q_i) - \Psi_B(Q_i)), \quad (7b)$$

$$U_{r,s}(Q_i) = \langle \alpha_r(z) | \frac{1}{2} K_i(z) (Q_i - Q_i^0(z))^2 | \alpha_s(z) \rangle. \quad (7c)$$

Since the both forms of a molecular system A and B are symmetric the expression $K_i(z) (Q_i - Q_i^0(z))^2$ is the symmetric function of z , too. Hence, the effective interaction operators U_{p^+,p^-} and U_{p^-,p^+} vanish due to the symmetry.

Eqs. (6a, b) can be written uniformly

$$[T(Q_i) + \frac{1}{2} \langle \alpha_p | K_i(z) (Q_i - Q_i^0(z))^2 | \alpha_p \rangle + E_p] \Phi^s(Q_i) = E \Phi^s(Q_i), \quad (8)$$

where p goes through the values of p^+ and p^- , $\Phi^s(Q_i)$ is a set of states $\Phi^+(Q_i)$ and $\Phi^-(Q_i)$, respectively.

To solve Eq. (8) the explicit form of an effective potential $U_{p,p}(Q_i)$ is necessary. We can write

$$U_{p,p}(Q_i) = \frac{1}{2} K_i^p Q_i^2 - L_i^p Q_i + D_i^p, \quad (9)$$

where

$$K_i^p = \langle \alpha_p | K_i(z) | \alpha_p \rangle, \quad (10a)$$

$$L_i^p = \langle \alpha_p | K_i(z) Q_i^0(z) | \alpha_p \rangle, \quad (10b)$$

$$D_i^p = \frac{1}{2} \langle \alpha_p | K_i(z) (Q_i^0(z))^2 | \alpha_p \rangle. \quad (10c)$$

Using then a displaced coordinate

$$q_i = Q_i - \frac{L_i^p}{K_i^p} \quad (11)$$

one can write the Eq. (8) in the form

$$(T(q_i) + \frac{1}{2} K_i^p q_i^2 + W_i^p) \Phi^s(q_i) = E \Phi^s(q_i), \quad (12)$$

where

$$W_i^p = D_i^p - \frac{1}{2} \frac{(L_i^p)^2}{K_i^p} + E_p. \quad (13)$$

The solution of the Eq. (12) leads to the following eigenvalues:

$$E = \hbar\omega_i^p(n + \frac{1}{2}) + W_i^p, \quad (14a)$$

where

$$\omega_i^p = (K_i^p/m)^{1/2}, \quad (14b)$$

and m is the reduced mass of the i -th normal vibration.

Although the harmonic character of the normal vibration has been kept, there are two important differences when compared to a system where the LAV does not exist:

- (i) the equilibrium position of a normal vibration is displaced (see Eq. (11)),
- (ii) the frequency of a normal vibration depends on a state of LAV (see Eqs. (14b) and (10)).

Now the problem emerges of an appreciation of the order of magnitude calculations of both effects. This can be evaluated by the comparison of the theoretical spectrum with the experimental one.

The discussion of the selection rules for molecules with LAV leads to the conclusion that the transitions $|n, p\rangle \leftrightarrow |n \mp 1, p\rangle$ or $|n, p\rangle \leftrightarrow |n, p \mp 1\rangle$ are the most intensive [11] (n, p are the quantum numbers of harmonic vibration and LAV respectively).

Excitations of the harmonic vibrations will be discussed further.

During these excitations the LAV state remains unchanged and the term W_i^p in Eq. (14a) is the same in the ground and excited states of the molecule. Hence the displacement of the equilibrium position does not affect the transition energy.

The influence of LAV on the normal vibration force constant can be studied separately. For exact calculations the functional dependence $K_i(z)$ is needed.

In the approximate calculations this dependence can be described in the more simple form:

$$K_i(z) = k_i + \frac{1}{2} c_i z^2, \quad (15a)$$

where

$$c_i = \left(\frac{\partial^2 K_i}{\partial z^2} \right)_0, \quad k_i = K_i(0). \quad (15b)$$

Therefore, the effective force constant of the i -th normal vibration of a molecule in the p -th LAV state is

$$K_i^p = k_i + \frac{1}{2} c_i \langle \alpha_p | z^2 | \alpha_p \rangle. \quad (16)$$

The value of the constant c_i may be considered as a measure of the interaction of the i -th normal vibration with LAV. Introducing the Eq. (16) into Eq. (14b), expanding the expression in a series and retaining only terms linear in c_i/k_i , one gets the approximate dependence of the frequency of the normal vibration on the LAV state

$$\omega_i^p = \omega_i^0 (1 + f_i \langle \alpha_p | z^2 | \alpha_p \rangle), \quad (17a)$$

where

$$f_i = \frac{1}{4} \frac{c_i}{k_i}, \quad \omega_i^0 = (k_i/m)^{1/2}. \quad (17b)$$

From Eqs. (14a), (17a) one can obtain the energy of the transition $|n, p\rangle \leftrightarrow |n \mp 1, p\rangle$:

$$\Delta E = \hbar \omega_i^0 (1 + f_i \langle \alpha_p | z^2 | \alpha_p \rangle). \quad (18)$$

3. Application to the disilyl ether

A molecule of the disilyl ether satisfies the above mentioned assumptions. The nonlinearity of this molecule was suggested by McKean [4] and Carl and Pitzer [5] and confirmed later by an electron diffraction study of the vapour, which gave a Si—O—Si angle of 144.1 ∓ 0.9 [12]. Due to the large value of this angle the potential of the bending vibration has two symmetric minima. Such a model of the bending vibration was studied by Thorson and Nakagawa [7] and experimentally supported by the works of Aronson et al. [2, 3].

In the former, the effort was undertaken to interpret the complex structure of the disilyl ether i.r. spectrum in the regions of SiO stretching modes: antisymmetric near 1105 cm^{-1} and symmetric near 606 cm^{-1} . But, neither the origin of the 1222 cm^{-1} nor 593 cm^{-1} bands was explained.

The following characteristic features of the i.r. spectrum of the disilyl ether have been distinguished up to now [2-6, 15]:

1. Three bands are observed in a region of the SiO symmetric stretching mode at 96 K: 606.6 cm^{-1} of the lower intensity and $595.3, 593.3 \text{ cm}^{-1}$ of higher intensity. No bands are observed at room temperature.

2. At room temperature the broad asymmetric band attributed to the SiO antisymmetric stretching mode is observed near 1105 cm^{-1} . At lower temperature (96 K) this band becomes sharper and shifts to 1080 cm^{-1} .

3. The broad band of low intensity near 1222 cm^{-1} which appears only in a gas phase is interpreted by McKean [4] as a combination tone $\nu_{\text{SiO}}(\text{asym}) + 2\delta_{\text{SiOSi}}$ but even the author himself stressed that the similar line in the spectrum of the silicon crystal containing oxygen impurities is interpreted as a transition from the excited levels of LAV [13, 14].

4. The broad band of low intensity near 68 cm^{-1} observed in a gas phase is assigned as SiOSi bending mode. This band does not change distinctly during the deuteration [3]. In the spectrum of a solid state at 75 K a few bands of different intensity between 75 and 106 cm^{-1} [15] are observed.

The aim of the paper is to show that all the above mentioned characteristic features of the $(\text{SiH}_3)_2\text{O}$ i.r. spectrum can be interpreted on the basis of the interaction of LAV with the remaining vibrations of the molecule.

Eq. (18) is a basic to our analysis. Its numerical value can be obtained when the wave functions of LAV is known. In order to obtain the wavefunctions it is supposed that

the LAV potential is given by a two-parameter polynomial function of the form

$$V(z) = -Az^2 + Bz^4, \quad (19)$$

where A, B are constants which depend on the barrier height V_h and the distance d between minima.

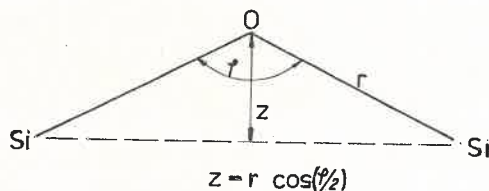


Fig. 1. Large amplitude vibration coordinate z used in $(\text{SiH}_3)_2\text{O}$

Fig. 1 shows the LAV coordinate which was chosen in the calculations, performed numerically by the standard method of solving the Schrödinger equation with double minimum potential [16].

The distance between minima of the LAV was taken from the geometry of $(\text{SiH}_3)_2\text{O}$ [12], which gave $d = 1.0072 \text{ \AA}$.

The reduced mass for the bending vibration was calculated under the assumption that the mass of the silyl group was concentrated at the silicon atom. It gave the values 12.72 a.u. and 12.95 a.u. for $(\text{SiH}_3)_2^{16}\text{O}$ and $(\text{SiD}_3)_2^{16}\text{O}$, respectively.

It should be pointed out that the potential barrier for the bending mode is low, which is in accordance with McKean's paper [6]. It is caused not only by the large value of the SiOSi angle but mainly by the presence of free electron pairs on oxygen which may overlap with empty $3d$ orbitals of the silicon atoms. Thus the inversion of the molecule connected with a change of the hybridization is facilitated. A similar phenomenon is well known for nitrogen compounds [18].

The analysis of the complex structure of bands ascribed to stretching SiO vibrations was carried out with the use of Eq. (18). The constants ω_i^0 and f_i were calculated so as to fit the experimental spectrum. The intensities corresponding to the different states α_p in Eq. (18) were calculated on the base of Crawford's [17] formula, with an additional assump-

TABLE I
Vibrational frequencies, constants of coupling between LAV and harmonic modes, calculated from Eq. (21)

| Mode | ν_i (cm^{-1}) | ω_i^0 (cm^{-1}) | k_i (mdyn \AA^{-1}) | c_i (mdyn \AA^{-3}) | f_i (\AA^{-2}) |
|---------------------------------|---------------------------------|--------------------------------------|-------------------------------------|-------------------------------------|--------------------------------|
| Solid | | | | | |
| $\nu_{\text{SiO}}(\text{sym})$ | 595.3 | 621.5 | 7.1 | -5.5 | -0.19 |
| $\nu_{\text{SiO}}(\text{asym})$ | 1080.0 | 1116.7 | 4.7 | -2.8 | -0.15 |
| Gas | | | | | |
| $\nu_{\text{SiO}}(\text{asym})$ | 1105.0 | 1142.5 | 4.9 | -2.8 | -0.14 |

tion that the dipole transition moments were independent of the LAV state of a molecule. In this approximation the intensity of a transition depended only on the Boltzman factor of the appropriate LAV level at a temperature T .

The values of constants taken to the calculations are listed in Table I. Comparing with a standard vibrational analysis a new parameter c_i appears, that describing the interaction between the LAV and the i -th normal vibration. The fourth order constants K_{ii33} which describe the interaction between bending and stretching modes were estimated for CO_2 to be equal to 0.8 milidyne Å [19]. The larger values of c_i in $(\text{SiH}_3)_2\text{O}$ may be explained by the stronger anharmonicity of a bending mode potential in this molecule than in CO_2 .

4. Discussion

SiO symmetric stretching mode

It is assumed that the three bands in a region 600 cm^{-1} are due to the SiO symmetric stretching mode coupled with LAV. The comparison of the theoretical and experimental [6] spectra at 96 K is presented in Fig. 2. A few lines in the theoretical spectrum results from

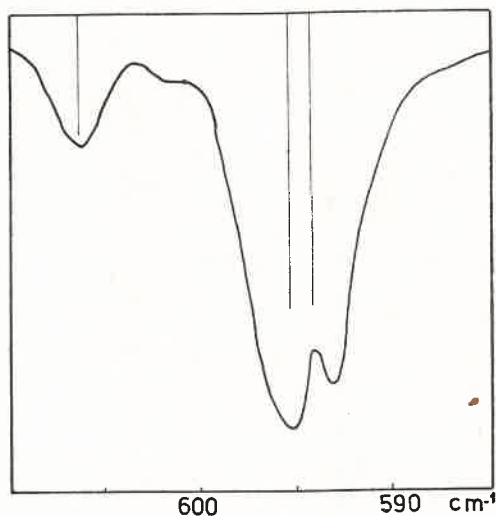


Fig. 2. Comparison of the theoretical and experimental [6] infrared spectrum due to $\nu_{\text{SiO}}(\text{sym})$ in $(\text{SiH}_3)_2\text{O}$ at 96 K

a change in the symmetry of a molecule excited to the LAV states lying over the potential barrier. In these states $(\text{SiH}_3)_2\text{O}$ has a center of symmetry and that is the reason for the fully symmetric vibration being inactive in the infrared. It is also the reason why the bands near 600 cm^{-1} are not observed in a gas phase. At higher temperatures the states lying over the barrier are strongly occupied and at the same time the bands become broader so the weak broad absorption bands cannot be distinguished from the background.

SiO antisymmetric stretching mode

This mode is infrared active for any symmetry of the disilyl ether molecule and so the numerous bands due to the coupling with LAV give broad asymmetric band (Fig. 3). In accordance with the experimental results [4, 6, 15] this band becomes broader at a higher temperature (Fig. 3).

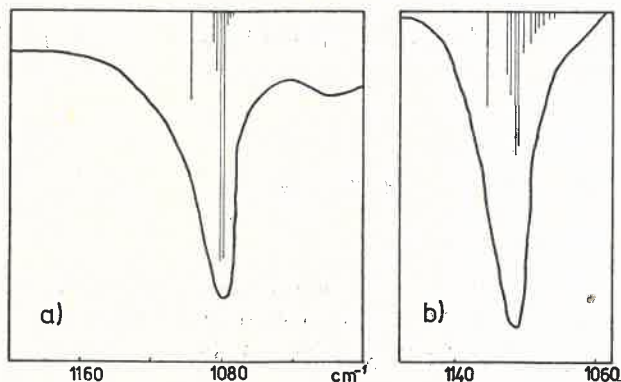


Fig. 3. Comparison of the theoretical and experimental infrared spectrum due to $\nu_{\text{SiO}}(\text{asym})$ in $(\text{SiH}_3)_2\text{O}$ at 96 K (experimental from [6]) and 293 K [15].

The 1222 cm^{-1} band

The origin of this band is still obscure. It may be interpreted as a combination band of a "hot band" type $\nu_{\text{SiO}}(\text{asym}) + \delta_{\text{SiOSi}}(1^+ \rightarrow 2^-) = 1105 + 119 = 1224 \text{ cm}^{-1}$. It would explain why this band is observed in a gas phase only, because one of the transitions would take place from the excited state. It is however still difficult to say why the following combination bands are not observed $\nu_{\text{SiO}}(\text{asym}) + \delta_{\text{SiOSi}}(0^+ \rightarrow 1^-) = 1105 + 90 = 1195 \text{ cm}^{-1}$ or $\nu_{\text{SiO}}(\text{asym}) + \delta_{\text{SiOSi}}(0^- \rightarrow 1^+) = 1105 + 69 = 1174 \text{ cm}^{-1}$. The values of 69 cm^{-1} , 90 cm^{-1} and 119 cm^{-1} were calculated numerically using the solution of the LAV eigenproblem with the potential function given by Eq. (19) and barrier to inversion equal to 125 cm^{-1} , as energy differences between energy levels cited above.

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