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Absolute Intensity Measurement of the ν_4 Band of Fluoroform by the Use of a Tunable Diode-laser Source

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The absolute infrared absorption intensities have been measured for the $P_{35}(35)$ and $P_{36}(36)$ lines, which belong to the ν_4 fundamental of fluoroform, by the use of a tunable diode–laser source. The observed intensity, Γ, was $5360+220$ cm^2 mol^{-1}. This intensity value was compared with that observed by the conventional method.

The absorption intensities of the vibration spectra of gaseous molecules have been discussed as the intensities integrated over the whole absorption bands. This has been largely due to the fact that the limited resolution of a dispersion-type spectrometer is insufficient to observed individual vibration-rotation lines. Therefore, the experimental method based on the theory of Wilson and Wells[1)] has conventionally been employed. In their method, the total pressure in the absorption cell is raised so that the rotational fine structures are completely smeared out, giving the band a smooth contour; this reduces the error resulting from the finite instrumental line-width. The disadvantage of this method is that the observed intensity value can be spoiled by some systematic errors. The two main origins of the systematic errors are:

1) the existence of hot bands originating from the combinations between the vibrational mode in question and the other modes,

and

2) the existence of the accidental coincidence of vibrational-energy levels.

Item 2) can further be divided into two categories: the anharmonic resonance (Fermi resonance) and the Coriolis interaction.

A high-resolution method has an advantage over the conventional method with respect to these problems. In the high-resolution method, it is enough to observe the intensities of several vibration-rotation lines in determining the intensity for the whole band. Since the instrumental line-width can be narrower than a Doppler width, two peaks whose frequency separation is larger than the Doppler width can be observed separately. Usually the molecular constants of the hot bands are slightly different from those of the fundamentals. Therefore, it is possible to detect this slight difference and to observe a spectrum corresponding to a single vibration-rotation transition. As for the problem of resonances, it should be remembered that it is the vibration-rotation levels that really interact with each other. Therefore, even if there are degeneracies with respect to the vibrational levels, only some vibration-rotation levels are considerably perturbed. The other vibration-rotation levels may be too far from their counter levels. Thus, it is possible to estimate the pure intensity for the vibration by observing the resonance-free transitions to these unperturbed vibration-rotation energy levels.

The purpose of this study is to examine the experimental possibility of intensity observation for a vibration spectrum by the use of a tunable diode-laser source spectrometer and to compare the intensity thus observed with that observed by the conventional method. Fluoroform was chosen because we have already determined its molecular constants on the ν_4 fumdamental.[2)] The vibrational intensity for the ν_4 fundamental has also been reported as determined by the use of a conventional method.[3)]

Experimental

Commercial fluoroform of a 99.95% purity was distilled several times just before the measurement. The sample cell was made of a Pylex tube (30 mm in diameter and 150 cm in length) with CaF_2 windows at its ends. The end planes of the Pylex tubes had been ground by means of a diamond grinder to make an angle of about 88° to the optical axis of the tube, thus avoiding interference. In order to produce the optimum transmittance under an appropriate pressure, it was often necessary to use several sample cells in a series. These cells were connected to a usual glass and grease manifold. The temperature of the sample was believed to be equal to the room temperature.

The measurement of the sample pressure is a critical problem in this kind of work. In the present experiment, a variable-inductance transducer (Tsukasa Sokken, model P90DL channeled to a special carrier amplifier) was connected to the vacuum system. By introducing air into the system, we calibrated the transducer against an MKS Baratron. We could not use the Baraton itself for our pressure measurements because the surface of the diaphragm is corroded by fluoride and so can be damaged by the sample fluoroform. The nonlinearity of the P90DL was estimated to be 4% up to 200 mTorr.[††] This figure can serve to indicate the relative accuracy of the instrument as long as the Baratron is accurate. Although the transducer is rather sensitive to the temperature change, we did not use any thermostatting equipment in this work, for the room temperature was controlled well enough. It was recognized that the pressure of the system increased by 2—3% during the intensity measurement; this increase was ascertained to stem from the evaporation of the vacuum grease.

A laser diode, in a closed-cycle refrigerator operating at about 20 K, served as the source of monochromatic radiation. The emitted energy was focused on the entrace slit of a grating monochromator, which served both for the coarse frequency calibration and for the isolation of discrete laser modes. A mechanical vibrating chopper, operating at 400 Hz, was placed immediately before the entrance slit. The laser from the exit slit of the monochromator passed through the sample cells and was focused onto a HgCdTe or PbSnTe detector kept at 77 K. The chopped signal was amplified and fed to a lock-in amplifier, whose reference was obtained from the chopper. The DC signal

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[††] 1 Torr = 133.322 Pa.

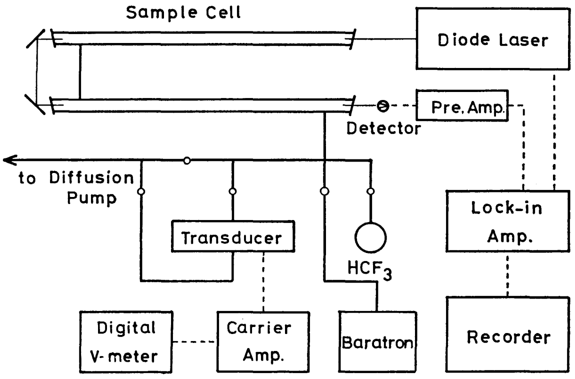

Fig. 1. The block diagram of the experimental arrangement for the intensity measurement.

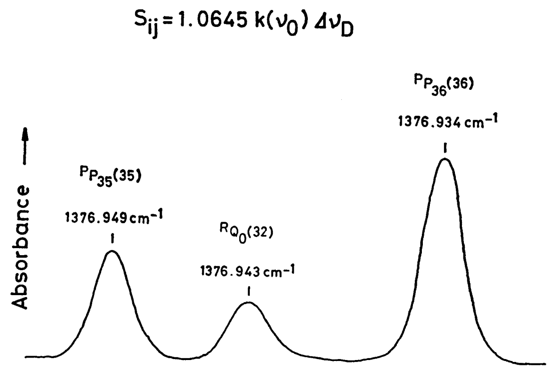

Fig. 2. The spectra for $P_{35}(35)$ and $P_{36}(36)$ of the ν_4 fundamental of fluoroform.

was channeled to an X-T recorder. The signal was strong enough for us to record lines with a high signal-to-noise ratio with a rather short time constant (300 ms) in comparison with the time needed to record an absorption line. Lines were identified in reference to the neighbouring lines. The FWMH (full-width at half maximum) was measured relative to the separation of three line peaks, with the middle one being measured. Figure 1 illustrates the experimental arrangement.

Results and Discussion

Observed Spectra. Figure 2 shows the spectra observed for the $^PP_{35}(35)$ and $^PP_{36}(36)$ lines of fluoroform. The length of the cell was 300 cm, and the pressure was 13.6 mTorr. The observation was made at 293 K. As the accurate frequencies had already been determined for these lines,[2)] the FWHM's could be estimated for these two lines. They were 59.7 MHz for $^PP_{35}(35)$ and 63.3 MHz for $^PP_{36}(36)$. It is probable that these two line-shapes are governed by the Doppler broadening, for the calculated Doppler width is 60.5 MHz in this frequency region (HCF_3= 70, T=293 K). This postulation seems reasonable if the following three points are taken into account:

1) the line-width due to the collision broadening is of the order of 0.1 MHz (the pressure-broadening parameter for fluoroform is 18 MHz/Torr[4)]),

2) the instrumental line-width can be narrower than 10^{-4} cm^{-1} (3 MHz),

and

3) the synthetic spectra calculated from the precise molecular constants[2)] predict no overlapping from other lines with considerable intensities.

Determination of the Line Intensity. The absorption intensity associated with the transition from the energy level, i, to another energy level, j, is defined by this relation:

$$S_{ij} = \int_{-\infty}^{\infty} k(\nu)\mathrm{d}\nu, \tag{1}$$

where $k(\nu)$ is the absorption coefficient which appears in the Lambert-Beer law:

$$I(\nu) = I_0(\nu)\exp(-k(\nu)\chi). \tag{2}$$

In Eq. 2, I_0 and I correspond to the intensities for the incident and transmitted light respectively. χ is a measure of the number per unit of area of the absorbing molecules occurring along the direction of the propagation of the radiation in the sample gas. If the absorbing molecules are at a certain concentration, n, and are contained in a space with a certain length, l, in the direction in which the radiation travels

$$\chi = nl. \tag{3}$$

Knowledge about the dependence of the absorption coefficient on the frequency is needed to estimate S_{ij} from Eq. 1. That is, the explicit expression for the distribution function;

$$k(\nu) = S_{ij}f(\nu-\nu_0), \tag{4}$$

must be known. In the present study, f can be considered to have the form of a Doppler profile under appropriate conditions. Defining $\Delta\nu_D$ as a FWHM of the Doppler limited-absorption line, the following normalized distribution function is obtained:

$$f(\nu-\nu_0) = \frac{(\ln 2/\pi)^{1/2}}{(\Delta\nu_D/2)}\exp[-(\ln 2)\{(\nu-\nu_0)/(\Delta\nu_D/2)\}^2]. \tag{5}$$

By combining Eqs. 4 and 5, one can get this expression:

$$S_{ij} = 1.0645\, k(\nu_0)\Delta\nu_D, \tag{6}$$

which shows that only knowledge about the absorption coefficient at the peak frequency is required to evaluate the line intensity as long as the line shape is approximated by a Doppler profile.

The absolute line intensities estimated from Eq. 6 are summarized in Table 1. In the estimation, we used the theoretically estimated Doppler width, $\Delta\nu_D$= 60.5 MHz, instead of the experimentally observed linewidths, because the experimentally observed linewidths were not accurate enough for the quantitative work; this may be due to the irregularity in the scan rate of the electric current fed to the diode.

Determination of Transition Moment for the ν_4 Fundamental. The absolute line intensity defined by Eq. 1 can have another form in the quantum-mechanical expression. The time-dependent perturbation theory has shown that:

$$S_{ij} = \frac{8\pi}{3hc}(N_j-N_i)\nu_{ij}|\mu_{ij}|, \tag{7}$$

where h is Planck's constant; c, the velocity of light; N_s, the molecular density of the energy level, E_s (E_j> E_i); ν_{ij}, the transition frequency, and μ_{ij}, the transition dipole moment. Suppose that the molecules are

TABLE 1. TRANSITION DIPOLE MOMENT DEDUCED FROM ABSORPTION LINES IN ν_4 OF HCF_3

Line	Pressure / mTorr	Intensity S / cm² atm	$\lvert\mu_{ij}\rvert$ / D	$\left(\frac{\partial\mu_x}{\partial Q_4}\right)\langle 0\lvert Q_4\rvert v_4=1\rangle\rvert/D$
$^{P}P_{35}(35)$	13.6	0.153	0.110	0.111
	21.7	0.163	0.113	0.115
$^{P}P_{36}(36)$	13.6	0.310	0.112	0.114
	21.7	0.302	0.111	0.113

a) $D(\text{Debye}) = 10^{-18}\ g^{1/2}\ cm^{5/2}\ s^{-1}$.

in thermal equilibrium; that is, the molecules follow the Boltzmann distribution. Then, the density of molecules in the energy level, E_s, can be expressed as;

$$N_s = Ng_s\exp(-E_s/kT)/Z, \tag{8}$$

where N is the total molecular density and g_s, the degree of the degeneracy of the level, s. The estimation of g_s has been discussed in the previous paper.[2] Z is the total partition function, which can be evaluated by computor calculation. In this evaluation, we considered the rotational levels belonging not only to the vibrational ground state, but also to the $v_3=1$ and $v_6=1$ states. As the band origins are: $\nu_3=700$ cm^{-1} and $\nu_6=507$ cm^{-1}, the number of molecules in these energy levels at room temperature cannot be neglected. The vibrational-energy levels higher than 1000 cm^{-1} ($2\nu_6$, ν_2, ν_5, $\nu_3+\nu_6$, ν_4, $2\nu_3$, *etc.*) were neglected because the distribution density is very small. Then, Z can be expressed as the sum of the partition functions for three vibrational levels:

$$Z = Z_0 + Z_3 + Z_6. \tag{9}$$

For example, the explicit formula for Z_0 is:

$$Z_0 = \sum_{J=0}^{\infty}\sum_{J=-J}^{J}(2J+1)g_K g_I\exp(-E_{JK}/kT), \tag{10}$$

where E_{JK} is equal to the $E(J,K)$ of our previous paper,[2] and:

$$\left.\begin{aligned} g_K &= 1 \text{ for } K=0,\\ g_K &= 2 \text{ for } K\neq 0,\\ g_I &= 2 \text{ for } K=3n\ (n=1,\ 2,\ 3,\ \cdots), \text{ and}\\ g_I &= 1 \text{ for } K\neq 3n. \end{aligned}\right\} \tag{11}$$

The summation was executed until the term newly added became less than 10^{-10} of the sum theretofore. Z_3 and Z_6 were calculated in the same way, special attention being paid to the symmetry species of the vibration-rotation energy levels ($v_3=1$, A_1; $v_6=1$, E). The result was:

$$\begin{aligned} Z &= 45836 + (3.21\times10^{-2})\times45991 + (8.26\times10^{-2})\times91875\\ &= 54904, \end{aligned} \tag{12}$$

where (3.21×10^{-2}) and (8.26×10^{-2}) are the Boltzmann factors for $v_3=1$ and $v_6=1$ respectively. The transition dipole moments thus obtained are shown in Table 1.

On calculating the transition moment from the observed line intensities, we have to pay much attention to the mixing of the energy levels. In the case of the ν_4 fundamental of fluoroform, the possible perturbations are the x-y type Coriolis interaction with $2\nu_3$ and the l-type resonance. Fortunately, for the cases of $^{P}P_{35}(35)$ and $^{P}P_{36}(36)$ we do not have to consider the existence of the x-y type Coriolis interaction, because there are no counter levels in the $2\nu_3$ state.[5] The presence of the l-type resonance is not a critical problem for the determination of the transition moment. The degree of the mixing can be calculated exactly, for the eigenvectors can be calculated from the constant q_4.[6] However, there are no interacting pairs for these transitions.[7] In other words, $|0,\ 1\colon\ J,\ J,\ -1>$ remains the eigenfunction of the overall Hamiltonian, and J, k, and l arc good quantum numbers. The matrix elements of the direction cosine can then, readily be calculated.[8]

Now, the transition moment corresponding to the ν_4 fundamental can be derived. By expanding the components of the electric dipole moment with respect to the normal coordinates, we obtain:

$$\mu_x = (\mu_x)_0 + \sum_k\left(\frac{\partial\mu_x}{\partial Q_k}\right)_{Q_k=0}Q_k + \cdots \tag{13}$$

and by neglecting the terms higher than the quadratic, we can express the matrix element of μ_x by this relation:

$$\langle 0|\mu_x|v_4=1\rangle = \left(\frac{\partial\mu_x}{\partial Q_4}\right)\langle 0|Q_4|v_4=1\rangle. \tag{14}$$

The constant term of Eq. 13 vanishes so long as the anharmonicity is neglected. The numerically estimated values of Eq. 14 are summarized in Table 1.[8]

Comparison with the Results Obtained from the Conventional Method. The observed transition-moment values were converted into the absolute absorption-intensity values in order to compare the present results with the absorption intensities obtained by conventional method.[3] The relation between the absolute intensity, Γ, and the transition moment is:

$$\Gamma = \frac{8\pi^3}{3hc}(N_j-N_i)\left|\left(\frac{\partial\mu_x}{\partial Q_4}\right)\langle 0|Q_4|v_4=1\rangle\right|^2. \tag{15}$$

This equation has the same form as Eq. 7 when Γ is replaced by S_{ij}/ν_{ij}. $|\mu_{ij}|^2$ can be written for a vibrational transition as:

$$\begin{aligned} |\langle v''|\mu_F|v'\rangle|^2 &= |\langle 0|\mu_x|v_4=1\rangle|^2 + |\langle 0|\mu_y|v=1\rangle^2\\ &= 2|\langle 0|\mu_x|v_4=1\rangle|^2. \end{aligned} \tag{16}$$

The coefficient of 2 corresponds to the degeneracy of the vibration, which is designated as k in Eq. 15. Again, the vibration-rotation partition functions were considered for the estimation of N_s. In Table 2, the Γ values calculated from Eq. 15 are compared with those obtained by the conventional method. The error for Γ was considered to arise mainly from the errors in the pressure measurement. The direct comparison of these intensity values is not possible because

TABLE 2. ABSOLUTE INTENSITIES Γ/cm^2 mol^{-1}

5360±220	Present result
6360±312	S. Saeki *et al.*[a)]
4960±240	[b)]

a) S. Saeki, M. Mizuno, and S. Kondo, *Spectrochim. Acta, Part A*, **32**, 403 (1976). b) The intensity for the ν_4 fundamentaal calculated from the value of a), assuming $T=293$ K.

the intensity values observed by the conventional method contain not only the absolute intensity for the ν_4 fundamental, but also the absolute intensities for such hot bands, like $\nu_6 \rightarrow \nu_6+\nu_4$ and $\nu_3 \rightarrow \nu_3+\nu_4$, or overtones like $2\nu_3$. For the subtraction of the contributions from these hot band, knowledge about the types of transitions and the intensities of these hot bands is necessary. As the symmetry species of ν_6 is E, the resultant level, $\nu_3+\nu_6$, has the symmetry of A_1+A_2+E. The direct product of the species of these two states:

$$E \times (A_1+A_2+E) = A_1 + A_2 + 3E$$

shows the types of transition. The intensity of the A_1+A_2 type band is supposed to be quite weak, for it is governed by a higher-order derivative of the dipole moment. The $\nu_3 \rightarrow \nu_3+\nu_4$ transition belongs to E. In order to discuss the overtone problem, it is necessary to know the magnitude of $|\langle 0|\mu_z|v_3=2\rangle|$. However, as we do not see any bands with considerable intensities in the 1400 cm^{-1} region of the survey spectra, $2\nu_3$ is supposed to be quite weak, and so its contribution to Γ might be negligible. Thus, we can estimate the relative intensities of these hot bands by calculating the Boltzmann factors.

Although Saeki *et al.* do not describe the temperature explicitly in their report,[3)] we assumed that their intensity measurement had been carried out at 293 K. Then, the intensity value of Ref. 3 can be corrected for the hot-band effects. The intensity value of 6360 cm^2 mol^{-1} is reduced to:

$$6360 \times \frac{1}{1+3\exp\left(-\dfrac{507}{293\,k}\right)+\exp\left(-\dfrac{700}{293\,k}\right)} = 4960.$$

This intensity value agrees with our present result within the limits of experimental error. This, in turn, suggests that the present experimental procedure is effective enough to observe vibrational intensities with a high accuracy.

Effect of x-y Type Coriolis Interaction on Line Intensity. As the method is established for determining the line-intensities of individual rotation-vibration lines, it is of some interest to see the effects of an x-y type Coriolis interaction on line-intensities. For this purpose, we observed the line-intensities for the $^{\mathrm{P}}\mathrm{P}_{J-6}(J)$ series lines, because it has been established in our previous work[2)] that the x-y type Coriolis interaction affects the energy levels of this line-series considerably.

A part of the observed results are summarized in Table 3. In can be seen from the table that the effective transition moment, $|\mu_{1\mathrm{J}}|$, decreases in magnitude with the increase in J and K values for $v_4=1$. Using the spectral data for the $2\nu_3 \leftarrow \nu_3$ band obtained by Graner *et al.*,[9)] together with the molecular constants related to the ν_4 band,[2)] we can ascertain that the energy level of the $|v_4=1, J, K=J-6>$ state is lower than the of $|v_3=2, J, K=J-5>$ for $J>36$, and *vice versa* for $J<36$. Therefore, the intensity behaviour of Table 3 may be explained by Coriolis coupling with the $2\nu_3$ band, whose intensity is rather weak in comparison with that of ν_4.

TABLE 3. LINE INTENSITES OF $^{\mathrm{P}}\mathrm{P}_{J-6}(J)$

Line	S/cm^2 atm^{-1}	$\mu_{1\mathrm{J}}/D$
$^{\mathrm{P}}\mathrm{P}_{24}(30)$	0.277	0.121
$^{\mathrm{P}}\mathrm{P}_{27}(33)$	0.237	0.117
$^{\mathrm{P}}\mathrm{P}_{30}(36)$	0.191	0.111

D(Debye) $=10^{-18}$ g$^{1/2}$ cm$^{5/2}$ s^{-1}.

If we take a Coriolis interaction and a l-type resonance into account, the wave-function of an excited state may be expressed as:

$$\begin{aligned}\psi' &= a\psi'_{+}(v_4=1, J, K+1) + b\psi'_0(v_3=2, J, K)\\ &\quad + c\psi'_{-}(v_4=1, J, K-1),\end{aligned} \tag{17}$$

where a, b, and c are constants. As the effect of the l-type resonance is negligible in the present case,[2)] Eq. 17 can be simplified as:

$$\left.\begin{aligned}\psi'_1 &= \cos\beta\psi'_0(v_3=2, J, K) + \sin\beta\psi'_{-}(v_4=1, J, K-1)\\ \psi'_2 &= -\sin\beta\psi'_0(v_3=2, J; K) + \cos\beta\psi'_{-}(v_4=1, J, K-1)\end{aligned}\right\}, \tag{18}$$

where:

$$\cos 2\beta = \frac{\Delta E}{2r}, \text{ and } \sin 2\beta = \frac{-\xi_{334}}{r}[J(J+1)-K(K-1)]^{1/2}$$

with

$$r = \left[\left(\frac{\Delta E}{2}\right)^2 + \xi^2_{334}\{J(J+1)-K(K-1)\}\right]^{1/2},$$

In the above relations, ΔE represents the energy difference between two unperturbed states, $|v_3=2, J, K>$ and $|v_4=1, J, K-1>$. The transition moment corresponding to the transition from the ground state, ψ'', is:

$$\begin{aligned}\langle\psi''|\mu|\psi'_2\rangle &= -\sin\beta\langle\psi''|\mu|\psi'_0\rangle + \cos\beta\langle\psi''|\mu|\psi'_{-}\rangle\\ &= -\sin\beta\cdot M_r\cdot M_k{}^k + \cos\beta\cdot M_s\cdot M_k{}^{k-1},\end{aligned} \tag{19}$$

where:

$$M_r = \left(\frac{\partial^2\mu_z}{\partial Q_3{}^2}\right)\langle 0|Q_3{}^2|v_3=2\rangle$$

and

$$M_s = \left(\frac{\partial\mu_x}{\partial Q_4}\right)\langle 0|Q_4|v_4=1\rangle$$

and $M_{k'}{}^{,k'}$ is a direction cosine matrix element. Thus, the rotation-vibration line-strength is shown to be proportional to this value:

$$\begin{aligned}|\langle\psi''|\mu|\psi'_2\rangle|^2 &= \cos^2\beta(M_sM_k{}^{k-1})^2 - \sin 2\beta M_rM_sM_k{}^kM_k{}^{k-1}\\ &\quad + \sin^2\beta(M_rM_k{}^k)^2\\ &= (\cos^2\beta - \alpha\sin 2\beta + \alpha^2\sin^2\beta)(M_sM_k{}^{k-1})^2,\end{aligned} \tag{20}$$

where:

$$\alpha = \frac{M_rM_k{}^k}{M_sM_k{}^{k-1}}.$$

According to the experimental results of Table 3, the line internsity of the ν_4 band decreases with the decrease in the energy difference between the levels interacting with each other through the Coriolis resonance. Therefore, the second term of Eq. 20 is positive; that is,

$$\alpha \sin 2\beta > 0$$

and, accordingly;[10)]

$$\xi_{334} M_r M_s > 0. \qquad (21)$$

The relation of Eq. 21 has been referred to as an "positive perturbation," following Mills, Smith, and Duncan.[11)] As the $v_3=2$ state has not yet been studied with sufficient accuracy, though, the quantitative analysis of line intensities based upon Eq. 20 is left for the future. We can only conclude at this stage that the observed line-intensity values show that the perturbation is positive.

References

1) E. B. Wilson, Jr., and A. J. Wells, *J. Chem. Phys.*, **14**, 578 (1946).

2) S. Sofue, K. Kawaguchi, E. Hirota, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **54**, 897 (1981).

3) S. Saeki, M. Mizuno, and S. Kondo, *Spectrochim. Acta, Part A*, **32**, 403 (1976).

4) C. H. Townes and A. H. Shawlow, "Microwave Spectroscopy," Dover Publications, New York (1955).

5) The matrix elements of the Hamiltonian for the Coriolis interaction between ν_4 and $2\nu_3$ are expressed as:

$$\langle v_3=2,\ v_4=0;\ J, K, l=0\ |H_c|\ v_3=0,\ v_4=1;\ J, K\pm1,\ l=\pm1\rangle = \pm\xi_{334}[J(J+1)-K(K\pm1)]^{1/2}.$$

Notice that $J>K$.

6) For the definition of q_4, see Ref. 2.

7) The perturbed energies can be obtained from the diagonalization of a 2×2 matrix of the form:

$$\begin{bmatrix} E(J,\ K-1,\ -1) & W \\ W & E(J,\ K+1,\ +1) \end{bmatrix}.$$

8) The following relations are used, where D_{fF} is a matrix element of a direction cosine matrix:

$$|\langle J,\ k|D_{xF}|J+1,\ k\pm1\rangle|^2 = \frac{(J\pm k+1)(J\pm k+2)}{2(J+1)(2J+1)}$$

$$|\langle J,\ k|D_{xF}|J,\ k\pm1\rangle|^2 = \frac{(J\mp k)(J\pm k+1)}{2J(J+1)}$$

$$|\langle J,\ k|D_{xF}|J-1,\ k\pm1\rangle|^2 = \frac{(J\mp k)(J\mp k+1)}{2J(2J+1)}.$$

9) G. Graner, R. Anttila, and J. Kaouppinen, *Mol. Phys.*, **38**, 103 (1979).

10)

$$\sin 2\beta = \frac{M_r}{M_s}\frac{M_k{}^k}{M_k{}^{k-1}}(-\xi_{334})[J(J+1)-K(K-1)]^{1/2}/r$$

As M_K^K/M_K^{K-1} is negative, the product, $\xi_{334}M_rM_s$, is positive. Therefore, we obtain this relation:

$$\xi_{334}\left(\frac{\partial^2\mu_z}{\partial Q_3{}^2}\right)\left(\frac{\partial\mu_x}{\partial Q_4}\right) > 0.$$

11) I. M. Mills, W. L. Smith, and J. L. Duncan, *J. Mol. Spectrosc.*, **16**, 349 (1965); C. DiLauro and I. M. Mills, *ibid.*, **21**, 386 (1966).