*The Distribution Function of Internal Displacement Coordinates in Linear XY_2 Molecules**

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Since the motion of atoms in a molecule is dependent on the interatomic force field, it must be of great help for understanding the physical significance of the potential field to consider the probability distribution function of the interatomic displacements. The calculation of the probability function is simple for a diatomic molecule which is treated as a one-dimensional oscillator. In this case the distribution of the interatomic displacements is described by a Gaussian function, if the interatomic potential is assumed to be a simple harmonic one. The effect of the cubic potential constant would be illustrated by resulting asymmetry of the distribution curve. In this work the distribution function is calculated for linear XY_2 molecules, and a schematical interpretation of intramolecular motion is presented by means of a distribution map. Numerical computation of the distribution map is carried out for carbon dioxide and carbon disulfide.

The Probability Distribution Function

The probability distribution function is given in a straight-forward manner by the vibrational wave functions expressed in terms of the normal coordinates,

$$P=\sum_{v} w_v \psi_v{}^* \psi_v \tag{1}$$

where w_v is the normalized Boltzmann factor of the v-th vibrational state**. The vibrational Hamiltonian of a linear XY_2 molecule consisting of the zeroth- and the first-order terms, is

$$H=H^{(0)}+H^{(1)} \tag{2}$$

where $H^{(0)}$ stands for the terms of the kinetic energy and the harmonic potential energy, while $H^{(1)}$ is given by

$$H^{(1)}=hc\,[k_{111}q_1{}^3+k_{122}q_1(q_{2a}{}^2+q_{2b}{}^2)+k_{133}q_1q_3{}^2] -\left(\frac{h}{\pi^2 c\omega_1 I}\right)^{1/2}\langle E_{\text{rot}}\rangle q_1 \tag{3}$$

The first term of $H^{(1)}$ is the cubic part of the potential function and the second term is the energy decrease due to the centrifugal stretching, where $\langle E_{\text{rot}}\rangle$ is the mean rotational energy of the molecule(1). The quartic and higher-order terms of the potential function are ignored in the present treatment. The coordinates q's are dimensionless normal coordinates.

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* A preliminary report of this work was presented at the International Conference on Magnetism and Crystallography, Kyoto, 1961.

** A set of quantum numbers designating the vibrational state is symbolically expressed by a single letter v.

1) Y. Morino and E. Hirota, This Bulletin, 31, 423 (1958).

The subscript 1 corresponds to the totally symmetric vibration, $2a$ and $2b$ to the doubly degenerate, and 3 to the antisymmetric vibration, respectively.

The wave function ψ_v is obtained by the first-order perturbation theory according to the equation

$$\psi_v=\psi_v^0-\sum_{v'}{}' \frac{\langle v'\,|H^{(1)}|\,v\rangle}{E_{v'}^0-E_v^0}\psi_{v'}^0 \tag{4}$$

as a linear combination of the zeroth-order wave functions ψ_v^0. All non-vanishing coefficients of $\psi_{v'}^0$ are calculated as shown in Appendix I, by substituting Eq. 3 for $H^{(1)}$. By the use of Eq. 4, Eq. 1 is rewritten as

$$P(q_1, q_{2a}, q_{2b}, q_3)=\sum w_v\psi_v^{0*}\psi_v^0 - \sum_v w_v \sum_{v'}{}' \frac{\langle v'\,|H^{(1)}|\,v\rangle}{E_{v'}^0-E_v^0}(\psi_v^{0*}\psi_{v'}^0+\psi_v^0\psi_{v'}^{0*}) \tag{5}$$

Since there hold the relations

$$\psi_v^0=\prod_s \psi_{v_s}^0(q_s), \qquad s=1,\ 2a,\ 2b \text{ and } 3$$

and

$$w_v=\prod_s \chi_s^{v_s}/\sum_{v_s}\chi_s^{v_s}, \left(\chi_s=\exp\left(-\frac{hc\omega_s}{kT}\right)\right)$$

every term of Eq. 5 can be calculated as a product of the summations over single vibrational quantum number. It should be mentioned that this type of calculation was performed by Reitan in his thesis²⁾, although his method of calculation seems to be a little more tedious than that of the present work. The essential part of the calculation is reported in Appendix II.

As the result of the calculation, we have

$$P(q_1, q_{2a}, q_{2b}, q_3)=N[1+a_1q_1+a_{111}q_1^3 + a_{122}q_1(q_{2a}^2+q_{2b}^2)+a_{133}q_1q_3^2] \times \exp\left[-\frac{q_1^2}{T_1}-\frac{(q_{2a}^2+q_{2b}^2)}{T_2}-\frac{q_3^2}{T_3}\right] \tag{6}$$

$$T_s=\coth(hc\omega_s/2kT)$$

with the following expressions for the coefficients;

$$a_1=-\frac{2k_{111}}{\omega_1}\left(\frac{1-\chi_1}{1+\chi_1}\right)^2 + \frac{4k_{122}\omega_2\gamma_{122}^+}{\omega_1(1+\chi_1)(1-\chi_2)(1+\chi_2)} + \frac{2k_{133}\omega_3\gamma_{133}^+}{\omega_1(1+\chi_1)(1-\chi_3)(1+\chi_3)}+\frac{2\langle E_{\mathrm{rot}}\rangle}{b_1T_1f_{11}r_e} \tag{7a}$$

$$a_{111}=-\frac{2k_{111}(1-\chi_1)(1+10\chi_1+\chi_1^2)}{3\omega_1(1+\chi_1)^3} \tag{7b}$$

$$a_{122}=-\frac{2k_{122}}{(1+\chi_1)(1+\chi_2)^2}\left\{\frac{2\chi_2(1-\chi_1)}{\omega_1}-\gamma_{122}^-\right\} \tag{7c}$$

$$a_{133}=-\frac{2k_{133}}{(1+\chi_1)(1+\chi_3)^2}\left\{\frac{2\chi_3(1-\chi_1)}{\omega_1}-\gamma_{133}^-\right\} \tag{7d}$$

and

$$\gamma_{1ss}^\pm=\left\{\frac{-1+\chi_1\chi_s^2}{\omega_1+2\omega_s}\pm\frac{-\chi_1+\chi_s^2}{\omega_1-2\omega_s}\right\} \tag{7e}$$

where b_1 is designated by Eq. 9, and f_{11} is the force constant for the symmetric stretching vibration.

Because of the accidental degeneracy of ω_1 and $2\omega_2$, the second term of Eq. 7e would fail to be a good approximation. It will, however, be shown in Appendix III that the same expression can be used without any serious error even in the case of strong degeneracy.

The distribution function in terms of the normal coordinates is converted to the expression in terms of Δz_1, Δz_2 and $\Delta\rho$, the internal Cartesian displacements; Δz denotes the relative displacements of the atom X to Y along the molecular axis and $\Delta\rho$ is the relative displacement perpendicular to the axis. $\Delta\rho^2$ is sometimes written as $\Delta x^2+\Delta y^2$. The displacements of the two X—Y atom-pairs are designated by Δz_1 and Δz_2, respectively.

These internal coordinates are related to the normal coordinates by the following relations,

$$\Delta z_1=b_1q_1+b_3q_3 \tag{8a}$$

$$\Delta z_2=b_1q_1-b_3q_3 \tag{8b}$$

and

$$\Delta\rho^2=b_{22}(q_{2a}^2+q_{2b}^2) \tag{8c}$$

The coefficients b's are given by

$$b_1=\left(\frac{h\mu_{\mathrm{Y}}}{8\pi^2c\omega_1}\right)^{1/2} \tag{9a}$$

$$b_3=\left[\frac{h}{8\pi^2c\omega_3}(\mu_{\mathrm{Y}}+2\mu_{\mathrm{X}})\right]^{1/2} \tag{9b}$$

and

$$b_{22}=\frac{h}{8\pi^2c\omega_2}(\mu_{\mathrm{Y}}+2\mu_{\mathrm{X}}) \tag{9c}$$

where μ_{X} and μ_{Y} are the reciprocal masses of the atom X and Y, respectively.

By these relations together with the followings,

$$q_{2a}=b_{22}^{-1/2}\Delta\rho\cos\varphi \tag{10a}$$

$$q_{2b}=b_{22}^{-1/2}\Delta\rho\sin\varphi \tag{10b}$$

where φ is the azimuthal angle, the probability distribution function $P(q_1, q_{2a}, q_{2b}, q_3)$ is transformed to the expression in terms of Δz_1, Δz_2, $\Delta\rho$ and φ, as

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2) A. Reitan, thesis, Institutt for Teoretiske Kjemi, Norges Tekniske Høgskole (1958).

$$P(\Delta z_1,\ \Delta z_2,\ \Delta\rho,\ \varphi)=N\Big[1+\frac{a_1}{2b_1}(\Delta z_1+\Delta z_2)$$

$$+\frac{a_{111}}{(2b_1)^3}(\Delta z_1+\Delta z_2)^3+\frac{a_{122}}{2b_1b_{22}}\Delta\rho^2(\Delta z_1+\Delta z_2)$$

$$+\frac{a_{133}}{2b_1(2b_3)^2}(\Delta z_1+\Delta z_2)(\Delta z_1-\Delta z_2)^2\Big]$$

$$\times\ \Delta\rho\ \exp\Big[-\frac{\Delta\rho^2}{b_{22}T_2}-\frac{(\Delta z_1+\Delta z_2)^2}{(2b_1)^2T_1}$$

$$-\frac{(\Delta z_1-\Delta z_2)^2}{(2b_3)^2T_3}\Big] \qquad (11)$$

In order to obtain a two-dimensional probability function $P(\Delta z,\ \Delta\rho)$, Eq. 11 is integrated over φ and over either one of Δz_1 and Δz_2. The calculation leads to the following result;

$$P(\Delta z,\ \Delta\rho)=N'\ [1+A_1\Delta z+A_{111}\Delta z^3+A_{122}\Delta z\Delta\rho^2]$$

$$\times\ \Delta\rho\ \exp\Big[-\frac{\Delta\rho^2}{\langle\Delta\rho^2\rangle}-\frac{\Delta z^2}{2\langle\Delta z^2\rangle}\Big] \qquad (12)$$

where

$$A_1=\frac{a_1b_1T_1}{2\langle\Delta z^2\rangle}+\frac{3a_{111}b_1T_1b_3{}^2T_3}{8\langle\Delta z^2\rangle^2}$$

$$+\frac{a_{133}b_1T_1T_3(b_1{}^2T_1-2b_3{}^2T_3)}{8\langle\Delta z^2\rangle^2} \qquad (13a)$$

$$A_{111}=\frac{a_{111}b_1{}^3T_1{}^2}{8\langle\Delta z^2\rangle^3}+\frac{a_{133}b_1T_1b_3{}^2T_3{}^2}{8\langle\Delta z^2\rangle^3} \qquad (13b)$$

$$A_{122}=\frac{a_{122}b_1T_1T_2}{2\langle\Delta z^2\rangle\langle\Delta\rho^2\rangle} \qquad (13c)$$

and

$$\langle\Delta z^2\rangle=\frac{b_1{}^2T_1+b_3{}^3T_3}{2} \qquad (13d)$$

$$\langle\Delta\rho^2\rangle=b_{22}T_2 \qquad (13e)$$

It is noted that $P(\Delta z,\ \Delta\rho)$ describes the relative motion of the end atom Y to the central atom X, the coordinate axes Δz and $\Delta\rho$ being fixed on the rotating plane defined by the triangle Y—X—Y.

The Probability Distribution Function of the Interatomic Distances r_{XY} and r_{YY}

The distribution function $P(\Delta z,\ \Delta\rho)$ given by Eq. 12 is further transformed to a one-dimensional distribution function in terms of

Δz																					
+0.1 A	00	01	01	02	02	02	02	02	02	01	01	01	01	00	00	00	00	00	00	00	
	00	01	02	03	04	04	04	04	04	03	02	02	01	01	01	00	00	00	00	00	
	00	02	05	06	08	08	08	08	07	06	05	04	03	02	01	01	01	00	00	00	
	00	04	08	11	13	14	14	14	12	10	08	06	05	03	02	02	01	01	00	00	
	00	07	14	19	22	24	24	22	20	17	14	11	08	06	04	03	02	01	01	00	
	00	11	21	29	34	36	37	34	31	26	21	16	12	09	06	04	03	02	01	01	
	00	15	29	40	48	52	52	49	43	37	30	23	17	13	09	06	04	02	01	01	
	00	20	38	53	63	68	68	64	57	49	40	31	23	17	12	08	05	03	02	01	
	00	24	46	64	76	82	82	78	69	59	48	38	28	21	14	10	06	04	02	01	
	00	27	51	71	84	91	92	87	78	67	54	43	32	23	16	11	07	04	03	02	0.2 A
0.0	00	28	53	73	87	94	94	89	80	69	56	44	33	24	17	11	07	05	03	02	$\Delta\rho$
	00	26	49	68	82	88	89	85	76	65	54	42	32	23	16	11	07	05	03	02	
	00	22	43	59	71	77	77	73	66	57	47	37	28	21	14	10	06	04	02	01	
	00	18	34	47	56	61	61	58	53	45	38	30	23	17	12	08	05	03	02	01	
	00	13	24	34	40	44	44	42	38	33	27	22	17	12	09	06	04	02	01	01	
	00	08	16	22	27	29	29	28	25	22	18	15	11	08	06	04	03	02	01	01	
	00	05	10	13	16	17	18	17	15	13	11	09	07	05	04	02	02	01	01	00	
	00	03	05	07	09	09	10	09	08	07	06	05	04	03	02	01	01	01	00	00	
	00	01	02	03	04	05	05	04	04	04	03	02	02	01	01	01	00	00	00	00	
	00	01	01	01	02	02	02	02	02	02	01	01	01	01	00	00	00	00	00	00	
−0.1 A	00	00	00	01	01	01	01	01	01	01	01	00	00	00	00	00	00	00	00	00	

Fig. 1a. CO_2

Δz																					
+0.1 A	00	01	02	03	04	05	05	05	05	05	05	04	04	03	02	02	01	01	01	01	
	00	02	04	06	07	08	09	09	09	09	08	07	06	05	04	03	03	02	01	01	
	00	03	07	10	12	14	15	15	15	14	13	12	10	09	07	06	04	03	02	02	
	00	05	10	15	19	21	23	24	23	22	20	18	16	13	11	09	07	05	04	03	
	00	08	15	22	27	31	34	35	34	32	30	27	23	20	16	13	10	08	06	04	
	00	11	21	30	37	43	46	48	47	45	41	37	32	27	23	18	14	11	08	06	
	00	14	27	39	49	56	60	62	61	58	54	49	42	36	30	24	19	15	11	08	
	00	17	33	48	59	68	74	76	75	72	67	60	52	45	37	30	24	19	14	10	
	00	20	38	55	68	79	85	88	87	83	77	70	61	52	44	36	28	22	17	12	
	00	21	41	59	74	85	92	95	95	91	85	77	67	58	48	39	31	25	19	14	
0.0	00	22	42	61	76	87	95	98	97	94	87	79	70	60	50	41	33	26	20	15	0.2A $\Delta\rho$
	00	21	41	58	73	84	91	94	94	90	84	77	68	58	49	40	32	25	19	15	
	00	19	36	52	65	75	82	85	85	82	77	70	62	53	45	37	30	23	18	14	
	00	16	31	44	55	64	69	72	72	70	65	59	53	46	39	32	26	20	16	12	
	00	12	24	35	44	50	55	57	57	55	52	47	42	37	31	26	21	17	13	10	
	00	09	18	26	32	37	41	42	42	41	39	36	32	28	23	19	16	13	10	07	
	00	06	12	18	22	26	28	29	30	29	27	25	22	19	17	14	11	09	07	05	
	00	04	08	11	14	17	18	19	19	19	18	16	15	13	11	09	07	06	05	04	
	00	02	05	07	09	10	11	11	12	11	11	10	09	08	07	06	05	04	03	02	
	00	01	03	04	05	06	06	06	06	06	06	06	05	04	04	03	03	02	02	01	
−0.1 A	00	01	01	02	02	03	03	03	03	03	03	03	03	02	02	02	01	01	01	01	

Fig. 1b. CS_2

Fig. 1. Calculated values of the distribution function $P(\Delta z, \Delta\rho)$.

the instantaneous displacement of the interatomic distance δr_{XY}. In this case, the transformation is not linear but it is given by

$$\delta r_{XY} = \Delta z + \Delta\rho^2/2r_e + \cdots\cdots, \quad (\delta r = r - r_e) \tag{14}$$

to the first-order of approximation. The calculation leads to the result

$$P(r_{XY}) = \frac{1}{(2\pi\langle\delta r^2\rangle)^{1/2}}\left\{1 + \left(A_1 + A_{122}\langle\Delta\rho^2\rangle + \frac{\langle\Delta\rho^2\rangle}{2r_e\langle\delta r^2\rangle}\right)\delta r + A_{111}\delta r^3\right\}\exp\left(-\frac{\delta r^2}{2\langle\delta r^2\rangle}\right) \tag{15}$$

where A's are defined by Eq. 13's.

It is seen that asymmetry is introduced into the Gaussian function by linear and cubic terms of δr. The $P(r)$ function is important in the study of electron diffraction by gaseous molecules, because it is closely connected with the molecular intensity curve and the radial distribution curve obtained by the diffraction study[3]. The empirical asymmetric parameters determined by the analysis of the radial distribution curve will be related to the spectroscopic force constants through this equation. It is accordingly expected that better interpretation of the radial function will be attainable on the basis of intramolecular force field.

The distribution function for the Y—Y distance is calculated more simply, because the transformation is linear as shown below;

$$\delta r_{YY} = \Delta z_1 + \Delta z_2 = 2b_1 q_1 \tag{16}$$

The $P(r_{YY})$ is therefore obtained from Eq. 6 through integration over q_{2a}, q_{2b} and q_3, as

$$P(r_{YY}) = \frac{1}{(2\pi\langle\delta r^2\rangle)^{1/2}}\{1 + A'_1\delta r + A'_{111}\delta r^3\} \times \exp\left(-\frac{\delta r^2}{2\langle\delta r^2\rangle}\right) \tag{17}$$

with

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[3] K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **35**, 1945 (1961).

$$A'_1=\frac{1}{2b_1}\left(a_1+a_{122}T_2+\frac{1}{2}A_{133}T_3\right)$$

and

$$A'_{111}=a_{111}/8b_1^3$$

Numerical Examples: CO_2 and CS_2

The probability distribution function $P(\Delta z, \Delta\rho)$ was numerically calculated for carbon dioxide and for carbon disulfide, respectively. The molecular constants used in the calculation are listed in Table I, together with the cubic potential constants k and the linear and cubic coefficients A of $P(\Delta z, \Delta\rho)$ obtained. The schematic diagrams of $P(\Delta z, \Delta\rho)$ are computed with an arbitrary normalizing-factor and arranged in rows so as to make correspondence to the point specified by the coordinates $(\Delta z, \Delta\rho)$, as seen in Figs. 1a and 1b. The contour lines are drawn on the diagrams, and the distribution maps thus obtained are shown in Fig. 2a for CO_2 and in Fig. 2b for CS_2, respectively.

TABLE I. MOLECULAR CONSTANTS OF CO_2 AND CS_2

	CO_2[a)]	CS_2[b,c)]
ω_1	$1354.85\ cm^{-1}$	$671.36\ cm^{-1}$
ω_2	$673.00\ cm^{-1}$	$398.62\ cm^{-1}$
ω_3	$2396.49\ cm^{-1}$	$1551.92\ cm^{-1}$
α_1	$0.00120\ cm^{-1}$	$0.000156\ cm^{-1}$
α_2	$-0.00072\ cm^{-1}$	$-0.000256\ cm^{-1}$
α_3	$0.00309\ cm^{-1}$	$0.000711\ cm^{-1}$
k_{111}	$-45.07\ cm^{-1}$	$-14.90\ cm^{-1}$
k_{122}	$73.81\ cm^{-1}$	$50.10\ cm^{-1}$
k_{133}	$-252.95\ cm^{-1}$	$-129.56\ cm^{-1}$
A_1	$1.8\ A^{-1}$	$1.2\ A^{-1}$
A_{111}	$309\ A^{-3}$	$170\ A^{-3}$
A_{122}	$-114\ A^{-3}$	$-100\ A^{-3}$

a) C. P. Courtoy, *Ann. Soc. Sci. Bruxelles*, I **73**, 5 (1959).
b) B. P. Stoicheff, *Can. J. Phys.*, **36**, 218 (1958).
c) A. H. Guenther, T. A. Wiggins and D. H. Rank, *J. Chem. Phys.*, **28**, 682 (1958).

These maps illustrate the relative motion of the end atom Y to the central atom X. The Δz axis lies on the equilibrium molecular axis. The point specified by $\Delta z=0$ and $\Delta\rho=0$ is the equilibrium position of the Y atom. The location of the atom X is far down out of the figures in the negative direction, specified by $\Delta z=-r_e$ and $\Delta\rho=0$.

It is easily seen in the diagrams of $P(\Delta z, \Delta\rho)$ that in the region of small $\Delta\rho$, the outer region of Δz is more favorable, and the inner region of Δz becomes more favorable as $\Delta\rho$ increases. This is caused by the negative contribution of the coupling term between bending and stretching, or A_{122}, to the distribution function. This general tendency of the probability distribution corresponds to a classical picture of the bending motion that the two X—Y bonds are bent at the central atom and the end atom Y moves along a circular locus which is slightly shifted outwards by the stretching anharmonicity.

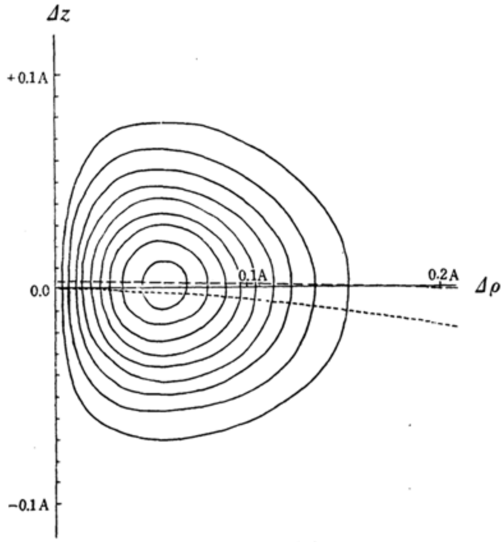

Fig. 2a. CO_2

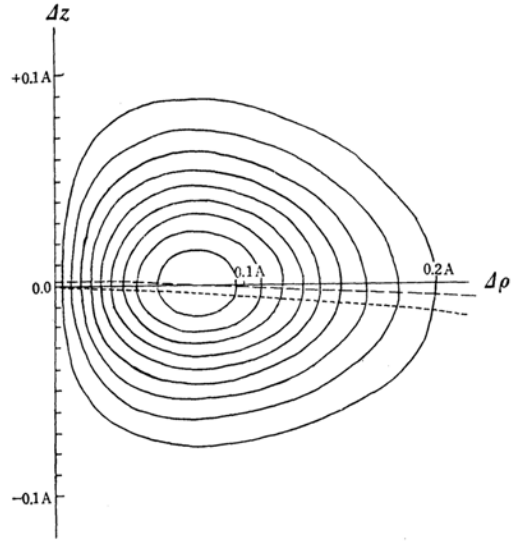

Fig. 2b. CS_2

Fig. 2. Contour map of the probability-distribution.

—— shows the ridge
- - - is the circular locus drawn by keeping the X—Y distance constant

It may be accordingly suggested that the intramolecular potential can be described better and more simply in terms of internal coordinates, i.e., the bond-stretching δr and the bending angle $\delta\rho$, rather than in terms of Cartesian coordinates. The force constants for the expression of the potential energy in terms of the internal coordinates are expected to have more distinct physical significance and therefore to be transferable among the chemical bonds of the same kind. An extensive study on the anharmonic force constants has been carried out along this line, and it was found that the most part of the constant k_{122} comes from the quadratic stretching force constants through coordinate transformation[4].

A more careful examination of the distribution map reveals that according as $\Delta\rho$ increases, the ridge in the map runs more and more outwards than the circular locus which is drawn by keeping the X—Y distance constant. In other words, it is easier for a bond to stretch when the bending motion takes place. Such an interaction term as $L_3\delta r\delta\alpha^2$ with a negative value of L_3, is therefore expected to improve the description of the intramolecular potential field. As a matter of fact, the predicted value of k_{122} was found to be in complete agreement with the observed value by introducing $L_3=-0.5$ md./A for CO_2, in addition to the main contribution from the quadratic stretching constants; while a smaller value $L_3=-0.1$ md./A is necessary to get the agreement for CS_2[4], corresponding to the fact that the extent of the outward shift is seen to be more appreciable in the case of CO_2 than CS_2.

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Appendix I. Non-vanishing Coefficients of Eq. 4

$(v=v_1,\ v_s,\ v_{s'})$ v'	$\dfrac{\langle v'\lvert H^{(1)}\rvert v\rangle}{E_{v'}^0-E_v^0}$
$v_1+1,\ v_s,\ v_{s'}$	$\frac{3k_{111}}{\omega_1}\left(\frac{(v_1+1)^3}{8}\right)^{1/2}-\left(\frac{h}{\pi^2c\omega_1I}\right)^{1/2}$ $\times\frac{\langle E_{\text{rot}}\rangle}{hc\omega_1}\left(\frac{v_1+1}{2}\right)^{1/2}$ $+\sum_s\frac{k_{1ss}}{\omega_1}\left(\frac{v_1+1}{2}\right)^{1/2}\left(v_s+\frac{1}{2}\right)$
$v_1+3,\ v_s,\ v_{s'}$	$\frac{k_{111}}{3\omega_1}\left[\frac{(v_1+1)(v_1+2)(v_1+3)}{8}\right]^{1/2}$
$v_1+1,\ v_s+2,\ v_{s'}$	$\frac{k_{1ss}}{\omega_1+2\omega_s}\left(\frac{v_1+1}{2}\right)^{1/2}$ $\times\frac{[(v_s+1)(v_s+2)]^{1/2}}{2}$
$v_1+1,\ v_s-2,\ v_{s'}$	$\frac{k_{1ss}}{\omega_1-2\omega_s}\left(\frac{v_1+1}{2}\right)^{1/2}\frac{[v_s(v_s-1)]^{1/2}}{2}$
$v_1-1,\ v_s,\ v_{s'}$	$-\frac{3k_{111}}{\omega_1}\left(\frac{v_1^3}{8}\right)^{1/2}$ $+\left(\frac{h}{\pi^2c\omega_1I}\right)^{1/2}\frac{\langle E_{\text{rot}}\rangle}{hc\omega_1}\left(\frac{v_1}{2}\right)^{1/2}$ $-\sum_s\frac{k_{1ss}}{\omega_1}\left(\frac{v_1}{2}\right)^{1/2}\left(v_s+\frac{1}{2}\right)$
$v_1-3,\ v_s,\ v_{s'}$	$-\frac{k_{111}}{3\omega_1}\left[\frac{v_1(v_1-1)(v_1-2)}{8}\right]^{1/2}$
$v_1-1,\ v_s+2,\ v_{s'}$	$-\frac{k_{1ss}}{\omega_1-2\omega_s}\left(\frac{v_1}{2}\right)^{1/2}$ $\times\frac{[(v_s+1)(v_s+2)]^{1/2}}{2}$
$v_1-1,\ v_s-2,\ v_{s'}$	$-\frac{k_{1ss}}{\omega_1+2\omega_s}\left(\frac{v_1}{2}\right)^{1/2}\frac{[v_s(v_s-1)]^{1/2}}{2}$

Appendix II. Calculation of the Summation over Vibrational States

It is easily shown that the summations over vibrational states appearing in Eq. 5 can be reduced to the products of some of the following summations:

$$F_0=\sum_v w_v\,|\phi_v{}^0|^2$$

$$F_1=\sum_v w_v\left(\frac{v+1}{2}\right)^{1/2}\phi_{v+1}{}^0\phi_v{}^0$$

$$F_2=\sum_v w_v\left[\frac{(v+1)^3}{8}\right]^{1/2}\phi_{v+1}{}^0\phi_v{}^0$$

$$F_3=\sum_v w_v[(v+1)(v+2)]^{1/2}\phi_{v+2}{}^0\phi_v{}^0$$

$$F_4=\sum_v w_v\left[\frac{(v+1)(v+2)(v+3)}{8}\right]^{1/2}\phi_{v+3}{}^0\phi_v{}^0$$

where $\phi_v{}^0$ is a non-perturbed wave function of a harmonic oscillator with the vibrational quantum number v.

As well known F_0 is given by[5,6],

$$F_0=\pi^{1/2}\left[\tanh\frac{hc\omega}{2\boldsymbol{k}T}\right]^{1/2}\exp\left[-\left(\tanh\frac{hc\omega}{2\boldsymbol{k}T}\right)q^2\right] \tag{AII-1}$$

By the use of the recursion formula,

$$\phi_{v+1}{}^0=\left(\frac{2}{v+1}\right)^{1/2}q\phi_v{}^0-\left(\frac{v}{v+1}\right)^{1/2}\phi_{v-1}{}^0$$

F_1 is rewritten as,

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[4] K. Kuchitsu, T. Iijima and Y. Morino, International Symposium on Molecular Structure and Spectroscopy, Tokyo, Japan, 1962.

[5] F. Bloch, *Z. Phys.*, 73, 295 (1932).

[6] Series of Modern Physics; "Statistical Mechanics", Iwanami Co., Ltd., Tokyo (1955), p. 212.

$$F_1 = q\sum_v w_v \phi_v{}^0 \phi_v{}^0 - \chi \sum_v w_{v-1}\left(\frac{v}{2}\right)^{1/2} \phi_v{}^0 \phi_{v-1}{}^0$$
$$= qF_0 - \chi F_1$$

where

$$\chi = \exp\left(-\frac{hc\omega}{\boldsymbol{k}T}\right)$$

Therefore we have,

$$F_1 = \frac{1}{1+\chi} qF_0 \qquad \text{(AII-2)}$$

Similarly,

$$F_2 = \sum_v w_v \left(\frac{v+1}{2}\right) q\phi_v{}^0\phi_v{}^0 - \sum_v w_v\left(\frac{v+1}{2}\right)\left(\frac{v}{2}\right)^{1/2}$$
$$\times \phi_v{}^0 \phi_{v-1}{}^0 = \frac{q}{2}G + \frac{q}{2}F_0 - \chi F_2 - \frac{1}{2}\chi F_1$$

Therefore,

$$F_2 = \frac{1}{1+\chi}\left(\frac{1}{2}qG + \frac{1}{2}qF_0 - \frac{1}{2}\chi F_1\right) \qquad \text{(AII-3)}$$

where

$$G = \sum_v w_v v \phi_v{}^0 \phi_v{}^0$$
$$= -\frac{1}{\sum_v \chi^v} \frac{\partial}{\partial\left(\frac{hc\omega}{\boldsymbol{k}T}\right)}[F_0 \cdot \sum_v \chi^v]$$
$$= \left\{\frac{\chi^2}{1-\chi^2} + \frac{2\chi}{(1+\chi)^2} q^2\right\} F_0 \qquad \text{(AII-4)}$$

Inserting Eqs. AII-2 and AII-4 into AII-3, we have,

$$F_2 = \frac{1}{1+\chi}\left[\frac{1-\chi+\chi^2}{2(1-\chi^2)} q + \frac{\chi}{(1+\chi)^2} q^3\right] F_0$$

and

$$F_3 = 2qF_1 - G - F_0 = \left\{-\frac{1}{1-\chi^2} + \frac{2}{(1+\chi)^2} q^2\right\} F_0$$

$$F_4 = \frac{1}{2}qF_3 - F_2 - \frac{1}{2}F_1$$
$$= \frac{1}{1+\chi}\left\{-\frac{3}{2(1-\chi^2)} q + \frac{1}{(1+\chi)^2} q^3\right\} F_0$$

Appendix III. The Effect of Fermi Resonance on the Probability Distribution Function

In order to simplify the discussion, let us consider a resonance between state I ($v_1=1$, $v_2=0$) and state II ($v_1=0$, $v_2=2$), connected by a coupling term $hck_{122}q_1q_2{}^2$, and calculate the probability distribution function $P = w_1|\phi_{\text{I}}|^2 + w_2|\phi_{\text{II}}|^2$, both by an ordinary first-order perturbation treatment and more rigorously by solving the secular determinant.

As the result of the first-order treatment, we have the perturbed wave functions as

$$\phi_{\text{I}} = \phi_{10}{}^0 - a_{20}\phi_{20}{}^0 - a_{22}\phi_{22}{}^0 - a_{00}\phi_{00}{}^0 - a_{02}\phi_{02}{}^0$$

and

$$\phi_{\text{II}} = \phi_{02}{}^0 - a_{12}\phi_{12}{}^0 - a_{14}\phi_{14}{}^0 - a_{10}\phi_{10}{}^0$$

where

$$a_{20} = \frac{k_{122}}{2\omega_1}, \qquad a_{12} = \frac{3k_{122}}{2\sqrt{2}\,\omega_1}$$

$$a_{22} = \frac{k_{122}}{\sqrt{2}\,(\omega_1+2\omega_2)}, \quad a_{14} = \frac{\sqrt{3}\,k_{122}}{\sqrt{2}\,(\omega_1+2\omega_2)}$$

$$a_{00} = -\frac{k_{122}}{2\sqrt{2}\,\omega_1}, \qquad a_{10} = \frac{k_{122}}{2(\omega_1-2\omega_2)}$$

$$a_{02} = -\frac{k_{122}}{2(\omega_1-2\omega_2)}$$

These wave functions are expressed more simply as

$$\phi_{\text{I}} = \phi_{10}{}^{(1)} - a_{02}\phi_{02}{}^0$$

and

$$\phi_{\text{II}} = \phi_{02}{}^{(1)} - a_{10}\phi_{10}{}^0$$

where $\phi^{(1)}$ includes all terms except for the term having a resonance denominator.

Accordingly we have,

$$P = w_1{}^0|\phi_{10}{}^{(1)}|^2 + w_2{}^0|\phi_{02}{}^{(1)}|^2 + \frac{w_1{}^0 - w_2{}^0}{\omega_1 - 2\omega_2} k_{122}\phi_{10}{}^0\phi_{02}{}^0 \qquad \text{(AIII-1)}$$

$$w_1{}^0 = \exp\left(-\frac{hc\omega_1}{\boldsymbol{k}T}\right), \qquad w_2{}^0 = \exp\left(-\frac{2hc\omega_2}{\boldsymbol{k}T}\right)$$

On the other hand, in a rigorous treatment, we consider the wave functions ϕ_{I} and ϕ_{II} to be expressed as

$$\phi_{\text{I}} = a\phi_{10}{}^{(1)} + b\phi_{02}{}^{(1)}$$
$$\phi_{\text{II}} = b\phi_{10}{}^{(1)} - a\phi_{02}{}^{(1)}$$

by the linear combinations of $\phi_{10}{}^{(1)}$ and $\phi_{02}{}^{(1)}$ which include contributions from non-resonant states as defined above. The secular determinant is established as*,

$$\begin{vmatrix} \omega_1 - E & k_{122}/2 \\ k_{122}/2 & 2\omega_2 - E \end{vmatrix} = 0$$

As a solution of the determinant, we have,

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* This secular determinant is not correct for the case of linear XY_2 type molecules, because the ω_2 normal vibration is doubly degenerate. By denoting two degenerate modes as ω_{2a} and ω_{2b}, we have to diagonalyse the energy matrix consisting of the elements among three states, ($v_1=1$, $v_{2a}=0$, $v_{2b}=0$), ($v_1=0$, $v_{2a}=2$, $v_{2b}=0$) and ($v_1=0$, $v_{2a}=0$, $v_{2b}=2$), where the perturbation term is $hck_{122}q_1(q_{2a}{}^2+q_{2b}{}^2)$.

The secular determinant is,

$$\begin{vmatrix} 2\omega_2 - E, & k_{122}/2, & 0 \\ k_{122}/2, & \omega_1 - E, & k_{122}/2 \\ 0 & k_{122}/2, & 2\omega_2 - E \end{vmatrix} = 0$$

Therefore we have,

$$E_1 = \omega_1 + \epsilon$$
$$E_2 = 2\omega_2 - \epsilon$$
$$E_3 = 2\omega_2$$

where

$$\epsilon = \frac{1}{2}\{-\delta + (\delta^2 + 2k_{122}{}^2)^{1/2}\}$$

and

$$\phi_1 = a\phi_{100} + b\left(\frac{1}{\sqrt{2}}\phi_{020} + \frac{1}{\sqrt{2}}\phi_{002}\right)$$
$$\phi_2 = b\phi_{100} - a\left(\frac{1}{\sqrt{2}}\phi_{020} + \frac{1}{\sqrt{2}}\phi_{002}\right)$$
$$\phi_3 = \frac{1}{\sqrt{2}}\phi_{020} - \frac{1}{\sqrt{2}}\phi_{002}$$

with

$$a = \frac{k_{122}}{(2\epsilon^2 + k_{122}{}^2)^{1/2}}, \qquad b = \frac{\sqrt{2}\,\epsilon}{(2\epsilon^2 + k_{122}{}^2)^{1/2}}$$

$$E_{\mathrm{I}}=\omega_1+\varepsilon$$
$$E_{\mathrm{II}}=2\omega_2-\varepsilon$$

where

$$\varepsilon=\frac{1}{2}\{-\delta+(\delta^2+k_{122}^2)^{1/2}\}$$

and

$$\delta=\omega_1-2\omega_2$$

$$a=\frac{k_{122}}{(4\varepsilon^2+k_{122}^2)^{1/2}},\qquad b=\frac{2\varepsilon}{(4\varepsilon^2+k_{122}^2)^{1/2}}$$

The probability distribution function is rewritten as

$$\begin{aligned}P&=w_1|\psi_{\mathrm{I}}|^2+w_2|\psi_{\mathrm{II}}|^2\\&=(w_1a^2+w_2b^2)\,|\psi_{10}{}^{(1)}|^2+(w_1b^2+w_2a^2)\,|\psi_{02}{}^{(1)}|^2\\&\quad+2(w_1-w_2)\,ab\psi_{10}{}^{(1)}\psi_{02}{}^{(1)}\end{aligned}$$

The term $w_1a^2+w_2b^2$ can be replaced by $w_1{}^0$, since $w_1\cong w_2\cong w_1{}^0$ and $a^2+b^2=1$. Similarly we have $w_1b^2+w_2a^2=w_2{}^0$. In the third term, $\psi_{10}{}^{(1)}\psi_{02}{}^{(1)}$ can be approximated by $\psi_{10}{}^0\psi_{02}{}^0$. Thus we have

$$P=w_1{}^0|\psi_{10}{}^{(1)}|^2+w_2{}^0|\psi_{02}{}^{(1)}|^2+2(w_1-w_2)\,ab\psi_{10}{}^0\psi_{02}{}^0 \tag{AIII-2}$$

The zeroth-order term $w_1{}^0|\psi_{10}{}^{(1)}|^2+w_2{}^0|\psi_{02}{}^{(1)}|^2$ is just equal to the corresponding expression in Eq. AIII-1.

In the case of weak resonance, i. e., $|\delta|\gg k_{122}$, we have

$$2(w_1-w_2)\,ab\cong(w_1{}^0-w_2{}^0)\,k_{122}/\delta$$

which is equivalent to the resonance-term of Eq. AIII-1.

In the case of strong degeneracy, i. e., $|\delta|\ll k_{122}$,

$$2(w_1-w_2)\,ab\cong-\frac{hck_{122}}{\boldsymbol{k}T}\exp\left(-\frac{hc\omega_1}{\boldsymbol{k}T}\right) \tag{AIII-3}$$

because,

$$2ab=1$$

and

$$w_1-w_2=-\frac{2hc\varepsilon}{\boldsymbol{k}T}\exp\left(-\frac{hc\omega_1}{\boldsymbol{k}T}\right)$$

where $\varepsilon=k_{122}/2$. On the other hand, the resonance term of Eq. AIII-1 yields in the limit of $\delta\rightarrow0$,

$$\lim_{\delta\to0}\frac{w_1{}^0-w_2{}^0}{\delta}k_{122}=-\frac{hck_{122}}{\boldsymbol{k}T}\exp\left(-\frac{hc\omega_1}{\boldsymbol{k}T}\right)$$

which is equal to Eq. AIII-3. This result seems to make sure the validity of Eq. AIII-1 even in the case of strong degeneracy.

The ratio of the resonance-term of Eq. AIII-1 to that of Eq. AIII-2 is evaluated at several values of δ, in the case of $k_{122}=50\,\mathrm{cm}^{-1}$. As shown in Table II, no appreciable discrepancy is found between the numerical values of the two expressions throughout the whole region of δ. Therefore, it seems most likely that the probability distribution function obtained in this article holds to a good approximation even in the case of an accidental degeneracy, although complicated manipulation of the summation over upper vibrational states have not been performed in this supplementary note.

TABLE II. RATIO OF THE RESONANCE TERMS CALCULATED BY THE TWO METHODS

δ cm^{-1}	Ratio
5	1.00
10	0.97
20	0.98
50	0.98
100	0.98
150	1.01
250	0.99