Calculation of the Widths for Isotropic Parts of Highly-polarized Raman Lines: Vibrational Relaxation of Infrared-inactive Levels

Masao Kakimoto and Tsunetake Fujiyama*

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

**Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158*

(Received December 25, 1973)

A theoretical calculation is made to explain the widths of the isotropic parts of polarized Raman lines in liquids. The calculation is based on the model of the intermolecular resonance-type vibrational relaxation through the vibration-dependent term of the Lennard-Jones atom-atom interaction. The result is applied to the Raman lines of liquid nitrogen, oxygen, and carbon disulfide, and compared with the experimental data.

It is known that a polarized Raman line consists of two parts, the isotropic and anisotropic parts, and that the former originates from the trace, and the latter, from the anisotropy, of a scattering tensor.[1,2] Because the trace of a tensor is independent of any rotation of coordinates, the isotropic part does not reflect the rotational motion of molecules. The widths of the isotropic parts are very narrow in general and are considered to be related to the decay of the vibrationally-excited state or the vibrational relaxation. The anisotropic part, on the other hand, contains information not only about the vibrational relaxation, but about the molecular rotational motion (or the reorientational motion in the case of condensed phases). The line-shape of the anisotropic part is expressed as a convolution of two curves which give the line-shapes due to vibrational relaxation and rotational motion respectively. Many authors have tried, both from theoretical[2–6] and experimental[2,7–12] aspects, to extract information about the reorientational motion of molecules in liquids from the observed line-shape of a Raman line. However, very few but Valiev[13] have reported any theoretical evaluation of the widths of the isotropic part. The present work will be concerned with the calculation of the width of the isotropic part of a highly-polarized Raman line which is infrared-inactive, or with the calculation of the transition probability for vibrational relaxation of an infrared-inactive level.

Previously, the present authors[14] reported a theoretical evaluation of the vibrational-relaxation widths appearing in the infrared spectra. Those results were, however, confined to infrared-active vibrational levels, because dipole matrix elements are necessary to cause transitions. In the present case, a similar model is not applicable since a vibrational transition has no transition moment. Any attempt to seek an interaction which causes vibrational relaxation ends to failure so long as we confine ourselves to *molecule-to-molecule*-type interactions. Valiev[13] used an exchange interaction *between atoms* which participate in a molecular vibration and estimated only the order of magnitude for the vibrational-relaxation width. Our model is similar to that of Valiev, but differs in the following two points: first, the use of a more realistic potential function of the Lennard-Jones type for an interatomic interaction, and second, the use of a model of the resonance exchange of vibrational quanta between two molecules.

Theory

Consider a pair of two homonuclear diatomic molecules, the interaction geometry of which is shown in Fig. 1. The interaction potential between two atoms,

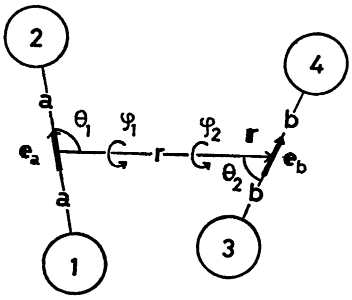

Fig. 1. A diagram showing a geometry of interacting two diatomic molecules.
1, 2, 3, and 4 indicate the atoms. $\mathbf{e}_a$ and $\mathbf{e}_b$ are unit vectors.

i and j, is written as $V(r_{ij})$, since the interaction, for which the Lennard-Jones potential is anticipated, is a function of the interatomic distance, r_{ij}, alone. Then the total intermolecular interaction, V, is:

$$V = \sum_{(i,j)} V(r_{ij}) \tag{1}$$

where (i, j) means all the pairs of interacting atoms, (1,3), (1,4), (2,3), and (2,4). The interatomic distances, r_{ij}'s, are the functions of r, θ_1, θ_2, φ_1, φ_2, a, and b (see Fig. 1):

$$\begin{aligned} r_{24} = r\Big[1 - \frac{2}{r}(a\cos\theta_1 - b\cos\theta_2) + \frac{1}{r^2}\{a^2 + b^2 \\ - 2ab(\sin\theta_1\cos\varphi_1\sin\theta_2\cos\varphi_2 \\ + \sin\theta_1\sin\varphi_1\sin\theta_2\sin\varphi_2 + \cos\theta_1\cos\theta_2)\}\Big]^{1/2} \end{aligned} \tag{2}$$

and similar equations for the others.[15] As the molecules undergo vibrations, a and b, and hence r_{ij}'s also, change in magnitude. Therefore, we expand V in a series of the small changes of the bond distances, Δa and Δb, and retain only the term which is bilinear on Δa and Δb:

$$V' = \frac{\partial^2 V}{\partial a \partial b} \Delta a \Delta b \tag{3}$$

which, by virtue of Eq. (1), yields:

$$V' = \sum_{(i,j)}\left[\frac{\partial^2 V(r_{ij})}{\partial r_{ij}^2}\frac{\partial r_{ij}}{\partial a}\frac{\partial r_{ij}}{\partial b} + \frac{\partial V(r_{ij})}{\partial r_{ij}}\frac{\partial^2 r_{ij}}{\partial a \partial b}\right]\Delta a \Delta b \tag{4}$$

Note that $\frac{\partial^2 V(r_{ij})}{\partial r_{ij}^2}$ and $\frac{\partial V(r_{ij})}{\partial r_{ij}}$ are common for all the (i,j) pairs. Therefore, they are written simply as $\frac{\mathrm{d}^2 V}{\mathrm{d}r^2}$ and $\frac{\mathrm{d}V}{\mathrm{d}r}$ respectively. On calculating the differentials in Eq. (4), we expand the square bracket in Eq. (2) in powers of $1/r$ and neglect the terms of orders higher than $(1/r)^2$. This approximation, and hence its validity, are similar to those of a dipole-dipole interaction.[15] Some manipulation leads to:

$$V' = \left[\frac{\mathrm{d}^2 V}{\mathrm{d}r^2}\frac{4ab}{r^2}X + \frac{\mathrm{d}V}{\mathrm{d}r}\frac{4ab}{r^3}Y\right]\Delta a \Delta b \tag{5}$$

where:[16]

$$X = 1 + (\mathbf{e}_\mathrm{a}\cdot\mathbf{e}_\mathrm{b})^2 + 8\left(\mathbf{e}_\mathrm{a}\cdot\frac{\mathbf{r}}{r}\right)^2\left(\mathbf{e}_\mathrm{b}\cdot\frac{\mathbf{r}}{r}\right)^2 - 6(\mathbf{e}_\mathrm{a}\cdot\mathbf{e}_\mathrm{b})\left(\mathbf{e}_\mathrm{a}\cdot\frac{\mathbf{r}}{r}\right)\left(\mathbf{e}_\mathrm{b}\cdot\frac{\mathbf{r}}{r}\right) - 2\left(\mathbf{e}_\mathrm{a}\cdot\frac{\mathbf{r}}{r}\right)^2 - 2\left(\mathbf{e}_\mathrm{b}\cdot\frac{\mathbf{r}}{r}\right)^2 \tag{5a}$$

and:

$$Y = -1 - 2(\mathbf{e}_\mathrm{a}\cdot\mathbf{e}_\mathrm{b})^2 - 15\left(\mathbf{e}_\mathrm{a}\cdot\frac{\mathbf{r}}{r}\right)^2\left(\mathbf{e}_\mathrm{b}\cdot\frac{\mathbf{r}}{r}\right)^2 + 12(\mathbf{e}_\mathrm{a}\cdot\mathbf{e}_\mathrm{b})\left(\mathbf{e}_\mathrm{a}\cdot\frac{\mathbf{r}}{r}\right)\left(\mathbf{e}_\mathrm{b}\cdot\frac{\mathbf{r}}{r}\right) + 3\left(\mathbf{e}_\mathrm{a}\cdot\frac{\mathbf{r}}{r}\right)^2 + 3\left(\mathbf{e}_\mathrm{b}\cdot\frac{\mathbf{r}}{r}\right)^2 \tag{5b}$$

The vector products appearing in Eqs. (5a) and (5b), and hence X and Y, are written in terms of the spherical harmonics normalized to unity, $Y_l^m(\theta_\mathrm{a},\varphi_\mathrm{a})$, $Y_l^m(\theta_\mathrm{b},\varphi_\mathrm{b})$, and $Y_l^m(\theta_r,\varphi_r)$, where $(\theta_\mathrm{a},\varphi_\mathrm{a})$, $(\theta_\mathrm{b},\varphi_\mathrm{b})$, and (θ_r,φ_r) are the polar coordinates of $\mathbf{e}_\mathrm{a}$, $\mathbf{e}_\mathrm{b}$, and $\mathbf{r}$ respectively in a laboratory-fixed coordinate system. Though these expressions are too lenghty to be written here, the following relations will be necessary later:

$$\begin{aligned} \int X^2 \mathrm{d}\tau' &= \frac{2^{10}}{5^2}\pi^3 \\ \int Y^2 \mathrm{d}\tau' &= \frac{2^{13}}{3\times 5^2}\pi^3 \\ \int XY \mathrm{d}\tau' &= -\frac{2^{11}\times 7}{3^2\times 5^2}\pi^3 \end{aligned} \tag{6}$$

where $\mathrm{d}\tau' = \sin\theta_\mathrm{a}\sin\theta_\mathrm{b}\sin\theta_r \mathrm{d}\theta_\mathrm{a}\mathrm{d}\varphi_\mathrm{a}\mathrm{d}\theta_\mathrm{b}\mathrm{d}\varphi_\mathrm{b}\mathrm{d}\theta_r\mathrm{d}\varphi_r$, and where integrations are carried out over the entire configuration space.

Now, consider that the two molecules are initially on the vibrational states of $v_\mathrm{a}=1$ and $v_\mathrm{b}=0$ respectively, where v_a and v_b are the vibrational quantum numbers. Then, the transition probability for a coupled transition, $(v_\mathrm{a}, v_\mathrm{b})=(1, 0)\rightarrow(0, 1)$, is given by:[17]

$$\frac{1}{\hbar^2}\int_{-\infty}^{\infty}\langle M(0)M(t)\rangle_\mathrm{av}\, \mathrm{e}^{-i(\omega_\mathrm{a}-\omega_\mathrm{b})t}\mathrm{d}t \tag{7}$$

where ω_a and ω_b are the vibrational angular-frequencies and where M means the matrix element of V':

$$M = \langle 01|V'|10\rangle \tag{8}$$

The average, denoted by $\langle\ \rangle_\mathrm{av}$ in Eq. (7), may be regarded either as a time-average or, if M is ergodic, as an ensemble average. The latter concept is used later in calculating the average. To obtain a probability, $P(1\rightarrow 0)$ for ,one of the interacting molecules undergoing a transition, $1\rightarrow 0$, one integrates Eq. (7) over ω_b and takes the square root:[18]

$$P(1\rightarrow 0) = \frac{1}{\hbar}\left[\langle|M|^2\rangle_\mathrm{av}\right]^{1/2} \tag{9}$$

We then insert Eq. (5) into Eq. (9), keeping in mind that $2\Delta a$ and $2\Delta b$ are the normal coordinates, Q_a and Q_b respectively, of vibrations. Further, when the interacting two molecules are of the same species, we can write:

$$a = b$$

and:

$$\langle 1|Q_\mathrm{a}|0\rangle = \langle 1|Q_\mathrm{b}|0\rangle = \sqrt{\frac{\hbar}{2m\omega}} \tag{10}$$

where m is the reduced mass and where $\omega=\omega_\mathrm{a}=\omega_\mathrm{b}$. Thus,

$$P(1\rightarrow 0) = \frac{a^2}{2m\omega}\left[\left\langle\left(\frac{\mathrm{d}^2 V}{\mathrm{d}r^2}\right)^2\cdot\frac{1}{r^4}X^2\right\rangle_\mathrm{av} + 2\left\langle\frac{\mathrm{d}^2 V}{\mathrm{d}r^2}\frac{\mathrm{d}V}{\mathrm{d}r}\frac{1}{r^4}XY\right\rangle + \left\langle\left(\frac{\mathrm{d}V}{\mathrm{d}r}\right)^2\cdot\frac{1}{r^6}Y^2\right\rangle_\mathrm{av}\right]^{1/2} \tag{11}$$

To proceed further, an analytical expression for V is necessary. The best that is available, that has a simple form and whose parameters are determined well, may be the Lennard-Jones potential:

$$V(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6\right] \tag{12}$$

The averages of Eq. (11) are calculated as:

$$\langle F\rangle_\mathrm{av} = W\int F\mathrm{d}\tau \tag{13}$$

where:

$$\mathrm{d}\tau = r^2\mathrm{d}r\mathrm{d}\tau'$$

and where W is a normalization constant which is determined, from the condition that n molecules are contained in 1 cm^3, to be:

$$W = \frac{n}{(4\pi)^2} \tag{14}$$

A lower limit, a_0, exists for the parameter, r, the physical meaning of which is that no two molecules can come closer than a_0. Remembering the relations of Eq. (6), we finally obtain:

$$P(1\rightarrow 0) = \frac{8}{5}\frac{a^2}{m\omega}\sqrt{n\pi}\,4\varepsilon\left[A\frac{r_0^{24}}{a_0^{29}} - B\frac{r_0^{18}}{a_0^{23}} + C\frac{r_0^{12}}{a_0^{17}}\right]^{1/2} \tag{15}$$

where

$$A = \frac{4\times 1909}{29},\quad B = \frac{4\times 1123}{23},\quad \text{and } C = \frac{661}{17}.$$

Comparison with the Experimental Data

To check the validity of our model as used in the present theory, the widths of the isotropic Raman lines of liquid N_2 and O_2 were calculated by means of Eq.

Table 1.

Molecule	(cm^{-1})[b]	FWHM[a] (cm^{-1})		Used parameters		
		Obsd[b]	Calcd	$2a$(Å)[c]	ε/k(K)[d]	r_0(Å)[d]
N_2	2331	0.067 ± 0.004	0.037	1.0976	35.7	2.789
O_2	1555	0.117 ± 0.008	0.067	1.2074	35.7	2.789
CS_2	656	$0.50\ \pm0.02$	0.72	3.108	124.0	3.418

a) Full-width at half-maximum, calculated from Eq. (15) through the relation; $\mathrm{FWHM}=P(1\rightarrow0)/\pi c$, where c is the velocity of light. b) See Ref. 19. c) See Ref. 22. d) See Ref. 23.

(15) and compared with the observed ones.

The Raman lines of liquid N_2 and O_2 are extremely narrow; therefore, the widths cannot be measured precisely with a conventional grating spectrometer. Clements and Stoicheff[19] have reported the most reliable data to date; they made their observations by the use of a Fabry-Perot interferometer.

In the calculations of the theoretical widths, the values of n are estimated from the values of the molecular weight and density.[20] Since the Lennard-Jones parameters, ε and r_0, are not available for an N···N or O···O pair, they are transferred from those for an Ne pair. The estimation of a_0 is the most difficult problem, although the results are rather sensitive to it. We arbitrarily, mainly because of the ease of calculation, put a_0 equal to r_0.[21] The results are shown in Table 1.

The conclusion of Eq. (15) is also applicable to the estimation of the width for the totally-symmetric vibration of CS_2, although it is a triatomic molecule. In this case, Q_a is $\sqrt{2}\Delta a$ instead of $2\Delta a$; therefore Eq. (15) should be multiplied by a factor of two. The values of ε and r_0 are transferred from those of Ar. The result for CS_2 is also included in Table 1.

As may be seen from Table 1, the agreement between the calculated and the experimental values is fairly good. This agreement may confirm the validity of the model used in the present theory. There may be many causes for the broadening of the isotropic part of a Raman line, but it can be concluded that the resonance exchange of the vibrational quanta through the interatomic interaction is the most important.

The authors are indebted to all the members of the Shimanouchi Laboratory for their helpful correspondence about this work. They are particularly grateful to Professor Takehiko Shimanouchi of the University of Tokyo for giving them the opportunity of publishing this work.

References

1) G. Placzek, "The Rayleigh and Raman Scattering," U. S. At. Energy Comm. UCRL-TRANS-526(L), 1962 [translated from *Marx Handbuch der Radiologie*, 2nd ed., Vol. 6, Akademische Verlagsgesellschaft, Leipzig (1934), Pt. II, pp. 205—374].

2) F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, **56**, 404, 413 (1972).

3) K. A. Valiev and L. D. Eskin, *Opt. Spectrosc.*, **12**, 429 (1961); K. A. Valiev, *ibid.*, **13**, 282 (1962).

4) R. G. Gordon, *J. Chem. Phys.*, **42**, 3658 (1965).

5) S. Bratos and E. Marechal, *Phys. Rev.*, **A4**, 1078 (1971).

6) L. A. Nafie and W. L. Peticolas, *J. Chem. Phys.*, **57**, 3145 (1972).

7) M. F. Crawford, H. L. Welsh, and J. H. Harrold, *Can. J. Phys.*, **30**, 81 (1952).

8) A. V. Rakov, *Opt. Spectrosc.*, **7**, 128 (1959).

9) M. Scotto, *J. Chem. Phys.*, **49**, 5362 (1968).

10) J. P. Perchard, W. F. Murphy, and H. J. Bernstein, *Mol. Phys.*, **23**, 499 (1972).

11) J. H. R. Clarke and S. Miller, *Chem. Phys. Lett.*, **13**, 97 (1972).

12) K. T. Gillen and J. E. Griffiths, *ibid.*, **17**, 359 (1972).

13) K. A. Valiev, *Soviet Phys. JETP*, **13**, 1287 (1961).

14) M. Kakimoto and T. Fujiyama, This Bulletin, **45**, 2970 (1972).

15) See, for example, M. Bersohn, and J. C. Baird, "An Introduction to Electron Paramagnetic Resonance," Benjamin, New York (1966), Appendix B-1.

16) All the quantities subscripted with a or b in the text hereafter correspond to the left and the right molecules, respectively, in Fig. 1.

17) See, for example, R. Zwanzig, *J. Chem. Phys.*, **34**, 1931 (1961), Eqs. (3)—(9).

18) K. A. Valiev, *Opt. Spectrosc.*, **11**, 253 (1961), Eq. (24). The integration over ω_b must be carried out only within a certain limited range, $[\omega_a-\alpha,\ \omega_a+\alpha]$, because ω_b cannot spread over so widely. In obtaining Eq. (9) of the text, one is putting the integral

$$\int_{\omega_a-\alpha}^{\omega_a+\alpha}\int_{-\infty}^{\infty}\frac{\langle M(0)M(t)\rangle_{\mathrm{av}}}{\langle|M|^2\rangle_{\mathrm{av}}}\mathrm{e}^{-i(\omega_a-\omega_b)t}\mathrm{d}t\mathrm{d}\omega_b$$

equal to 1. Although there is no theoretical reason to choose the value of 1, this simplification is permissible because we concern here only with the order of magnitude and because there is no way to estimate the correct value for α. In the limit of $\alpha\rightarrow\infty$, the final result (Eq. (11) or (15)) becomes about 2.5 (*i.e.* $\sqrt{2\pi}$) times larger.

19) W. R. L. Clements and B. P. Stoicheff, *Appl. Phys. Lett.*, **12**, 246 (1968): Though the spectra they measured contain not only isotropic but anisotropic parts, the widths reported may be regarded as those of isotropic parts, because of very low depolarization degrees.

20) "International Critical Tables," National Research Council, McGraw-Hill, New York (1928).

21) r_0 is the distance at which the potential has the value zero. If we choose, instead, a_0 to be the distance at which the potential has the value $(3/2)kT$ the results become about 3.3 times larger for N_2 and O_2, and about 3.6 times larger for CS_2. This may be an overestimation, since we do not take a radial distribution function into account. Anyhow, the present model gives the correct order of magnitude.

22) "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958).

23) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).