

**MOLECULAR FRAME DISTORTION AND MOLECULAR PAIR POLARIZABILITY**

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The contribution of frame distortion to the collision-induced polarizability of the isotropic molecules CH<sub>4</sub>, CF<sub>4</sub>, CCl<sub>4</sub> and SF<sub>6</sub> is estimated and found to be negligible

**1. Introduction**

Collision-induced light scattering (CIS) refers to the scattering by clusters of interacting atoms or molecules. The cluster polarizability determines the intensity of the scattered light. Several mechanisms have been invoked to account for this cluster polarizability. The dipole-induced-dipole (DID) interaction [1] and electron overlap during close encounters have been most frequently applied [2]. For interacting molecules, another possible mechanism, frame distortion, has been proposed [3]. While this mechanism has received some attention in the literature [4,5], no quantitative estimate has been made of the magnitude of its effect. It is the purpose of this note to calculate in an approximate manner its contribution to the intensity of the scattering by those molecules of tetrahedral and octahedral symmetry, which have been most thoroughly studied [4-7]. It is concluded that in these cases the effect of the interaction is negligible.

**2. Calculation**

In order to determine the frame-distortion contribution to the pair polarizability we must first estimate the distortion of the molecular frame during a collision and then estimate the change in the molecular polarizability resulting from this distortion.

If the intermolecular potential is taken to be of the

Lennard-Jones 6-12 form, the force acting on the molecule during a collision is

$$F(r) = -dV(r)/dr = (24\epsilon/\sigma)(2x^{-13} - x^{-7}), \quad (1)$$

where  $x = r/\sigma$ ,  $r$  is the intermolecular distance and  $\epsilon$  and  $\sigma$  are the usual potential parameters. We make the further assumption that the intermolecular force is felt only by that part of the molecular frame which is nearest to the point of contact between the molecules. We have considered special cases where the intermolecular force vector lies along a two-fold or a three-fold axis of a tetrahedral MX<sub>4</sub> molecule, and causes bond bending and compression of either one, two or three bonds while the rest of the molecular frame remains rigid. The bond stretching and bond bending force constants of the valence-force model,  $k_s$  and  $k_b$ , are evaluated from the frequencies of vibrational Raman fundamentals. Since the molecular vibrational frequencies are much larger than the inverse collision time, the molecular frame responds essentially instantaneously to the applied forces. For an accurate estimate of the frame distortion one would have to determine the true forces acting on the atoms during the collision, use the correct intramolecular force field to determine the atomic displacements, and do this for all relative orientations of each molecule of the colliding pair.

Having estimated the molecular frame distortion during a collision, the next step is to calculate the resulting polarizability increment. The depolarized CIS intensity depends on the anisotropic polarizability increment induced in the colliding pair. Using the bond-polarizability model we may calculate the frame-distortion polarizability increment. The frame-distortion

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Table 1  
Molecular parameters

	$\epsilon/k^a$ (K)	$\sigma^a$ (Å)	$R_{MX}$ (Å)	$k_s^b$ (mdyn/Å)	$k_s/R_{MX}^2$ <sup>b)</sup> (mdyn/Å)	$24\epsilon/\sigma$ (mdyn)	$\alpha^c$ (Å <sup>3</sup> )	$\bar{\alpha}'_{MX}$ (Å <sup>2</sup> )	$\gamma_{MX}$ (Å <sup>3</sup> )	$\gamma'_{MX}$ (Å <sup>2</sup> )	$A^h$ (Å <sup>4</sup> )
CH <sub>4</sub>	148.2	3.82	1.091	5.04	0.416	$1.29 \times 10^{-2}$	2.642	1.130 <sup>d)</sup>	0.279 <sup>d)</sup>	2.05 <sup>d)</sup>	1.0
CF <sub>4</sub>	152.5	4.70	1.323	9.23	0.713	$1.07 \times 10^{-2}$	2.937	1.00 <sup>e)</sup>	0.512 <sup>e)</sup>	1.97 <sup>e)</sup>	2.2
CCl <sub>4</sub>	327	5.88	1.776	4.40	0.331	$1.84 \times 10^{-2}$	10.59	2.20 <sup>f)</sup>	2.11 <sup>f)</sup>	4.47 <sup>f)</sup>	—
SF <sub>6</sub>	200.9	5.51	1.584	6.72	—	$1.21 \times 10^{-2}$	4.549	1.23 <sup>g)</sup>	—	—	—

a) Ref [11]    b) Ref [12]    c) At 4880 Å, refs [13,14]    d) Ref [15]    e) Data from ref. [16] analyzed as in ref [17].  
 f) Data from ref [18] analyzed as in ref [17]    g) Ref [16]    h) Refs [9,10]

anisotropic polarizability increment induced on a single molecule will have the form

$$\beta_{FD}(r) = -[C(\gamma_{MX}/R_{MX})(k_s/R_{MX}^2)^{-1} + D \gamma'_{MX}/k_s] F(r), \quad (2)$$

where  $\gamma_{MX}$  and  $\gamma'_{MX}$  are the bond anisotropy and its derivative and  $R_{MX}$  is the M-X bond length. The coefficients  $C$  and  $D$  depend on the orientation of the molecule with respect to the director of the force  $F$ . The bond polarizabilities are determined from the intensities of vibrational Raman bands. Values of the parameters in eq. (2) are presented in table 1 for several molecules.

The total intensity of CIS is specified by the zeroth spectral moment,  $\phi^{(0)}$ , which may be expressed as [8]

$$\phi^{(0)} = 4\pi \int_0^\infty dr r^2 g(r) \beta^2(r), \quad (3)$$

where  $g(r)$  is the radial distribution function,  $g(r) = \exp[-V(r)/kT]$ , and  $\beta(r)$  is the polarizability anisotropy of the colliding pair of molecules. The largest contribution to  $\beta(r)$  comes from the DID mechanism and has the value [1]

$$\beta_{DID}(r) = (6\alpha^2/\sigma^3)x^{-3}, \quad (4)$$

where  $\alpha$  is the polarizability of a single molecule. The total scattered intensity  $\phi_{DID+FD}^{(0)}$ , including the contributions due to both the DID and FD distortion mechanisms, is calculated by substituting

$$\beta^2(r) = (\beta_{DID} + 2\beta_{FD})^2 \approx \beta_{DID}^2 + 4\beta_{DID}\beta_{FD} \quad (5)$$

into eq (3). The last approximation follows because

$$\beta_{FD} \ll \beta_{DID}.$$

The size of the FD contribution to the scattered intensity, in terms of the dominant DID contribution, may be expressed as

$$\begin{aligned} \phi_{FD}^{(0)}/\phi_{DID}^{(0)} &= (\phi_{DID+FD}^{(0)} - \phi_{DID}^{(0)})/\phi_{DID}^{(0)} \\ &= 0.13 (\sigma^3/\alpha^2)(\beta_{FD}/F) 24\epsilon/\sigma, \end{aligned} \quad (6)$$

where the integrals have been evaluated using  $\epsilon/kT = 0.52$ .

In table 2 are presented estimates of  $\phi_{FD}^{(0)}/\phi_{DID}^{(0)}$  for several molecules. For the tetrahedral molecules we have calculated  $\beta_{FD}/F$  for three orientations of the molecule with respect to the direction of the intermolecular force and used the average of these three values of  $\beta_{FD}/F$  to compute  $\phi_{FD}^{(0)}$ . For SF<sub>6</sub> we have used an approximate expression for  $\beta_{FD}/F$  in terms of  $k_s$  and  $\bar{\alpha}'_{MX}$ , the isotropic bond polarizability derivative.

Frame distortion decreases the scattered intensity of the translational CIS by one percent or less.

Since  $\beta_{FD}$  depends on the orientation of the molecule with respect to the direction of the intermolecular force  $F$ , frame distortion can give rise to a collision-induced rotational scattering (CIRS) spectrum as well as a translational CIS spectrum [9,10]. The intensity of the CIRS spectrum will be given by eq. (3) with  $\beta^2(r)$  replaced by the average of the angle dependent part of  $\beta^2(r)$  over all orientations of each molecule with respect to the intermolecular axis. As before, frame distortion is not the dominant mechanism. The main contribution to the CIRS intensity comes from

Table 2  
Calculated quantities

	$-\beta_{FD}/F$ a) ( $\text{\AA}^3/\text{mdyn}$ )	$\phi_{FD}^{(0)}/\phi_{DID}^{(0)}$ b)	$\phi_{FD,CIRS}^{(0)}/\phi_{A,CIRS}^{(0)}$ c)
CH <sub>4</sub>	0.41 d) 0.65 c) 0.32 f)	$-0.6 \times 10^{-2}$	$4 \times 10^{-2}$
CF <sub>4</sub>	0.21 d) 0.58 e) 0.26 f)	$-0.6 \times 10^{-2}$	$3 \times 10^{-2}$
CCl <sub>4</sub>	1.02 d) 3.80 e) 1.69 f)	$-0.9 \times 10^{-2}$	—
SF <sub>6</sub>	0.57 h)	$-0.7 \times 10^{-2}$	—

a) Per molecule

b)  $\beta_{FD}$  is taken as the average of the three orientations in the first column. The sign of the FD term is negative when the bond polarizability values are all positive.

c) The angle-dependent part of  $\beta_{FD}$  is taken to have an amplitude which is half the difference of the largest and smallest values of  $\beta_{FD}$  in the first column.

d)  $C = 0$ ,  $D = 1$  in eq. (2), compression of a single bond,  $F$  along the three-fold axis.

e)  $C = 1.06$ ,  $D = 0$  in eq. (2), bending and compression of two bonds  $F$  along the two-fold axis.

f)  $C = 0.44$ ,  $D = 0.11$  in eq. (2); bending and compression of three bonds,  $F$  along the three-fold axis.

h) The average of d, e and f, with the approximations [17]  $2\gamma_{MX}/R_{MX} \approx \gamma'_{MX}/2 \approx \bar{\alpha}'_{MX}$  and  $k_s/R_{MX} \approx k_s/10$ , has been used to obtain the approximate expression  $-\beta_{FD}/F \approx 3.1 \bar{\alpha}'_{MX}/k_s$ .

$$\Delta\beta_A^2 = 36(8/7)(\alpha^2 A^2/a^8)x^{-8}, \quad (7)$$

where  $\Delta\beta_A^2$  is the mean-square pair polarizability anisotropy arising through the dipole-quadrupole tensor  $\mathbf{A}$ . This tensor is specified by the single parameter  $A$  for tetrahedral molecules. Substituting  $\beta^2 = \Delta\beta_A^2 + 4\Delta\beta_A\Delta\beta_{FD}$  into eq. (3) we obtain the result.

$$\phi_{FD,CIRS}^{(0)}/\phi_{A,CIRS}^{(0)} = 0.20(\sigma^4/\alpha A)(\Delta\beta_{FD}/F)24\epsilon/\sigma. \quad (8)$$

The values of  $\phi_{FD,CIRS}^{(0)}/\phi_{A,CIRS}^{(0)}$  shown in the third column of table 2 are computed using  $\Delta\beta_{FD}/F$  estimated as half the difference between the largest and smallest values of  $\beta_{FD}/F$  in column one of table 2. Frame dis-

tortion only accounts for a few percent of the total intensity of the CIRS spectrum.

Therefore, in the cases considered, the frame distortional contribution to the collision-induced scattering intensity is negligible.

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### References

- [1] L. Silberstein, *Phil. Mag.* 33 (1917) 92, 521.
- [2] W.M. Gelbart, *Advan. Chem. Phys.* 26 (1974) 1.
- [3] J.A. Bucaro and T.A. Litovitz, *J. Chem. Phys.* 54 (1971) 3846.
- [4] J.H.K. Ho and G.C. Tabisz, *Can. J. Phys.* 51 (1973) 2025.
- [5] H.E. Howard-Lock and R.S. Taylor, *Can. J. Phys.* 52 (1974) 2436.
- [6] D.P. Shelton, M.S. Mathur and G.C. Tabisz, in: *Molecular spectroscopy of dense phases*, eds. M. Grossmann, G. Elkomoss and J. Ringeissen (Elsevier, Amsterdam, 1976) p. 555.
- [7] F. Barocchi, M. Zoppi, D.P. Shelton and G.C. Tabisz, *Can. J. Phys.* 55 (1977) 1962.
- [8] H.B. Levine, *J. Chem. Phys.* 56 (1972) 2455.
- [9] A.D. Buckingham and G.C. Tabisz, *Opt. Letters* 1 (1977) 220.
- [10] A.D. Buckingham and G.C. Tabisz, *Mol. Phys.* 36 (1978) 583.
- [11] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, *Molecular theory of gases and liquids* (Wiley, New York, 1954) p. 1111.
- [12] G. Herzberg, *Infrared and Raman spectra of polyatomic molecules* (Van Nostrand, Princeton, 1945).
- [13] H.E. Watson and K.L. Ramaswamy, *Proc. Roy. Soc. A* 156 (1936) 144.
- [14] Landolt-Börnstein, *Zahlenwerte und Funktionen*, Band 11, Teil 8 (Springer, Berlin, 1962).
- [15] D. Bermejo, R. Escribano and J.M. Orza, *J. Mol. Spectry.* 65 (1977) 345.
- [16] W.F. Murphy, W. Holzer and H.J. Bernstein, *Appl. Spectry.* 23 (1969) 211.
- [17] R.J.H. Clarke and P.D. Mitchell, *J. Mol. Spectry.* 51 (1974) 458.
- [18] H.W. Schrotter and H.W. Klockner, in *Topics in current physics*, Vol. 11, ed. A. Weber (Springer, Berlin, 1979) p. 123.