

## Binary collision-induced light scattering by isotropic molecular gases

### I. Details of the experiment and the argon spectrum

by D. P. SHELTON† and G. C. TABISZ  
Department of Physics, University of Manitoba,  
Winnipeg, Manitoba, Canada R3T 2N2

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An experiment to measure the two-body collision-induced light scattering spectrum of Ar, CH<sub>4</sub>, CD<sub>4</sub>, CF<sub>4</sub> and SF<sub>6</sub> is described. Contrary to previous studies, the argon spectral intensity is shown to exceed that of the predictions of the first order dipole-induced-dipole model for the pair polarizability anisotropy. It is demonstrated empirically that this intensity can be accounted for by second-order quantum mechanical effects. The spectral profile is analysed in terms of various modifications to the pair polarizability. The main object of this study is to provide a basis for comparison with the molecular spectra described in paper II of this series.

#### 1. INTRODUCTION

The present study of molecular gases represents a continuation of our previous work on the collision-induced scattering (CIS) by relatively low density gases [1-3]. The essential features of the effect of CIS may be easily described. The total dipole moment induced in a pair of molecules by the electric field associated with an incident light beam differs in general from the sum of the dipoles induced in the individual molecules placed in the same electric field. The incremental polarizability depends on the intermolecular separation and, as the molecules move past one another, the amplitude of the scattered wave is modulated by the encounter. This modulation introduces frequency components into the scattered wave which are not present in the usual Rayleigh scattering by individual molecules. The collision-induced spectrum is thus shifted in frequency from the incident and Rayleigh scattered light. If the scattering molecules have an isotropic polarizability, then the Rayleigh light is polarized in the same sense as the incident light. The CIS spectrum is, however, depolarized as the incremental polarizability is generally anisotropic. The more rapid is the modulation, the larger is the frequency shift. Molecular velocities are of the order of 5 Å/ps at 300 K and the effective interaction between molecules occurs within a range of about 2.5 Å of the distance of closest approach. The modulation occurs for about 1 ps, a period long compared to that of the oscillation of the incident light, which is one of the order of 10<sup>-15</sup> s in the visible region.

† Present address: Department of Theoretical Chemistry, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England.

The CIS spectrum appears therefore as a broad depolarized tail on the Rayleigh spectrum.

The scattering from pairs of molecules becomes conveniently observable in gases at densities of about 1 mol/l. The time interval between successive collisions is about 5 ps and there are seldom more than two molecules participating in a collision; at these densities the intensity of the CIS will increase with the square of the density. At somewhat higher densities, collisions involving three molecules become more frequent and a density cubed term becomes significant in the virial expansion of the intensity in terms of the density (see § 3). The sign of this so-called three-body term is usually negative [3] and thereby reduces the intensity from that due to two-body encounters alone. At densities greater than 10 mol/l, clusters of interacting molecules are so large that a description based on a model of independent collisions becomes inadequate [4]. The experiments reported here are conducted in a range 0.5–5 mol/l where the CIS spectrum is easily observable and interpretation in terms of binary collisions is possible (after correction for contributions due to three-body effects).

Frequency shifts of allowed rotational Raman lines lie in the same region as does the collision-induced scattering; their intensities are usually much stronger and they are also depolarized. In order to avoid complications from such allowed spectra, molecules of tetrahedral and octahedral symmetry are chosen for the present study; their dipole polarizabilities are invariant under rotation and no allowed rotational Raman transitions arise. The particular molecules selected are  $\text{CH}_4$ ,  $\text{CD}_4$ ,  $\text{CF}_4$  and  $\text{SF}_6$ .

The object of these papers is to compare the scattering by colliding pairs of isotropic atoms (Ar) and molecules in order to elucidate the mechanisms involved. In paper I, the argon spectrum is scrutinized thoroughly. It has been the subject of much previous attention [5–7]. The present study reveals new information on the magnitude of the scattered intensity. The argon discussion also provides a clear basis for identification of distinctive features of the molecular spectra; these form the subject of paper II which is the following paper. The most significant result is the confirmation of *collision-induced rotational* Raman scattering by these molecules. The theory and preliminary work on this effect has been presented earlier [8].

The thorough elucidation of binary CIS is considered a prerequisite to an understanding of the more complicated three-body and higher  $N$ -body CIS processes which occur in high density gases and liquids. Even in the two body case, the molecular dynamics of the collision and the nature of the induced polarizability increments are linked in the description of the scattering spectrum. Both the intensity and spectral distribution must be studied since, roughly, the dynamics govern the shape and width of the spectrum while the cluster polarizability determines the total intensity. In this study it is assumed that intermolecular potentials are known sufficiently well and emphasis placed on the incremental polarizability.

## 2. EXPERIMENTAL DETAILS

The apparatus used is essentially that of conventional laser Raman spectroscopy and is described in detail elsewhere [1, 8]. Light from an argon ion laser at 4880 Å is incident upon the sample cell; the light scattered at 90° is collected,

passed through a double monochromator and detected by photon counting techniques. A half wave plate and nicol prism in the incident laser beam and a sheet polarization analyser in the scattered beam permit the selection of polarization geometry. In the present experiments if the laser light is considered to propagate along the  $x$ -axis polarized in the  $z$ -direction, then the observed light is scattered along the  $y$ -axis polarized in the  $x$ -direction; this geometry is often referred to as VH scattering. Some features of the apparatus deserve specific description as they are necessary to measure the scattered intensity and spectral profile with precision.

In a typical spectrum, the total number of counts actually recorded varies markedly with frequency shifts; e.g. for argon there can be 1600 counts/s at the spectral peak but only 0.6 counts/s at  $120\text{ cm}^{-1}$  from the peak. The background count rate of the photomultiplier tube, RCA Quantacon (No. 31034), used as a detector is about 0.6 counts/s. The accuracy of spectral measurements is limited by this background and counting statistics. The maximizing of the scattered light signal is consequently one of the main objectives of the experiment. Low frequency spectral measurements meet with a different problem whose solution is incompatible with this objective. Superimposed on the CIS spectrum at zero frequency shift is a strong narrow line commonly referred to as stray light which originates chiefly from Rayleigh scattering and from scattering by dust particles in the sample. Stringent precautions are necessary. The cell walls are blackened and the interior is fitted with field stops about the incident beam and in front of the collection arm window. A blackened off-axis wedge serves as a backdrop in the focal region of the beam. The fused quartz cell windows are anti-reflection coated. Dust scattering is reduced by flushing and filling the cell through a series of sintered metal filters, the finest blocking passage of particles larger than  $5\text{ }\mu\text{m}$ .

In order to obtain information about the CIS spectrum near zero frequency shift, narrow spectrometer slits must be used so that only a small portion of the spectrum is obliterated by the instrumentally broadened Rayleigh line. However, in the double monochromator, the detected signal increases as the square of the spectral slit width and measurement of the weaker signal at large frequency shift is favoured by wide slits. The only way to reconcile these conflicting requirements is to make separate scans with narrow and wide slits for small and large frequency shift regions, respectively.

Another limitation at small frequency shifts is the finite dynamic range capability of the signal processing electronics. These electronics are optimized for low signal conditions (photon counting) and at count rates of  $10^4/\text{s}$  or more deadtime losses must be accounted for. When the signal from the far spectral tail is large enough to be measured, the peak intensity of the CIS spectrum can exceed the linear response region of the electronics.

The desired spectral measurements require the preparation of gas samples at room temperature with pressures in the range 10 to 100 atm. The sample handling equipment is arranged to allow the cell to be purged, the gases to be purified and filtered as necessary, and mixed gas samples to be prepared of controlled composition. The argon used is of commercial ultra high purity grade (99.999 mol per cent) and the hydrogen is 99.95 mol per cent purity. (The other molecular gases are discussed in paper II.) The preparation of a sample begins by filling the system to 1 atm of  $\text{H}_2$  gas and then introducing the

sample of gas. If a series of measurements are to be made at successively higher sample densities, then the sample for each measurement is made by adding more gas to the previous sample. The density of the  $H_2$  gas, which serves as an internal standard for determining the scattered light intensity is fixed by the amount initially placed in the system. The total pressure is measured to  $\pm 0.3$  atm. The total gas system contains 1–10 per cent  $H_2$  with usually less than 0.1 per cent of other impurities. The sample density is calculated assuming a binary mixture of  $H_2$  and the sample gas. The PVT data used is that of Gosman *et al.* [9] for argon and that of [10] for  $H_2$  and  $H_2$ -Ar mixtures.

### 3. DATA ANALYSIS

Once a series of spectra are obtained from samples of known density and composition, the data must be reduced to a form which is directly comparable with theoretical predictions. The binary CIS spectrum is obtained from the raw data by (i) applying instrumental corrections, (ii) accounting for impurities and (iii) fitting a virial expansion to the measured intensities.

- (i) The probability that a photon entering the spectrometer is detected depends on both its frequency and polarization. The response of the spectrometer-detector system is measured with a tungsten ribbon lamp source which has been calibrated by the National Research Council of Canada against a standard black body source. The response of the system also depends on slit width for slits narrower than  $1 \text{ cm}^{-1}$ .
- (ii) The only significant impurities in the samples studied are  $N_2$  and  $O_2$ . These result in a weak rotational Raman spectrum superimposed on the CIS spectrum. If the impurity concentration in a given sample is known, then its rotational spectrum may be calculated, suitably pressure broadened and subtracted from the CIS spectrum. The concentration of the  $N_2$  and  $O_2$  may be assayed spectroscopically by comparing the intensity of the rotational lines of  $N_2$  and  $O_2$  in a low pressure sample (of measured density) to the intensity of the  $S(1)$  line of a sample of  $H_2$  (of measured density).

The major constituents of the systems studied are in fact  $H_2$  and the sample  $X$ ; the CIS spectrum consists of contributions arising from  $X$ - $X$ ,  $H_2$ - $X$  and  $H_2$ - $H_2$  collisions. Because of the low concentrations of  $H_2$  and its small polarizability, the  $H_2$ - $H_2$  spectrum is ignored. The  $H_2$ - $X$  spectrum makes, however, a small but significant contribution to the total intensity and must be subtracted. Since the intensity is only a few per cent of the  $X$ - $X$  intensity, a rough approximation to the true  $H_2$ - $X$  spectrum suffices. From direct observation, the  $H_2$ - $H_2$  spectrum may be represented by an exponential of the form  $I(\omega) = A \exp(-\omega/50)$  on the Stokes side where  $A$  is a constant and  $\omega$  is the frequency shift in  $\text{cm}^{-1}$ . The collision time for a  $H_2$ - $X$  collision is determined by the inverse square root of the reduced mass of the pair and corresponds to an exponential decay constant of about  $36 \text{ cm}^{-1}$  for the samples studied. For purposes of subtracting the  $H_2$ - $X$  spectra, they are approximated by an exponential shape whose integrated intensity is given by the dipole-induced-dipole (DID) model (see § 4).

- (iii) The intensity of the  $X$ - $X$  spectrum may be represented by a power series in the density [3, 11],

$$I(\omega) = I^{(2)}(\omega)\rho_x^2 + I^{(3)}(\omega)\rho_x^3 + I^{(4)}(\omega)\rho_x^4 + \dots, \quad (1)$$

where  $\rho_x$  is the density of  $X$ . The leading term is  $I^{(2)}(\omega)\rho_x^2$  since the CIS spectrum arises from the interaction of at least two molecules. Over the range of densities of the present experiments, the spectrum is adequately described by just the two- and three-body terms,  $I^{(2)}(\omega)\rho_x^2$  and  $I^{(3)}(\omega)\rho_x^3$ . When the four-body term becomes important, it will appear first at small frequency shifts [12]. The two- and three-body spectra are obtained from a series of spectra at different densities by first normalizing the intensities to the  $S(1)$  line intensity of  $H_2$ , then multiplying by  $\rho_{H_2}/\rho_x^2$  and fitting a straight line of the form  $B + C\rho_x$  at a series of separate frequencies. The coefficients of the fit  $B$  and  $C$  are then just  $I^{(2)}(\omega)$  and  $I^{(3)}(\omega)$ . Figure 1 shows the two-body spectrum,  $I^{(2)}(\omega)$ , for argon; the intensity scale is the scattering cross-section  $(d^2 s/d\Omega d\omega)_{CIS}$  relative to that of the  $H_2 S(1)$  line,  $(ds/d\Omega)_{H_2 S(1)}$ , where  $s$  is the total scattering cross section and  $\Omega$  is the solid angle.

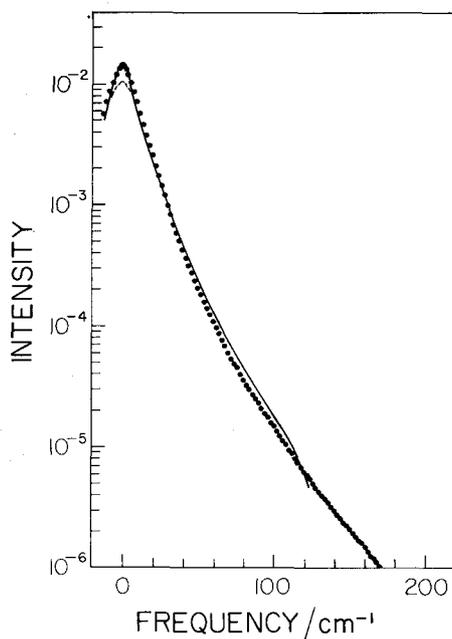


Figure 1. Comparison of the experimental and calculated spectrum for argon. The experimental two-body spectrum is indicated by  $\dots$  plotted every  $2 \text{ cm}^{-1}$ . The spectrum calculated using the first order DID model  $\beta(x) = x^{-3}$  is shown by the solid line. The  $---$  near zero frequency shift is the calculated spectrum ignoring the contribution of bound dimers. The vertical scale is the scattering cross section relative to that of the  $H_2 S(1)$  line.

## 4. THE ARGON SPECTRUM : TOTAL INTENSITY

The total intensity of the scattered light may be expressed as the zeroth moment  $\phi^{(0)}$  of the spectrum. Levine [13] shows that

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

where  $r$  is the intermolecular distance,  $\beta(r)$  is the pair polarizability anisotropy and  $g(r)$  is the radial distribution function. The major contribution to  $\beta(r)$  is usually considered to be the dipole-induced-dipole (DID) interaction [5, 7]. The interaction between the molecules and the electric field  $\epsilon$  associated with the light beam is described as follows:  $\epsilon$  induces a dipole moment  $\mu^{(1)}$  in molecule 1 of the pair and the field  $\mathbf{F}$  due to  $\mu^{(1)}$  induces a dipole in molecule 2. This gives a contribution to the pair polarizability anisotropy which varies as  $r^{-3}$ . The interaction may be taken to higher orders. Silberstein [14] first elucidated the effect and showed that classically

$$\beta(r) = 6\alpha^2 r^{-3} + 6\alpha^3 r^{-6} + \dots, \quad (3)$$

where  $\alpha$  is the polarizability of an individual molecule.

Experimentally, the zeroth moments of the two- and three-body spectra may be obtained by integrating  $I^{(2)}(\omega)$  and  $I^{(3)}(\omega)$ . It is preferable, however, to obtain this moment by fitting  $I^{(2)} + I^{(3)} \rho_x$  to a plot of  $I(\rho)/\rho^2$  versus  $\rho$  where  $I(\rho)$  is the integrated intensity of the spectrum obtained from the sample of density  $\rho$ . The advantage lies in the fact that each spectrum is represented by a single point

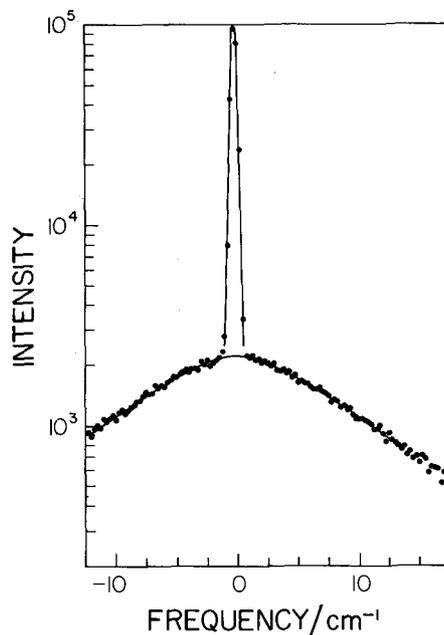


Figure 2. Extrapolation to zero frequency of the CIS spectrum of argon. The number of counts is plotted against frequency. The sample pressure is 5.3 mol/l (120 atm) and the spectral slit width is 0.5 cm<sup>-1</sup>. The CIS spectrum may be followed down to a frequency shift of 1 cm<sup>-1</sup>. The extrapolation is indicated by the solid line. The sharp peak about zero frequency is the stray light.

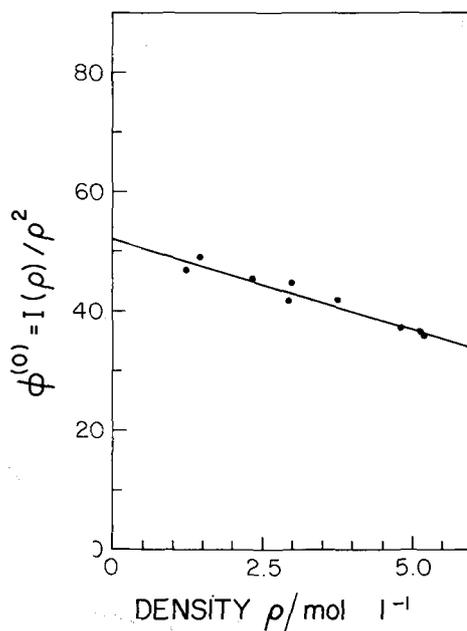


Figure 3. Extrapolation of the zeroth moment for argon. The zero intercept gives the intensity due to binary collisions. The dots represent spectra taken at different densities  $\rho$ . The downward slope as density increases represents the effect of three-body scattering.

and it is thereby easier to assess critically the quality of the fit in terms of statistical and systematic uncertainties.

The measurement of the zeroth moment is difficult because the central part of the spectrum which contributes most of the total intensity is partially obscured by the Rayleigh line (figure 2). Unless the spectrum is scanned with sufficiently high resolution, the extrapolation of the spectrum to zero frequency shift will be unreliable. The narrow slit width, however, greatly reduces the observed intensity and eventually counting statistics will limit the small frequency shift region of an argon spectrum at high resolution. The extrapolation to zero frequency shift for this spectrum contributes only a small uncertainty to the determination of the integrated intensity; for low density spectra, in particular, it is usually the counting statistics and not the extrapolation which limit the accuracy of the integrated intensity. A plot of  $I/\rho^2$  versus  $\rho$  is given for argon in figure 3. A straight line adequately represents the data and justifies the neglect of the four-body contribution. For the molecules studied,  $\phi^{(0)}$  is at least five times as large for argon (see paper II). For argon, we obtain  $\phi^{(0)} = 52.1 - 3.05 \rho$  where  $\phi^{(0)}$  is given in units of  $\text{\AA}^0$  and  $\rho$  is in mol/l. The first term is due to binary collisions while the second arises from three-body encounters. The uncertainty in the measurement is about  $\pm 5$  per cent.

A number of laboratories have made measurements of the zeroth moment of argon; these results disagree with each other and with theoretical predictions, being in the range 0.5 to 0.8 times the first order DID result for  $\phi^{(0)}$ . This situation prompted us and the group led by Barocchi at CNR, Firenze, Italy, to

$\phi^{(0)}$  for argon at room temperature.

| $\phi_{\text{expt}}^{(0)}/\text{\AA}^9$ | $\phi_{\text{expt}}^{(0)}/\phi_{\text{calc}}^{(0)\dagger}$ | Method                      |
|---|--|-----------------------------|
| 52.1 $\pm$ 3 (a)                        | 1.12   | Spectral profile            |
| 49.4 $\pm$ 3 (b)                        | 1.06   | Spectral profile $\ddagger$ |
| 50.1 $\pm$ 4 (c)                        | 1.08   | Spectral profile $\S$       |
| 25.7 $\pm$ 2.5 (d)                      | 0.55   | Spectral profile            |
| 33.5 $\pm$ 5.0 (e)                      | 0.72   | Spectral profile            |
| 35.8 $\pm$ 3 (f)                        | 0.77   | Depolarization ratio        |
| 30.2 $\pm$ 4.4 (g)                      | 0.65   | Kerr effect                 |

$\dagger$  The calculated value is 46.6  $\text{\AA}^9$ .

$\ddagger$  We have taken  $(\alpha_{\parallel} - \alpha_{\perp}) = 0.316 \text{\AA}^3$  at 5145  $\text{\AA}$  for  $\text{H}_2$  rather than 0.314  $\text{\AA}^3$  and adjusted their result accordingly.

$\S$  To obtain  $\phi^{(0)}$  we have normalized our spectral profile to their measured intensity at 12  $\text{cm}^{-1}$ .

(a) This work, (b) reference [15], (c) reference [6], (d) reference [11], (e) reference [23], (f) reference [24], (g) reference [25].

make a careful comparison of independent measurements of  $\phi^{(0)}$ . A principle difference between our method and theirs lies in the treatment of the  $\text{H}_2$  standard. As described in §§ 2 and 3, we use an internal standard technique measuring the CIS and  $\text{H}_2$  spectra in the same scan thereby eliminating the effect of focusing or alignment changes in the optics. Barocchi uses an external standard, wherein the cell is filled first with pure  $\text{H}_2$  for the standard spectrum, emptied and then filled with a pure gas sample for the CIS measurements. This procedure eliminates the correction for the interaction between the sample and  $\text{H}_2$  molecules which must be accounted for in our method. In other respects, the approaches are similar although the spectrometers, gratings and photomultipliers are of different commercial manufacture. In addition to our group and that of Barocchi, the group of Frommhold *et al.* has also made accurate absolute intensity measurements for Ar. They use an external standard and make the standard and CIS intensity measurements at the same frequency. These results are given in the table along with those of other workers. Our value and those of Barocchi [15] and of Frommhold [6] agree and have an average value of 50.9  $\text{\AA}^9$ , which is about 1.1 times the first order DID calculation of 46.6  $\text{\AA}^9$ . (In this calculation,  $\beta(r) = 6\alpha^2 r^{-3}$  and  $g(r) = \exp(-V(r)/kT)$ . The intermolecular potential of Smith [16] is used for  $V(r)$  and  $\alpha = 1.679 \text{\AA}^3$  at 4880  $\text{\AA}$  [18].) These values of  $\phi^{(0)}$  clearly disagree, however, with those of previous studies. We can only suggest reasons for errors in earlier reports.

- (i) The variation in spectral sensitivity between zero frequency and the  $\text{H}_2$   $S(1)$  line has not been taken into account.
- (ii) The effect of the negative three-body contribution has not been considered. At 40 atm (1.5 mol/l), the three-body term is already 10 per cent of the two-body intensity.

- (iii) Unless the specific intent of the experiment is accurate absolute intensity measurements, the results are likely to be affected by systematic errors due to features of the experiment which are of little consequence if only the spectral shape is desired. As a final consideration it must be noted that our value can be no more accurate than the value of the  $H_2$  polarizability anisotropy ( $\alpha_{\parallel} - \alpha_{\perp}$ ) of  $0.317 \text{ \AA}^3$  at  $4880 \text{ \AA}$  that we have used. We have considered static [19] and dynamic [20] calculations and measurements at  $6328 \text{ \AA}$  [21] and  $4880 \text{ \AA}$  [22] in arriving at this value.

In the past, the values of  $\phi^{(0)}$  less than  $\phi_{DID}^{(0)}$  have been accounted for by the empirical device of including a negative term in  $\beta(r)$  due to an electron overlap interaction [5]. Recent *ab initio* calculations by Clarke *et al.* [26] and Oxtoby [27] suggest that the magnitude of the electron overlap interaction term may not be sufficiently large to decrease the scattered intensity significantly. Consequently, there no longer seems to be a reason to expect that  $\phi^{(0)}$  should be lower than the DID prediction for low density spectra.

##### 5. THE ARGON SPECTRUM : THE SPECTRAL PROFILE

The profile of the two-body spectrum for argon at 300 K is given in figure 1. In this section, the result is compared with theoretical calculations of the spectral shape. The first comparison is made assuming a DID model. It will be convenient to present the discussion in terms of  $\beta(x)$  where  $x=r/\sigma$  and  $\beta(r) = (6\alpha^2/\sigma^3)\beta(x)$  where  $\sigma$  is the molecular radius; the numerical method of calculation selectively follows that of Lallemand [23] and Frommhold *et al.* [6]. First the correlation function [23],

$$C(\tau) = \langle \beta(t)\beta(t+\tau)P_2[\mathbf{u}(t) \cdot \mathbf{u}(t+\tau)] \rangle \quad (4)$$

is evaluated;  $P_2$  is the second Legendre polynomial and  $\langle \dots \rangle$  denotes an ensemble average.  $C(\tau)$  is treated in two steps. The classical orbits of the colliding molecules are computed for a given energy and impact parameter. Then  $C(\tau)$  is Fourier transformed and the resulting frequency spectrum is interpolated at intervals of  $1 \text{ cm}^{-1}$ . This procedure results in a downward turn of the profile for argon beyond  $100 \text{ cm}^{-1}$  which is spurious (figures 1, 4, and 5) and is due to the choice of time interval  $\Delta\tau$  between the times  $\tau$  at which  $C(\tau)$  is evaluated. The interval has been chosen such that the low and intermediate frequency spectrum is accurately calculated. Below  $100 \text{ cm}^{-1}$ , the calculated spectrum is accurate to about 1 per cent. The spectrum is normalized so that the CIS intensity is expressed in units of the  $H_2 S(1)$  line scattering cross-section per unit frequency interval, when both gases are maintained at unit density ( $1 \text{ mol/l}$ ). Finally, the spectrum is corrected for the Boltzmann asymmetry. There is no universally accepted procedure for making this correction. In this work, it is assumed that  $I_{\text{classical}} = (I_{\text{Stokes}} + I_{\text{Anti-Stokes}})/2$ . The 'corrected' Stokes spectrum is obtained by multiplying  $I_{\text{classical}}$  by  $\exp(\omega/2kT)$  where  $2kT = 410 \text{ cm}^{-1}$  at room temperature. The correction to the anti-Stokes side is the inverse of this factor.

Spectral contributions involving free particles are not the only ones. Scattering by bound dimers is also possible but is responsible for only about 10 per cent of the total intensity, under the conditions of the present experiments, and is

confined to the region of small frequency shift. The problem of calculating the spectral profile is treated rigorously by Frommhold *et al.* [6] and by Prengel and Gornall [28]. The dimer contribution is handled properly only with quantum mechanics. Since the primary interest of the present work is the high frequency profile, a crude approximation to the dimer spectrum suffices. The spectrum is considered to be due to rigid, freely rotating pairs with an intermolecular separation fixed at the minimum of the intermolecular potential. The rotational constant of  $(\text{Ar})_2$  is  $0.60 \text{ cm}^{-1}$ . The shape of the band is taken as that of the rigid rotor and its intensity is adjusted to match the difference between the total scattered intensity and the free (unbound) contribution.

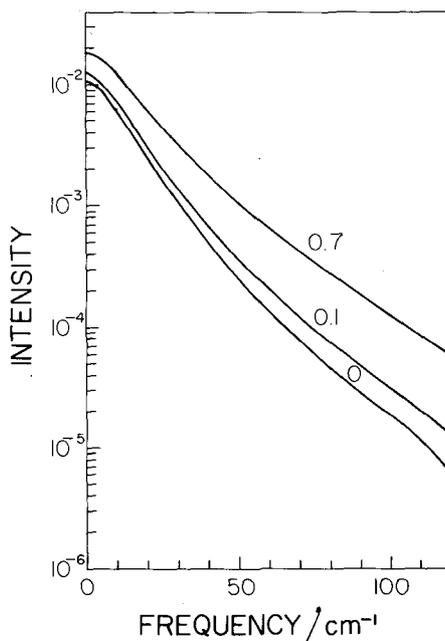


Figure 4. The effect of a short range term in  $\beta(x)$  on the spectral profile for argon. The three spectra are calculated with  $\beta(x) = x^{-3} + Ax^{-6}$  where  $A$  is 0, 0.1 and 0.7. Only the unbound dimer spectra are plotted.

First consider  $\beta(x) = x^{-3}$ , i.e. a first order DID form. Figure 1 shows the computed spectrum together with the experimental result. The agreement of the profiles is good, especially since no free parameters are involved. The bound dimer spectrum is somewhat too narrow while the unbound spectrum is somewhat too wide. This agreement of the gross features arises because the spectral width is determined by the molecular diameter and velocity and is relatively insensitive to the form of the pair polarizability function; the intensities, however, do not agree. Recall that our  $\phi_{\text{expt}}^{(0)}$  is  $50.9 \text{ \AA}^9$  and  $\phi_{\text{DID}}^{(0)}$  is  $46.6 \text{ \AA}^9$ . It is evident that the simple DID model is not sufficient. From (3), the classical point dipole DID expression for  $\beta(x)$  is

$$\beta(x) = x^{-3} + (\alpha/\sigma^3)x^{-6} + \dots \quad (5)$$

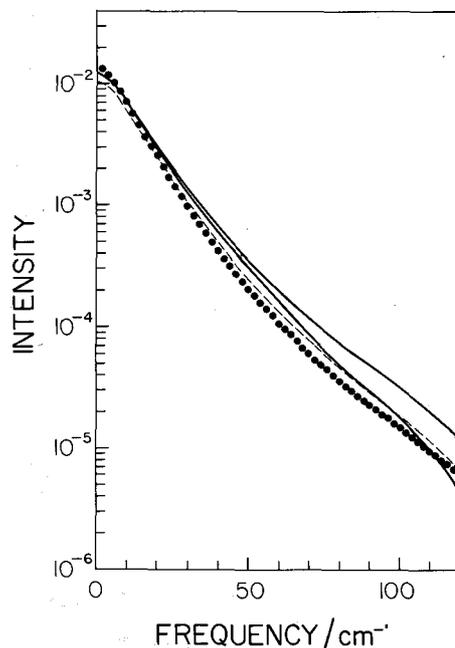


Figure 5. The effect of a negative exponential term in  $\beta(x)$ . The dotted line . . . is the experimental spectrum. The lower solid line is obtained with  $\beta(x) = x^{-3} + 0.17x^{-6} - 0.66 \exp(-14.21(x-0.8))$ . The upper solid line is computed with  $\beta(x) = x^{-3} + 0.11x^{-6}$  and the dashed line --- with  $\beta(x) = x^{-3}$ .

A quantum mechanical perturbation calculation for  $(\text{He})_2$  gives [29]

$$\beta(x) = x^{-3} + 2.00 (\alpha/\sigma^3)x^{-6} + \dots \quad (6)$$

while a model due to Clarke [30], which takes into account the second hyperpolarizability, gives  $1.95 (\alpha/\sigma^3)$  and  $1.29 (\alpha/\sigma^3)$  as the coefficients of the  $x^{-6}$  term of  $\beta(x)$  for  $(\text{He})_2$  and  $(\text{Ar})_2$ , respectively. When the coefficient of the  $x^{-6}$  term of  $\beta(x)$  for argon is adjusted to make  $\phi_{\text{calc}}^{(0)}$  agree with  $\phi_{\text{expt}}^{(0)}$ , the form of  $\beta(x)$  is

$$\beta(x) = x^{-3} + 1.58 (\alpha/\sigma^3)x^{-6} + \dots \quad (7)$$

which is plausible in the light of these calculations. In figure 4, spectra are shown computed for argon with coefficients of the  $x^{-6}$  term of 0, 2.5 and  $15 \alpha/\sigma^3$ . The profile swings upward as the  $x^{-6}$  term increases so that the spectrum becomes relatively more intense at high frequencies as the short range component becomes larger. No abrupt changes in shape are, however, introduced by the short range term. Comparison with figure 1 shows that with  $\beta(x) = x^{-3}$ , the intensity is already greater than observed at large frequency shifts. Inclusion of non-zero  $x^{-6}$  term makes the disagreement at high frequencies even worse.

A mechanism which decreases  $\beta(x)$  at short range would counteract the tendency for the high frequency spectrum to be too intense. Electron overlap has been invoked to account for such a phenomenon. To see the effect of electron overlap on the shape of the spectrum, we include in  $\beta(x)$  a small term

which falls exponentially with distance at the same rate as the repulsive part of the intermolecular potential [17] and which sharply reduces  $\beta(x)$  at short range. The size of the negative contribution is chosen arbitrarily to be equal to one half the value of the  $x^{-6}$  term at the distance of closest approach at 300 K. Then

$$\beta(x) = x^{-3} + 0.17x^{-6} - 0.66 \exp(-14.21(x-0.8)). \quad (8)$$

In this model, the  $x^{-6}$  term and exponential cancel at  $x=0.8$ , a distance at which very few collisions occur at 300 K. The resulting spectrum is shown in figure 5. Again there is no abrupt change in shape accompanying changes in  $\beta(x)$  but the relative intensity at high frequency is reduced in the expected manner. The calculated spectrum is however too intense in the intermediate frequency range. By a suitable choice of the three parameters in (8), the calculated spectrum can be forced to fit the observed, but in order to decide whether the resulting parameters are physically meaningful, a better theoretical understanding of the form and origin of  $\beta(x)$  must be awaited. It should not be forgotten, that the detailed shape of the spectrum depends on the intermolecular potential as well as on the pair polarizability.

## 6. SUMMARY

The conclusions of the present work on argon may be summarized as follows.

- (i) The first order DID model of the pair polarizability yields a good approximation to the spectral shape. The shape is relatively insensitive to the form of  $\beta(r)$  and depends mainly on the collision dynamics.
- (ii) The experimentally observed zeroth moment at 300 K is  $50.9 \pm 2 \text{ \AA}^9$ , about 1.1 times the first order DID prediction.
- (iii) To account for the discrepancy between the observed and calculated total intensities, additional terms must be included in  $\beta(r)$ . An  $r^{-6}$  term tends to increase the intensity at intermediate and high frequencies and makes the shape of the calculated spectrum deviate even further from the shape of the observed spectrum than it does for the first order DID model. This tendency can be partially countered by a negative exponential term in  $\beta(r)$ . It must be emphasized that, in general, the shape favours a long range form for  $\beta(r)$ .
- (iv) While total intensity is sensitive to  $\beta(r)$ , experimentally it is difficult to obtain information on the form of  $\beta(r)$  because the measured quantities are averaged over all values of  $r$  accessible to the colliding molecules. Data on  $\phi^{(0)}$  as a function of temperature and thereby of the range of  $r$  being probed would be very helpful. Separation of the CIS spectrum into  $N$ -body components has only been performed at room temperature to date.

The present study on argon while valuable in itself also provides a basis for comparison with molecular spectra, where internal degrees of freedom play a role in the induction process. This is the subject of paper II of this series.

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