

The three body correlation spectrum in collision induced light scattering by isotropic molecular gases

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

and F. BAROCCHI and M. ZOPPI
Istituto di Elettronica Quantistica del CNR,
via Panciatichi 56/30, 50127 Firenze, Italy

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The three body correlation spectra in the collision induced light scattering by gaseous Ar, CH₄, CF₄ and SF₆ at 295 K are reported. The zeroth and second frequency moments are compared with calculations based on a pairwise additive triplet cluster polarizability. It is found that the experimental results may be accounted for with the use of the first order dipole-induced dipole model for the polarizability. The spectra may be used to distinguish between the suitability of various intermolecular potentials ; modern potentials give excellent results for Ar and CH₄ and a Lennard-Jones 28-7 potential best describes the CF₄ and SF₆ spectra.

1. INTRODUCTION

The term collision induced scattering refers to the light scattering by a cluster of interacting atoms or molecules which shows features not present in the scattering by the isolated species [1]. Spectra of compressed gases have most frequently been analysed in terms of two body interactions. Spectral features due to three and four body correlations have been shown to be experimentally accessible [2, 3, 4]. Three body correlation spectra, for example, contain information on three body dynamics in somewhat the same way as two body spectra relate to two body dynamics. It must be emphasized, however, that the so-called three body correlation spectra have contributions from the induced polarizability both of a pair and of a triplet cluster of molecules (see § 3).

A derivation of theoretical expressions for the zeroth and second intensity moments of three body spectra has been given earlier by some of us [5]. More recently, the roles of many body correlations in the scattering process have been the subject of a careful molecular dynamics calculation [6]. A comparison of the two and three body correlation Rayleigh and Raman scattering has been made [7]. A theoretical and experimental study of three body contributions to a related phenomenon, the Kerr Effect, has been reported for a number of

† Present address : Department of Physics, University of Toronto, Toronto, Ontario, Canada.

simple molecular gases [8]. In view of this activity, we present in this paper new data on the three body correlation spectra of Ar, CH₄, CF₄ and SF₆ and compare them with calculations of spectral moments based on the dipole-induced dipole (DID) approximation. The spectra given here were taken at the University of Manitoba, while the calculations were performed at CNR, Firenze.

2. EXPERIMENTAL DETAILS

The experiment has been described in detail elsewhere [9]. The argon laser line at 4880 Å was used for excitation. In the experimental geometry, if the incident laser beam was considered to propagate along the *x*-axis, polarized in the *z*-direction, the observed light was scattered along the *y*-axis, polarized in the *x*-direction. The spectra were recorded for frequency shifts up to 200 cm⁻¹ at 295 K and at gas pressures from 10 to 100 atmospheres. Experiments were performed with both narrow and wide slits in order to measure the profile accurately at small and large frequency shifts. Absolute scattered intensities were determined by comparison with the known intensities of the rotational Raman lines of molecular hydrogen, which was added to the sample gases in small quantities to provide an internal standard.

For a given sample, spectra were taken at a series of pressures and the resulting set of spectra fitted to a power series of the form,

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

where $I(\omega)$ is the intensity at frequency shift ω and ρ is the density. $I^{(2)}(\omega)$, $I^{(3)}(\omega)$, $I^{(4)}(\omega)$, . . . are spectra identified with two, three, four, . . . body correlations in the gas, respectively [2]. The density expansion (1) is valid only in a restricted density-frequency regime [10]. The present analysis has been made within the appropriate ranges. A discussion of $I^{(2)}(\omega)$ has been published previously [9, 11]. $I^{(3)}(\omega)$ is the subject of the present paper. No contribution to $I(\omega)$ from $I^{(4)}(\omega)$ could be detected at the densities used here.

The three body spectrum $I^{(3)}(\omega)$ for each of the sample gases is given in figures 1 to 4 (Stokes side only). As has always been found, $I^{(3)}(\omega)$ is negative and reduces the scattered intensity from that due to the dominant two body interactions. A noteworthy feature of these spectra is the flattening of the profiles at small frequency shifts. Previous reports [2, 3, 4] showed $I^{(3)}(\omega)$ to decrease in a nearly exponential manner from zero frequency shift.

The *m*th spectral moment of the *n*-body spectrum is defined as

$$\phi_m^{(n)} = \int_{-\infty}^{\infty} \omega^m I^{(n)}(\omega) d\omega. \quad (2)$$

The zeroth moment is just the total intensity of the spectrum and may be calculated in two ways from the present data : (i) by integrating $I^{(3)}(\omega)$ directly and (ii) by fitting the expression $\phi_0^{(2)} + \phi_0^{(3)}\rho$ to a plot of $I(\rho)/\rho^2$, where $I(\rho)$ is the integrated intensity of the total spectrum obtained from the sample at density ρ . Both methods were used in order to assess the error in determining $I^{(2)}(\omega)$ and $I^{(3)}(\omega)$ and consequently in evaluating the moments. Only the Stokes profiles were experimentally measured ; the anti-Stokes sides were obtained by multiplying them by the Boltzmann factor, $\exp(-\omega/kT)$. In

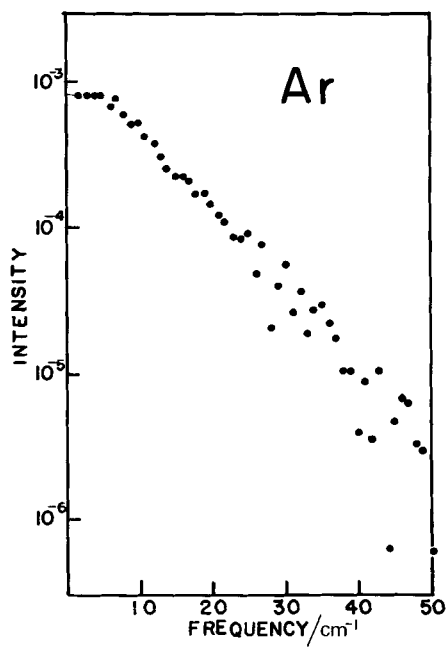


Figure 1. The three body correlation spectrum of argon at 295 K. Intensities are measured relative to the S(1) line of H₂. Points are shown every 1 cm⁻¹. The solid line shows the extrapolation to zero frequency.

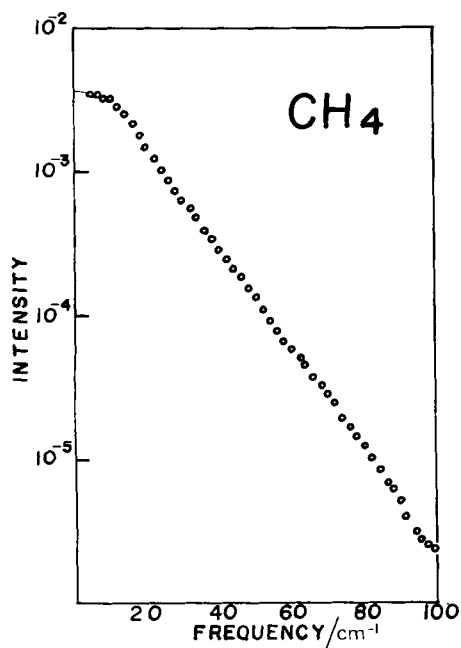


Figure 2. The three body correlation spectrum of CH₄ at 295 K. Intensities are measured relative to the S(1) line of H₂. Points are shown every 2 cm⁻¹. The solid line shows the extrapolation to zero frequency.

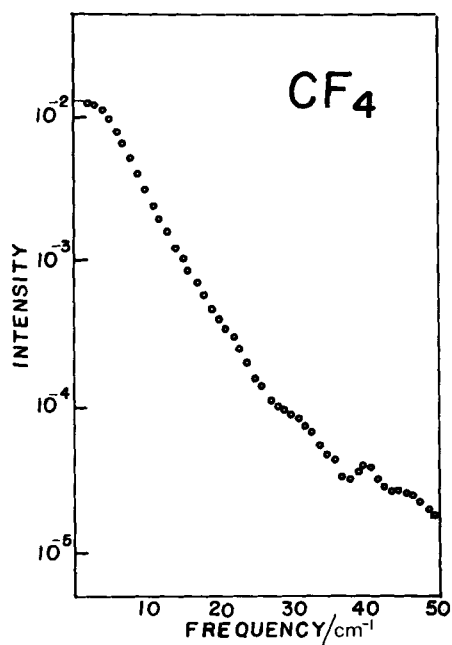


Figure 3. The three body correlation spectrum of CF_4 at 295 K. Intensities are measured relative to the S(1) line of H_2 . Points are shown every 1 cm^{-1} . The solid line shows the extrapolation to zero frequency.

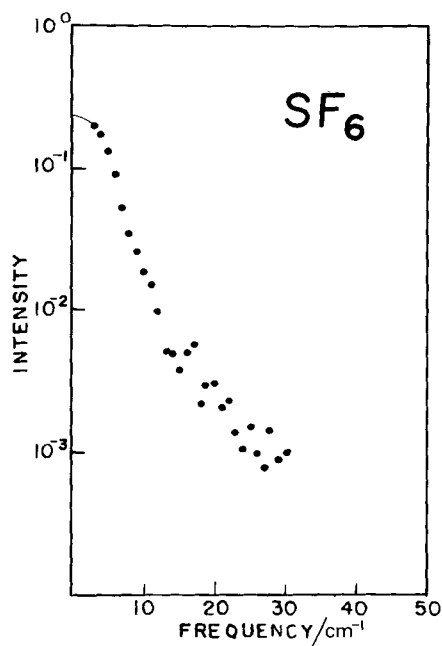


Figure 4. The three body correlation spectrum of SF_6 at 295 K. Intensities measured relative to the S(1) line of H_2 . Points are shown every 1 cm^{-1} . The solid line shows the extrapolation to zero frequency.

method (i), $I^{(3)}(\omega)$ can be determined accurately from the experiment only at frequency shifts greater than 2 cm^{-1} and an extrapolation must be made to zero frequency shift in order to perform the integration; this extrapolation is shown in the figures. Details on method (ii) are given in [9]. Accuracy in determination of the second moment is limited by the uncertainty of the observed intensity at high frequency shifts. This uncertainty rendered evaluation of higher moments impossible. The moments are given in table 1. The units of $\phi_0^{(3)}$ and $\phi_2^{(3)}$ are \AA^{12} and $\text{\AA}^{12} \text{ s}^{-2}$ where ρ is expressed as atoms/ \AA^3 . ($1 \text{ mole/litre} = 6.025 \times 10^{-4} \text{ atoms/\AA}^3$.)

Table 1. Values of the zeroth and second moments.

	Expt	$-\phi_0^{(3)}$ ($\text{\AA}^{12} \times 10^{23}$)		Expt	$-\phi_2^{(3)}$ ($\text{\AA}^{12} \text{ s}^{-2} \times 10^{28}$)	
		Calc†	Exp/calc		Calc†	Exp/calc
Ar	5.1 ± 0.4 (a)	4.91 (c)	1.04	2.4 ± 0.9 (a)	1.86 (c)	1.29
	5.0 ± 0.5 (b)	5.04 (d)	1.01	2.5 ± 0.9 (b)	2.24 (d)	1.07
CH ₄		31.5 (e)	1.17		28.2 (e)	1.52
	37 ± 6	32.7 (f)	1.13	43 ± 13	35.8 (f)	1.20
		34.6 (g)	1.07		65.3 (g)	0.66
CF ₄		48.4 (h)	0.99		5.42 (h)	1.85
	48 ± 10 †	51.8 (i)	0.93	10 ± 3	10.6 (i)	0.94
		52.9 (j)	0.91		11.3 (j)	0.88
SF ₆		289 (k)	2.01		25.8 (k)	2.40
	580 ± 110	293 (l)	1.98	62 ± 19	17.7 (l)	3.50
		283 (m)	2.05		59.1 (m)	1.05
		306 (n)	1.90		46.5 (n)	1.33

† $\phi_0^{(3)}$ is calculated from equation (11) and $\phi_2^{(3)}$ from equation (12).

‡ The value given in [11] is incorrect. The polarizabilities α_0 at 4880 \AA are: Ar, 1.679 \AA^3 [15]; CH₄, 2.642 \AA^3 [16]; CF₄, 2.937 \AA^3 [16] and SF₆, 4.549 \AA^3 [16].

(a) Present work.

(b) Reference [4].

(c) 12-6 potential: $\epsilon/k = 119.8 \text{ K}$, $\sigma = 3.405 \text{ \AA}$ [17].

(d) Barker potential [13].

(e) 12-6 potential: $\epsilon/k = 148.2 \text{ K}$, $\sigma = 3.82 \text{ \AA}$ [17].

(f) 20-6 potential: $\epsilon/k = 217 \text{ K}$, $\sigma = 3.557 \text{ \AA}$ [18].

(g) 28-7 potential: $\epsilon/k = 310 \text{ K}$, $\sigma = 3.40 \text{ \AA}$ [19].

(h) 12-6 potential: $\epsilon/k = 152.5 \text{ K}$, $\sigma = 4.70 \text{ \AA}$ [20].

(i) 28-7 potential: $\epsilon/k = 288 \text{ K}$, $\sigma = 4.20 \text{ \AA}$ [21].

(j) 28-7 potential: $\epsilon/k = 315 \text{ K}$, $\sigma = 4.33 \text{ \AA}$ [19].

(k) 12-6 potential: $\epsilon/k = 259 \text{ K}$, $\sigma = 5.01 \text{ \AA}$ [22].

(l) 12-6 potential: $\epsilon/k = 200.9 \text{ K}$, $\sigma = 5.51 \text{ \AA}$ [20].

(m) 28-7 potential: $\epsilon/k = 439 \text{ K}$, $\sigma = 4.68 \text{ \AA}$ [21].

(n) 28-7 potential: $\epsilon/k = 414 \text{ K}$, $\sigma = 5.03 \text{ \AA}$ [19].

3. CALCULATION OF SPECTRAL MOMENTS

Barocchi, Neri and Zoppi [5] have derived theoretical expressions for $\phi_0^{(3)}$ and $\phi_2^{(3)}$. In their treatment they consider the three body polarizability to be due to molecules acting in pairs and neglect the irreducible three body polarizability; this approach is consistent with the usual pair potential approximation. Then in the molecular frame, they find

$$\phi_0^{(3)} = V^2 [\langle \beta_{12}^2 \rangle_1 + 2 \langle \beta_{12} \beta_{13} P_2(\cos \Theta_{23}) \rangle_0] \quad (3)$$

and

$$\begin{aligned} \phi_2^{(3)} = \frac{V^2 kT}{\mu} & \left[\left\langle \left(\frac{d\beta_{12}}{dr_{12}} \right)^2 + 6 \left(\frac{\beta_{12}}{r_{12}} \right)^2 \right\rangle_1 \right. \\ & + \left\langle \left(\frac{d\beta_{12}}{dr_{12}} \right) \left(\frac{d\beta_{13}}{dr_{13}} \right) \cos \Theta_{23} P_2(\cos \Theta_{23}) \right\rangle_0 \\ & + 6 \left\langle \left(\frac{d\beta_{12}}{dr_{12}} \right) \left(\frac{\beta_{13}}{r_{13}} \right) \sin^2 \Theta_{23} \cos \Theta_{23} \right\rangle_0 \\ & \left. + 6 \left\langle \left(\frac{\beta_{12}}{r_{12}} \right) \left(\frac{\beta_{13}}{r_{13}} \right) \cos^3 \Theta_{23} \right\rangle_0 \right]. \quad (4) \end{aligned}$$

β_{ij} is the polarizability anisotropy of the pair (i, j), r_{ij} is the distance between i and j and Θ_{23} is the angle of the axial 'molecule' (1, 2) relative to 'molecule' (1, 3). V is the sample volume, k is Boltzmann's constant, T is the absolute temperature and μ is the reduced mass of an interacting pair of molecules. The averages are performed with the two and three body distribution functions. The two body distribution function is

$$g(r_{12}) = g_0(r_{12}) + g_1(r_{12})\rho + \dots, \quad (5)$$

where

$$g_0(r_{12}) = \exp(-U(r_{12})/kT), \quad (6)$$

$$g_1(r_{12}) = g_0(r_{12}) \int_V f(r_{13})f(r_{23}) dr_3 \quad (7)$$

and

$$f(r_{ij}) = g_0(r_{ij}) - 1 \quad (8)$$

is the Ursell-Mayer function; $U(r_{ij})$ is the pair potential. The three body distribution function is given to lowest order in ρ as

$$g_0(r_{12}, r_{13}, r_{23}) = g_0(r_{12})g_0(r_{13})g_0(r_{23}). \quad (9)$$

Then quantities in brackets $\langle \dots \rangle_1$ represent contributions due to a pair of molecules averaged over the first density correction to the two body distribution function, namely $g_1(r_{12})$. The quantities in brackets $\langle \dots \rangle_0$ give the pairwise additive contribution from a cluster of three molecules averaged over the three body distribution function $g_0(r_{12})g_0(r_{13})g_0(r_{23})$. It is worth noting that the difference between the true three body distribution function and the lowest order approximation (9) used here is proportional to at least ρ (neglecting the irreducible three body potential) and thus has no effect on the ρ^3 term which we are considering.

If the first order dipole-induced dipole (DID) form is assumed for $\beta(r)$,

$$\beta(r) = 6\alpha_0^2 r^{-3}, \quad (10)$$

where α_0 is the polarizability of an isolated molecule, then (3) and (4) become

$$\phi_0^{(3)} = 36(4\pi)^2 \alpha_0^4 [J_5(T') + 3\bar{J}_{2,2,2}(T') - \bar{J}_{2,2,0}(T')], \quad (11)$$

$$\phi_2^{(3)} = 540(4\pi)^2 (\alpha_0^4/\sigma^2)(kT/\mu) [J_7(T') + (1/2)\{5\bar{J}_{3,3,3}(T') - 3\bar{J}_{3,3,1}(T')\}], \quad (12)$$

where

$$J_k(T') = \int_0^\infty dz \int_0^z dy \int_{z-y}^{z+y} dx x^{-k} y z g_0(x) f(y) f(z), \quad (13)$$

$$\bar{J}_{h,k,i}(T') = \int_0^\infty dz \int_0^z dy \int_{z-y}^{z+y} dx xy^{-h} z^{-k} W^i g_0(x) g_0(y) g_0(z), \quad (14)$$

$$W = (z^2 + y^2 - x^2)/2yz. \quad (15)$$

x , y and z are space variables reduced with respect to σ and T' is kT/ϵ , the reduced temperature, where σ and ϵ are potential parameters.

A computer programme was written [5] to evaluate (13) and (14) by a method similar to that of Levine and McQuarrie [12]. Calculations were performed for several types of potentials: the Lennard-Jones 12-6, 20-6 and 28-7 forms and the Barker argon potential [13]. These particular potentials were used in our earlier work on two body spectra [9, 11, 14] and thus provide a consistency needed for meaningful comparisons.

The quantities in square brackets in (11) and (12) are respectively the reduced moments $\bar{\phi}_0^{(3)} = \phi_0^{(3)}/(4\pi)^2 36\alpha_0^4$ and $\bar{\phi}_2^{(3)} = \phi_2^{(3)}/(4\pi)^2 (540\alpha_0^4/\sigma^2)(kT/\mu)$. These are given in table 2 at a series of values of T' for the 12-6 and 28-7 potentials. (A similar table for the Barker potential appears in [5].) Calculations based on interpolation within this table are sufficiently accurate for comparison with experiment. The individual contributions of J_5 and $(3\bar{J}_{2,2,2} - \bar{J}_{2,2,0})$ to $\bar{\phi}_0^{(3)}$ are plotted in figure 5 for the 12-6 potential. There is a range of T' , roughly

Table 2. Reduced moments for the Lennard-Jones potential.

T	12-6 $\bar{\phi}_0^{(3)}$	$\bar{\phi}_2^{(3)}$	T^*	28-7 $\bar{\phi}_0^{(3)}$	$\bar{\phi}_2^{(3)}$
0.8	-0.0660	-0.0457	0.64	-0.112	-0.114
0.9	-0.0998	-0.0555	0.71	-0.125	-0.097
1.0	-0.114	-0.0565	0.75	-0.127	-0.0881
1.2	-0.121	-0.0518	0.94	-0.125	-0.0605
1.4	-0.121	-0.0457	1.0	-0.123	-0.0549
2.0	-0.114	-0.0325	1.25	-0.115	-0.0386
2.5	-0.109	-0.0260	1.50	-0.109	-0.0283
3.0	-0.106	-0.0216	1.75	-0.106	-0.0237
4.0	-0.102	-0.0161	2.00	-0.103	-0.0197
5.0	-0.0991	-0.0128	2.50	-0.0998	-0.0147
8.0	-0.0943	-0.00765	3.0	-0.0966	-0.0118

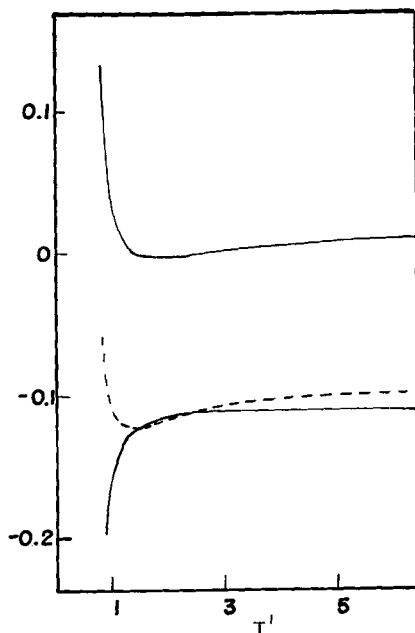


Figure 5. The reduced moment $\bar{\phi}_0^{(3)}$ as a function of reduced temperature T' . The upper solid curve is the contribution of J_5 and the lower solid curve is the contribution of $(3\bar{J}_{2,2,2}, -\bar{J}_{2,2,0})$. The dashed curve is $\bar{\phi}_0^{(3)}$. The calculation is made with the Lennard-Jones 12-6 potential.

between 1.1 and 5, in which the contribution of J_5 to the moment may be neglected ($\lesssim 10$ per cent). Consequently, in this range, the polarizability correlation in the triplet cluster dominates the moment, which thus directly reflects three body distribution properties. The equivalent region for $\bar{\phi}_2^{(3)}$ is 1.1 to 2.4. For the 28-7 potential, these ranges are shifted to lower T' and are 0.7 to 2.5 and 0.7 to 2.0 for $\bar{\phi}_0^{(3)}$ and $\bar{\phi}_2^{(3)}$ respectively.

Specific values of the moments for each of the molecules studied are compared with experimental values in table 1.

4. DISCUSSION

To begin the discussion we shall detail the comparison between calculated and observed moments, as a function of potential. For Ar the agreement is excellent for both moments with the 12-6 and Barker potentials; the Barker values are the better, particularly for $\phi_2^{(3)}$. Three potential forms are tried for CH_4 , the 12-6, 28-7 and a 20-6 approximation to the modern numerical potential of Matthews and Smith [18]. All provide adequate results for $\phi_0^{(3)}$ but only the 20-6 gives agreement for $\phi_2^{(3)}$. For CF_4 both the 12-6 and 28-7 potentials give satisfactory values of $\phi_0^{(3)}$. The 28-7 value of $\phi_2^{(3)}$ is in good agreement; the 12-6 value is only 50 per cent of the experimental one. All the calculated values of $\phi_0^{(3)}$ for SF_6 are too low by a factor of two regardless of whether the 12-6 or 28-7 potential is used. The 28-7 potential, however, yields good values of $\phi_2^{(3)}$ while those of the 12-6 which are too low by large factors.

We now review briefly a corresponding comparison of moments for the two body correlation spectrum $I^{(2)}(\omega)$. For Ar the use of the Barker potential gives results for $\phi_0^{(2)}$ and $\phi_2^{(2)}$ in good agreement with the experiment (3 and 20 per cent, respectively [11, 14]). For the molecules calculation of $\phi_2^{(2)}$ and $\phi_2^{(3)}$ is complicated by the occurrence of induced rotational transitions [23]. These constitute only 5 per cent or less of the total two body intensity. They nevertheless contribute significantly to the second moment as they produce broad high frequency tails on the spectra [11]. Such transitions should also appear in the three body spectra but would be very weak and they are neglected in the present analysis. This assumption is supported by the lack of dramatic change in slope of the high frequency tail in the molecular spectra in figures 2 to 4. The observed three body spectra would thus seem to be due only to translational scattering. Therefore, the following discussion involves only $\phi_0^{(2)}$ for the molecular spectra. The calculation of $\phi_0^{(2)}$ for CH_4 with the Matthews and Smith potential is in accord (~ 3 per cent) with the measured value [11]. For CF_4 , a 28-7 potential [21] gives a value of $\phi_0^{(2)}$ in agreement (~ 2 per cent) with experiment while the 12-6 value is 50 per cent too small [11]. For SF_6 , one 28-7 potential [19] gives $\phi_0^{(2)}$ only 1 per cent different from experiment while another set of parameters [21] gives a value 35 per cent too high; the 12-6 values are very low [11]. Finally, it should be noted that the $I^{(3)}(\omega)$ are considerably narrower than the $I^{(2)}(\omega)$ even when the broad tails of $I^{(2)}(\omega)$ are ignored [3, 11].

The success in accounting for both the two and three body moments of Ar and CH_4 with the use of modern precise potentials shows that when reliable information (on the polarizability and potential) is available an accurate detailed description of the scattering process can be given. No good calculation of the zero moments of SF_6 emerges, however. This result is consistent with other experiments on SF_6 , which measure quantities related to ϕ_0 , namely the depolarization ratio [24] and Kerr virial coefficients [8], whose unexpectedly large values are not understood. Buckingham and Clarke-Hunt [25] tried to explain such data in terms of the distribution of polarizable matter throughout the molecule but concluded that the intermolecular potential must be better specified before definite statements can be made.

The 28-7 potential has been devised primarily for large quasi-spherical molecules such as CF_4 and SF_6 , but excluding CH_4 [19]. Thus its failure for CH_4 and success with CF_4 and SF_6 (table 1) might be expected. (We find the use of the parameters of reference [21] to give calculated moments in best agreement with experiment.) Posch and Litovitz [26] used a 28-7 potential to analyse their induced scattering results for fluid SF_6 . Birnbaum and Sutter [27] also used it to determine molecular multipole moments in their study of collision induced absorption in gaseous SF_6 . We have found it to be particularly appropriate to account for $\phi_2^{(3)}$ which is very sensitive to the slope of the repulsive wall for the heavy scatterers CF_4 and SF_6 , and Xe and Kr [5]. Since $\phi_2^{(3)}$ for SF_6 is thus correctly given, the excess intensity in $\phi_0^{(3)}$ would appear to lie near zero frequency shift.

Finally we shall consider the relative intensity of the three and two body scattering and compare our results to those of other studies. At a density of 1 mol l^{-1} the present data and those of [11] give the ratio $\phi_0^{(3)}/\phi_0^{(2)}$ in units of 1 mol^{-1} as follows: Ar, 6.0×10^{-2} ; CH_4 , 7.8×10^{-2} ; CF_4 , 11×10^{-2} ; and SF_6 ,

30×10^{-2} . The density ρ^* at which the two and three body intensities are equal is in mol l^{-1} : Ar, 17 (370 Amagat); CH_4 , 13 (290 Amagat); CF_4 , 9.2 (210 Amagat); and SF_6 , 3.3 (74 Amagat). Gharbi and Le Duff [7] give this intensity ratio for CF_4 as 13.2×10^{-2} at 1 mol l^{-1} corresponding to a ρ^* of 7.6 mol l^{-1} (170 Amagat). The ratio of the third Kerr and second Kerr virial coefficients should be equal to $\phi_0^{(3)}/\phi_0^{(2)}$. Dunmur *et al.* [8] find the Kerr ratio in 1 mol l^{-1} to be: CH_4 , 12×10^{-2} , CF_4 , 4.8×10^{-2} ; and SF_6 , 21×10^{-2} . Despite the large discrepancies between the Kerr and scattering ratios, they are in agreement within the quoted errors of the two experiments.

5. CONCLUSION

The principal conclusions of the present study may now be given. To within experimental error, the three body correlation spectra may be described with the first order DID model for the cluster polarizability. They thereby provide information on mainly long range interactions. Such a result is perhaps not surprising. Only two bodies can overlap strongly and the third body in a triplet cluster must be relatively distant. Long time processes therefore are probed and the spectrum should appear at low frequency shifts. Indeed, molecular dynamics experiments verify this hypothesis [6]. The agreement between experiment and calculation is encouraging and shows that measurements of $I^{(3)}(\omega)$ are important, particularly to gain information on the isotropic part of the intermolecular potential. This is the first study to use three body correlation spectra to distinguish between the suitability of various potentials to describe collision induced scattering.

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