

The spectral profile of the collision-induced translational light scattering by gaseous CH_4

Determination of the pair polarizability anisotropy†

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The two-body purely translational, collision-induced light scattering spectra of $\text{CH}_4\text{-CH}_4$, $\text{CH}_4\text{-Ar}$, and $\text{CH}_4\text{-Xe}$ at 295 K are deduced by subtraction of the collision-induced rotational Raman scattering component from the total spectrum. For $\text{CH}_4\text{-CH}_4$, the zeroth moments of the total and purely translational spectrum are $205.4 \pm 14 \text{ \AA}^9$ and $203.8 \pm 14 \text{ \AA}^9$ respectively. The $\text{CH}_4\text{-CH}_4$ translational moments are used to evaluate the parameters in an expression for the pair polarizability anisotropy. Although some ambiguity exists, a model is thus obtained for the extra-DID contributions which is consistent with the inert gas case.

1. INTRODUCTION

The collision-induced depolarized Rayleigh scattering by inert gases may be considered as a translational Raman scattering [1]. The relative kinetic energy of the interacting molecules is altered in the scattering process. Spectra of isotropic molecules show, in addition, an induced rotational component [2, 3]. In the first paper of this series [4], hereafter referred to as I, new measurements of the

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spectrum of CH_4 were reported together with an accurate description of the shape and intensity of the induced rotational wing. In the present paper, the pure translational component and its spectral moments are obtained from these results. The profile and the moments are then analysed by a method developed for inert gas spectra [5] in order to determine the parameters of a model for the pair polarizability anisotropy.

2. TRANSLATIONAL SPECTRUM

In I, the rotational wing of the two-body spectra arising from $\text{CH}_4\text{-CH}_4$, $\text{CH}_4\text{-Ar}$ and $\text{CH}_4\text{-Xe}$ encounters was shown to be very well reproduced by the theory of collision-induced rotational Raman scattering due to Buckingham and Tabisz [2, 3]. This description involves high order molecular multipole polarizabilities and dipoles induced by intermolecular field gradients. Theoretical spectra were generated from intensity expressions from [3] and with appropriate translational broadening functions for each rotational line. Estimates of the magnitude of the dipole-quadrupole polarizability \mathbf{A} of CH_4 were obtained. The uniformly good description of the profile beyond 250 cm^{-1} as well as the consistency among the values of $|A|$ obtained from the various $\text{CH}_4\text{-X}$ spectra give confidence that the contribution from long-range interactions dominates the rotational spectrum in the frequency range studied ($0\text{-}450\text{ cm}^{-1}$). The purely translational component of the spectrum may then be obtained through subtraction from the total experimental spectrum of the theoretical rotational spectrum, fitted to the high frequency wing. Figure 6 of I illustrates how the spectrum consists of rotational and translational components. For such a separation to be appropriate, translational-rotational coupling must be assumed negligible. The translational components so obtained are shown in figures 1-3 and the intensities are recorded in table 1. These are the first reported purely translational light scattering spectra of isotropic molecules.

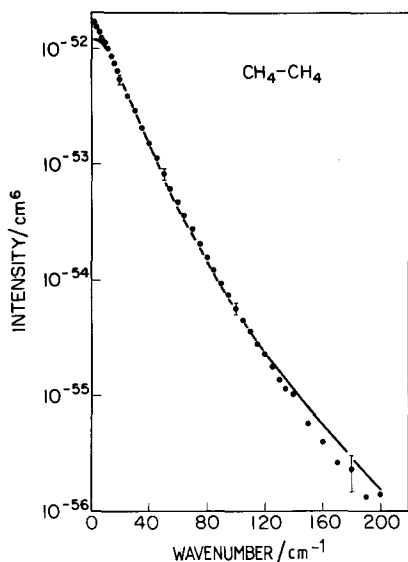


Figure 1. The purely translational spectrum of $\text{CH}_4\text{-CH}_4$. The solid line is the theoretical curve generated with equation (2) and the parameters of model 2 (table 3).

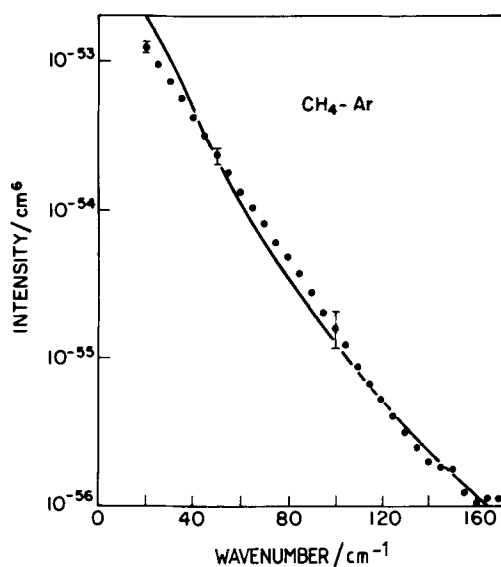


Figure 2. The purely translational spectrum of $\text{CH}_4\text{-Ar}$. The solid line is the theoretical curve generated with equation (2) and the parameters in table 3.

Some comment on these spectra is required. Excitation was at 5145 \AA . Details on the measurement of the total spectra are given in I. Absolute intensities were measured by using the intensity of the induced two-body argon spectrum at 20 cm^{-1} as the standard in an external calibration procedure; the average value of the argon intensity determined by Barocchi *et al.* [6] was adopted, namely $(8.83 \pm 0.40) \times 10^{-54} \text{ cm}^6$. The $\text{CH}_4\text{-CH}_4$ spectral intensity was measured at

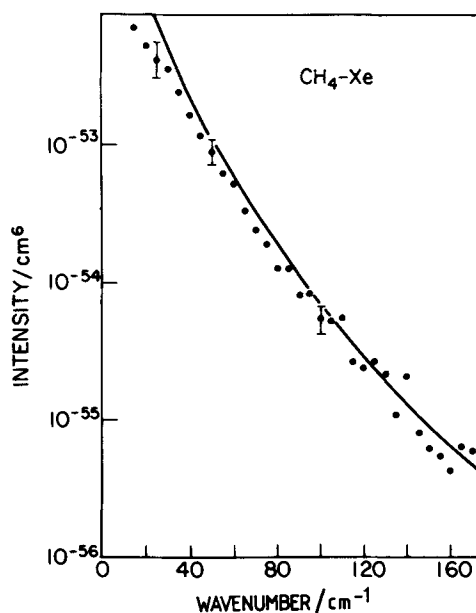


Figure 3. The purely translational spectrum of $\text{CH}_4\text{-Xe}$. The solid line is the theoretical curve generated with equation (2) and the parameters in table 3.

Table 1. Intensities (cm^6) of the two-body $\text{CH}_4\text{-X}$ pure translational spectrum with 5145 Å (Stokes side).

$\Delta\nu/\text{cm}^{-1}$	$\text{CH}_4\text{-CH}_4$	$\text{CH}_4\text{-Ar}$	$\text{CH}_4\text{-Xe}$
2	1.67×10^{-52}		
4	1.52×10^{-52}		
6	1.39×10^{-52}		
8	1.26×10^{-52}		
10	1.13×10^{-52}		
20	$(5.44 \pm 0.27) \times 10^{-53}$	$(1.26 \pm 0.06) \times 10^{-53}$	$(5.06 \pm 1.74) \times 10^{-53}$
30	2.85×10^{-53}	7.30×10^{-54}	3.23×10^{-53}
40	1.53×10^{-53}	4.14×10^{-54}	1.64×10^{-53}
50	$(8.41 \pm 0.68) \times 10^{-54}$	$(2.36 \pm 0.18) \times 10^{-54}$	$(8.75 \pm 0.62) \times 10^{-54}$
60	4.89×10^{-54}	1.39×10^{-54}	5.05×10^{-54}
70	2.77×10^{-54}	8.26×10^{-55}	2.61×10^{-54}
80	1.57×10^{-54}	4.78×10^{-55}	1.25×10^{-54}
90	9.40×10^{-55}	2.81×10^{-55}	7.70×10^{-55}
100	$(5.75 \pm 0.49) \times 10^{-55}$	$(1.65 \pm 0.38) \times 10^{-55}$	$(5.42 \pm 0.20) \times 10^{-55}$
120	2.24×10^{-55}	5.73×10^{-56}	2.35×10^{-55}
140	1.03×10^{-55}	$(2.14 \pm 0.75) \times 10^{-56}$	$(2.06 \pm 0.28) \times 10^{-55}$
160	3.80×10^{-56}	1.14×10^{-56}	3.06×10^{-56}
180	2.26×10^{-56}	5.20×10^{-57}	2.91×10^{-56}
200	$(1.36 \pm 0.8) \times 10^{-56}$	$(1.94 \pm 1.7) \times 10^{-57}$	$(1.70 \pm 1.1) \times 10^{-56}$

20 cm^{-1} in several independent low-density experiments at Manitoba and Firenze and found to be $(5.44 \pm 0.27) \times 10^{-53}\text{ cm}^6$. The units [cm^6] are defined in [6]. The object of the observation of CH_4 spectra reported in I was accurate measurement of the weak, high frequency, rotational wing. Consequently broad spectral slit widths were used. As a result, the spectral profile nearer to the exciting line than 10 cm^{-1} was considered unreliable. In the $\text{CH}_4\text{-CH}_4$ case, higher resolution measurements [$\frac{1}{2}\text{ cm}^{-1}$] of Shelton and Tabisz [7] were available. These were scaled to match the present data at 20 cm^{-1} and thus gave the profile in the range $2\text{--}20\text{ cm}^{-1}$. (The profile described by the measurements of Shelton and Tabisz is correct despite the error in the absolute intensities to be discussed in §3). A gaussian extrapolation was made from 2 to 0 cm^{-1} . The errors shown in table 1 represent both the spread in the intensity of the total spectrum among several experiments and the uncertainties introduced in the subtraction procedure.

3. MOMENTS OF THE $\text{CH}_4\text{-CH}_4$ SPECTRUM

Since the $\text{CH}_4\text{-CH}_4$ spectrum is specified from 0 to 450 cm^{-1} , its first few spectral moments can be determined. The n th moment $\phi^{(n)}$ is defined as

$$\phi^{(n)} = (-)^{n/2} \int_{-\infty}^{\infty} \omega^n I(\omega) d\omega \quad (1)$$

The values of $\phi^{(0)}$, $\phi^{(2)}$ and $\phi^{(4)}$ for both the total spectrum and the translational component are given in table 2. In order to estimate $\phi^{(4)}$, it was necessary to extrapolate exponentially the total spectrum from 450 cm^{-1} and the translational component from 250 cm^{-1} . Since the spectra were measured at low density, these are two-body moments.

Table 2. Experimental moments of the CH₄-CH₄ spectrum.

	Total	Translational	Rotational†
$\phi^{(0)}/\text{\AA}^9$	205.4 ± 14	203.8 ± 14	1.6 ± 0.2 (1.61)
$\left(\frac{\phi^{(2)}}{\text{\AA}^9 \text{s}^{-2}}\right) \times 10^{-27}$	-5.61 ± 0.56	-3.75 ± 0.38	-1.86 ± 0.2 (1.80)
$\left(\frac{\phi^{(4)}}{\text{\AA}^9 \text{s}^{-4}}\right) \times 10^{-54}$	8.1 ± 4	0.60 ± 0.15	7.5 ± 4 (6.2)

† The values in brackets are those obtained from the calculated spectrum in I.

A most important feature of these results are the values for $\phi^{(0)}$ and $\phi^{(2)}$, which are significantly lower than those reported earlier by us [7, 8]. The present results were shown to be the more accurate through a critical reassessment of the earlier experiments. The values of 285 and 281.5 \AA^9 published by Shelton and Tabisz [7] for $\phi^{(0)}$ (total) and $\phi^{(0)}$ (trans) were found to be overestimated due to a difficulty in handling the hydrogen gas sample used as an internal intensity standard in those experiments. It would appear that the hydrogen was swept into and trapped in a gauge during the filling of the pressure cell; insufficient time was allowed for diffusion of the H₂ into the cell and for complete mixing before measurements began. Computer modelling of the gas handling system of those experiments with Fick's law and the continuity equation quantitatively confirmed that this effect was indeed a source of error. This simulation shows that the spectral moments of CH₄ given in references [7] and [9] should be scaled by a factor of about 0.73 which brings the two-body moments into accord with the present values. The moments of the three-body spectrum of CH₄ [7, 9] should also be scaled by this factor but will not be as reliable as the two-body moments. The results for Ar, CF₄ and SF₆ in [7] and [9] remain unchanged. The experiment of Barocchi *et al.* [8] was performed without calibration of the intensity response of the spectrometer-detector system as a function of frequency. The ITT FW-130 photomultiplier used has a marked frequency dependent response. The large separation of 700 cm^{-1} between the exciting line and the S(1) line of H₂, the intensity standard, would give rise to an overestimate of $\phi^{(0)}$ and $\phi^{(2)}$. The importance of calibration of the response of the system for accurate intensity determinations cannot be overemphasized.

Let us now compare the value of $205.4 \pm 14 \text{\AA}^9$ of $\phi^{(0)}$ of the total spectrum with other determinations. Values in \AA^9 from depolarization measurements are 192 \AA^9 [10], 200 \AA^9 [11], 218 ± 31 [12] and 205 ± 73 [13]; from integrated spectral intensities, they are 187 [14] and 195 [15]. There is, thus, substantial agreement among values from depolarization ratio and spectral measurements. The Kerr measurements give a somewhat higher value of 255 ± 36 [16].

4. PAIR POLARIZABILITY FOR THE TRANSLATION SPECTRUM

In this section, the parameters of a model for the pair polarizability anisotropy responsible for the translational spectrum are obtained. The method used is that thoroughly described by Bafle *et al.* [5] for inert gas spectra. The polarizability anisotropy is taken to be of the form:

$$\beta(X) = \frac{6\alpha_0^2}{b^3} (X^{-3} + A^*X^{-6} - B^* \exp(-X/X_0)), \quad (2)$$

where α_0 is the polarizability of the free molecule, R is the intermolecular distance, b is the distance corresponding to the potential minimum, X is R/b , and A^* , B^* and X_0 are parameters. The first term is the first order DID contribution and the second term attempts to account for all intermediate range effects; the third describes overlap induction. Analytical expressions for the first few $\phi^{(n)}$ as functions of $\beta(X)$ and of the intermolecular potential have been derived [5]. Substitution of (2) into them and comparison with experimental values leads to equations in A^* , B^* and X_0 . For a given pair of moments $\{\phi^{(0)}, \phi^{(2)}\}$ and a particular X_0 , a set of quadratic equations in A^* and B^* is obtained and solved with a specified potential. Then $\phi^{(4)}$ is calculated and compared with the experimental value. If there is an agreement between these values for $\phi^{(4)}$, then a lineshape $D(\omega)$ is computed with the equations [5, 17]:

$$D(\omega) = 6/45k_0 k_s^3 \int_0^\infty dv P(v) \int_0^\infty db 2\pi b v \Gamma(\omega), \quad (3)$$

where

$$\Gamma(\omega) = 1.5 \left\{ \int_0^\infty \beta(t) \cos [2\phi(t) + \omega t] dt \right\}^2 + \left\{ \int_0^\infty \beta(t) \cos \omega t dt \right\}^2 + 1.5 \left\{ \int_0^\infty \beta(t) \cos [2\phi(t) - \omega t] dt \right\}^2. \quad (4)$$

$P(v)$ is the Maxwell distribution for the relative velocity v , and b is the impact parameter. $\phi(t)$ is the angle swept by the radius vector connecting the two interacting molecules, with $t = 0$ and $\phi(0) = 0$ at closest approach. The calculated symmetric classical profile is then corrected for detailed balance [17, 18] and compared with the experiment. This procedure was performed for values of X_0 in the range 0.05 to 0.2 in steps of 0.0005 for several intermolecular potentials. α was taken as 2.642 \AA^3 .

The analysis was performed at both Firenze and Manitoba. A calculation of the parameters A^* and B^* for a given set of $\phi^{(0)}$ and $\phi^{(2)}$ for 60 values of the parameter X_0 requires less than 3 s of CPU-time on the Amdahl 470/V8 computer at the University of Manitoba; the calculation of one spectral profile requires about 15 minutes of CPU-time for 30 frequency points.

A number of aspects of the CH_4 scattering makes this analysis intrinsically less reliable than that in the case of inert gas spectra. The induced rotational spectrum, which must be subtracted from the total experimental profile to give the translational spectrum, dominates the spectrum at high frequencies. Therefore the small uncertainty in the rotational component renders the translational profile ambiguous beyond approximately 150 cm^{-1} . $\phi^{(0)}$ and $\phi^{(2)}$ are thus unaffected by the uncertainties in the rotational spectrum but the uncertainty in $\phi^{(4)}$, while relatively small, is enough to limit severely the usefulness of this moment as a criterion for choosing the 'best' polarizability model.

The moment analysis consequently gives a fairly broad range of acceptable X_0 -values for a given pair of $\phi^{(0)}$ and $\phi^{(2)}$. Line shapes calculated with a representative selection of the possible models differ significantly only at high frequencies, where the uncertainties of the experimental profile are large, and therefore provide little additional help in choosing a preferred model for $\beta(R)$. (Table 3, figure 4.)

Table 3. Parameters of the pair polarizability anisotropy for $\text{CH}_4\text{-CH}_4$.

Model	A^*	B^*	X_0	$R_0/\text{Å}$	$\Delta_1/\%$	$\Delta_2/\%$	$\phi_{\text{calc}}^{(0)}/\text{Å}^9\eta$	$\left(\frac{\phi_{\text{calc}}^{(2)}}{\text{Å}^9\text{s}^{-2}}\right) \times 10^{-27}\eta$	$\left(\frac{\phi_{\text{calc}}^{(4)}}{\text{Å}^9\text{s}^{-4}}\right) \times 10^{-53}\eta$	$\left(\frac{\phi_{\text{calc}}^{(6)}}{\text{Å}^9\text{s}^{-6}}\right) \times 10^{-80}\eta$
$\text{CH}_4\text{-CH}_4^\dagger$	1	2160	0.0945	0.392	0.5	10.8	203.8	3.75	6.33	4.03
	2	631	0.135	0.56	5.6	9.0	217.2	3.79	6.86	7.54
	3	465	0.139	0.58	3.8	12.6	203.8	3.50	6.40	7.24
	4	298	0.118	0.49	4.1	19.5	203.8	3.94	8.14	7.76
$\text{CH}_4\text{-Ar}^\ddagger$		327	0.137	0.53						
$\text{CH}_4\text{-Xe}^\S$		409	0.127	0.53						

† Effective R₁MK potential at 295 K: $\alpha_{\text{CH}_4} = 2.642 \text{ Å}^3$, $b = 4.14 \text{ Å} [4]$.

‡ $\alpha_{\text{Ar}} = 1.679 \text{ Å}^3$, $b = 3.88 \text{ Å}$.

§ $\alpha_{\text{Xe}} = 4.2 \text{ Å}^3$, $b = 4.719 \text{ Å}$.

|| Calculated from 20 cm^{-1} to 200 cm^{-1} .

¶ Classical moments.

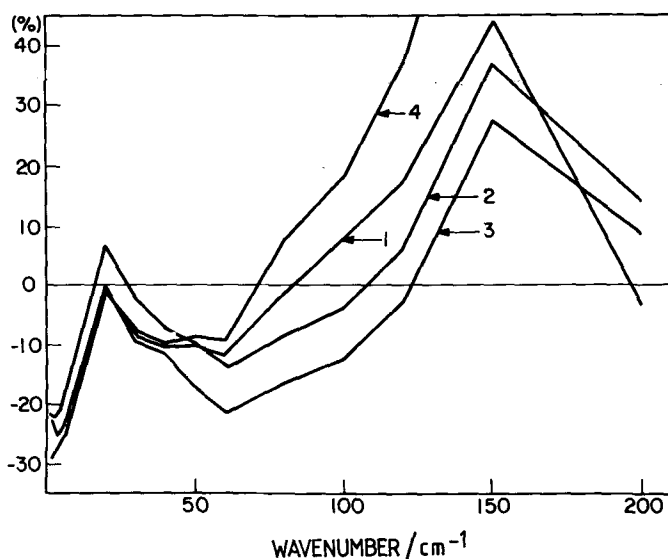


Figure 4. The relative difference $((I_{\text{calc}} - I_{\text{expt}})/I_{\text{expt}}) \times 100$ as a function of frequency for the four polarizability models for $\text{CH}_4\text{-CH}_4$ in table 3. Below 20 cm^{-1} , the omission of the dimer contribution to the spectrum in the lineshape calculation is evident.

A second complication arises because the intermolecular potential of CH_4 is not as accurately known as those for the inert gases. The models one derives for the pair polarizability are potential dependent and can only be applied together with the potential adopted for the analysis. Furthermore, the errors introduced by using isotropic models for the potential and pair polarizability are unknown.

In order to appreciate the uncertainties caused by the fact that the potential is not accurately known, the complete analysis was performed for several of the potentials described in I: the effective RMK-potential [4], the angular average of the original RMK-potential [19, 20], the angular average of the modified RMK-potential [20] and the Kr-Kr-potential [21]. Profiles calculated for different potentials, with polarizability models which give approximately the same set of moments, are not experimentally distinguishable; the largest relative differences in calculated intensity are of the order of 3 per cent (out to about 300 cm^{-1}) and vary very slowly with frequency. The most important aspect of the choice of potential energy model is that an outward shift of the potential wall causes the extra-DID part of the polarizability to increase (i.e. become less negative) in order to offset the slightly larger average separation of the molecules. An increase in the well depth causes very little change in the extra-DID part.

A further complication arises from the fact that the CH_4 molecule is sufficiently light that quantum corrections may be important. Expressions for the quantum corrections to the classical moments, up to order \hbar^2 have been derived [18]. For the pair polarizability models considered in this study, the first quantum correction to $\phi^{(0)}$ and $\phi^{(2)}$ is small (< 1 per cent), but it is significant for $\phi^{(4)}$. For the final models selected (table 3), this correction to $\phi^{(4)}$ is between 5 and 13 per cent and is small compared to the error in the experimental value of $\phi^{(4)}$, 25 per cent (table 2). Full quantum mechanical lineshape calculations for CH_4 induced absorption spectra have recently been reported [22]. However, in

view of the difficulties in accurately determining the high frequency tail of the experimental translation Raman spectrum, it was felt that such time-consuming profile calculations were not justified in the present study.

There is a small discrepancy between the calculated and experimental profile between 0 cm^{-1} and 150 cm^{-1} , where the rotational contribution does not significantly complicate the analysis, which cannot be removed for any choice of parameters A^* , B^* and X_0 (figure 4). The accuracy of the profile calculations is confirmed by comparing the moments of the calculated profiles with the theoretical values. There is excellent agreement, usually within 1 per cent, for $\phi^{(6)}$ for all profiles calculated, whereas $\phi^{(0)}$, $\phi^{(2)}$ and $\phi^{(4)}$ are too low. These discrepancies in the moments can be quantitatively attributed to the omission of the bound states in the profile calculations [23].

Model 1 reproduces the moments, has a very small A^* and a short-range exponential term. With model 2, the calculated $\phi^{(0)}$ is at the experimental upper limit, $\phi^{(2)}$ is in close agreement with experiment, and the exponential is of long-range. For models 3 and 4, $\phi^{(0)}$ is reproduced but $\phi^{(2)}$ is, respectively, too low and too high.

Bafle *et al.* [5] use the weighted root mean square deviation as a criterion for assessing agreement between calculation and experiment for the moments (Δ_1) and the profiles (Δ_2). These are given in table 3. As in the case of the inert gases, the short-range model 1 yields a profile which deviates strongly from quasi-exponential behaviour, but for $\text{CH}_4\text{-CH}_4$ this does not occur until high frequencies ($300\text{--}400\text{ cm}^{-1}$), a region which is obscured by the rotational spectrum.

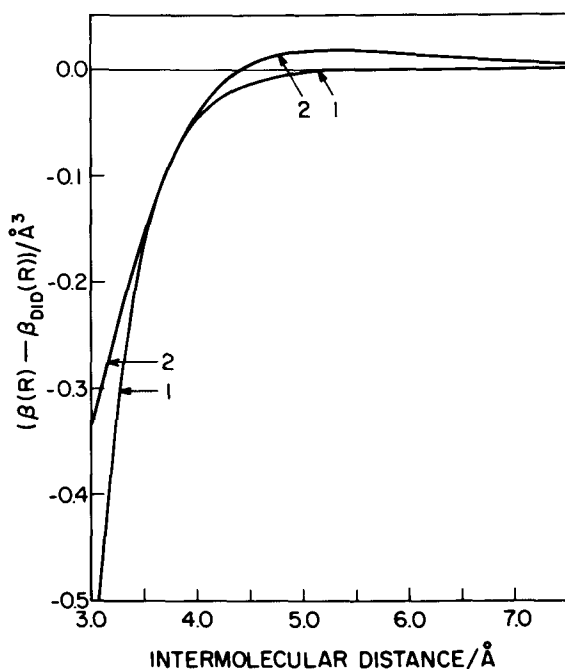


Figure 5. The extra-DID contribution of the pair polarizability $(6\alpha_0^2/b^3)(A^*(b/R)^6 - B^* \exp(-R/R_0))$ plotted as a function of intermolecular distance for models 1 and 2 of $\text{CH}_4\text{-CH}_4$ (table 3).

Table 4. Parameters of the pair polarizability anisotropy for CH₄ and the inert gases.

	A^*	B^*	X_0	$R_0/\text{\AA}$	$\alpha_0/\text{\AA}^3$	$b/\text{\AA}$
Ar [5]	0.62	850	0.138	0.52	1.68	3.763
Kr [24]	0.216	964	0.120	0.48	2.54	4.012
Xe [24]	0.0124	631	0.110	0.48	4.166	4.3623
CH ₄	0.343	631	0.135	0.56	2.642	4.147

Consequently, the short-range model cannot be directly deemed unsuitable as for the inert cases. In figure 1, the profile computed with model 2 is compared with experiment.

Figure 5 shows the extra-DID terms of the pair polarizability ($6\alpha_0^2/b^3$)($A^*X^{-6} - B^* \exp(-X/X_0)$) for models 1 and 2 plotted as a function of distance. A quantitative investigation of the role of the moments reveals that $\phi^{(0)}$ and $\phi^{(2)}$ allow a determination of the extra-DID contribution only for $3.5 \text{ \AA} < R < 4.5 \text{ \AA}$; $\phi^{(4)}$ and $\phi^{(6)}$ are required to specify it for $3 \text{ \AA} < R < 3.5 \text{ \AA}$. Recall that only $\phi^{(0)}$ and $\phi^{(2)}$ are well known in the present case.

The parameters of the long-range exponential polarizability model for the inert gases are compared with CH₄ in table 4. The extra-DID contributions for these are plotted in figure 6. There is a consistency evident, particularly in the range parameter.

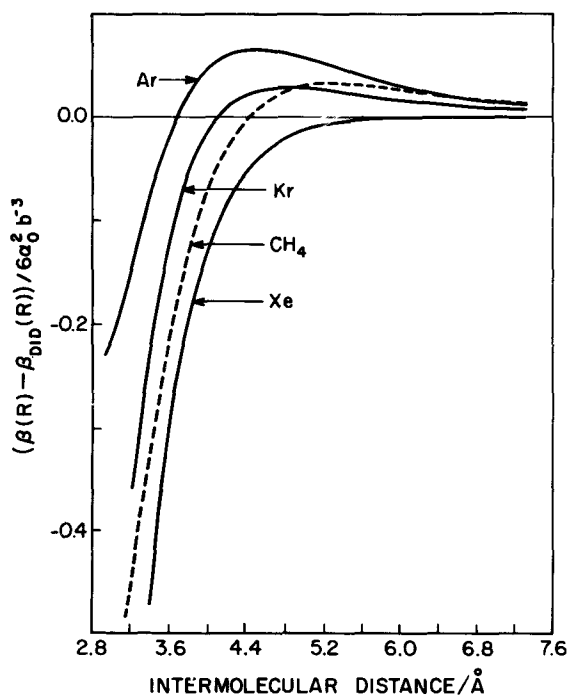


Figure 6. The reduced pair polarizability $(\beta(R) - \beta(R)_{\text{DID}})/6\alpha_0^2 b^{-3} = A^*(b/R)^6 - B^* \exp(-R/R_0)$ plotted as a function of intermolecular distance for Ar, Kr, Xe and CH₄ (table 4).

5. CH₄-Ar AND CH₄-Xe

The translational spectra of CH₄-Ar and CH₄-Xe could not be subjected to a similar moment analysis since they were not measured at the low frequencies necessary to specify $\phi^{(0)}$. Nevertheless, the parameters in the pair polarizability expression (2) were estimated by scaling them from those found for Kr-Kr as explained in I. These parameters are included in table 3 and should be regarded only as defining a mathematical expression suitable for calculation of the spectral profile. That they represent an adequate approximation is evident from figures 2 and 3 where the computed profiles are compared with experiment.

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