

An experimental and numerical study of high-frequency Raman scattering in argon gas

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The depolarized binary collision induced spectrum of argon gas has been measured, at room temperature, over an extended frequency domain not fully explored previously with comparable accuracy, and ranging from 2 to 400 cm⁻¹. In addition, theoretical spectra were calculated with different interaction models proposed in the literature. The comparison of experimental and theoretical spectra allows us to analyse the different theoretical models, in particular for short-distance interactions characterized through the high-frequency part of the spectra.

1. Introduction

Binary collision induced scattering by low density gases is related to interaction induced pair polarisabilities [1–3]. This effect has been widely studied in the Rayleigh wings of atomic gases and of molecular gases. For molecules, generally, most of the scattering intensity observed for the Rayleigh band comes from the monomolecular rotational Raman bands which appear when the molecular tensor is anisotropic. On the contrary, for atoms, or isotropic molecules, there is no permanent monomolecular rotational contribution to the Rayleigh scattering wing, and the study of translational induced scattering is a good way to determine interaction induced polarisabilities. However, this method implies that the intermolecular potential is known with sufficient accuracy. This is the case for atomic gases, and in particular for argon. For this atom, several theoretical calculations of the collision induced polarisability have been published [4–7]. Calculated scattering spectra of argon, computed using these different polarisability models, generally agree with observed scattering spectra for low frequency shifts. In this frequency range, scattered intensities are mainly due to long distance interactions, which are well de-

scribed by a dipole induced dipole (DID) model. For higher frequency shifts, however, DID interactions alone are not sufficient to give correct account of the scattering process, and interactions of shorter and shorter range must be considered. Up to now, binary collision induced scattering in argon has been measured with satisfactory accuracy for frequencies shifts up to 250 cm⁻¹ [8,9]. At higher frequencies, only one spectrum has ever been proposed [10], with very low accuracy. It is one purpose of this work to measure the high frequency scattered intensities, with good accuracy up to 400 cm⁻¹. In addition, the experimental data obtained are compared with theoretical spectra calculated using classical trajectories in association with different interaction models published in the literature.

2. Experimental

The green line (5145   ) of an argon laser operating at 2 W was used to excite the gas contained in a four-window high-pressure cell. The light scattered at right angle was analysed with a holographic double monochromator. Special attention has been paid to reduce parasitic light originating in reflection or

scattering at the laser frequency and entering the monochromator. Indeed, due to the imperfection of the monochromator, this parasitic light may produce spurious additional intensities up to frequency shifts as high as several hundreds of cm^{-1} from the laser frequency, when large slit widths ($>4 \text{ cm}^{-1}$) are used. We thus have utilized a blackened tube and diaphragms inside the high pressure cell, and multilayer antireflection coatings for the cell windows. Moreover, the gas was introduced into the cell about one day prior to the experiment, in order to minimize any light coming from dust. We used high purity argon gas from Air Liquide, with residual impurities of about 1 ppm, and filtered it through a $4 \mu\text{m}$ dust filter. PVT data were calculated from ref. [11]. On coming out of the monochromator, Raman light was detected by a bi-alkali photomultiplier associated to a photon counter. Our experiment was monitored by a computer, which served for the processing of the data in the following way, in order to increase the accuracy of the measurement. For each frequency, five measurements of the scattering intensity n are first performed; then a middle value n_m is calculated, and an interval $[n_{\min}, n_{\max}]$ is defined; the lower value n_{\min} is given by

$$n_{\min} = n_m - (an_m^{1/2} + b),$$

and the higher value n_{\max} by

$$n_{\max} = n_m + (an_m^{1/2} + b),$$

where a and b are two constants adjusted to experimental conditions. If any one of the five data lies outside the interval $[n_{\min}, n_{\max}]$, new measurements are performed, and the procedure is repeated until five measurements lying within the correct interval are obtained. It has been checked [12] that this method may improve accuracy, with no bias to the estimation, when instabilities appear in the experiment. Using counting times as long as about one hour to collect one value of intensity at a given frequency shift, we were able to measure intensities corresponding to signals lower than one tenth of the photomultiplier dark count. The overall spectral response of the detection system, including spectrometer and photomultiplier, has been checked with a calibrated OSRAM spectral lamp, and the experimental spectra have been corrected for the variation

of the spectral sensitivity of the instrument.

3. Numerical computation

Theoretical spectra were calculated numerically, using classical trajectories to describe the relative motion of a pair of argon atoms in a binary collision, and following a procedure detailed previously [13]. For the calculation, a pair potential of interaction $V(r)$ is selected together with an anisotropy $\beta(r)$ of the polarisability of the pair, r being the particle separation. Initial conditions are specified by a velocity at infinity of magnitude g , and an impact parameter b . The resulting relative trajectory, defined in a plane by radius $r(t)$ and polar angle $\theta(t)$, is calculated, starting from the point of closest approach, and using a fourth-order Runge-Kutta algorithm to solve the first-order differential equation of the orbit [14]. The autocorrelation function $C(\tau)$ of the scattered electric field is evaluated as [15]

$$C(\tau) = \langle \beta[r(t)]\beta[r(t+\tau)] \times \{3 \cos^2[\theta(t) - \theta(t+\tau)] - 1\} \rangle, \quad (1)$$

where $\langle \rangle$ denotes a time and ensemble average over all possible trajectories, with statistical weight $bg^3 \exp(-mg^2/2kT) dg dm$, m being the reduced mass of the pair.

The spectral distribution $I_C(\nu)$ of the scattered intensity is deduced as the Fourier transform of $C(\tau)$, and it is expressed here as a function of the spatial Raman frequency shift ν (in cm^{-1}) for the scattered light. A correction taking into account the detailed balance principle and the frequency dependence of the scattering when photon counting is performed, is then applied to yield the intensity as

$$I_F(\nu) = I_C(\nu) \exp(hc\nu/2kT - 3\nu/\nu_L), \quad (2)$$

where $\nu_L = 1/\lambda_L$, with $\lambda_L = 5145 \text{ \AA}$, is the spatial frequency (in cm^{-1}) of the incident light.

The calibration of the spectrum $I_F(\nu)$ in absolute units (in cm^6) is performed through the medium of its zero-order moment. First, the zero-order moment due to free atomic pairs is computed as

$$m_{0,F} = \int_{-\infty}^{\infty} I_F(\nu) d\nu. \quad (3)$$

Second, the total zero-order moment (including contribution of bound dimers) is evaluated in absolute units (in cm^5) through the equation [16]

$$m_0 = \frac{8\pi}{15} \left(\frac{2\pi}{\lambda_L} \right)^4 \int_0^\infty \beta^2(r) \exp\left(-\frac{V(r)}{kT}\right) r^2 dr. \quad (4)$$

For argon gas at room temperature, the relative contribution of dimers to the integrated collision induced scattering has been evaluated to be about 10% [17], so the calibration of the calculated spectrum $I_F(\nu)$ is obtained through the identification of $\frac{10}{9}$ of $m_{0,F}$ to the value m_0 as given by eq. (4).

A natural unit of length in the problem is given by the Lennard-Jones diameter of an argon atom, $\sigma = 3.41 \text{ \AA}$. At temperature $T = 295 \text{ K}$, a mean quadratic velocity can be deduced as $u_0 = (2kT/m)^{1/2}$. A natural unit of time follows as $t_0 = \sigma/u_0$. In the numerical computation, the time sampling of $r(t)$, $\theta(t)$ and $C(\tau)$ was $\Delta t = 0.01t_0$, and the calculation was carried out at most up to $1675t_0$. This large time domain is necessary for the definition of $C(\tau)$, in order to obtain after Fourier transform good accuracy over the whole frequency range. In the averaging procedure, g was sampled with step $\Delta g = 0.2u_0$ in the interval $[0, 21u_0]$, and b with step $\Delta b = 0.2\sigma$ in the interval $[0, 25\sigma]$. As a test of the accuracy of the computation, the discretization steps Δt , Δg and Δb were divided by two, and the extent of the corresponding integration domains were multiplied by two, the resulting changes in the calculated spectrum then did not exceed a few percent.

Various interaction potentials $V(r)$ have been tested and are discussed in section 4. The anisotropies $\beta(r)$ that were tested are:

(i) a DID model of anisotropy where

$$\beta(r) = 6\alpha_0^2/r^3 + 6\alpha_0^3/r^6, \quad (5)$$

with $\alpha_0 = 1.68 \times 10^{-24} \text{ cm}^3$;

(ii) a self-consistent field (SCF) model of anisotropy [4,18];

(iii) two different anisotropies, given in ref. [5], and calculated with a perturbational model using two different basis sets of functions. Here we shall denote by CC the polarisability model using the basis set proposed by Clementi [19], and by CS the model using the basis set of Sitter and Hurst [20].

4. Results and discussion

For argon gas at room temperature, we have measured the depolarized scattering spectral intensities $I_{\parallel}(\nu)$ obtained with a laser beam linearly polarized parallel to the scattering plane. The behavior of scattering intensities when the gas density increases, has been studied for several frequency shifts ν ranging from 2 to 400 cm^{-1} , in order to determine density conditions preserving good signal to noise ratio while keeping to binary-interaction conditions. In this study, the effect, on the scattering intensities, of the local field and of the variation of the index of refraction, has been taken into account. For the highest frequencies (ν around 400 cm^{-1}), the intensity $I_{\parallel}(\nu)$ increases proportionally to the square of the gas density, up to 255 amagat. For the lowest frequencies ($2 < \nu < 6 \text{ cm}^{-1}$), a quadratic dependence of $I_{\parallel}(\nu)$ is observed only for small densities, typically below 10 amagat. We show the values of $I_{\parallel}(\nu)$ measured as a function of argon density, at 5, 10 and 30 cm^{-1} in fig. 1a, and at 150 and 200 cm^{-1} in fig. 1b. From our result, we have deduced density conditions that we adopted to record scattering spectra induced by binary pairs of argon atoms. In the low frequency part, up to 30 cm^{-1} , we used argon at 6 and 10 amagat; then, up to 150 cm^{-1} , the density was about 30 amagat; and for the highest frequency

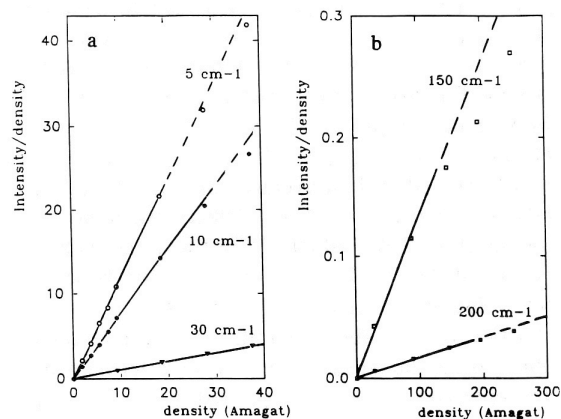


Fig. 1. Depolarized scattering intensity from argon gas divided by density, in arbitrary units, versus density in amagat, and measured at several frequency shifts ν : (a) $\nu = 5 \text{ cm}^{-1}$ (open circles), $\nu = 10 \text{ cm}^{-1}$ (full circles), $\nu = 30 \text{ cm}^{-1}$ (triangles); (b) $\nu = 150 \text{ cm}^{-1}$ (open squares), $\nu = 200 \text{ cm}^{-1}$ (full squares).

domain, data were obtained with densities from 60 to 240 amagat. In these conditions, we were able to measure the binary spectrum of argon gas at room temperature from 2 to 400 cm^{-1} . We employed several slit functions for the monochromator; resolutions of 0.5 to 0.7 cm^{-1} were selected for the low frequency part, and larger resolutions, up to 4 cm^{-1} , for the high frequency part.

The absolute scattering intensities of argon were evaluated by comparison to rotational line intensities published for several diatomic molecules as standards of intensity [21,13]. We conducted two types of experiments with the same experimental conditions. The first one was to measure the signal S_a (in counts/s) scattered by argon gas at a particular frequency shift ν_0 . The second one was to measure the frequency integrated intensity S_r^i (in cm^{-1} counts/s) corresponding to a well resolved reference rotational line of a molecule B serving as a standard. If the integrated cross section of the reference line ($d\sigma/d\Omega$)_{||} is known, the argon pair intensity at ν_0 per unit of frequency shift, $I_{||}^p(\nu_0)$, can be calculated from

$$I_{||}^p(\nu_0) = \left(\frac{d\sigma}{d\Omega} \right)_{||} \frac{S_a}{S_r^i} \frac{2n_r}{n_a^2}, \quad (6)$$

where n_a and n_r are the number density of argon and molecule B, respectively. Using as reference line the rotational line $S_0(1)$ of hydrogen with an anisotropy $\gamma = 0.3198 \times 10^{-24} \text{ cm}^3$ [22], we measured for argon at frequency shift $\nu_0 = 20 \text{ cm}^{-1}$, $I_{||}^p(20 \text{ cm}^{-1}) = 9.06 \times 10^{-54} \text{ cm}^6$. Another experiment using the rotational line $S_0(2)$ of nitrogen as the reference, and with an anisotropy $\gamma = 0.714 \times 10^{-24} \text{ cm}^3$ [23], gave $I_{||}^p(20 \text{ cm}^{-1}) = 9.12 \times 10^{-54} \text{ cm}^6$. Finally, from our results we deduced an average value for the experimental pair intensity of low density argon gas at a frequency shift $\nu_0 = 20 \text{ cm}^{-1}$, for the Stokes side, as $I_{||}^p(20 \text{ cm}^{-1}) = (9.09 \pm 0.70) \times 10^{-54} \text{ cm}^6$. Based on this value of the intensity at $\nu_0 = 20 \text{ cm}^{-1}$, we were able to express in absolute units the experimental intensities for the anisotropic Stokes scattering which are reported in table 1 and plotted in fig. 2. Overall typical experimental uncertainties are shown in fig. 2a, that include the uncertainties on the absolute value of the reference line used for the calibration. Our experimental spectrum of fig. 2 is in good agreement with the other experimental spectra published

Table 1

Depolarized scattering intensities $I_{||}$, measured at several frequency shifts ν , from argon gas at 295 K and for binary interaction conditions.

ν (cm^{-1})	$I_{ }$ (cm^6)	ν (cm^{-1})	$I_{ }$ (cm^6)
2	4.39×10^{-53}	170	8.53×10^{-58}
3	4.33×10^{-53}	180	5.53×10^{-58}
4	4.21×10^{-53}	190	3.57×10^{-58}
5	4.05×10^{-53}	200	2.39×10^{-58}
6	3.85×10^{-53}	210	1.65×10^{-58}
7	3.63×10^{-53}	220	1.14×10^{-58}
8	3.35×10^{-53}	230	8.81×10^{-59}
9	2.99×10^{-53}	240	5.54×10^{-59}
10	2.59×10^{-53}	250	4.17×10^{-59}
20	9.09×10^{-54}	260	3.10×10^{-59}
30	3.51×10^{-54}	270	2.16×10^{-59}
40	1.50×10^{-54}	280	1.70×10^{-59}
50	6.98×10^{-55}	290	1.18×10^{-59}
60	3.34×10^{-55}	300	9.25×10^{-60}
70	1.63×10^{-55}	310	6.75×10^{-60}
80	8.55×10^{-56}	320	5.24×10^{-60}
90	4.64×10^{-56}	330	3.89×10^{-60}
100	2.60×10^{-56}	340	3.27×10^{-60}
110	1.47×10^{-56}	350	2.08×10^{-60}
120	8.79×10^{-57}	360	1.76×10^{-60}
130	5.21×10^{-57}	370	1.27×10^{-60}
140	3.25×10^{-57}	380	8.91×10^{-61}
150	2.03×10^{-57}	390	7.16×10^{-61}
160	1.21×10^{-57}	400	6.39×10^{-61}

up to 250 cm^{-1} [8,9]. For the higher frequency part, up to 400 cm^{-1} , important significant discrepancies are found with the previously published experimental spectrum [10].

From the data of table 1, and from an extrapolated value for the zero shift intensity as shown in fig. 3, we calculated the integrated intensity, or zero-order spectral moment m_0 , for the anisotropic scattering of low density argon gas excited by the green light of an argon laser ($\lambda_L = 5145 \text{ \AA}$). We found $m_0 = (1.28 \pm 0.11) \times 10^{-51} \text{ cm}^5$. This result takes into account the Stokes and anti-Stokes intensities scattered by each argon pair. Our intensity value measured at $\nu_0 = 20 \text{ cm}^{-1}$ is consistent with previous results published independently by two laboratories [8]. For the lowest frequency domain (ν of the order or below 10 cm^{-1}), however, our data of table 1 are significantly below values reported in ref. [8]. This difference could be attributed to a very careful elimination, in our experiment, of parasitic light that may occur at low frequency shifts. Moreover, our

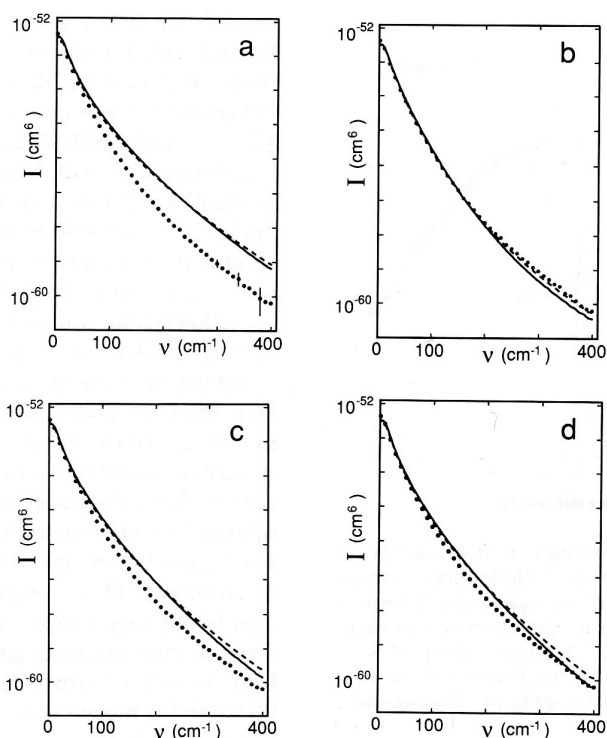


Fig. 2. Binary scattering spectra for argon gas at 295 K. The intensities are given in cm^6 , versus frequency shift ν in cm^{-1} . Full circles: experimental data; dashed line: calculated spectra with a Lennard-Jones potential [24]; solid line: calculated spectra with an Aziz potential [27]. Different models for the anisotropy of the polarisability have been used: (a) DID anisotropy given by eq. (5); (b) SCF model [4]; (c) CC model [5]; (d) CS model [5]. Typical experimental error bars are shown in (a); for $\nu \leq 250 \text{ cm}^{-1}$ error bars correspond roughly to the diameter of the full circles.

zero-order spectral moment m_0 is lower than previously published ones [8,9] deduced from spectral intensity measurements and given in table 2. When compared to theoretical values, our experimental m_0 appears lower than DID result. With more elaborate polarisability models [5,4], the theoretical values of m_0 that we calculated come closer to experiment.

From the measurement of the binary spectral intensities it is possible, in principle, to determine the induced polarisabilities for the colliding argon pair. At long intermolecular distance, the pair polarisability anisotropy is well described by the DID model. At short distance, the validity of this model breaks down. It is one of the purposes of this work to use our experimental intensities, measured over an extended frequency domain, to test different theoretical polarisability models proposed for the argon pair.

To achieve this, it is first desirable to identify the

influence of the intermolecular potential on the scattering spectral shape. Several models of the potential $V(r)$ have been tested in this study: (1) a Lennard-Jones potential with parameters $\sigma = 3.41 \text{ \AA}$ and $\epsilon = 165.4 \times 10^{-23} \text{ J}$ [24], that stands for a classic reference of interaction potential; (2) a Bobetic-Barker [25] potential; (3) a Barker-Fisher-Watts [26] potential; (4) an Aziz HFDTCS2 potential [27], that represent a more recent and satisfactory interaction potential for argon. With the same anisotropy $\beta(r)$, the spectra calculated with potentials (2)–(4) are very similar and display differences that are smaller than the uncertainties on the experimental spectrum. Potentials (2)–(4) are three recent realistic potentials for argon that differ only slightly. The outcome of the calculation suggests that, for the frequency range studied in this work, once a “reasonable” potential has been chosen, the calculated

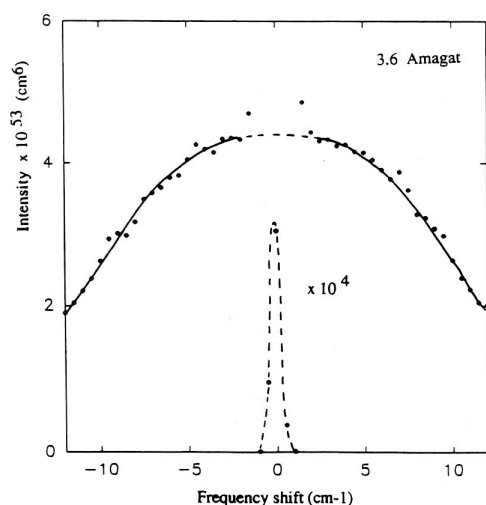


Fig. 3. Depolarized scattering intensity $I_{\parallel}(\nu)$ from argon gas, in cm^6 , versus frequency shift ν in cm^{-1} . The spectrum has been obtained at 295 K, with argon at 3.6 amagat, and a slit function of 0.7 cm^{-1} . Experimental data are given for Stokes and anti-Stokes sides from -12 to 12 cm^{-1} . In order to fall into the scale of the figure, the very intense line at zero frequency due to parasitic light, has been plotted after a division by 10^4 of its magnitude.

Table 2

Depolarized scattering intensity $I_{\parallel}(20 \text{ cm}^{-1})$ measured at the frequency shift $\nu = 20 \text{ cm}^{-1}$, and zero-order moment m_0 for the depolarized scattering intensity from argon gas at 295 K and binary interaction conditions. Our results are compared with published values obtained by Barocchi and Zoppi [8] (BZ), Proffit and Frommhold [8] (PF), Shelton and Tabisz [9] (ST). m_0 is calculated in \AA^9 from $m_0 = \frac{15}{2} (\lambda_L/2\pi)^4 \int_{-\infty}^{\infty} I_{\parallel}(\nu) d\nu$. Theoretical values of m_0 were obtained using the Aziz potential [27] and different polarisability models: DID model of eq. (5); SCF model [4], CS model [5] with Sitter and Hurst [20] basis set; CC model [5] with Clementi [19] basis set

		$I_{\parallel}(20 \text{ cm}^{-1}) \times 10^{54} (\text{cm}^6)$	$m_0 (\text{\AA}^9)$
experiment	this work	9.09 ± 0.7	42.8 ± 3.8
	BZ [8]	8.94 ± 0.57	49.4 ± 3
	PF [8]	8.71	50.1 ± 4
	ST [9]		52.1 ± 3
theory	DID		48.8
	SCF [4]		43.2
	CS [5]		43.2
	CC [5]		45.6

spectra that follow are not significantly influenced by small details of the potential. The Lennard-Jones potential (1) is a less elaborate potential, that shows noticeable differences with the group of potentials (2)–(4), and visible differences are induced on the high frequency part of the calculated spectra that may be significant. To illustrate this point, we show in figs. 2a–2d, in each one of the four panels, two calculated spectra, using either the recent Aziz potential [27], or the much older Lennard-Jones potential [24]. In the following, we will consider for the discussion the spectra calculated with the recent Aziz potential.

Among the various polarisability models tested here, the DID model leads to the highest scattering intensities. Moreover, as shown in fig. 2a, the DID spectrum lies above the experimental spectrum, except for low frequencies ($\nu < 20 \text{ cm}^{-1}$). This indicates that in addition to the DID interaction, a negative contribution must be included to the pair polarisability. This contribution, coming in play at high frequencies, can be attributed mostly to short distance interactions originating in overlapping effects. As such, it is partly taken into account in other polarisability models that we studied. The calculated spectrum of fig. 2c, based on the CC model, brings an improvement to the DID results, but still remains too high above experiment. The CS model leads to the spectrum of fig. 2d which is even closer to experimental data, although discrepancies still exist for middle frequencies. These two polarisability models CC and CS differ only at short distances: they are significantly different only for intermolecular distances $r < 6a_0$ (a_0 is the Bohr radius), and they become roughly equal for $r > 7a_0$. Since the spectra calculated with these two polarisabilities are notably different, this demonstrates that we are probing very short range interactions, and that the choice of the basis set significantly influences the calculation of the resulting spectrum. The SCF model of fig. 2b is in good agreement both with the full quantum spectrum calculated by Frommhold up to 250 cm^{-1} [18], and with experiment. This calculated spectrum of fig. 2b stays close to experimental data up to 200 cm^{-1} , and then gradually moves below for higher frequencies, to deviate of an amount that is slightly greater than experimental uncertainties. This may point out some small inaccuracy of the SCF polarisability at short distances of interaction.

5. Conclusion

We have measured anisotropic binary scattering intensities for argon gas, in a frequency domain which had not been fully explored previously with comparable accuracy, and ranging from 2 to 400 cm^{-1} . We have compared our experimental spectrum with theoretical spectra calculated using classical trajectories in association with different interaction models of the literature. We observed that when using recent realistic interaction potentials for argon, the resulting calculated spectra do not significantly differ. We further identified that, in the framework of our calculation, the SCF model of refs. [4,18] and the CS model of ref. [5] yield the best agreement with experiment. However small significant discrepancies still exist in the spectra for middle or high frequencies with both of these models, suggesting that the validity of these models gradually breaks down as interaction distances become shorter and shorter. In addition, this work shows that argon scattering intensities measured over an extended frequency range (up to 400 cm^{-1}) allow one to probe the behavior of the polarisability for intermolecular distances smaller than the molecular diameter. Our results bring new elements for improving the description of the induced polarisability of a pair of argon atoms, and the characterization of short distance interactions in rare gases.

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