Depolarized-light-scattering spectrum from gaseous hydrogen at 50 K: The density-squared component

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The density-squared component of the depolarized-light-scattering spectrum of hydrogen at 50 K has been measured. This contribution is compared with the results of a theoretical model that considers both the wings of the rotational lines and the interaction-induced spectral components. The overall agreement is good, but some inconsistencies remain in the region between the rotational lines. Probable reasons for such a discrepancy are discussed.

In hydrogen, as in any other gas composed of linear molecules, the collision-induced contribution to the depolarized spectrum is superimposed with the allowed rotational Raman lines arising from the anisotropy of the polarizability of a single molecule. It is often assumed that the two contributions should be separable for molecular systems of small momentum of inertia since, in the gas phase, the collision time is much shorter than the time Consequently, the pressurecollisions. between broadened allowed rotational lines are much sharper than the induced spectra, masking the latter only over a limited range of frequencies. Indeed, the depolarized-lightscattering (DLS) spectrum of hydrogen in the frequency interval between 20 and 250 cm⁻¹ has been successfully analyzed even when any contributions from the allowed spectrum are ignored.^{1,2}

Recently, the DLS spectrum of hydrogen at room temperature has been measured at frequencies up to 850 cm⁻¹ (Ref. 3) which includes the rotational $S_0(0)$ to $S_0(8)$ lines. For further tests, an analogous series of measurements was performed in hydrogen at a cryogenic temperature which we report in this paper.

The experimental setup and the analysis of the data are similar to those described in Ref. 3. The depolarized spectra of hydrogen were measured in the range 10-800 cm⁻¹, at ten different densities, from 20 to 530 amagats. The series of measurements were taken starting at the highest density, corresponding to a pressure of about 90 bars. The gas sample was kept at 50 K for many days to ensure equilibration of the ortho-para concentration (mainly induced by the walls of the scattering cell), decreasing the density of subsequent recordings of spectra. As the cold hydrogen gas was flowing out of the cell, a small amount of warm gas from one pipe entered the cell. The concentration of orthohydrogen was, therefore, not constant during the experiment. However, from the observed ratio of the $S_0(0)$ and $S_0(1)$ lines, we found it to vary from a minimum of 26% to a maximum of 40% at the highest and lowest density, respectively. This variation of the para-ortho concentration has been accounted for in the calculation of the allowed spectrum.

We have determined the density variation of the depolarized spectrum of H_2 in the whole frequency range between 10 and 800 cm⁻¹ in much the same way as explained in Ref. 3. For every frequency of the measured spectra, and from a range of densities where only the quadratic component was significant, we have derived the spectral component $D_{\parallel}^{(2)}(v)$ (Refs. 4 and 5) of the double-differential scattering cross section per unit volume, defined as in Eq. (41) of Ref. 3, for comparison with a theory⁵ which is based on the binary collision approximation.

Solid circles in Fig. 1 represent the measured spectrum $D_{\parallel}^{(2)}(\nu)$ as functions of frequency ν in absolute intensity units on a logarithmic scale. The present determination of the translational two-body spectrum gives a slightly less intense spectrum than the one previously reported.¹ However, we feel more confident about the present result which is based on a much larger set of experimental data, taken at a variety of densities.

As mentioned previously, the spectral component $D_{\parallel}^{(2)}(\nu)$ is composed of both the allowed and the induced spectra. Since, experimentally, these two contributions cannot be separated, a theoretical modeling of both contributions is desirable for an analysis of such measurements.

Recently, two of us (A.B. and M.M.) have proposed a theory based on the binary collision approximation to calculate the DLS spectrum far from the Raman lines, and to account for both the allowed and the interaction-induced components.⁵ For the wings of the allowed rotational lines, the theory relies on a perturbative treatment of the pair dynamics in terms of the anisotropic component of the intermolecular potential. The theory was

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FIG. 1. Experimental two-body spectrum (\bullet) in absolute intensity units. Error bars are shown whenever they exceed the size of the circles. The solid line represents the calculation, namely the sum of the collision-induced contribution ($\cdot \cdot \cdot \cdot$) and the collisionally broadened, allowed line wings (- - -).

successfully tested with the low-density DLS spectrum of hydrogen at room temperature.⁵

Calculated induced two-body spectra are also shown in Fig. 1 (solid line). The induced contribution (smalldotted line) has been calculated from the lowest-order dipole-induced dipole (DID) approximation of the pair polarizability $A_{\Lambda}(\lambda_1, \lambda_2, L; R)$ terms, and the spherical part of the pair interaction potential given in Ref. 6; we accounted for the following terms: $\lambda_1, \lambda_2, \Lambda$, L=0,0,0,2; 0,2,2,2; and 2,0,2,2.

Pressure broadening of the unshifted rotational Raman lines (mainly the $J=1\rightarrow J=1$ transition) is indicated by the dashed line. It is almost negligible above 15 cm⁻¹.

This gives a more rigorous justification, though *a posteriori*, of the analysis of this frequency range of the DLS spectrum of hydrogen in terms of induced contributions only.^{1,2} The discrepancy between experiment and theory, evident at high-frequency shifts, is mostly due to the assumption of the DID model for the polarizability.

In order to check the effect of the short-range contributions to the pair polarizability, we will now consider the first three translational spectral moments. For the determination of the measured moments of a translational DLS spectrum, some extrapolations to low and high frequencies are needed. In order to avoid including part of the $Q_0(1)$ line in the calculation of the spectral moments, the experimental spectra were truncated at 15 cm^{-1} . An estimation of the contribution at lower frequencies was made as an average of a flat spectrum of intensity equal to the one measured at 15 cm^{-1} and an exponentially extrapolated spectrum. One-half of the difference between the two results is added to the estimated error. For the high-frequency region, in order to avoid the contribution of the $S_0(J)$ lines, we have extrapolated the spectrum beyond 240 cm^{-1} with the help of a function which is known to account for the observed curvature of the spectral shape in a semilogarithmic plot. A lower limit is determined from imposing a purely exponential shape. The difference between the two distinct contributions to the moments was also added to the estimated error.

The experimental moments of the induced two-body spectrum at 50 K are reported in Table I, together with the results of the theoretical [quantum-mechanical (QM)] calculation. We also report available results at room temperature.³ The QM calculations based on the theory⁷ consider three different models of the pair polarizability anisotropy $\beta(R)$. Specifically, we assume⁸⁻¹⁰

$$\beta(R) = \frac{6\alpha_0^2}{R^3} + \frac{A}{R^6} - Be^{-R/R_0} , \qquad (1)$$

	M_0 (error) (10 ⁻⁵² cm ⁵)		M_1 (error) (10 ⁻⁵¹ cm ⁴)		M_2 (error) (10 ⁻⁴⁹ cm ³)	
		T=50 K				
Present experiment ^a	0.96	(0.06)	1.52	(0.06)	1.70	(0.14)
QM theory (DID)	1.07		2.02		2.89	
QM theory (RG) (Ref. 10)	0.95		1.35		1.51	
QM theory (MRG) (Ref. 8)	1.04		1.75		2.19	
		T=297 K				
Experiment (Ref. 3)	1.27	(0.03)	1.84	(0.27)	8.3	(0.6)
QM theory (DID)	1.22		2.83		13.91	
QM theory (RG) (Ref. 10)	0.96		1.41		6.65	
QM theory (MRG) (Ref. 8)	1.13		2.11		9.77	

TABLE I. Spectral moments of the pure translational part of the two-body spectrum of hydrogen at 50 and 297 K. The calculations are performed within the framework of quantum mechanics, using Eq. (1) for the polarizability anisotropy, and different choices of parameters. The isotropic intermolecular pair potential was assumed after Ref. 6.

^aThe large difference between the integrated intensity reported in Ref. 1 and the present result is due to the fact that, in Ref. 1, a part of the $Q_0(1)$ line intensity has been incorrectly included into the calculation of the translational zeroth moment. Note also that the value of the second moment in Ref. 1 was incorrect due to a typographical error and should read 1.77 instead of 2.77.

where α is the trace of the H₂ polarizability ($\alpha = 5.58a_0^3$). Our first model is given by A = B = 0 (DID model). For this case, the agreement with the experiment is very poor (Table I). We also added short-range terms to the anisotropy using $A = 1457a_0^9$ and either $B = 1781.4a_0^3$ [rare-gas (RG) model, Ref. 10] or $B = 822a_0^3$ [modified rare-gas model (MRG), Ref. 8]. The isotropic pair interaction potential of Ref. 3 was assumed. Table I shows that the experimental results for the first three spectral moments are intermediate between the two latter calculations. The slight discrepancy for the zeroth moment at room temperature is attributed to the large fraction of orthohydrogen and, consequently, to the large contribution to the low-frequency spectrum of the $Q_0(J)$ rotational Raman line which probably was not properly subtracted from the induced spectrum. In fact, the allowed contribution to the DLS spectrum of hydrogen at room temperature becomes negligible only for frequency shifts above 35-40 $cm^{-1}.5$

Next we have considered the high-frequency spectral region. Figure 2 shows the rototranslational contribution to the depolarized induced spectrum of hydrogen, which extends roughly from 250 to 800 cm^{-1} . The computations of the pressure-broadened Raman lines include two significant terms of the anisotropy of the potential, namely V_{202} and V_{224} . The results of Ref. 5 indicate that the interference of the pressure-broadened allowed lines and the induced spectral component is negligible; it has not been included in the present computations. In the region from 250 to 800 cm^{-1} , the contributions from the translational interaction-induced part and the pressurebroadened allowed lines are more clearly discernible. Moving closer to the rotational Raman lines, the allowed components of the spectrum increase and eventually become larger than the induced spectrum. Moreover, in the same region, the effect of different ortho-para concentration becomes discernible. Due to the combined effect of a much higher population of the J=0 state and a steeper slope of the translational Rayleigh wing at 50 K relative to the room-temperature spectra (cf. Fig. 1 of Ref. 5), the present translational component (small-dotted line), mainly due to the $A_2(002; R)$ term, now gives a larger contribution (by a factor of 3-4) to the intensity in the region of the $S_0(0)$ line than at 297 K. Nevertheless, in the vicinity of the Raman transitions, the most important contributions come from the broadened allowed lines (dashed line). In this region the agreement with the calculation is better. In the far wings, and in the region between the $S_0(0)$ and $S_0(1)$ lines, the calculations give insufficient intensity. At room temperature, theoretical predictions were too low between the $S_0(1)$ and $S_0(2)$ lines (Fig. 2 of Ref. 5), but they matched the experimental results in the region between the $S_0(0)$ and $S_0(1)$ lines (Fig.



FIG. 2. Same as in Fig. 1, in the region of the rotational allowed Raman transitions $S_0(0)$ and $S_0(1)$. The solid lines are the theoretical results assuming a concentration of parahydrogen equal to 74 or 60% of the total (plotted as thin and thick lines, respectively).

1 of Ref. 5). However, if we assume that induced intensities are overestimated by the DID model and that, at 297 K, such contribution is still important in the frequency range between $S_0(0)$ and $S_0(1)$, we recognize that the small underestimate of the intensity will be a general feature of the calculation.

In conclusion, we note that, at present, there is substantial agreement between theory and experiment for the interaction-induced depolarized spectrum of dimolecular hydrogen at low frequencies in the purely translational spectrum. Agreement is also seen in the (near) wings of the rotational Raman lines. The far wings of the rotational Raman lines, however, and the spectral region between the lines, show differences between the present theory and the experiments. This frequency region is the one where the anisotropic part of the intermolecular potential is important, and we feel that, to some extent, the inconsistencies are due to the generally poor knowledge of the anisotropy of the intermolecular potential at near range. In fact, the high-frequency spectral contributions come mainly from the energetic (short-time) collisions, which are extremely sensitive to the details of the potential at short ranges. Given the well-known lack of experiments that probe this region, the present experimental technique might become a useful (though indirect) test of the anisotropy of the intermolecular potential of hydrogen.

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