
Dynamic Aspects of Light Scattering by Gases [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1979 **293**, 407-412
doi: 10.1098/rsta.1979.0107

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Dynamic aspects of light scattering by gases

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Light scattering experiments involving the rotational Raman and depolarized Rayleigh spectra of H₂, D₂ and HD have been performed. From the collisional broadening and collisional frequency shift of these lines, it is possible to infer much about the dynamics of molecular collisional processes. In particular, the elastic and inelastic contributions to the linewidths can be separated by studying their temperature dependence over a range 25–300 K. Moreover, measuring the linewidths as a function of *ortho-para* composition permits a study of the rather strong influence of resonance collisions. The results will be compared with scattering theory calculations based on the distorted wave Born approximation.

1. INTRODUCTION

For many years the rotational Raman lines have been an abundant source of information about the molecular properties of matter. The most extensively investigated aspect, the displacement of a particular Raman line from the exciting light, is commonly used for the determination of molecular structure parameters. Another important feature, the shape of the line, is the main subject of this paper. The spectral line shape is dependent on the density of the scattering medium and is determined by the time evolution of the molecular translational and rotational states. Because those states are perturbed by molecular interactions, the line shape can be used to extract information on intermolecular collision processes (Berne & Pecora 1976; Knaap & Lallemand 1975).

In the absence of collisions, the spectral line shape is determined by natural broadening and Doppler broadening. Since the natural linewidth is very small, the spectral line shape of a Raman line of a gas at very low density reflects the velocity distribution of the scattering molecules. When the density is slightly increased, the molecular translational motion is no longer free, but becomes influenced by intermolecular collisions, and so the linewidth is thereby related to the diffusional motion of the radiating molecules. The rotational motion of the molecules is also influenced by collisions, and since the amplitude, frequency and phase of the scattered light wave are dependent on the internal molecular state, such collisions can, in general, disturb the radiation process and thus give rise to collisional line broadening and a shift of the central line frequency (collisional line shift). At higher densities, where the mean free path of the molecules becomes considerably smaller than the wavelength of the light, the collisional broadening dominates over the broadening due to the diffusional motion. The spectral line shape can then be described by a Lorentzian profile (Gersten & Foley 1968):

$$I(\nu) = \frac{I_0}{\pi} \frac{\Delta\nu_{\frac{1}{2}}(\rho)}{(\nu - \nu_R)^2 + \Delta\nu_{\frac{1}{2}}(\rho)^2}, \quad (1)$$

where ν is the spectral frequency, I_0 is the integrated line intensity, $\Delta\nu_{\frac{1}{2}}$ is the halfwidth of the line, dependent on the density, ρ . The central frequency, ν_R , of the Raman line, is, for Stokes rotational Raman lines, given by

$$\nu_R = \nu_0 - (E_f - E_i) h^{-1} - \Delta\nu_s(\rho), \quad (2)$$

[197]

where ν_0 is the frequency of the exciting light and $(E_f - E_i)h^{-1}$ is the Raman frequency displacement corresponding to the energy difference between the unperturbed initial and final levels of the spectroscopic transition. The term $\Delta\nu_s(\rho)$ is the (density dependent) collisional line shift, taken to be positive when the line shifts away from ν_0 . The terms $\Delta\nu_{\frac{1}{2}}(\rho)$ and $\Delta\nu_s(\rho)$ are proportional to the density, provided that the density is not so high that ternary or higher order collisions occur at an appreciable rate. In figure 1 a schematic picture of the line spectrum at different densities is given. We shall restrict ourselves to that region of the binary collision regime where the collisional broadening is predominant.

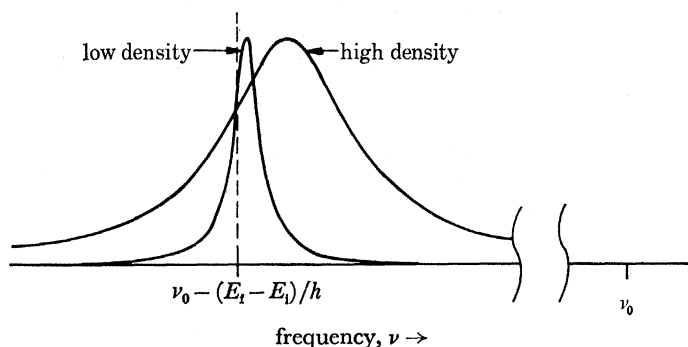


FIGURE 1. Sketch of the spectral profile of a Raman line.

Many different collisional processes contribute to the observed cross section for a particular Raman line, and it is usually not possible to disentangle the various contributions. For better insight with regard to the processes that lead to the broadening and shift of the Raman lines, it would, of course, be quite useful if such a separation could be achieved on an experimental level. For this reason, an investigation of the hydrogen isotopes (H_2 , D_2 , HD) is very interesting. Because of the large energy separations between the rotational levels, only a few rotational states are appreciably occupied, even at room temperature. For H_2 and D_2 the interpretation is further simplified, since transitions between *ortho* and *para* states are forbidden for these homonuclear molecules. This makes rotational-translational energy transfer by collisions even more improbable.

Obviously, it is most desirable to change the occupation of translational and rotational states by temperature variation. For the hydrogen isotopes a large experimental temperature range is available, because the gas phase exists, at moderate densities, down to 25 K, where only one or two rotational levels are occupied. When the line broadening effect is then measured as a function of the *ortho-para* composition, and the results are extrapolated to the limit of the pure modifications, linewidths are obtained which arise from only a very small number of possible collision processes.

Another very attractive aspect of hydrogen is that the mass difference between the isotopes is relatively large. Hence the velocity and rotational energy level distributions are significantly different, while the intermolecular potentials are closely related.

2. EXPERIMENTAL

The apparatus used to measure the broadening and shift of the rotational Raman lines at low temperatures was very similar to the one used by Keijser *et al.* (1974*a, b*) for the investigation of the depolarized Rayleigh line and the rotational Raman lines at room temperature.

For the present measurements a new type of scattering cell was devised which could be used at temperatures between 5 and 300 K. It was mounted in an optical cryostat. A schematic diagram of the optics is given in figure 2. A beam of horizontally polarized light from an Ar ion laser was focused into the scattering cell. The light scattered at right angles to the laser beam passed through a polarizer which was set to transmit only the horizontally polarized component. For the spectroscopic analysis a Fabry-Pérot interferometer was used in combination with a small monochromator. The monochromator was set to transmit only the particular Raman line under investigation, while the interferometer could then be used to measure the spectral line with high resolution. The transmitted light was detected by a low noise photomultiplier together with photon counting equipment.

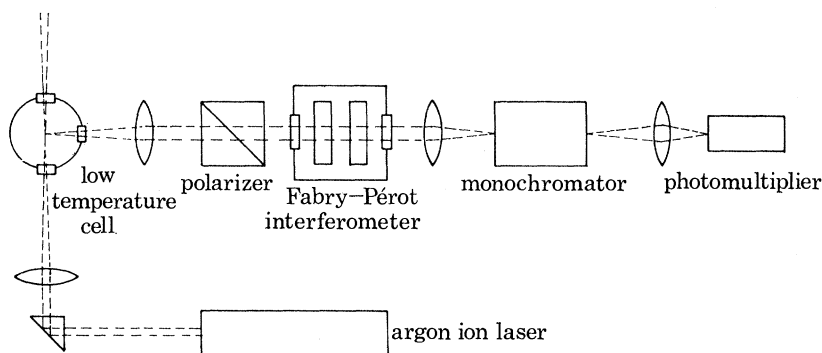


FIGURE 2. Schematic diagram of the experimental arrangement.

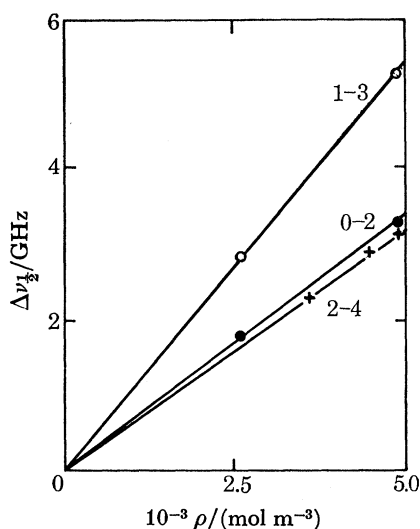


FIGURE 3. The collisional halfwidths for $n\text{-H}_2$ (for Stokes rotational Raman transitions ($\Delta j = 2$)) as a function of density at 77.8 K. ●, 0-2; ○, 1-3; +, 2-4.

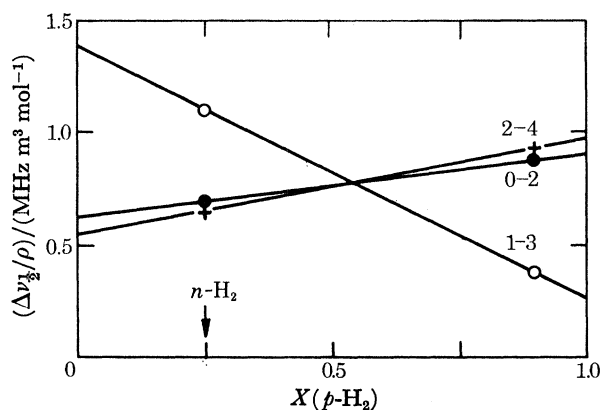


FIGURE 4. The line broadening coefficients for H_2 as a function of the $p\text{-H}_2$ concentration at 77.8 K. ●, 0-2; ○, 1-3; +, 2-4.

After applying some corrections (e.g. for the instrumental width) the true Raman line is obtained. The line was found to be Lorentzian (see equation (1)). The linewidth due to collisional broadening $\Delta\nu_{\frac{1}{2}}$ is plotted (in figure 3) against density for some typical cases. From such plots the broadening coefficients $\Delta\nu_{\frac{1}{2}}/\rho$ are obtained. These broadening coefficients are,

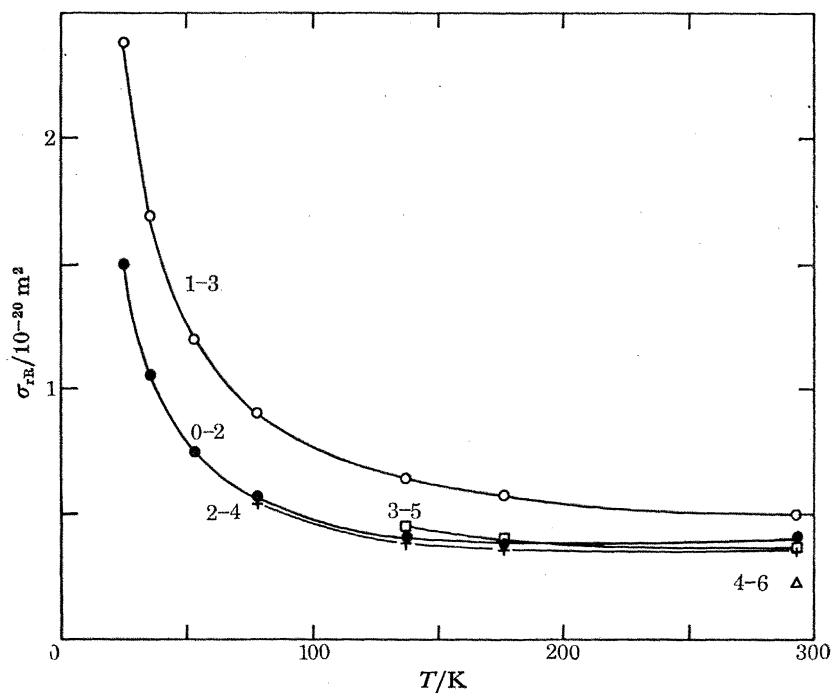


FIGURE 5. The line broadening cross sections for $n\text{-H}_2$ as a function of temperature.
 ●, 0-2; ○, 1-3; +, 2-4; □, 3-5; △, 4-6.

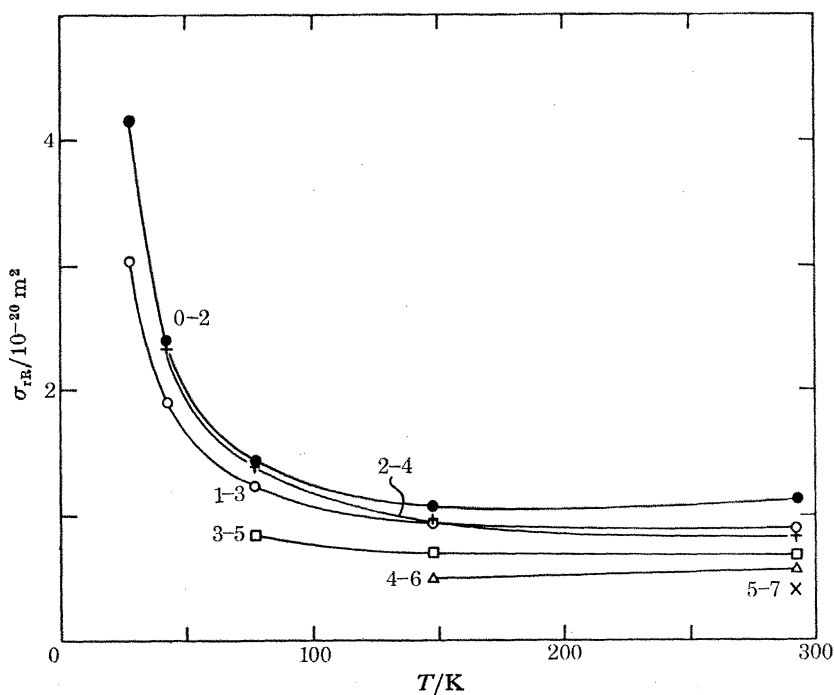


FIGURE 6. The line broadening cross sections for $n\text{-D}_2$ as a function of temperature.
 ●, 0-2; ○, 1-3; +, 2-4; □, 3-5; △, 4-6; ×, 5-7.

in the binary collision régime, linear functions of the *ortho-para* concentration (see figure 4). By extrapolation, the values of $\Delta\nu_{\frac{1}{2}}/\rho$ for the pure *ortho* and *para* components are obtained.

For a discussion of the observed behaviour of the line broadening in terms of molecular collision processes, it is useful to express the collisional broadening coefficients in terms of effective cross sections for the rotational Raman lines according to the relation

$$\sigma_{\text{rR}} = 2\pi\Delta\nu_{\frac{1}{2}}/n\langle v \rangle_0. \quad (3)$$

In this formula, n is the number density and $\langle v \rangle_0$ is the relative velocity given by

$$\langle v \rangle_0 = \left(\frac{8k_{\text{B}}T}{\pi\mu} \right)^{\frac{1}{2}}, \quad (4)$$

where k_{B} is the Boltzmann constant, T is the absolute temperature and μ the reduced mass of the collision partners. The Raman line broadening cross sections are presented in figures 5–8, where the cross sections are plotted as a function of the temperature.

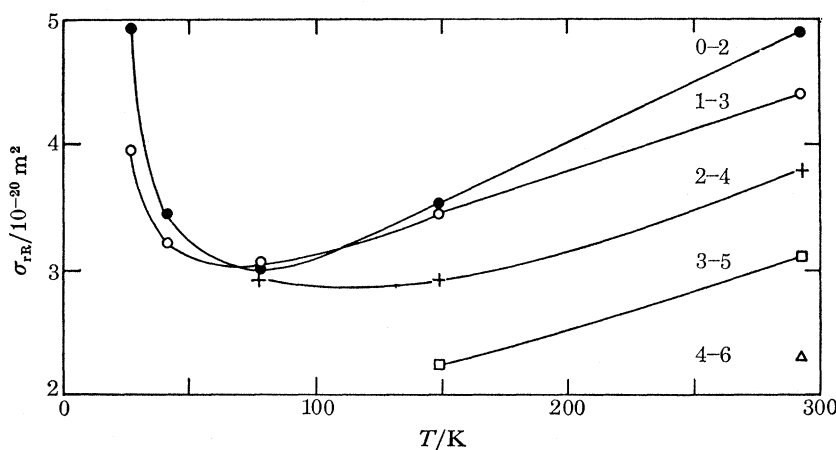


FIGURE 7. The line broadening cross sections for HD as a function of temperature. ●, 0-2; ○, 1-3; +, 2-4; □, 3-5; △, 4-6.

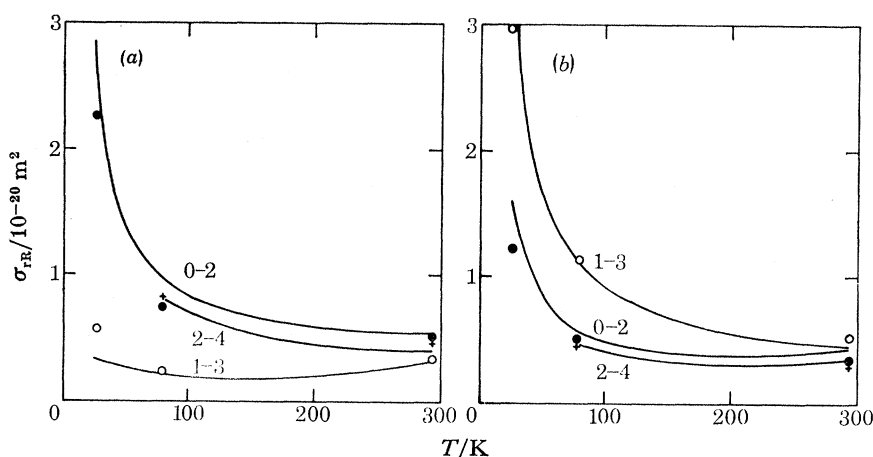


FIGURE 8. (a) The line broadening cross sections as a function of temperature in (the limit of pure) *p*-H₂ (J even). ●, 0-2; ○, 1-3; +, 2-4; □, 3-5; △, 4-6. —, Theoretical calculations based on distorted wave Born approximation (Coombe & Köhler (1980)). (b) The line broadening cross sections as a function of temperature in (the limit of pure) *o*-H₂ (J odd). ●, 0-2; ○, 1-3; +, 2-4; □, 3-5; △, 4-6. —, Theoretical calculations based on distorted wave Born approximation (Coombe & Köhler (1980)).

Theoretically, the results can be discussed treating the angle dependent part of the intermolecular potential as a perturbation. Calculations have been performed on the basis of distorted wave Born (d.w.B.a.) calculations in which the translation is also treated quantum mechanically (Moraal 1974; Coombe & Köhler 1980) and on the basis of the Born approximation with the translation treated classically (Van Kranendonk 1963).

At higher temperatures one finds, for HD, a cross section that is considerably larger than for H₂ and D₂ (see figures 5–7). This is directly related to the strong $P_1(\cos \chi)$ term in the intermolecular potential for HD, which is present because the centre of mass does not coincide with the centre of action of the intermolecular force.

For H₂ and D₂ the calculations (Moraal 1974; Van Kranendonk 1963) indicate a dominant contribution from the quadrupole–quadrupole interaction. At the lowest temperatures only very few (elastic and inelastic) collision processes are possible (i.e. molecules are in the $j = 0$ or $j = 1$ states). The measurements of the linewidths as a function of *ortho*–*para* composition of H₂ between 20 and 40 K permit a critical comparison with a recent theoretical calculation (Coombe & Köhler 1980).

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie and has been made possible by financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek.

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Discussion

A. D. BUCKINGHAM (*University Chemical Laboratory, Cambridge, U.K.*). Dr Knaap has beautifully demonstrated through Raman rotational line broadening in hydrogen that intermolecular resonance forces can shorten the lifetime of a particular rotational state. It might be possible to employ double resonance techniques to extend the technique to heavier molecules. By pumping power into a gas at a resonance frequency the Boltzmann distribution is disturbed; observations of the change in the rotational Raman scattering resulting from the pump would determine the efficiency of collisions in bringing about molecular transitions between the particular quantum states involved in the pumping and Raman transitions. Double resonance techniques have already proved useful in microwave spectroscopy (Oka 1973; Ronn & Wilson 1967).

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