

EVIDENCE FOR RESONANCE COLLISIONS IN ROTATIONAL ENERGY TRANSFER; RAMAN LINES OF H₂.

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We have shown that resonance collisions are important in rotational energy transfer by measuring Raman linewidths in various ortho-para H₂ mixtures. We find that the contribution of resonance collisions to the linewidths can exceed 40%.

Pressure broadening of Raman and infrared lines of simple molecules at moderate pressures arises from several different processes. Among these are elastic collisions, inelastic collisions, and also so-called resonance collisions in which the rotational energy given up by one molecule is exactly matched by the rotational energy picked up by its collision partner. As suggested by Van Kranendonk [1] in systems where the energy spacings between rotational levels are larger than the thermal energy, resonance collisions might be expected to be relatively more important (see also [2]). We therefore studied the rotational Raman lines of H₂, D₂ and HD.

The experimental arrangement was a conventional light scattering system [3] with a 600 mW Ar ion laser (5145 Å) in single mode operation. Light was focussed into a chamber which contained the sample gas at 293 K at pressures up to 124.5 atm. Scattered light was collected at right angles to the source. A Jarrell-Ash 25 cm monochromator was utilized to isolate a region of the spectrum containing the individual Raman line of interest. This line was then spectrally analyzed with a pressure scanned Fabry-Perot interferometer and standard photon counting equipment. The shapes of the Raman lines were analyzed by a Fourier transform technique. Careful analysis showed no deviations from a Lorentzian line shape [4].

The measured linewidths for the first five Stokes Raman lines ($\Delta J = +2$, S-branch) in normal hydrogen are shown in fig. 1. Previous results in H₂ have only been obtained for the S(0) and S(1) with which we agree [5, 6]. The linewidths as a function of J deviate markedly from the usual pattern that $\Delta\nu_{1/2}$ decreases

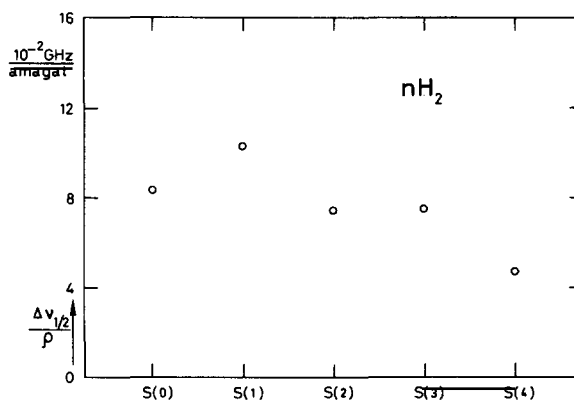


Fig. 1. Broadening coefficients of the first five rotational Raman lines in normal hydrogen. $\Delta\nu_{1/2}$ is the full width at half height.

monotonically with J [7]. There is a clear alternation in the measured widths,

A possible interpretation can be given as follows. In normal H₂ more than 2/3 of the molecules are in the $J=1$ state. Molecules in the $J=3$ state are special since they are the only ones that can undergo resonance collisions with abundant $J=1$ molecules.

If these resonance collisions are important a significantly shorter life time for molecules in the $J=3$ state results. This in turn causes extra broadening for the spectroscopic lines involving this state (in this case S(1) and S(3)).

To further test this hypothesis, we decided to vary the relative populations of the odd and even rotational states by making measurements for different mixtures of ortho and para hydrogen. This could easily be ac-

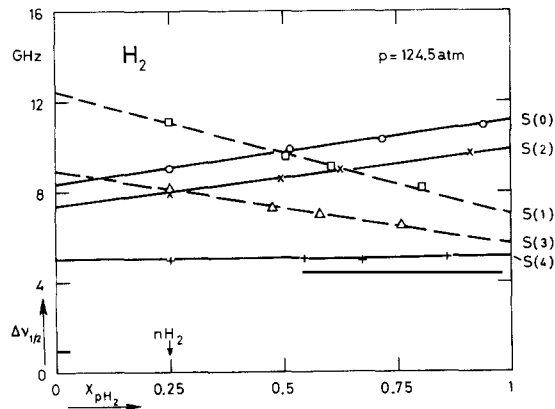


Fig. 2. Variation of the linewidths of the rotational Raman lines for H_2 as a function of mole fraction para H_2 . $\Delta\nu_{1/2}$ is the full width at half height.

completed by performing measurements on a sample of pure para hydrogen at 124.5 atm, which was allowed to convert slowly to normal hydrogen.

The measured linewidths as a function of mole fraction para hydrogen are given in fig. 2, for the first five Raman lines. The linewidths for all lines vary linearly with concentration as should be expected in a pressure region where binary collisions are dominant.

It is seen that the linewidths of the S(1) and S(3) lines decrease with increasing para concentration (dotted lines). At higher para concentrations (even rotational states) molecules with odd J undergo resonance collisions less frequently. On the other hand the molecules with even J will more often encounter collision partners in the even J states, with which resonance collisions can occur. This then also explains the increase of the linewidths of S(0) and S(2) (solid lines in fig. 2) as a function of the para concentration, further corroborating the importance of resonance collisions. In fact the contribution of resonance collisions in some of the lines exceeds 40% of the total linewidth. This implies that the angle dependent part of the H_2 potential must contain terms that allow for simultaneous

transitions of collision partners e.g. quadrupole-quadrupole interactions. A straight line trajectory calculation for Raman line broadening has been presented by Van Kranendonk [1, 8] which he applied to normal H_2 . We have extended these calculations to obtain the linewidths for ortho and para H_2 . Good agreement with respect to both magnitudes and slopes of the S(J) widths in fig. 2 is found if quasi-resonance collisions, i.e. collisions where the change of rotational energy of one molecule is only partially compensated by the rotational energy change of the collision partner, are weighted slightly less than suggested by Van Kranendonk.

We have also investigated the Raman lines of normal D_2 (S(0) through S(5)) and HD (S(0) through S(4)) which have not previously been studied. For nD_2 we find a similar but less pronounced alternation of the widths with J , while for HD the expected smooth J dependence was found. More details will appear in a later publication.

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