Pressure Narrowing of the Rotational Lines of the Fundamental Infrared Band of H_2 in Collision-Induced Absorption[1]

J. De Remigis[2], J. W. Mactaggart[2], and H. L. Welsh
Department of Physics, University of Toronto, Toronto, Ontario

Received September 8, 1970

The enhancement by argon of the pressure-induced fundamental infrared absorption band of hydrogen is studied for Ar densities in the range 8–820 amagat at 152 K. The half-width, $\Delta\nu_{1/2}$, of the quadrupole-induced $S_1(1)$ transition remains constant at 55 cm^{-1} up to ~300 amagat and then decreases to 25 cm^{-1} at the highest density. In the higher density range $\Delta\nu_{1/2}$ varies inversely as the density. The $S_1(1)$ line of H_2 in liquid H_2–Ar solutions shows a similar pressure narrowing for Ar densities in the range 640–833 amagat at 115 K.

Canadian Journal of Physics, **49**, 381 (1971)

The collision-induced fundamental infrared absorption band of hydrogen in hydrogen–argon gas mixtures has been studied as a function of the Ar density along the 152 K isotherm. For Ar densities in the range from ~300 amagat to 820 amagat, the highest density reached, the quadrupole-induced rotational lines show a marked, but hitherto unnoted, pressure narrowing. In this paper we present the observed characteristics of this new type of line narrowing; in the following note Zaidi and Van Kranendonk (1971) propose an explanation of the effect in terms of gas diffusion.

The experiments reported here for Ar densities from 8 to 820 amagat at 152 K were carried out with three absorption cells and cryostats of different designs. For the lowest densities, corresponding to total mixture pressures up to 8 atm, a multiple-traversal cell provided a path length up to 15 m. The intermediate density range, 90–600 amagat, was covered by a 20 cm double-pass cell used with pressures up to 200 atm. For the 600–800 amagat region a 48 cm single-pass cell was used with pressures up to 2000 atm. The cells were cooled in liquid nitrogen cryostats in which temperatures from 77 to 200 K could be maintained. The temperature of the 20 cm cell could be held constant to better than 0.05 deg during the experiments at 152 K; this stability was required for the 250–400 amagat range because of the proximity of the critical point of argon at 150.9 K and 300 amagat. The H_2 partial pressure in the mixtures was kept as low as was compatible with accurate absorption measurements; the H_2 number density constituted 0.5 to 3% of the total number density for total densities greater than 100 amagat but was higher (~50%) for the lowest density.

Figure 1 shows absorption profiles of the fundamental band for the extreme Ar densities used, 8 and 820 amagat. The curves refer to the enhancement of the H_2 absorption by H_2–Ar collisions, *i.e.*, the absorption given by the base density of hydrogen and due to H_2–H_2 collisions has been subtracted out. The three main features of the band are the Q_1 branch and $S_1(0)$ and $S_1(1)$ lines[3]; the profiles in Fig. 1 are normalized to give the same peak intensity for the $S_1(1)$ transition. The fine structure near the maxima of the low-density profile is due to transitions between bound states of H_2–Ar complexes (Kudian *et al.* 1965). The Q branch at the high density shows the well-known three components (Hare and Welsh 1958). Those marked Q_1 are due to short range (overlap) interaction, the minimum between them arising from intercollisional interference (Van Kranendonk 1968). The sharper $Q_1(1)$ component, uncovered by the splitting of the overlap Q branch at high densities, and the $S_1(0)$ and $S_1(1)$ lines constitute the part of the spectrum induced by the longer range interaction originating in the quadrupole moment of the H_2 molecule (Van Kranendonk 1957, 1958).

Of particular interest to us here is the decrease in the width of the quadrupole-induced components as the gas density is increased. In Fig. 1

[1]This research was supported in part by a grant from the National Research Council of Canada.

[2]Holder of a National Research Council Graduate Research Fellowship.

[3]$Q_1(J)$ and $S_1(J)$ refer to transitions for which $J = 0$ and $+2$, respectively, where J is the rotational quantum number of the ground vibrational state; the subscript 1 indicates the $v = 1 \leftarrow v = 0$ vibrational transition.

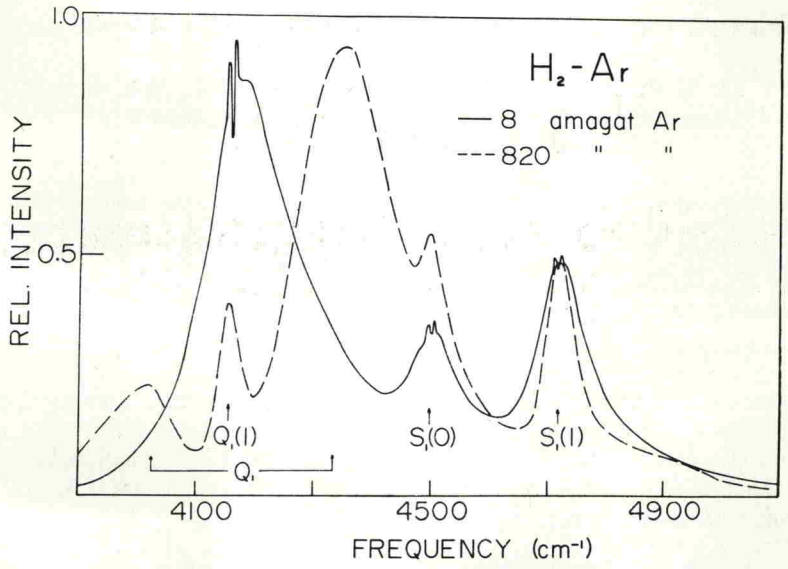

FIG. 1. The enhancement of the pressure-induced fundamental band of hydrogen by argon at 152 K for two Ar densities, 8 amagat and 820 amagat. The effect of special interest here is the pressure narrowing of the $S_1(1)$ line.

this effect is most readily evident for the $S_1(1)$ component which is relatively free from overlapping by the other components of the band. However, to delineate the effect more clearly it is necessary to isolate the $S_1(1)$ intensity from the overlapping tails of the Q and $S_1(0)$ components. This was accomplished in a systematic manner by fitting the entire fundamental band with a synthetic profile using a modified version of the analysis described by Watanabe and Welsh (1967); the details of the computation will not be given here. The computed version of the $S_1(1)$ feature was then removed from the synthetic profile which was in turn subtracted from the experimental spectrum leaving a reasonable approximation to the true $S_1(1)$ line. This translationally broadened profile of the $S_1(1)$ transition showed, of course, the well-known Boltzmann relation between the intensity distributions in the low- and high-frequency wings (Chisholm and Welsh 1954). When the Boltzmann factor is removed by multiplying the intensity distribution with the factor $[1 + \exp(-hc\Delta\nu/kT)]$, where $\Delta\nu$ is the distance from the H_2 frequency (*i.e.*, from the line maximum) the resulting symmetrical line shape is the Fourier transform of the autocorrelation function of the dipole moment induced during the collision; this line shape is amenable to theoretical analysis (Zaidi and Van Kranendonk 1971).

Figure 2 shows in (*a*) the observed spectrum in the region of the $S_1(1)$ line at the low and high densities and in (*b*) the corresponding isolated symmetrized $S_1(1)$ profiles; in both cases the profiles are normalized to give the same peak intensity. The half-width $\Delta\nu_{1/2}$ (one-half of the width at half intensity) of the symmetrized line decreases from 55 cm^{-1} at 8 amagat to 25 cm^{-1} at 820 amagat.

To obtain the form of the density dependence of $\Delta\nu_{1/2}$ the spectra for 17 different argon densities were reduced by the procedure outlined above; the results are shown in the log–log plot in Fig. 3. In the density range up to ~ 300 amagat $\Delta\nu_{1/2}$ remains effectively constant at 55 cm^{-1} and then decreases rather rapidly. Over much of the higher density range the decrease can be represented by a straight line of slope -0.89, *i.e.*, approximately -1, as in Fig. 3; this means that in this region $\Delta\nu_{1/2}$ varies as $1/\rho_{Ar}$. There is some indication that at the highest densities the rate of decrease of $\Delta\nu_{1/2}$ is less rapid than is given by this law.

At low densities the spectrum arises primarily from isolated binary collisions and $\Delta\nu_{1/2}$ is determined by the collision duration, τ_d, through the uncertainty relation, $\Delta\nu_{1/2} \approx (2\pi c\tau_d)^{-1}$. In the density range where binary collisions predominate $\Delta\nu_{1/2}$ is therefore constant and has a value characteristic of the range of the qua-