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# Pressure Narrowing of the Rotational Lines of the Fundamental Infrared Band of H<sub>2</sub> in Collision-Induced Absorption<sup>1</sup>

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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<sup>-1</sup> up to ~300 amagat and then decreases to 25 cm<sup>-1</sup> 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<sub>2</sub> in liquid H<sub>2</sub>-Ar solutions shows a similar pressure narrowing for Ar densities in the range 640–833 amagat at 115 K.

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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<sub>2</sub> partial pressure in the mixtures was kept as low as was compatible with

accurate absorption measurements; the H<sub>2</sub> 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<sub>2</sub> absorption by H<sub>2</sub>-Ar collisions, *i.e.*, the absorption given by the base density of hydrogen and due to H<sub>2</sub>-H<sub>2</sub> 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<sup>3</sup>; 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<sub>2</sub>-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<sub>2</sub> 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

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<sup>3</sup> $Q_1(J)$  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.

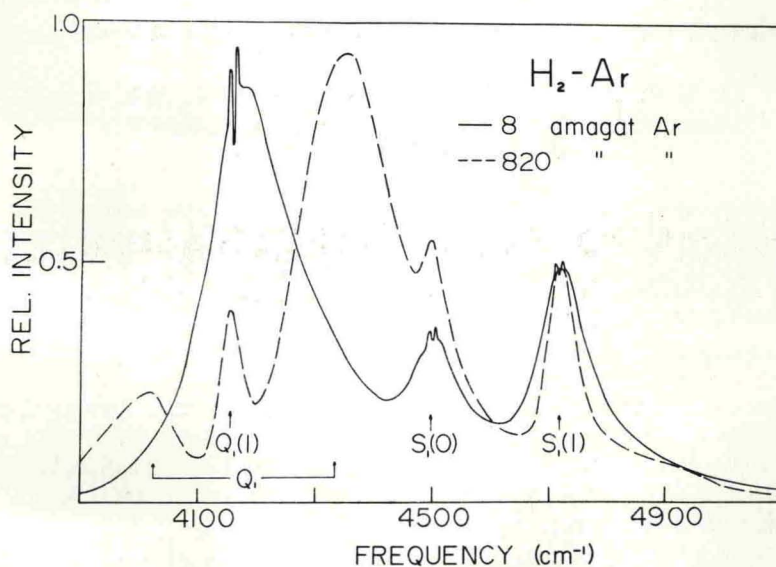


FIG. 1. The enhancement of the pressure-induced fundamental band of hydrogen by argon at 152 K for two Ar densities, 8 amagat and 820 amagat. The effect of special interest here is the pressure narrowing of the  $S_1(1)$  line.

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 auto-correlation 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  $55 \text{ cm}^{-1}$  at 8 amagat to  $25 \text{ cm}^{-1}$  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  $\sim 300$  amagat  $\Delta\nu_{1/2}$  remains effectively constant at  $55 \text{ cm}^{-1}$  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,  $\tau_d$ , through the uncertainty relation,  $\Delta\nu_{1/2} \approx (2\pi\epsilon\tau_d)^{-1}$ . 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-

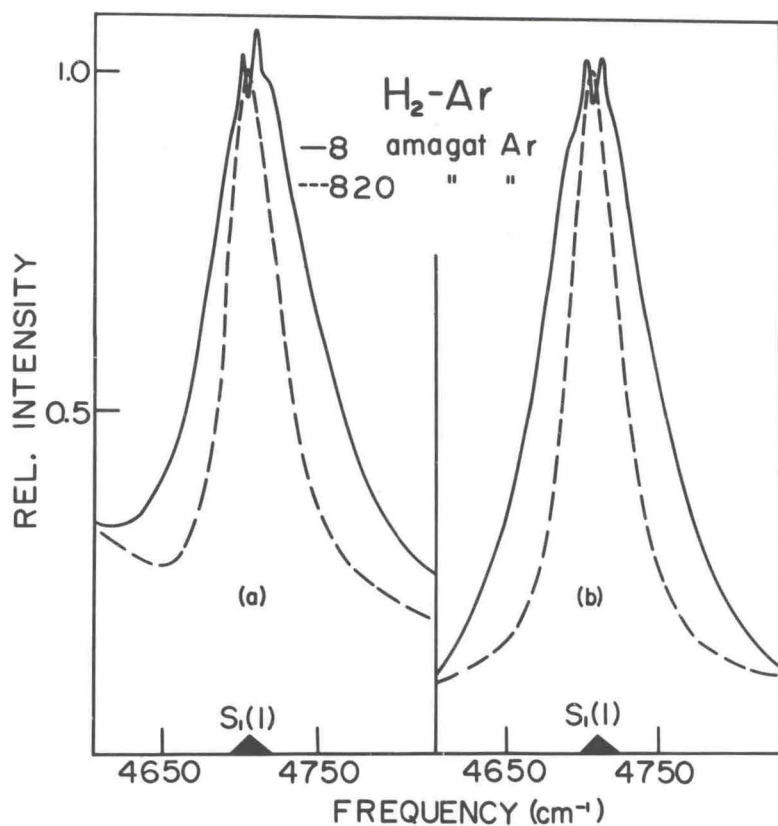


FIG. 2. (a) The observed spectrum in the region of the  $S_1(1)$  line at low and high densities, and (b) the isolated symmetrized  $S_1(1)$  lines.

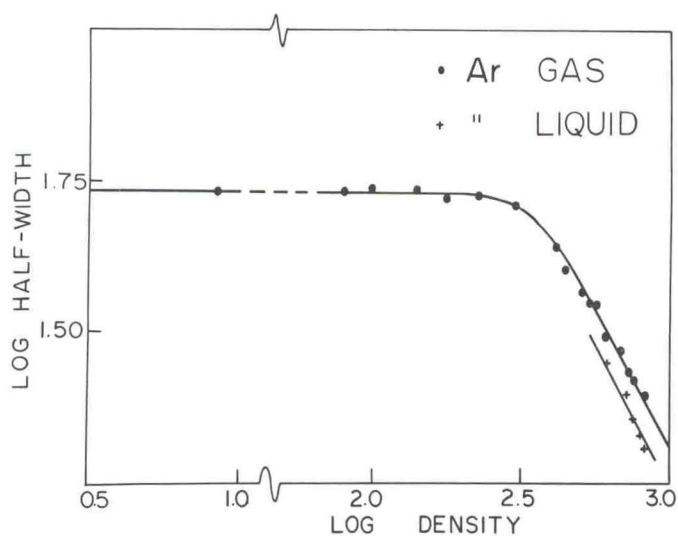


FIG. 3. Variation of the half-width  $\Delta\nu_{1/2}$  of the symmetrized  $S_1(1)$  line of hydrogen with the argon density in gaseous and liquid  $\text{H}_2$ -Ar systems.

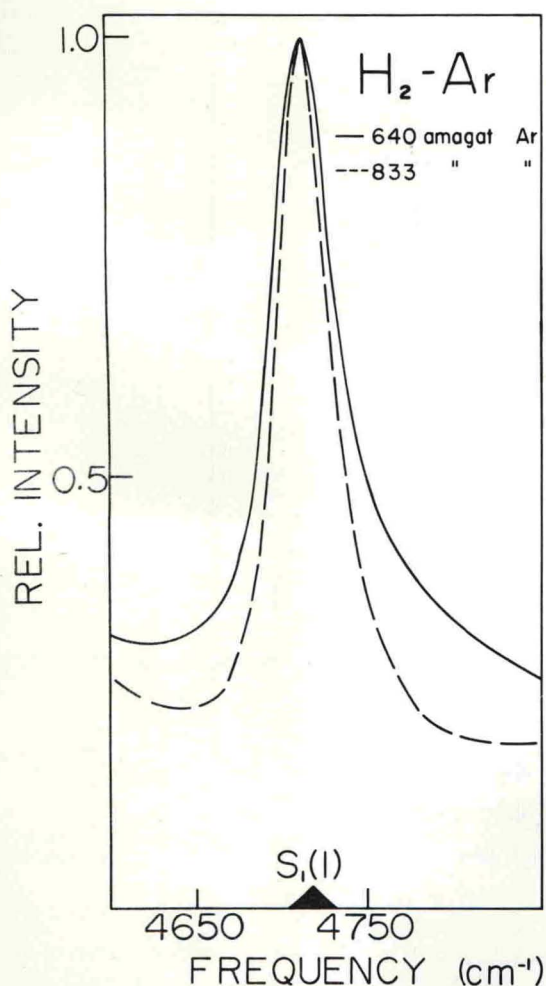


FIG. 4. The region of the  $S_1(1)$  line in the collision-induced spectrum of hydrogen in a liquid  $H_2$ -Ar system at 115 K under pressures of 19 and  $\sim 1500$  atm.

drupolar interaction. At higher densities the collision path of the  $H_2$  molecule is modified by the presence of nearby Ar atoms and the collision duration is effectively increased. As shown by

Zaidi and Van Kranendonk (1971) in the following note, this effect can be treated as a diffusion phenomenon and the experimental value of  $\Delta v_{1/2}$  can be used to calculate the diffusion coefficient of hydrogen in argon at high densities. In particular, their theory gives  $\Delta v_{1/2} \propto 1/\rho_{Ar}$  at high densities in accordance with the experimental result.

It is interesting to note that density narrowing is also present in the  $H_2$ -Ar liquid system and that the diffusion theory of Zaidi and Van Kranendonk seems to be also applicable in this case. The two spectra in Fig. 4 show the  $S_1(1)$  region for the liquid system at two densities, 640 and 833 amagat, obtained by pressurizing the liquid at 115 K up to  $\sim 1500$  atm; a significant narrowing of the  $S_1(1)$  line is evident. Values of  $\Delta v_{1/2}$  for a few densities in the range given above are plotted in Fig. 3. These indicate general agreement with the law,  $\Delta v_{1/2} \propto 1/\rho_{Ar}$ , as was found for the gaseous system. It might also be noted that the line for the liquid falls below that of the gas by an amount which is in good agreement with the  $\sqrt{T}$  variation expected for translational broadening and also for the diffusion coefficient. This emphasizes the essential similarity of collision-induced spectra of liquid and gaseous system which has been pointed out previously by Welsh and Kriegler (1969).

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