

DIRECT SPECTROSCOPIC EVIDENCE OF BOUND STATES  
OF  $(\text{H}_2)_2$  COMPLEXES AT LOW TEMPERATURES\*

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In an experiment designed to obtain indirect evidence for bound states in  $(\text{H}_2)_2$  complexes in hydrogen gas at low temperatures by observing a predicted increase in the collision-induced infrared absorption at temperatures less than  $40^\circ\text{K}$ , the expected diffuse absorption was accompanied by a number of relatively sharp lines. A frequency analysis of these lines showed that they could unquestionably be interpreted as transitions involving bound and virtual states of  $(\text{H}_2)_2$  complexes. The evidence is that there are probably two bound and at least two detectable virtual states in the  $(\text{H}_2)_2$  "molecule," which appears to have a dissociation energy of  $\sim 3.5 \text{ cm}^{-1}$  or  $\sim 10 \text{ cal/mole}$ .

In an earlier experiment<sup>1</sup> the integrated absorption coefficient of the pressure-induced fundamental infrared band of hydrogen was measured in the high-pressure gas over the temperature range  $376\text{--}80^\circ\text{K}$ . The observed rather rapid decrease of the coefficient with temperature was qualitatively explained in terms of the smaller average interaction of collision pairs at lower temperatures. The experimental temperature variation of the absorption was well reproduced over most of the range by Van Kranendonk's theory of pressure-induced absorption.<sup>2</sup> Since the quantum-mechanical corrections to the molecular-pair distribution function used by Van Kranendonk are valid for hydrogen only down to about  $180^\circ\text{K}$ , a completely quantum-mechanical calculation of the function was made by Poll<sup>3</sup> and applied to the problem of the induced fundamental infrared band. These calculations showed that two bound states of the  $(\text{H}_2)_2$  complex could have sufficient population at low temperatures to cause a sharp rise in the absorption coefficient as the temperature decreased below  $30^\circ\text{K}$ . An experiment was therefore designed to show this effect.

An optical path length of 13.6 m was produced by 62 traversals of a multiple-reflection absorption cell immersed in liquid hydrogen at  $20^\circ\text{K}$ . With 1 atm of gaseous hydrogen in the cell the absorption profile of the fundamental band was easily recorded, and the integrated

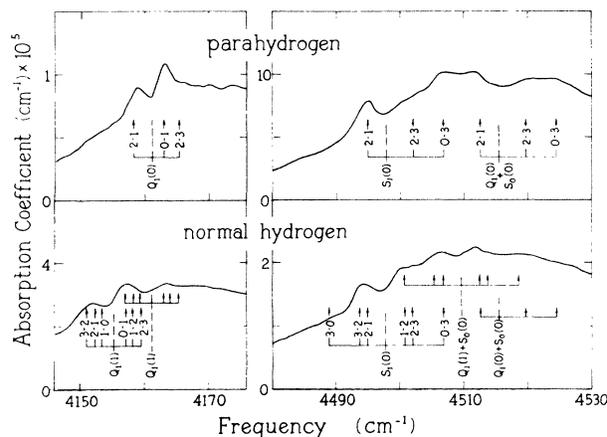


FIG. 1. The infrared spectrum of the fundamental band of gaseous hydrogen (1 atm,  $20^\circ\text{K}$ ) showing transitions ( $l'' \rightarrow l'$ ) between bound states of  $(\text{H}_2)_2$  complexes for (a) parahydrogen and (b) normal hydrogen.

absorption coefficient<sup>4</sup> showed the rise predicted by the theory of Poll. The band profile at lower resolution ( $5 \text{ cm}^{-1}$ ) showed the expected structure<sup>5</sup>; for example, in 98% parahydrogen the main features were a weak  $Q_1(0)$  branch ( $\Delta J=0$ ) and an  $S(0)$  group ( $\Delta J=+2$ ) consisting of the single transition  $S_1(0)$  and the double transition  $Q_1(0) + S_0(0)$ . However, at higher resolution ( $\sim 1 \text{ cm}^{-1}$ ) these rather diffuse features were observed to be accompanied by the finer structure shown in the absorption profiles in Fig. 1.

The analysis of the structure was easily made from the spectrum of parahydrogen [Fig. 1(a)]. The frequencies of the maxima, given in the first column of Table I, can be expressed in the form

$$\nu = \nu_{\text{H}_2} + (\nu_{l'} - \nu_{l''}),$$

where  $\nu_{\text{H}_2}$  is one of the "hydrogen" frequencies  $Q_1(0)$ ,  $S_1(0)$ , and  $Q_1(0) + S_0(0)$ , calculated from the constants of the free molecule. The  $\nu_{l'}$ 's are a set of four frequencies with  $l''=0, 2$  and  $l'=1, 3$ , the observed lines corresponding to the combinations ( $l'', l'$ ) given in the last column of Table I. The new components are

Table I. Fine-structure components in the pressure-induced infrared fundamental of gaseous parahydrogen at 20°K.

Wave number	H <sub>2</sub> transition	(H <sub>2</sub> ) <sub>2</sub> transition <i>l''</i> → <i>l'</i>
4158.9	Q <sub>1</sub> (0)	2 → 1
4163.0	Q <sub>1</sub> (0)	0 → 1
4494.8	S <sub>1</sub> (0)	2 → 1
4501.7(?)	S <sub>1</sub> (0)	2 → 3
4507.4	S <sub>1</sub> (0)	0 → 3
4512.0	Q <sub>1</sub> (0) + S <sub>0</sub> (0)	2 → 1
4519.4	Q <sub>1</sub> (0) + S <sub>0</sub> (0)	2 → 3
4524.0	Q <sub>1</sub> (0) + S <sub>0</sub> (0)	0 → 3

thus combination tones of the hydrogen frequencies as they occur in induced absorption with frequencies which arise from certain definite transitions between four states,  $\nu_0$ ,  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ . The average term values of these states are  $\nu_0 = 0$ ,  $\nu_1 = 1.9$ ,  $\nu_2 = 4.8$ , and  $\nu_3 = 9.1$  cm<sup>-1</sup>.

Since the fundamental band arises from the interaction of two hydrogen molecules, the structure observed can arise only from transitions between discrete levels of an (H<sub>2</sub>)<sub>2</sub> complex. The integer  $l$  introduced above must represent the quantum number of the angular momentum of the relative motion of the two H<sub>2</sub> molecules. In fact, if the term values given above are expressed as  $F(l) = B^{\text{eff}} l(l+1)$ , the values of  $B^{\text{eff}}$  give intermolecular distances in the range 4.2-4.6 Å. As might be expected, because of the large anharmonicity of the vibration of the two H<sub>2</sub> molecules in the intermolecular potential, these values are somewhat greater than the equilibrium distance, 3.3 Å, of the Lennard-Jones potential curve.

The interpretation given is confirmed by the calculations of Cohen *et al.*<sup>6</sup> and of Poll.<sup>3</sup> Using a Lennard-Jones potential these authors found that the (H<sub>2</sub>)<sub>2</sub> complex has two bound states,  $l=0$  and  $l=1$ , lying close to the asymptote of the intermolecular potential. The calculated separation of these states was 1.5 cm<sup>-1</sup>, in good agreement with the value 1.9 cm<sup>-1</sup> obtained from the spectrum. The states with  $l=2$  and  $l=3$  are apparently virtual or resonance states lying immediately above the asymptote of the intermolecular potential, as shown in Fig. 2, which has been drawn with the Lennard-Jones parameters  $\sigma = 2.95$  Å,  $\epsilon = 25.5$  cm<sup>-1</sup>, as given by Michels, De Graaff, and Ten Sel-dam.<sup>7</sup> It will be noted that the 0-1 transition,

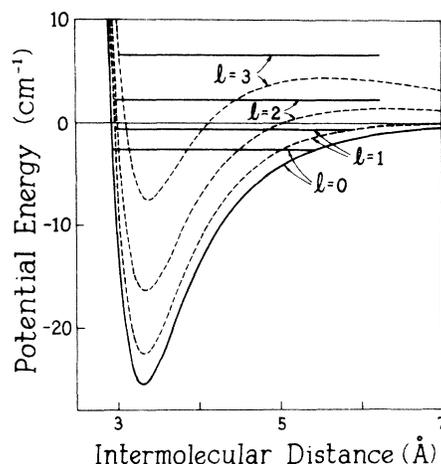


FIG. 2. The observed energy levels of the (H<sub>2</sub>)<sub>2</sub> complex superimposed on the Lennard-Jones potential ( $l=0$ ) and "effective" potential curves for  $l=1, 2$ , and  $3$ . The  $l=0$  level has been placed following the calculation of Poll, but should perhaps be 1 to 2 cm<sup>-1</sup> lower.

involving the two bound states, gives the sharpest line. Transitions involving one virtual state are less sharp, and the 2-3 transitions involving two virtual states are very broad but nevertheless detectable. Experimentally, the asymptote of the intermolecular potential curve thus appears to come between the  $l=1$  and  $l=2$  levels, in accordance with the theory.

The dashed curves in Fig. 2 represent "effective" potential curves given by the equation

$$V(l) = V(0) + l(l+1)h/8\pi^2 \mu c r^2,$$

where  $r$  is the intermolecular distance. When the  $l=0$  level is drawn as shown with a dissociation energy of 2.5 cm<sup>-1</sup>, following the calculation of Poll,<sup>3</sup> the quasibound  $l=2$  and  $l=3$  levels lie somewhat above the rotational barrier of the corresponding effective potential curve. The actual dissociation energy might therefore be as great as 4.5 cm<sup>-1</sup>. It is possible that calculations with an improved model of the intermolecular potential would confirm this.

The selection rules for  $l$ , as revealed by the analysis, are easily explained. With two parahydrogen molecules in the ground vibrational state, the complex (H<sub>2</sub>)<sub>2</sub> can exist for symmetry reasons only in the  $l=0$  and  $l=2$  states. These are the states which are actually observed as initial states. For the upper state of any transition in the fundamental band one of the H<sub>2</sub> molecules is in the  $v=1$  vibrational state, and the complex can presumably exist in any of the  $l$  states. For the transitions

accompanying the induced  $Q$  branch the transition moment is directed along the band, so that the selection rule is  $\Delta l = \pm 1$ , as observed. The  $S$  transitions are produced by quadrupole interaction of the molecular pair and involve the  $J=2$  state of one of the molecules as the final rotational state; from an analysis of the angular dependence of the induced dipole moment (Poll and Van Kranendonk<sup>8</sup>), it follows that the selection rules are  $\Delta l = \pm 1, \pm 3$ , as is observed. It is interesting to note that the transition  $l''=0 \rightarrow l'=1$  is predicted to be much weaker for the  $S$  transitions than for the  $Q$  branch, and is not, in fact, observed for the  $S$  transitions.

Bound-state structure was also observed for normal hydrogen [Fig. 1(b)]. Since the four states are all populated in this case, many more transitions are involved, and the individual transitions are not resolved. The calculated frequencies of the possible transitions for the  $Q$  and  $S(0)$  groups are shown in Fig. 1(b). It is evident that the observed spectrum is in good qualitative agreement with the calculated structure.

If a dissociation energy of  $3.5 \text{ cm}^{-1}$  is assumed for the  $(\text{H}_2)_2$  complex a calculation shows that only about 0.1% of the hydrogen molecules at 20°K are in bound states. This small fraction is, however, sufficient to give a pronounced

increase in the integrated intensity of the fundamental band in the range 40-20°K; this phase of the investigation will be discussed in detail elsewhere.<sup>4</sup>

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## DISTORTED-WAVE CALCULATION OF ROTATIONAL EXCITATION OF $\text{N}_2$ BY SLOW ELECTRONS\*

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Rotational excitation is usually an important energy-loss mechanism for low-energy ( $\lesssim 1 \text{ eV}$ ) electrons in a slightly ionized gas, and can be very significant in determining its electrical properties. For  $\text{N}_2$ , which is probably of greatest practical interest, there have existed some uncertainties in the value for the rotational cross section and some discrepancies between theory and experiment. This note shows that these difficulties can be resolved.

The theoretical expression widely used for the rotational cross section is that computed

by Gerjuoy and Stein<sup>1</sup> using the first Born approximation for a rigid-rotator molecule with an effective electron-molecular interaction  $V(\vec{r})$  due entirely to the electric quadrupole interaction. The GS expression is proportional to  $Q^2$ , where  $Q$  is the quadrupole moment of the molecule. A careful analysis of swarm experiments gives very good agreement with the GS theory if a value<sup>2</sup>  $|Q| = 1.04$  in units of  $ea_0^2$  is assumed for  $\text{N}_2$ . Quite recently the large differences between various experimental and theoretical values of  $Q$  have been resolved by