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Broad infrared absorption feature in solid D_2 and H_2 containing tritium

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A new infrared absorption feature in the low-temperature spectrum of solid D_2 and H_2 containing small amounts of tritium has been observed. The absorption can be interpreted as being due to electrons in bubblelike structures with diameters of approximately 9 Å.

We have observed a broad infrared absorption feature in solid D_2 and solid H_2 containing small amounts of radioactive tritium. The absorption, which is absent in pure samples of H_2 and D_2, occurs in the spectral region between $\nu = 4000\ \mathrm{cm}^{-1}$ and $\nu = 7000\ \mathrm{cm}^{-1}$ [Figs. 1(a) and 1(b) in which the absorption coefficient α is given by $\alpha = (1/l) \times \ln(I_0/I)$, where l is the path length]. The experimental method for obtaining these absorption spectra is essentially the same as that described in a previous publication.[1] The D_2 spectrum in Fig. 1(a) clearly shows some structure and appears to consist of two broad lines. A similar situation probably exists in H_2, shown in Fig. 1(b); however, the data below about $4500\ \mathrm{cm}^{-1}$ are much more unreliable than the rest of the spectrum because of the decrease of the emission of the quartz-halogen lamp used as a light source. This absorption does not occur in the pure D_2 or H_2 solid and is therefore due to the presence of the tritium impurity. In either case the effect only occurs if the temperature of the solid is sufficiently low. The results in Fig. 1 both refer to a sensor temperature of 4.7 K; the sample temperature is 5 to 6 K. We find that the absorption for a given T_2 concentration increases with the tritium irradiation time of the low-temperature solid. This effect is shown in Fig. 1(a) for the case of D_2; it also occurs in H_2. Note that it takes about 10 min to record a spectrum, and the shorter irradiation time shown in Fig. 1(a) therefore refers to a period of approximately 10 min. After 120 min no further change takes place; i.e., an equilibrium situation has been established.

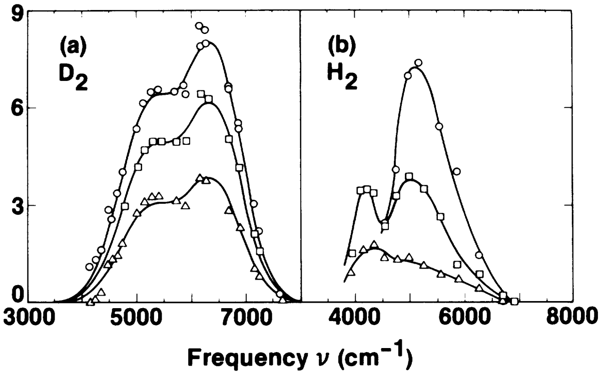

FIG. 1. Infrared absorption of tritium-doped solid hydrogen at 5 to 6 K. (a) refers to solid D_2 with 0.3% T; the curves of increasing intensity are for irradiation times of 10–20 min, 35–40 min, and 120 min, respectively. (b) refers to solid H_2; the curves of increasing intensity are for 5.5% T at 90 min, 7% T at 15 min, 16% T at 70 min, respectively.

The effect of different T_2 concentrations (at approximately the same irradiation times) is shown for the case of H_2 in Fig. 1(b). A similar situation occurs in D_2 except for the fact that the concentration of T_2 required for a similar absorption in D_2 is about two orders of magnitude smaller than that for H_2 [c.f. Fig. 1(a)]. The absorption in pure T_2 is so strong that with our 8-mm cell the signal is saturated and therefore no absorption coefficient can be determined.[1]

Of the two spectra in Fig. 1 the absorption in D_2 is much more accurate and forms the basis of the analysis which follows. It turns out that the absorption coefficient can be represented quite accurately by the sum of two Gaussians [indicated by the lines in Fig. 1(a)]. The width of these Gaussians is the same for the two lines and is also independent of the irradiation time; the full width at half height is $1200\ \mathrm{cm}^{-1}$ and the central wave numbers ν_1 and ν_2 are 5200 and $6400\ \mathrm{cm}^{-1}$. The strength of these lines is given by $S = \int \alpha(\nu)d\nu/\nu$, and the ratio S_1/S_2 for the two lines is also independent of the irradiation time. It is found that $S_1/S_2 = 0.75$ and $S = S_1 + S_2 = 1.7\ \mathrm{cm}^{-1}$ in the limit of long times [the upper curve in Fig. 1(a)].

We have previously reported on some other spectral features that are associated with the presence of T_2 radiation in host lattices of solid hydrogens.[2,3] The difference between those previously reported lines and the ones under discussion here is that the former are transitions which take place in the host molecules of the lattice, whereas the latter have, in all likelihood, no relation to the transitions in the host molecules. This is most clearly evident in the case of D_2 where the observed absorption takes place in a spectral region far removed from that of the molecular host species. For H_2 the absorption does partly overlap the region of the fundamental band but we regard this as not significant in this context. What is of significance is that the absorptions in D_2 and H_2 occur at roughly the same frequency and are therefore expected to be due to the same mechanism.

The previously observed lines were interpreted as being due to transitions between levels of host molecules that are Stark shifted by the electric field of ions created during the radioactive decay process of tritium; we refer to such transitions as "charge-induced" transitions. The charges responsible for this induction effect were considered to be those of positive ions and of electrons. It was argued that the electrons were located in holes or bubbles in the host lattice which are formed by balancing the electron zero-point energy with the bubble formation energy. If this interpretation is correct one would also expect to see absorption by the electron in its associated "box." The model of an electron trapped in a bubblelike structure in either a liquid or a solid is well known and has been discussed before; of particular interest is the case of electron bubbles in liquid helium[4] and in liquid and solid hydrogen.[5]

In line with the remarks just made, the simplest possible description would therefore be that of an electron in a box. In our previous work[3] we deduced a bubble diameter of 9.4 ± 1 Å from the measured Stark shifts of the D_2 molecule. Bubbles of this size also give rise to absorption by the electron of roughly the right frequency as is observed in the present work. To show this we consider the highly oversimplified case of an electron in a rectangular box of square cross section with dimensions $d_1 \times d_1 \times d_2$. The reason for considering a rectangular instead of a cubical box is the fact that the lattice is anisotropic with a different elastic constant along the c axis as compared with that perpendicular to it. Note that in a rectangular box the first excited state is slightly split, and under those conditions we would expect two closely spaced absorption lines as is observed. In addition, it is to be expected that the size of the box, which is mainly determined by the zero-point energy, is not the same in the ground state and in the first excited state. We have determined the increase of the box size in these two states from the requirement that the zero-point pressure be the same in both. We find that in the excited state all dimensions are increased by 15% as compared with those in the ground state. From the two frequencies ν_1 and ν_2 we can determine the size of the box in the ground state and find $d_1 = 8.7$ Å and $d_2 = 9.3$ Å. It is seen that the size of the box arrived at in this way from the electron spectrum agrees very well with that obtained earlier from the Stark shift of the D_2 molecule. This suggests that the present absorption is indeed due to electrons localized in a bubblelike structure. As pointed out above the size of the box in the excited state is 15% larger than that in the ground state, i.e., $d_1' = 10.0$ Å and $d_2' = 10.7$ Å. An electronic transition between two states with a different size of box is only possible if the nuclear coordinates do not change upon such a transition. This is analogous to the situation for electronic transitions in molecules which are governed by the Franck-Condon principle. Taking into account the fact that the size of the box is itself subject to a zero-point motion of the same order of magnitude as that of the unperturbed lattice it is clear that transitions can indeed take place.

The ratio of the intensities S_1 and S_2 of the two components making up the observed absorption feature is given by $d_2^2/2d_1^2$ in our model. Having determined d_1 and d_2 from the position of the lines, the ratio S_1/S_2 is predicted to be 0.6; as mentioned above the value obtained from our fitting procedure is 0.75. Considering the simplicity of the model used we regard this as satisfactory.

The total absorption intensity, which is given by

$$S = n\frac{4\pi^2}{3hc}\sum |\langle n_1n_2n_3|\vec{\mu}|n_1'n_2'n_3'\rangle|^2 \ , \tag{1}$$

allows us to determine the density of electron bubbles n; it is found to be 2×10^{16} or about 1 ppm. This number is of the same order of magnitude as the positive ion density which was obtained previously from the intensity of the Stark-shifted D_2 absorption. In expression (1), the quantity $\langle n_1n_2n_3|\vec{\mu}|n_1'n_2'n_3'\rangle$ denotes the matrix element of the electronic dipole moment between the electron-in-a-box states; the summation is over all states contributing to the observed intensity.

For simplicity, the intensity calculations above were done for a nonexpanding box, and for this reason the results should be regarded as order-of-magnitude estimates only. The main difference with the calculation including the expansion of the box would be the appearance in expression (1) of a Franck-Condon factor. Because this factor is smaller than 1, the value obtained for n should be regarded as a lower limit; it might well be an order of magnitude larger. In addition, the Franck-Condon factor for the ν_1 transition must be larger than that for the ν_2 transition. This will have the effect of increasing the calculated ratio S_1/S_2 above the value of 0.6 obtained before.

It is clear that it is also possible to describe the appearance of two lines in terms of two different kinds of holes each with a slightly different size. Taking these holes to be spherical and assuming the zero-point pressure to be the same in the ground and first excited states as before, we find diameters of 10 and 11 Å which are similar to the values obtained above.

As pointed out above the total intensity of the absorption increases with time and finally saturates [cf. Fig. 1(a)]. It turns out that the integrated intensity can be represented to within experimental accuracy with the expression

$$S = S_1(1-e^{-t/\tau_1}) + S_2(1-e^{-t/\tau_2}) \ ,$$

where $S_1 = 1.42\ \text{cm}^{-1}$, $S_2 = 0.28\ \text{cm}^{-1}$, $\tau_1 = 2.5\times10^3$ s, and $\tau_2 = 5\times10^2$ s. Less-accurate data taken at a higher temperature (sensor temperature 7.1 K) indicate a single-exponential behavior with a value for τ_1 of approximately 5×10^2 s.

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