Interference effects in the charge-induced spectrum of $\text{H}_2$ at 4.2 K

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The fundamental vibrational infrared-absorption spectrum of solid $\text{H}_2$ at 4.2 K has been measured while the sample was irradiated with a 15-MeV proton beam. The Stark-shifted molecular transitions resulting from molecules that are the nearest neighbours of localized electrons have been observed and are contrasted with the same transition previously observed in solid $\text{D}_2$. The differences are interpreted as evidence of an interference between the dipole of the localized electron and the charge-induced molecular dipole, a result of a coincidence in the frequencies of the molecular and electronic transitions.

On a mesuré le spectre d’absorption infrarouge vibrationnel fondamental de $\text{H}_2$ solide à 4.2 K, pendant que l’échantillon était irradié par un faisceau de protons de 15 MeV. Les transitions moléculaires avec déplacement Stark qui proviennent des molécules qui sont les plus proches voisines d’électrons localisées ont été observées et mises en contraste avec les mêmes transitions observées antérieurement dans $\text{D}_2$ solide. Les différences sont interprétées comme la preuve d’une interférence entre le dipôle de l’électron localisé et le dipôle moléculaire induit par la charge, par suite d’une coïncidence entre les fréquences des transitions moléculaire et électronique.

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1. Introduction

Recent experiments, in which the absorption spectra of polycrystals of solid hydrogens were recorded during (and after) irradiation by high-energy charged particles, have revealed a new kind of induced spectrum, thought to be due to the presence of free charges and thus called charge-induced spectra. In one type of experiment (1, 2), tritium was used either as a pure crystal or as a small admixture with another hydrogen. In these experiments the radiation was provided by the $\beta$-decay of the tritium. In the second type of experiment (3), a proton beam from an accelerator was used to irradiate the hydrogen polycrystalline sample.

In both types of experiments at temperatures below about 12 K, up to three new absorption lines were observed in the fundamental rotation–vibration band of the sample’s molecules. An example of such a spectrum is shown in Fig. 1 (adapted from ref. 3) for the case of proton irradiation of $\text{D}_2$ at 4.2 K. In all cases, one line (A) was observed to shift between 100 and 200 cm$^{-1}$ to lower frequency from the vibrational $Q$ line; another line (B) shifted between 10 and 20 cm$^{-1}$ to lower frequency from the $Q$ line, and a third weak line (D) shifted a similar amount to lower frequency from the $S_v$ (0) rotational line. Another very weak feature, originally labelled $C$, is sometimes observed between $A$ and $B$ (2).

The effect of the high-energy radiation is to ionize the hydrogen molecules; the new lines in the spectrum are interpreted as the Stark-shifted molecular transitions in the nearest neighbour molecules of the positively and negatively charged ionization fragments. For example, if the crystal is one of $\text{D}_2$, the A line is believed to be caused by vibrational transitions in $\text{D}_2$ host molecules around a $\text{D}_2^+$ ion. The large polarization energy of the ion–molecule pairs draws the nearest neighbour molecules into a distance of 2.4 Å from the ion; this distance is considerably less than the lattice spacing of $\text{D}_2$, which is 3.6 Å. The much smaller shift of the $B$ line from the $Q$ line indicates a charge–molecule separation of 5.5 Å, a distance greater than the lattice spacing. This is taken as evidence that the negative charge is an electron trapped in a bubblelike structure whose dimensions are determined by the polarization of the lattice and the zero-point motion of the electron (4). The $D$ line is the Stark-shifted rotational transition (analogous to the $S_v$ (0) transition) in the nearest neighbour molecules of the electron. Similarities of the timing of the growth and decay of the $B$ and $D$ lines confirm this interpretation, which attributes both to the same kind of charge centre (5).

![Fig. 1. The fundamental vibrational band of solid $\text{D}_2$ at 4.2 K. (a) with no proton-beam irradiation, (b) with the proton beam.](image-url)
Further confirmation of the electron-in-a-bubble model for the B and D lines was the observation (5-7) of the optical absorption of the electron itself. The frequency of this broad absorption gives a bubble radius of about 5 Å, in good agreement with that obtained from the Stark shift of the B line (7). The timing of the onset and decay of this electron-absorption further confirms this interpretation (5).

A remarkable feature of these new absorption lines is their persistence for long times following irradiation at very low temperatures. Detailed timing measurements can only be made in the case of the proton-beam irradiated samples (3, 5); and, for the case of D2 at 4.2 K, the B, D, and electron-absorption features grow to saturation in times on the order of a few minutes but decay, after turning off the beam, with times in the order of a few hours. At least in the case of D2, the charged species seem to be very stable. If, however, the temperature is raised to about 11 K, the features vanish very rapidly.

The frequency of the electron absorption depends only on the properties of the electron and on the elastic constants of the hydrogen lattice; the latter differ very little among the various isotopic species. Therefore, the electron absorption should appear at roughly the same frequency for all six molecular solids: H2, HD, HT, D2, DT, and T2; in D2 it lies between 4000 and 7000 cm⁻¹. The fundamental vibrational bands of the molecules occur at frequencies that vary with the molecule considered, ranging between 2458 cm⁻¹ for the Q line of T2 to 4150 cm⁻¹ for H2. A unique situation occurs for H2 in which the fundamental vibrational band and the electron-absorption frequencies overlap, thus creating the possibility of interference between the dipole of the localized electron and the charge-induced dipole in the host H2 molecules.

In this paper we report on observations of the charge-induced spectra in solid H2 at 4.2 K induced by proton-beam irradiation and contrast these with previously obtained results in other crystals, principally D2.

2. Results

The method of obtaining the spectra was identical with that used for the observation of the electron-absorption spectrum in D2 (5). An example of the spectra obtained is shown in Fig. 2 for the case of H2 at 4.2 K under irradiation with a 45-nA proton beam 15 MeV in energy. Figure 2a is the well-known spectrum of solid hydrogen with no external radiation; some of the spectral features are identified in the figure. Figure 2b is a spectrum of the same sample during irradiation. Comparison of Figs. 2a and 2b shows clear evidence of a new feature (B) to the low-frequency side of the Q1(1,0) line and a small change (D) to the low-frequency side of the Q1(1,0) + S0(0) line. There may also be a similar feature to the low-frequency side of the S0(1) line, but the evidence is not conclusive on the basis of the data of Figs. 2a and 2b alone. The inset in Fig. 2b is an expanded version of the region of the B feature.

Figure 3 shows two spectra taken over a broader spectral region than in Fig. 2; the plot is also expanded in the vertical direction so that the details of the spectral peaks are lost. The solid curve is for the nonirradiated sample, and the dashed curve is the spectrum under proton irradiation. It is clear that in addition to the B spectral feature, there is a broad absorption extending from below 4000 cm⁻¹ to about 7000 cm⁻¹; this is the electron absorption previously reported for D2 (5).

Comparison of Figs. 1 and 2 shows that the features produced by the irradiation are quite different for the case of H2 as compared with that for D2. For D2 (and also for T2, HT, DT, and HD with β-irradiation), the charge-induced features appear as symmetric absorption lines, whereas for H2, the B line appears quite asymmetric. In addition, there is no evidence of the A feature in the H2 spectra at any beam current used.

An even more striking contrast between H2 and D2 is in the timing of the onset and decay of the B-line and electron-line features. With the monochromator tuned to the position of maximum absorption, data are acquired at half-second (D2) or quarter-second (H2) intervals. Twenty channels of data are collected before the beam is turned on, and the mean of these
values yields \( I_0 \). The beam is terminated at some predetermined time (defined as zero), and both the turn-on and turn-off of the beam are performed without interrupting data acquisition. Figure 4 shows a comparison of the \( B \)-line timing curves for \( \text{H}_2 \) and \( \text{D}_2 \). As mentioned earlier, the turn-on and turn-off times in \( \text{D}_2 \) are a few minutes and a few hours respectively. In \( \text{H}_2 \) the turn-on times are shorter by a factor of two or three, but the turn-off times are reduced from a few hours to one or two minutes. We interpret this to mean that the charges in \( \text{H}_2 \) are much more mobile than those in \( \text{D}_2 \) at the same temperature.

### 3. Discussion

As discussed in a previous publication (2), we propose that the ions responsible for the observed lines are formed in a two-stage process. For the case of \( \text{H}_2 \), for example, in the first stage the beam produces \( \text{H}_2^+ \) ions and electrons, which both have a relatively high mobility in the lattice. In the second stage some of these ions and electrons become localized and therefore are able to produce Stark-shifted absorption lines. The localization of the positive ion probably takes place via the reaction

\[
\text{H}_2^+ + \text{H} \rightarrow \text{H}_2 + \text{H}^+
\]

where the \( \text{H}_2^+ \) ion (not being subject to resonant charge transfer with its neighbours) will have a very low mobility. The localization of the electron is assumed to take place via a lattice imperfection (for example, a vacancy), which allows the electron to form a bubble-like disturbance of the lattice with, presumably, a very low mobility. A similar mechanism will operate in \( \text{D}_2 \).

The experimental results discussed in the previous section, however, suggest that the mobility of the localized beam-induced charges is much higher in \( \text{H}_2 \) than in \( \text{D}_2 \). We would therefore expect that, at a given beam current, the populations of localized positive ions and electrons will be smaller in \( \text{H}_2 \) than in \( \text{D}_2 \). In \( \text{D}_2 \) the integrated intensity of the \( B \) line is about five times larger than that of the \( A \) line, but the induced dipoles responsible for the \( A \)-line absorption are much larger than those for the \( B \)-line absorption. This is because these dipoles are of magnitude \( \alpha q / R \), where \( \alpha \) is the polarizability of the molecules, \( q \) is the ion (or electron) charge, and \( R \) is its separation from the molecule.

We therefore conclude that the number of absorbing, positive ion sites is considerably smaller than the number of localized electrons in \( \text{D}_2 \). Apparently the same situation prevails in \( \text{H}_2 \), where no \( A \) line is observed at all. This indicates that an insufficient population of localized positive ions are observable within the accuracy of the beam experiment.

The presence of electron absorption and a feature at the \( B \)-line position in \( \text{H}_2 \) indicates an observable, localized, electron density. As mentioned in the previous sections, the electron absorption is considerably weaker than in the case of \( \text{D}_2 \).

The most interesting difference between the electron and \( B \)-line absorption spectra in \( \text{D}_2 \) and \( \text{H}_2 \) is the asymmetric shape of the \( B \) line in \( \text{H}_2 \). Since \( \text{H}_2 \) is the only case in which the \( B \) line and the electron absorption overlap in frequency, it is natural to assume that this effect is due to an interaction between the vibrational degrees of freedom of the molecules that are responsible for the \( B \)-line absorption and the electronic degrees of freedom, which, together with the localized lattice vibration, are responsible for the broad electron absorption.

To understand the asymmetric line shape in more detail, it should be noticed that, at frequencies near the \( B \)-line feature in \( \text{H}_2 \), there are two possible types of states that can be excited. The first type of state is one in which the electron in a bubble is in its ground state and one of the surrounding molecules is in an excited vibrational state. In the second type of state, it is the electron that is excited and the molecules that are all in their ground vibrational states. In the ground state, both the electron and the molecules are in their lowest states.

The electron absorption is caused by transitions between the ground state and the excited state \( \Psi_E \) in which the electron is excited. These states form a quasi-continuum owing to localized lattice vibrations, and the transitions to them give rise to the broad electron absorption. The transition dipole is given by \( \mu_e = er \), where \( r \) is the displacement of the electron from the centre of the bubble. This dipole does not give rise to transitions to the second type of excited states because it does not connect different vibrational states of the molecules. The charge-induced dipole is \( \mu_i = \alpha E \), where \( E \) is the electric field caused by the electron at the position, \( R \), of the molecule measured with respect to the centre of the cavity. This dipole does connect these states, and it gives rise to the \( B \)-line absorption. In contradistinction to the electron absorption, this absorption is quite sharp because it only involves two vibrational molecular states, viz., the ground state and the upper state \( \phi \), which can be regarded as being essentially discrete. This is the situation that is observed in \( \text{D}_2 \). In \( \text{H}_2 \) the discrete state \( \phi \) is resonant with the continuum \( \Psi_E \), and any interaction that mixes these states will allow absorption to take place via the cross product of the dipoles \( \mu_e \) and \( \mu_i \). In \( \text{H}_2 \), as pointed out earlier, the situation is such that the \( B \)-line intensity itself is expected to be either very small or perhaps negligible. The term that is caused by the cross product (or interference) between \( \mu_e \) and \( \mu_i \) is much larger than the pure \( B \)-line intensity, which is proportional to \( \mu_i^2 (\mu_e / \mu_i)^{-10^{-2}} \), and therefore allows a \( B \)-line feature to appear in \( \text{H}_2 \) that otherwise would be too weak to be observed. This feature is expected to be of roughly the same width as the \( B \) line itself, but...
has a special shape that is associated with the interaction of a
discrete state with a continuum.

Among the interactions that couple the discrete state \( \phi \) and
the continuum \( \Psi_E \), the dominant one is the polarization
interaction between the electron and the molecules, \( 1/2 \propto E^2 \)
(8). The electric field is of the form

\[
E = \frac{q}{|R - r|} = \frac{q}{R^2} + \frac{2r \cdot R}{R^4} + \ldots
\]

The term corresponding to \( q/R^3 \) in \( 1/2 \propto E^2 \) is the main term
responsible for the Stark shift of the molecular levels, whereas
the next term involving \( r \) does not contribute to the Stark shift
because the expectation value of \( r \) over any state of the electron
in the bubble is zero; it does, however, connect the states \( \phi \) and
\( \Psi_E \). It should be noted that this coupling term does not connect
the states \( \Psi_E \) among themselves. This situation, in which a
discrete state interacts with a continuum and in which the
continuum states themselves are not coupled, is completely
analogous to the phenomenon of autoionisation described in a
classic paper by Fano (9). There it is shown that such an
interaction gives rise to a characteristically asymmetric line
shape that has become known as a “Beutler-Fano lineshape.”
This is actually the shape that is observed for the \( B \) line of
hydrogen. Details of the calculation that has only been outlined
here will be published separately.

4. Summary

The charge-induced spectrum of solid H\(_2\) in the fundamental
band at 4.2 K under 15-MeV proton-beam irradiation has been
presented and compared with the analogous spectrum in D\(_2\). H\(_2\)
is unique among the hydrogens in that two different charge-
induced features, viz., the Stark-shifted lines of the fundamental
band and the broad electron absorption, are accidentally
coincident. While both of these features taken separately are
much weaker in H\(_2\) than in D\(_2\), the accidental coincidence gives
rise to an interference line shape that is quite prominent and
occurs at the expected position of the \( B \) line. The interpretation
that the interference is caused by a polarization interaction
between a trapped electron and a neighboring molecule not
only explains the otherwise anomalous line shape of the \( B \)
feature, but is consistent with our failure to observe a similar
line shape at the A-line position.

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