# Correct Assignment of the Hydrogen Vibrations of the Donor-Hydrogen Complexes in Si: A New Example of Fermi Resonance

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(Received 18 September 1995)

Three vibrational bands have been reported for the donor-H complexes in Si. The frequencies of two of these bands have been the benchmark for calculations of the structure of these complexes while the assignment of the third has been controversial. A new assignment of the vibrational spectra, based upon a Fermi resonance between the second harmonic of the hydrogen-wagging mode and the stretching fundamental, explains the presence of all three vibrational bands without the need for additional charge states or defect species that have been suggested previously.

PACS numbers: 78.30.Hv, 61.72.Ji

The passivation of defects and impurities in semiconductors by hydrogen has been studied intensely in recent years, with the dopant-hydrogen complexes being the best understood model systems [1–3]. Studies of the hydrogen vibrations of the defect complexes, coupled with theoretical calculations, have been responsible for much of the rapid progress in this field. The determination of the structure of the donor-H complexes in Si has provided an example of the power of this approach. The hydrogen vibrational spectra of P-H, As-H, and Sb-H in Si (Ref. [4]) consists of three bands observed near 810, 1560, and 1660 cm$^{-1}$ for each of the complexes. The 810 and 1560 cm$^{-1}$ bands were assigned to the H-wagging and stretching modes, respectively. (There are corresponding bands for the donor-D complexes.) The vibrational frequencies were found to be nearly independent of the donor which was taken as support for the defect structure originally proposed by Johnson, Herring, and Chadi [5] that is shown in Fig. 1(a) for Sb-H. Several groups have performed theoretical calculations of the vibrational frequencies [6–11] and have obtained results in good agreement with the experimental values to support and further refine the structural model. The assignment of the 1660 cm$^{-1}$ band has been controversial. Bergman *et al.* [4] suggested that the 1660 cm$^{-1}$ band might be due to a complex that involves the donor, H, and a plasma damage defect. Estreicher and Jones [10] have suggested that it might be due to an additional (positive) charge state of a donor-H complex. Korpas, Corbett, and Estreicher [12] and Liang, Haas, and Niesen [13] have suggested that there should be donor-H$_2$ complexes; these would present still another possibility for additional hydrogen modes. Given the important role the vibrational frequencies have played as the benchmark for theory and the suggested assignments of the 1660 cm$^{-1}$ band, it is essential that the hydrogen modes be correctly assigned.

In this paper, we present a new assignment [14] of the 1560 and 1660 cm$^{-1}$ vibrational bands of the donor-H complexes in Si and provide new data that help to confirm it. An important clue comes from the recognition that the second harmonic frequency of the H-wagging mode, $\omega_{2w} \approx 2 \times 810$ cm$^{-1}$, lies between the two high frequency bands. This suggests that if the second harmonic of the wagging mode and the H-stretching-mode fundamental were weakly coupled by anharmonic interactions, then vibrational transitions to these modes would *share the intensity of the allowed transition* to the H-stretching mode and give rise to both the 1560 and 1660 cm$^{-1}$ bands. The situation is similar for the donor-D complexes. This effect is well known as Fermi resonance in molecular spectroscopy [15–17] and has permitted Watkins *et al.* [18] to explain an anomalous isotope effect observed by Pajot *et al.* [19] for the D-stretching vibrations of the $^{11}$B-D and $^{10}$B-D complexes in Si.

Samples for our experiments were prepared by the implantation of P, As, or Sb into floating-zone Si wafers with ion energies of 30, 100, and 200 keV and a typical

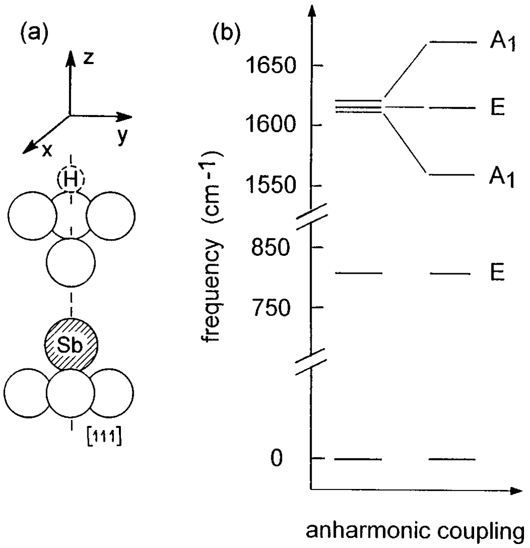

FIG. 1. (a) Structure of the Sb-H complex in Si. (b) Energy level diagram for the donor-H complexes in Si. The positions of the decoupled frequencies are shown on the left. The effect of a weak anharmonic perturbation is shown on the right.

0031-9007/96/76(7)/1154(4)$06.00

dose of $10^{15}$ cm$^{-2}$ for each energy. Following an activation anneal of 1150 °C for 30 s, the implanted wafers were exposed to an $H_2$ or $D_2$ plasma for up to 6 h at 120 °C. Infrared absorption spectra were measured at a resolution of 2 cm$^{-1}$ with a Bomem DA3.16 spectrometer equipped with an Infrared Laboratories 4.2 K bolometer with a cold filter. This detector has a flat baseline throughout the spectral range of interest which allowed the areas of broad absorption bands to be measured more accurately than in the previous study of the donor-H complexes. A list of the vibrational bands observed for the donor-H and donor-D complexes and their areas, relative to the area of the wagging band, is shown in Table I. The band areas differ substantially from those reported previously [4], especially for the 1660 cm$^{-1}$ band, because the earlier measurements were subject to large errors that resulted from estimating the baselines. New weak bands have also been observed near 1616 cm$^{-1}$ for the hydrogenated samples.

An energy level diagram for the hydrogen modes of the donor-H complexes is shown in Fig. 1(b). The presumed hydrogen mode frequencies are shown on the left for the approximation that there is no anharmonic coupling between the modes. The H-stretching mode transforms like the $A_1$ representation of the trigonal point group and the H-wagging mode transforms like $E$; the corresponding energy levels are shown by the high frequency line near 1620 cm$^{-1}$ and the line near 810 cm$^{-1}$, respectively. The second harmonic of the wagging mode transforms like the symmetrized product $E \times E$, or in terms of irreducible representations, $A_1 + E$ (Ref. [20]). These accidentally degenerate $A_1$ and $E$ components of the second harmonic of the wag can be split by anharmonic terms in the potential [16,17] and are shown by the two lower lying levels near 1620 cm$^{-1}$ in Fig. 1(b). We now consider the effect of anharmonic interactions that can mix and shift the modes. Only modes that transform like the same irreducible representation can be coupled by anharmonic terms in the potential. For the states shown in Fig. 1(b), the H-stretching fundamental and the $A_1$ component of the second harmonic of the wag can be mixed, as is shown on the right in Fig. 1(b).

TABLE I. Frequencies and band areas (which are proportional to the transition's intensity) for the hydrogen and deuterium modes observed in Si samples implanted with P, As, or Sb and exposed to $H_2$ or $D_2$ containing plasmas. The frequency units are cm$^{-1}$. The band areas are given relative to the band near 810 cm$^{-1}$ for the donor-H complexes and to the band near 585 cm$^{-1}$ for the donor-D complexes. Spectra were measured near 4.2 K.

| | $H_2$ plasma | | $D_2$ plasma | |
|---|---|---|---|---|
| | Frequency (cm$^{-1}$) | Relative strength | Frequency (cm$^{-1}$) | Relative strength |
| P | 809.5 | 1 | 584.7 | 1 |
| | 1555.4 | 0.62 | 1141.5 | 0.42 |
| | 1615.5 | 0.04 | | |
| | 1645.5 | 0.92 | 1215.5 | 0.98 |
| As | 809.9 | 1 | 584.4 | 1 |
| | 1561.0 | 0.61 | 1143.1 | 0.39 |
| | 1617.0 | 0.02 | | |
| | 1661.4 | 0.98 | 1222.0 | 1.29 |
| Sb | 809.5 | 1 | 584.4 | 1 |
| | 1561.8 | 0.65 | 1142.7 | 0.43 |
| | 1616.7 | 0.02 | | |
| | 1670.6 | 0.85 | 1218.1 | 1.04 |

The vibrational wave functions are labeled by the quantum numbers of the transverse H-wagging modes, $n_x$ and $n_y$, and of the longitudinal H-stretching mode, $n_z$. The wave functions for the component of the second harmonic of the wagging mode and the H-stretching fundamental that transform like $A_1$ can then be written as

$$|2w\rangle = (1/\sqrt{2})\,(|200\rangle + |020\rangle) \tag{1}$$

and

$$|s\rangle = |001\rangle, \tag{2}$$

respectively. The lowest order term of the anharmonic perturbation that can couple these wave functions is the cubic term,

$$H' = k_3(x^2 + y^2)z\,, \tag{3}$$

where the displacement coordinates are defined in Fig. 1(a). The energies of the coupled modes are given by the eigenvalues, $E_\pm$, of the following perturbation matrix, and the wave functions are given by the corresponding eigenvectors, $\alpha_\pm|s\rangle + \beta_\pm|2w\rangle$,

$$\begin{pmatrix} E_s - E_\pm & \eta \\ \eta & E_{2w} - E_\pm \end{pmatrix} \begin{pmatrix} \alpha_\pm \\ \beta_\pm \end{pmatrix} = 0\,. \tag{4}$$

Here $E_s$ and $E_{2w}$ are the decoupled energies of the H-stretching mode and the second harmonic of the wagging mode, respectively. $E_{2w}$ is related to the wagging mode frequency by $E_{2w} = 2E_w - \delta$, where $\delta$ is a small frequency shift due to anharmonicity that is taken to be inversely proportional to $\mu$, the reduced mass of the Si-H (or D) oscillator [21]. $\eta$ is the following matrix element of $H'$,

$$\eta = \langle 2w|H'|s\rangle = k_3\hbar^{3/2}(2\mu^3\omega_w^2\omega_s)^{-1/2}. \tag{5}$$

The eigenvalues of Eq. (4) are given by

$$\begin{aligned} E_\pm = {} & \tfrac{1}{2}(E_s + 2E_w - \delta) \\ & \pm \tfrac{1}{2}[(E_s - 2E_w + \delta)^2 + 4\eta^2]^{1/2}. \end{aligned} \tag{6}$$

Experimental values for $E_w$ for both the donor-H and donor-D complexes are given in Table I and the values of $\eta_D$ and $\delta_D$ for the donor-D complexes can be written in terms of $\eta_H$ and $\delta_H$ from their known dependences on the vibrational frequencies and the reduced mass $\mu$. Thus Eq. (6) can be used to fit the positions of the four strong high frequency bands for a donor-H complex, $E_\pm$(H), and the corresponding donor-D complex, $E_\pm$(D), with the four parameters $E_s(\mathrm{H})$, $E_s(\mathrm{D})$, $\eta_\mathrm{H}$, and $\delta_\mathrm{H}$. The values of these parameters, determined from a fit to the data in Table I, are given in Table II. (We note that it is the uncoupled mode energies, $E_w$ and $E_s$, that should be compared with theoretical calculations of vibrational frequencies.) Spectra for Sb-D and Sb-H are shown in Fig. 2, as an example, along with the positions of the uncoupled modes determined from our fit. For all of the donor-H and donor-D complexes, $E_s$ lies above $E_{2w}$, giving the higher energy band, $E_+$, greater stretching mode character and $E_-$ greater wagging-overtone character.

From Table I it can be seen that the ratio of the intensities of bands $E_+$ and $E_-$, $I_+/I_-$, for a donor-D complex is consistently greater than this ratio for the corresponding donor-H complex. The intensities of transitions to the admixed states, $I_+$ and $I_-$, are determined by the fraction of the H-stretching state $|s\rangle$ in the corrected wave functions because only the transition from the ground state to $|s\rangle$ is allowed for harmonic vibrations and has appreciable intensity. Thus the ratio of the intensities of the coupled modes is $I_+/I_- = \alpha_+^2/\alpha_-^2$. The intensity ratios calculated, without additional parameters, from the eigenvectors of the matrix in Eq. (4) are compared with the experimentally determined values in Table II. The calculated ratio of the intensities, $I_+/I_-$(calc), is greater for the donor-D complexes than for the donor-H complexes, in agreement with the experimental intensity ratios. Qualitatively, the uncoupled modes are closer in frequency for the donor-H complexes than for the corresponding donor-D complexes. Therefore, the second harmonic of the wagging mode and stretching fundamental are more strongly mixed for the donor-H complexes and more intensity is transferred to the lower frequency band, $E_-$, than for the donor-D complexes. These arguments are consistent with the positions of the uncoupled modes and the relative intensities of the bands shown in Fig. 2 for Sb-H and Sb-D. Further, the sum of the areas of the vibrational bands near 1560 and 1660 cm$^{-1}$ for the donor-H complexes and the sum of the areas of the bands near 1140 and 1220 cm$^{-1}$ for the donor-D complexes are approximately 1.5 (see Table I) *independent of the hydrogen isotope.* This constancy of the total intensity of the two high frequency bands for the donor-H and donor-D complexes does not depend on the details of the fit of our model to the data and is a strong confirmation that these two bands share the intensity of the allowed transition to the stretching fundamental as is required by our Fermi resonance model.

TABLE II. Parameters $\omega_s(\mathrm{H})$, $\omega_s(\mathrm{D})$, $\delta_\mathrm{H}$, and $\eta_\mathrm{H}$ used to fit the frequency positions of the vibrational bands of the donor-H and donor-D complexes given in Table I. Units for these parameters are cm$^{-1}$. The calculated and experimental ratios of the intensities of the two high frequency bands for each complex are also shown.

| | $\omega_s$ | $\delta_\mathrm{H}$ | $\eta_\mathrm{H}$ | $I_+/I_-$(calc) | $I_+/I_-$(expt) |
|---|---|---|---|---|---|
| P-H | 1612.1 | 28.9 | 44.6 | 1.6 | 1.3 |
| P-D | 1203.4 | | | 4.9 | 2.5 |
| As-H | 1627.1 | 24.9 | 47.3 | 2.0 | 1.8 |
| As-D | 1208.7 | | | 4.9 | 3.3 |
| Sb-H | 1621.3 | 7.6 | 54.4 | 1.2 | 1.3 |
| Sb-D | 1196.9 | | | 2.6 | 2.8 |

The new assignment of the hydrogen vibrations of the donor-H complexes is further supported by two additional observations. (i) A weak, previously unreported band is seen at 1616.7 cm$^{-1}$ in Fig. 2(b) for Sb-H. We assign this band to the transition to the $E$ component of the second harmonic of the wag which is predicted by our model. We note that the frequency of the $E$ component is greater than the frequency of the decoupled $A_1$ component, $\omega_{2w}$, as is typically observed in molecular spectroscopy [16]. The frequencies of the corresponding weak bands are given in Table I for P-H and As-H. (The signal to noise ratio was not sufficient for us to identify the corresponding bands in deuterated samples.) (ii) Bergman *et al.* [4] had noted that the three bands near 810, 1560, and 1660 cm$^{-1}$ anneal together. We have carefully reproduced this result for a sample containing Sb and hydrogen. These three bands decay together upon annealing which confirms that they all arise from the same defect center. The weak new band at 1616.7 cm$^{-1}$ also shows the same annealing behavior, supporting its assignment to a mode of the same donor-H complex.

Our new assignment of the vibrational spectra of the donor-H and donor-D complexes in Si, based upon a Fermi resonance between the second harmonic of the hydrogen-wagging mode and the stretching fundamental, explains for the first time the presence of all the observed hydrogen vibrational bands without the need for

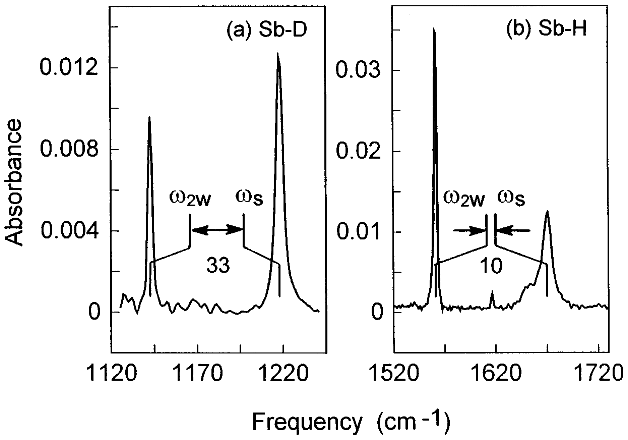

FIG. 2. Absorption spectra measured near 4.2 K for the two high frequency bands of the (a) Sb-D and (b) Sb-H complexes in Si. The positions of the decoupled frequencies and their separations (in cm$^{-1}$) are shown.

additional charge states or defect species. This model is confirmed by its ability to explain the isotope dependence of the relative intensities of the coupled modes and the presence of a new weak band that we have assigned to a transition to the $E$ component of the second harmonic of the H-wagging mode.

We acknowledge G. D. Watkins for numerous helpful discussions and S. J. Pearton and J. Lopata for the ion implantation and plasma treatment of our samples. This work was supported by NSF Grant No. DMR-9415404.

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