

Rotational-vibrational transitions of interstitial HD in Si

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The ir spectrum of interstitial HD in Si provides unique insight into the rotational motion of interstitial H₂ because the rotational-vibrational transitions for the heteronuclear HD molecule are subject to less restrictive selection rules. ir lines for transitions between rotational-vibrational states of the interstitial HD molecule with rotational quantum numbers $J=0, 1$, and 2 have been observed. The assignment of the rotational-vibrational spectrum of interstitial HD, with additional transitions that occur for HD but not for H₂ or D₂, is confirmed by uniaxial stress results.

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I. INTRODUCTION

The interstitial H₂ molecule was suggested by theory to be an important defect in semiconductors in the early 1980s.^{1,2} After many years, vibrational lines were discovered for interstitial H₂, HD, and D₂ in GaAs and Si to provide an unambiguous experimental identification of interstitial H₂ in a semiconductor host.³⁻⁷ Nonetheless, the vibrational spectrum for H₂ and its isotopic partners proved difficult to interpret and explain, especially for the Si host, and the microscopic properties of interstitial H₂ remained uncertain.^{8,9}

The vibrational line for H₂ in GaAs discovered by Raman spectroscopy was found to be split into two components separated by 8.2 cm⁻¹.^{3,7} These components were assigned to ortho- and para-H₂, leading to the conclusion that interstitial H₂ in GaAs is a nearly free rotator. In contrast to the situation in GaAs, the H₂ molecule in Si gave only a single H₂ vibrational line at 3618.4 cm⁻¹ and no evidence for an ortho-para splitting in its vibrational spectrum.⁴⁻⁶ To explain the absence of an ortho-para splitting, it was suggested that there must be a barrier that prevents rotation of the molecule.¹⁰ Uniaxial stress results for the 3618.4 cm⁻¹ line were also interpreted in terms of a static defect, reinforcing the suggestion that the H₂ molecule does not rotate.¹¹ However, several theoretical calculations for H₂ at a tetrahedral interstitial site in Si found a very small barrier to rotation, making it surprising that the H₂ molecule is static.^{10,12-16} In addition to the 3618.4 cm⁻¹ line for H₂ in Si, vibrational lines due to HD and D₂ were discovered at 3265.0 and 2642.6 cm⁻¹ (4.2 K), respectively.^{4,6} The HD line gave additional puzzles; its frequency is higher than would be predicted from the frequencies of the H₂ and D₂ lines¹¹ and its intensity is anomalously weak.¹⁷

The key to understanding the microscopic properties of interstitial H₂ in Si was the discovery of an additional vibrational line at 3191.1 cm⁻¹ for the HD molecule [Fig. 1(a)].¹⁸ This line appears at a sample temperature above ~20 K and lies 74 cm⁻¹ below the 3265.0 cm⁻¹ line previously assigned to HD. This 74 cm⁻¹ energy difference is close to the $J=0$ to 1 rotational transition energy for a free HD molecule, providing experimental evidence that the HD defect is, in fact, a nearly free rotator.

The 3191.1 cm⁻¹ line discovered for HD was assigned to a vibrational transition that occurs with the molecule in its

$J=1$ rotational state.^{16,18} The ir lines seen for H₂ and D₂ were assigned to corresponding transitions, also with these molecules in their $J=1$ rotational states (ortho for H₂ and para for D₂).^{16,18} In the tetrahedral field associated with the T_d interstitial site of the Si lattice, the $J=1$ state becomes T_2 , so that the $\Delta J=0$ ir transitions that are seen for H₂ and D₂ are $T_2 \rightarrow T_2$ transitions allowed by symmetry. The molecules in their $J=0$ states (para for H₂ and ortho for D₂) are not seen by ir spectroscopy because the $J=0$ state becomes A_1 , and $A_1 \rightarrow A_1$ transitions are forbidden in tetrahedral symmetry. This model was confirmed for interstitial H₂ and D₂ by ir experiments performed in conjunction with uniaxial stress in which the stress-induced splittings of the 3618.4 and 2642.6 cm⁻¹ lines were explained by $T_2 \rightarrow T_2$ transitions in full tetrahedral symmetry.¹⁹ Subsequent Raman experiments performed for H₂ in Si (which are not subject to the same selection rules as ir absorption experiments) found vibrational transitions for both the ortho and para species, providing a further confirmation that the interstitial H₂ defect is a nearly free rotator.²⁰

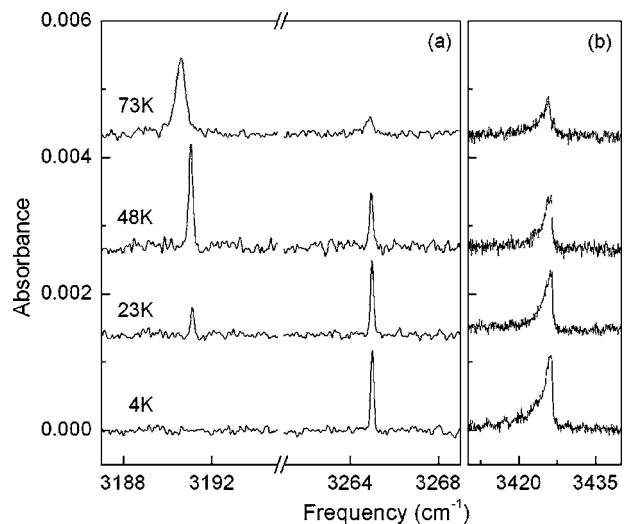


FIG. 1. Spectra measured as a function of temperature for (a) the 3191.1 and 3265.0 cm⁻¹ lines assigned previously to interstitial HD in Si and (b) a line at 3425 cm⁻¹ that is assigned to a rotational-vibrational transition in which the rotational quantum number changes from $J=0$ to 2.

The 3265.0 cm^{-1} line for HD that was initially the source of confusion was reassigned to a rotational-vibrational transition in which the rotational quantum number changes from $J=0$ to 1.^{16,18} Such a transition is not possible for the heteronuclear molecules H_2 and D_2 because the odd and even rotational states must occur on different (ortho and para) molecules. Further experiments for interstitial HD in Si, with its richer rotational-vibrational spectrum, proved challenging because of the weakness of the ir absorption lines associated with HD.

In the present paper, ir transitions of interstitial HD in Si between rotational-vibrational states with rotational quantum numbers $J=0, 1$, and 2 are studied. Furthermore, uniaxial stress has been used to test the assignment of the rotational-vibrational spectra that occur only for interstitial HD in Si.

II. EXPERIMENTAL PROCEDURE

H and D were introduced into lightly doped Si by annealing samples in sealed quartz ampoules that contained 0.7 atm of a mixture of H_2 and D_2 for 1 h at $1250\text{ }^\circ\text{C}$. The anneals were terminated by a rapid quench in water to room temperature. It was found in previous experiments that the concentration of interstitial H_2 molecules produced in this way is near $[\text{H}_2]=5 \times 10^{15}\text{ cm}^{-3}$.²¹ For ir absorption experiments made in the absence of stress, sample dimensions were typically $6 \times 6 \times 15\text{ mm}^3$. For uniaxial stress experiments, oriented samples were prepared with dimensions of typically $3 \times 4.5 \times 12\text{ mm}^3$. Stress was applied along the long axis of the sample, and the optical viewing direction was along the axis with a path length of 4.5 mm.

ir absorption spectra were measured with a Bomem DA3.16 Fourier transform spectrometer equipped with a KBr beam splitter and an InSb detector. A cooled (77 K) bandpass filter (2950 to 6310 cm^{-1}) was glued to the field of view shield inside the detector Dewar to increase the signal-to-noise ratio of the ir measurements. For absorption measurements made in the absence of stress, samples were cooled in a variable-temperature, cold-finger cryostat. The sample temperature was measured with a Chromel-Au 0.07 at. % Fe thermocouple that was attached to the sample holder at a position a few millimeters from the sample. Uniaxial stress experiments were performed with a push rod apparatus that was cooled in an Oxford CF 1204 cryostat using He contact gas. In this case, the temperature was measured with a RhFe resistance sensor mounted on the heat exchanger of the cryostat. A wire grid polarizer was placed in the ir beam path after the cryostat for uniaxial stress experiments made with polarized light.

III. ROTATIONAL-VIBRATIONAL TRANSITIONS OF INTERSTITIAL HD IN Si

Figure 1 shows spectra measured at different temperatures for a Si sample into which H and D had been introduced. At 4 K , ir lines at 3265.0 and 3425 cm^{-1} are seen. As the measurement temperature is increased, both of these lines decrease in intensity, while a new line at 3191.1 cm^{-1} appears and increases in intensity. The lines seen at 3265.0 and

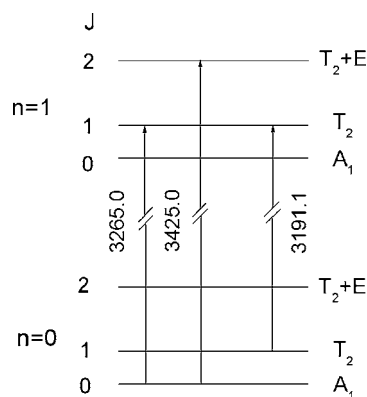


FIG. 2. Energy level diagram for the rotational-vibrational transitions of interstitial HD in Si.

3191.1 cm^{-1} have previously been assigned to interstitial HD in Si,^{16,18} whereas the 3425.0 cm^{-1} line has not. A search for additional transitions between the rotational-vibrational levels of HD found no additional ir absorption lines. The transitions giving rise to the 3265.0 and 3191.1 cm^{-1} lines are shown in the energy level diagram given in Fig. 2.

The 3425 cm^{-1} line shown in Fig. 1(b) has a transition energy 160 cm^{-1} greater than that of the 3265.0 cm^{-1} line. This energy is near twice the rotational transition energy of the HD molecule [$\hbar/(\mu r^2)=80.7\text{ cm}^{-1}$ for an internuclear separation of 0.788 \AA (Ref. 22)], suggesting the assignment of the 3425 cm^{-1} line to a rotational-vibrational transition of HD in which the rotational quantum number changes from $J=0$ to 2 (Fig. 2). A rotational state with $J=2$ becomes T_2+E in the tetrahedral field associated with the T_d interstitial site of the Si lattice.²³ A transition from the A_1 ground state to the T_2 component is allowed whereas the transition to the E component remains forbidden in tetrahedral symmetry.

The assignment proposed for the 3425 cm^{-1} line involves a transition that originates from the rotational-vibrational $J=0$ ground state of the HD molecule, similar to the transition giving rise to the 3265 cm^{-1} line. Therefore, if the assignments are correct, these ir lines should show a similar dependence on the measurement temperature, becoming weaker when the ground state is thermally depopulated, consistent with the ir data shown in Fig. 1.

A series of isochronal anneals has also been performed for a Si sample containing interstitial HD up to temperatures sufficient to remove the HD defect.⁴ The 3191.1 , 3265.0 , and 3425.0 cm^{-1} lines (measured at 75 , 4 , and 4 K , respectively) were eliminated together by an anneal near $300\text{ }^\circ\text{C}$ (30 min).²⁴ The correlated disappearance of these lines upon annealing supports their assignment to transitions of the same HD defect.

Based on its frequency position, temperature dependence, and annealing behavior, we assign the 3425 cm^{-1} line to a rotational-vibrational transition of HD in Si in which the rotational quantum number changes from $J=0$ to 2. The rotational-vibrational transitions observed in the ir spectrum for interstitial HD in Si reveal the rotational manifold that is expected for the vibrational levels of an interstitial molecule that is rotating nearly freely in the crystal lattice. A similar rotational-vibrational structure has not been observed in ir

and Raman spectra measured for interstitial H_2 or D_2 in Si which show only purely vibrational transitions.²⁵

IV. TEST OF ASSIGNMENTS OF THE IR LINES FROM UNIAXIAL STRESS DATA

The ir lines for the different transitions shown in Fig. 2 are predicted to have a different dependence on applied uniaxial stress, thereby providing a definitive test of their proposed assignments. Uniaxial stress experiments have not been attempted previously for interstitial HD in Si, in spite of their appeal as a test of the assignments of the rotational-vibrational transitions that are unique to HD, because of the weakness of the ir lines. The intensity of the ir line at 3618.4 cm^{-1} due to H_2 in Si is roughly 200 times weaker than is typical of other local vibrational modes in semiconductors.^{17,26} The intensity of the 3265.0 cm^{-1} line assigned to HD is expected to be an additional 20 times weaker than the H_2 line.²⁷ The experiments reported in the present paper were made possible by attention to details that affect the signal-to-noise ratio of the ir measurements. Several samples with a greater optical path length than those typically used for stress experiments were fabricated, and those with the strongest HD lines were selected for further ir measurements. The bandpass filter added to the InSb detector was found to improve the signal-to-noise ratio of ir measurements by a factor of ~ 4 . Ir measurements were made for only a few values of the stress applied along [001] and [110] directions with signal-averaging times of up to 8 h for each measurement.

The sharp lines due to HD at 3265.0 and 3191.1 cm^{-1} are the primary focus of these experiments. The line at 3618.4 cm^{-1} due to interstitial H_2 was present in the same samples and was also examined for comparison with the stress results for HD. The line at 3191.1 cm^{-1} has been proposed to be due to a $T_2 \rightarrow T_2$ transition that corresponds to the purely vibrational transitions seen for interstitial H_2 and D_2 in Si with the molecules in their $J=1$ rotational state.^{16,18} The line at 3265 cm^{-1} , however, has been proposed to be due to a rotational-vibrational transition that is possible only for HD in which the rotational quantum number changes from $J=0$ to 1. In the tetrahedral field, this would be an $A_1 \rightarrow T_2$ transition with a different stress-splitting pattern than has been seen previously for H_2 or D_2 . (The additional line at 3425 cm^{-1} is broader than the 3265.0 and 3191.1 cm^{-1} lines and showed only small shifts in its position under stress that were not well resolved in our measurements. The behavior of this line under stress was not studied further.)

Figures 3 and 4 show spectra for uniaxial stresses applied along the [001] and [110] directions, respectively, for the 3191.1 and 3265.0 cm^{-1} lines assigned to HD and also for the 3618.4 cm^{-1} due to H_2 that is present in the same sample. A comparison of the spectra shown in panels (a) and (c) of Figs. 3 and 4 shows that the 3191.1 cm^{-1} line seen for HD at elevated temperature (60 K) behaves similarly to the 3618.4 cm^{-1} line seen for H_2 at low temperature (8 K). Panel (b) in Figs. 3 and 4 shows that the 3265.0 cm^{-1} line seen for HD at 8 K has a different behavior under stress. The shifts and splittings of the 3191.1 and 3265.0 cm^{-1} lines measured

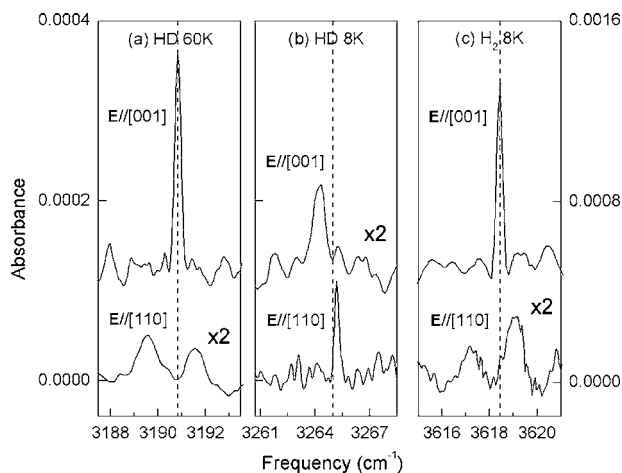


FIG. 3. Effect of stress (60 MPa) applied along the [001] direction for the (a) 3191.1 and (b) 3265.0 cm^{-1} lines assigned to interstitial HD in Si and for the (c) 3618.4 cm^{-1} line due to H_2 that was present in the same sample. The labels give the direction of the polarization of the probing light. For the 3265.0 and 3618.4 cm^{-1} lines, spectra were measured at 8 K with a resolution of 0.15 cm^{-1} and for the 3191.1 cm^{-1} line, at 60 K with a resolution of 0.3 cm^{-1} . The dashed vertical lines in each panel show the position of the ir line in the absence of stress.

for the [001] and [110] orientations of the applied stress are shown in Fig. 5.

Kaplyanskii²⁸ has determined the splittings of the representations of the T_d point group for stresses applied along the high-symmetry crystal directions and also the polarizations and relative intensities of the transitions between the split states. Energy level diagrams for the stress-induced splittings of the A_1 and T_2 levels are shown in Fig. 6. The stress data

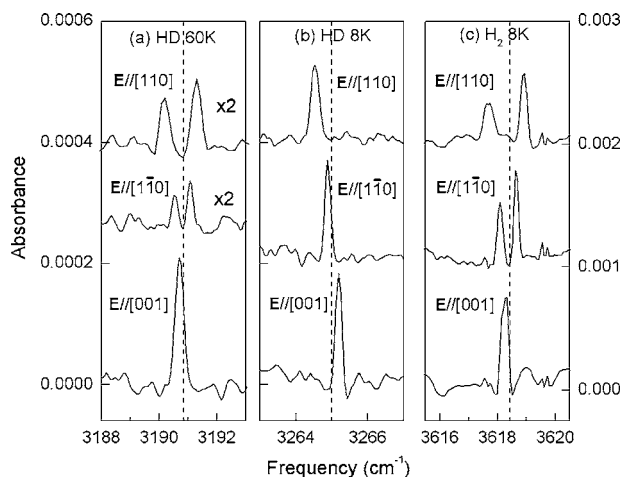


FIG. 4. Effect of stress (60 MPa) applied along the [110] direction for the (a) 3191.1 and (b) 3265.0 cm^{-1} lines assigned to interstitial HD in Si and for the (c) 3618.4 cm^{-1} line due to H_2 that was present in the same sample. The labels give the direction of the polarization of the probing light. For the 3265.0 and 3618.4 cm^{-1} lines, spectra were measured at 8 K with a resolution of 0.15 cm^{-1} and for the 3191.1 cm^{-1} line, at 60 K with a resolution of 0.3 cm^{-1} . The dashed vertical lines in each panel show the position of the ir line in the absence of stress.

tings of the rotational states for the components of the stress applied along the [001] and [111] directions, that have been determined experimentally. For example, for stress applied along a [001] direction, the stress data for HD show that the nondegenerate B_2 state lies below the E state, consistent with a negative value for B and the ordering of the stress-split levels shown in Fig. 6.

V. CONCLUSION

Interstitial H_2 and D_2 in Si each show single sharp vibrational lines in their ir absorption spectra and no additional lines that might be due to transitions between the levels of a manifold of rotational states. Interstitial HD, however, with its less restrictive selection rules, gives rise to a more interesting rotational-vibrational spectrum. The ir transitions observed for interstitial HD reveal the levels of the rotational manifold of a nearly free rotator with rotational quantum numbers $J=0, 1$, and 2 .

The 3191.1 and 3265.0 cm^{-1} ir lines due to interstitial HD show different behaviors under applied uniaxial stress, al-

lowing the assignments of the transitions to be unambiguously confirmed. The 3191.1 cm^{-1} line behaves similarly to corresponding purely vibrational transitions studied previously for interstitial H_2 and D_2 in Si. Stress data for the 3265.0 cm^{-1} line confirm its assignment to a rotational-vibrational transition that can occur only for the heteronuclear HD molecule in which the rotational quantum number changes from $J=0$ to 1 and reveal the signs of the parameters describing the stress-induced shifts that previously could not be determined. Uniaxial stress results provide a strong confirmation of the assignment of the rotational-vibrational spectra that underpin our understanding of the rotational motion of interstitial H_2 in Si, but that are seen only for interstitial HD.

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²⁵A rotational-vibrational transition in which the rotational quantum number changes from $J=0$ to 2 might also be possible for para- H_2 or ortho- D_2 in Si. Spectra measured for a Si sample that contained interstitial D_2 were examined near the frequency expected for such a transition ($\sim 2800 \text{ cm}^{-1}$), and no additional ir line was found. If a line had been present with an intensity greater than 0.05 times that of the D_2 line at 2642.6 cm^{-1} , it would have been detected in this experiment. An explanation for the presence of a $J=0$ to 2 rotational-vibrational transition that is seen only for HD is that the T_2 components of the states corresponding to $J=1$ and 2 can be mixed by the potential energy function that describes the rotational motion of the HD molecule in the Si lattice (see, for example, Ref. 16). For H_2 and D_2 , the $J=1$ and 2 states are present on different molecules and cannot be mixed.

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²⁷The intensity of the 3265.0 cm^{-1} HD line has been found to be 10 times weaker than the 3618.4 cm^{-1} H_2 line for equal concentrations of HD and H_2 (Ref. 17). Furthermore, when H and D are

introduced into a Si sample with equal concentration, only half of the molecules that are produced will be HD if a random pairing of the H and D isotopes is assumed. The combination of these factors will make the HD line at 3265.0 cm^{-1} 20 times weaker than the H_2 line in a Si sample containing only H.

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the vibrational transition energy and might depend on the isotopic mass of the H_2 molecule. However, the effect of the parameters A_x on the fit to the stress data is relatively small, so the possible dependence of A_x on isotope is subject to substantial experimental uncertainty.

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