Symmetry of Molecular H_2 in Si from a Uniaxial Stress Study of the 3618.4 cm^{-1} Vibrational Line

J. Anna Zhou and Michael Stavola
Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015

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Uniaxial stress has been used in conjunction with vibrational spectroscopy to probe the structure and microscopic properties of interstitial H_2 in Si. The stress splitting pattern observed for the 3618.4 cm^{-1} line assigned to H_2 is consistent with triclinic (C_1) symmetry of a static center. The piezospectroscopic tensor determined in these experiments suggests a near ⟨100⟩ orientation for the H_2 molecular axis. The low symmetry that has been found in these experiments on the 3618.4 cm^{-1} line is unexpected.

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Atomic hydrogen in semiconductors is mobile at room temperature and forms complexes with a variety of shallow- and deep-level impurities and defects, modifying their electrical properties [1,2]. Hydrogen's prevalence in the environment and its ability to alter the electrical properties of semiconductors have led to many studies of this "simple" impurity. In addition to being bonded to other defects, it has been proposed that H can be present in the form of H_n aggregates [3,4], sometimes with very high concentration. Two different H_2 dimers have been studied by theory [3], the isolated H_2 molecule located at a tetrahedral interstitial site and an alternative configuration called H_2^* where the two H atoms lie along a ⟨111⟩ direction, separated by a host atom to which they are bound. In spite of the proposed importance of these hydrogen dimers during indiffusion processes and H-related reactions, H_2 and H_2^* were not observed spectroscopically until recently [5–8]. In this paper, we report the use of uniaxial stress in conjunction with IR spectroscopy to probe the structure and properties of H_2 in Si. These data reveal a surprisingly low symmetry for H_2 in Si and important differences from the expectations of recent theoretical calculations [9–12].

The stretching vibration of an isolated interstitial H_2 molecule in a semiconductor was observed first in GaAs by Raman spectroscopy [6] with a frequency of 3934.1 cm^{-1} (77 K). The H_2 line is split by 8.2 cm^{-1}, leading to the conclusion that the H_2 molecule is freely rotating and that this doublet is due to the ortho and para nuclear spin states whose vibrational frequencies are split by rovibrational coupling. Subsequently, the stretching vibration of H_2 in Si was discovered at 3618.4 cm^{-1} (4.2 K) independently by Raman [7] and IR absorption [8] spectroscopies, and strong evidence was presented that this line is indeed due to an isolated molecule [8]. In both GaAs and Si, lines due to D_2 and HD were also observed, confirming the assignments. In further support of these assignments, theoretical calculations [9–12] find vibrational frequencies for H_2 in GaAs or Si that are shifted to lower frequency from the gas phase value by several hundred cm^{-1}, in agreement with experiment.

Several aspects of the results for H_2 in Si are surprising. In the gas phase, the stretching vibration of a homonuclear diatomic molecule does not give rise to an oscillating electric dipole moment and is IR inactive. The observation of a weak absorption line for interstitial H_2 in Si was, therefore, unexpected. Further, there is an important difference between H_2 in Si and in GaAs; no ortho-para splitting was observed for H_2 in Si, even at the high resolution (0.1 cm^{-1}) used in the IR absorption experiments [8]. To explain the absence of an ortho-para splitting, it was suggested that there must be a barrier of at least 0.17 eV that prevents rotation of the molecule [11]. It has been found by theory that ⟨100⟩, ⟨111⟩, and ⟨110⟩ orientations have similar energies [3,9–12], making it surprising that there is a substantial barrier to rotation and that the H_2 molecule in Si is static. Another important experimental observation is that the vibration line assigned to HD in Si is not split at 0.1 cm^{-1} resolution [13], suggesting that the two H atoms in the molecule remain equivalent. Based on the above results, a configuration with the H_2 molecule oriented along a ⟨110⟩ direction and displaced from the tetrahedral interstitial site along the perpendicular ⟨100⟩ direction (C_{2v} point group) was proposed [11]. This configuration gives rise to a weak vibrational transition moment along the ⟨100⟩ direction oriented perpendicular to the ⟨110⟩ molecular axis while still leaving the H atoms equivalent. Several of these recent suggestions are tested by our uniaxial stress experiments.

For our experiments, H was introduced into lightly doped Si by annealing samples in sealed quartz ampoules containing H_2 gas (~0.7 atm at room temperature) for 30 min at 1250 °C. These samples were then quenched to room temperature in ethylene glycol. Infrared spectra were measured with a Bomem DA3.16 Fourier transform spectrometer. The concentration of H_2 molecules produced in our samples was estimated from the area of the absorption line at 3618.4 cm^{-1} and the calibration (effective charge $q = 0.08e$) reported by Pritchard *et al.* [8]. For the [001] and [110] samples shown in Fig. 1, we found $[H_2] \approx 5 \times 10^{15}$ mol cm^{-3}. This concentration is consistent with the solubility of H at the

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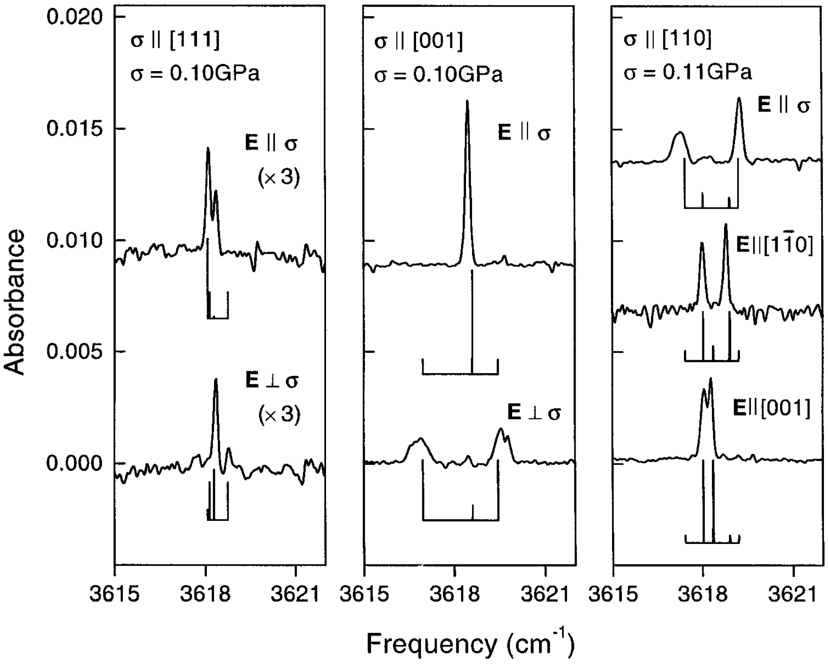

FIG. 1. Effect of stress σ on the 3618.4 cm^{-1} vibrational absorption line assigned to molecular H_2 in Si. The stress direction, magnitude of the stress, and polarization vector **E** for the incident light are given.

introduction temperature (1250 °C) [14]. For uniaxial stress measurements, oriented, bar-shaped samples with dimensions 3.5 × 3.5 × 10 mm^3 were prepared. Stress was applied with a push rod apparatus that was cooled to near liquid He temperature in an Oxford CF 1204 cryostat.

The effect of uniaxial stress on the 3618.4 cm^{-1} line is shown in Figs. 1 and 2. This stress-splitting pattern is consistent with a nondegenerate vibrational mode of a triclinic center (C_1 point group). The shifts of the stress-split components $\Delta\omega_i$ are given by

$$\Delta\omega_i = \sum_{ij} A_{ij}\sigma_{ji}\,, \tag{1}$$

where A_{ij} are the component of a symmetric piezospectroscopic tensor and σ_{ij}, defined here to be positive for compression, are the components of the stress tensor [15]. The polarization dependence of the spectra is determined by the direction of the transition moment **M** for the vibrational mode. For a C_1 center, symmetry does not restrict the choice of the transition moment direction. From the data for [001] stress, where each component is observed for just one polarization direction, it appears that **M** must lie near a ⟨100⟩ direction. From the data for [110] stress, however, it is found that **M** must be rotated away from ⟨100⟩ to explain the appearance of a distinct pair of lines for each of the polarization directions. To determine a transition moment direction that is consistent with the spectra for both stress orientations, the intensities of the stress-split components were written in terms of the polar and azimuthal angles θ and ϕ that characterize the direction of **M** in the defect coordinate system (Fig. 3). The polar and azimuthal angles were then varied to produce a fit to the observed intensity pattern for the [001] and [110] stress directions. (We have chosen **M** to be nearest the z axis in the defect coordinate system. This choice fixes A_3 as the parameter that describes the shift of the line observed for **E** ∥ σ for [001] stress.) With the transition moment direction determined, it was then

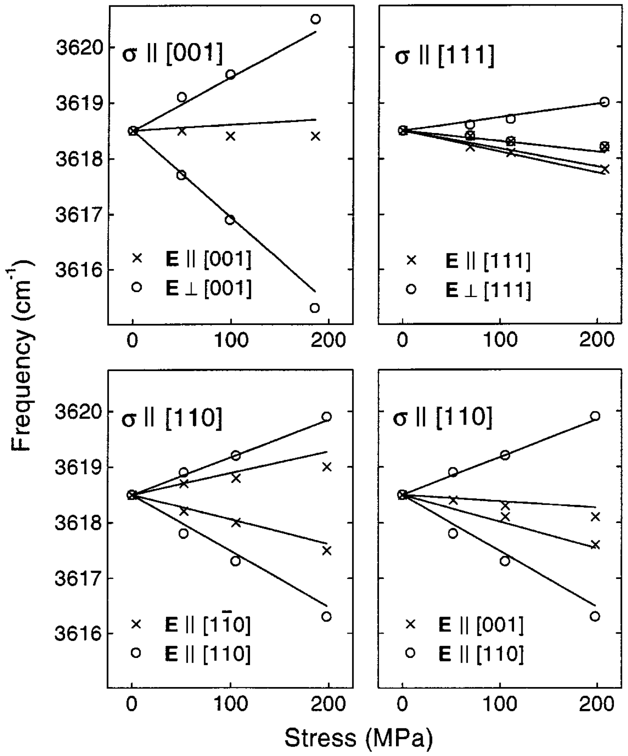

FIG. 2. Stress-induced frequency shifts vs the magnitude of the stress applied along the high symmetry crystal directions for the 3618.4 cm^{-1} line assigned to molecular H_2 in Si.

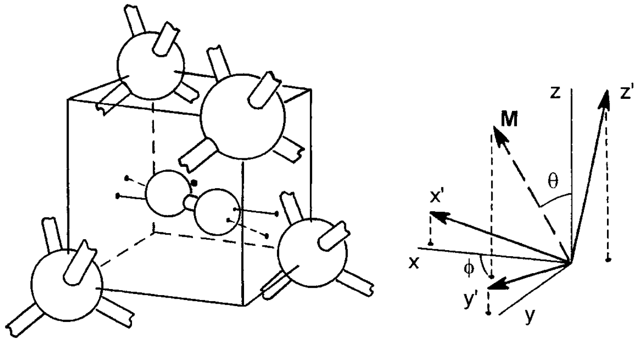

FIG. 3. A representative model for H_2 in Si is shown on the left. The molecular axis (dashed line) is rotated slightly from a $\langle 100 \rangle$ direction (solid line) and the center of mass is displaced from the tetrahedral interstitial position. The principal axes of the piezospectroscopic tensor and the direction of the IR transition moment **M** are shown on the right. The direction cosines for the principal axes are as follows: $x' = (0.979, -0.090, 0.183)$, $y' = (0.061, 0.986, 0.156)$, $z' = (-0.194, -0.142, 0.971)$.

possible to assign the vibrational lines observed for the three stress directions and to fit the line positions with Eq. (1). The positions and intensities of the stress-split components, determined with the piezospectroscopic tensor components given in Table I and with $\theta = 28°$ and $\phi = 45°$, are shown in Fig. 1 by the vertical lines. The direction of the transition moment is not precisely determined by our fit and there are a few weak components, especially for the [111] stress direction, that are not well accounted for by our model which assumes a static transition moment direction (i.e., a transition moment direction that is independent of the stress). The fit to the IR-line positions shown in Figs. 1 and 2 is satisfactory, with the positions of the lines differing from the fit by less than 0.15 cm^{-1} for $\sigma = 0.1$ GPa (Fig. 1).

Our uniaxial stress data reveal a surprisingly low symmetry for H_2 in Si and require a structural model with a lower symmetry than has been considered previously [3,9–12]. The structure we propose is based upon the form of the piezospectroscopic tensor whose largest components, A_1 and A_2, lie on the diagonal. The principal axes of the tensor are shown in Fig. 3 and are rotated by less than 14° from the $\langle 100 \rangle$ cube axes. The dominance of the effect of $\langle 100 \rangle$ stresses suggests that the H_2 molecule is oriented approximately along a $\langle 100 \rangle$ direction. A plausible further assumption is that it is stress along the molecular axis that raises the vibrational frequency. In this case, the polarization dependence observed for [001] stress, with the upward shifting line observed only for $\mathbf{E} \perp \sigma$, would be consistent with the H_2 molecular axis being aligned near x (or y), i.e., with the transition moment not along the molecular axis. These considerations lead to the model for H_2 in Si shown in Fig. 3. The molecular axis is rotated slightly away from a high symmetry $\langle 100 \rangle$ direction to be consistent with the C_1 symmetry found by our experiments. Furthermore, for C_1 symmetry, the molecule's center of mass is not required to be located at the tetrahedral interstitial site. While the piezospectroscopic tensor strongly suggests that the H_2 molecular axis is oriented near a $\langle 100 \rangle$ direction, there is not a direct connection between the principal axes of the piezospectroscopic tensor and the direction of the molecular axis. Therefore, the small rotation angle of the molecular axis away from $\langle 100 \rangle$ and the displacement of the molecule's center of gravity from the T_d interstitial site are not determined by our results, and Fig. 3 shows only a representative possibility.

TABLE I. The piezospectroscopic tensor components, in units cm^{-1}/GPa, for the H_2 molecule in Si. Both the labels introduced by Kaplyanskii [15] and the conventional tensor notation are given for the components.

A_1 (A_{xx})	A_2 (A_{yy})	A_3 (A_{zz})	A_4 (A_{xy})	A_5 (A_{yz})	A_6 (A_{xz})
9.6	−15.6	1.1	−1.8	−2.8	1.4

The relative intensities of the stress-split components were found to be independent of the applied stress (up to 0.2 GPa), showing that the center does not reorient at low temperature. Experiments were also performed to investigate whether the H_2 molecule could be aligned by stresses applied at elevated temperatures. For these experiments a stress of 0.2 GPa was applied at room temperature and maintained while the sample was slowly cooled to 4.2 K. (Both [001] and [111] stress directions were investigated.) Vibrational spectra were then measured to investigate whether a stress-induced alignment of the H_2 defect had modified the relative intensities of the stress-split components. No such alignment-related intensity changes were observed. If we assume a typical value for the stress-induced shift of the ground state energy ($\sim$10 meV/GPa) [16], then we find that a detectable alignment (determined by the Boltzmann factor for differently oriented defects at the temperature where an alignment would become frozen in [17]) should have been produced in our experiments if the molecule could reorient below roughly 60 K to establish an equilibrium alignment under stress. These results are in agreement with the analysis of Hourahine *et al.* [11] who concluded that there must be a barrier to rotation of at least 0.17 eV to explain the absence of a resolved ortho-para splitting for the 3618.4 cm^{-1} line and, therefore, that the H_2 molecule must be static for temperature below $\approx$70 K.

For the C_1 symmetry found in our experiments, the two H atoms in the molecule must be inequivalent, in apparent contradiction to the previous observation [13] that two vibrational lines are not observed for the HD molecule. We have repeated this measurement for a sample that contained H and D with a resolution of 0.05 cm^{-1}. We have found a single sharp line at 3265.0 cm^{-1}, in agreement with the previously published result, and with a full width at half maximum of 0.16 cm^{-1}. One possibility suggested by this result is that the H and D atoms are nearly equivalent and a small splitting of the HD line remains unresolved. However, the evidence suggests an alternative possibility, that the H and D atoms are sufficiently inequivalent for a particular arrangement of H and D to be favored energetically. In this case, the alternative arrangement, with the H and D interchanged, is not observed. This interesting latter possibility is supported by the frequency position of the HD line which is found to be inconsistent with the model commonly used to characterize the anharmonic shift of the vibrational frequency. The observed frequency position ω of a vibrational line is given by [17,18]

$$\omega = \omega_0 - B/m\,, \tag{2}$$

where $\omega_0 = (k/m)^{1/2}$ is the harmonic frequency, m is the reduced mass of the oscillator, and B is a parameter. The application of Eq. (2) to the H_2 (3618.4 cm^{-1}) and D_2 (2642.6 cm^{-1}) stretching frequencies gives anharmonic shifts of 406 cm^{-1} and 203 cm^{-1} for H_2 and D_2, respectively [19]. From this analysis, one then finds an anharmonic shift of 305 cm^{-1} for HD and thus an HD frequency of 3180 cm^{-1}. This value determined from Eq. (2) differs from the experimental frequency (3265.0 cm^{-1}) by 85 cm^{-1}. A similar analysis for the frequencies of H_2 and D_2 in GaAs or in gas phase is consistent with the HD line positions in these cases to within a few cm^{-1}. This remarkable shift of the HD line in Si from its expected position would be consistent with two inequivalent arrangements of H and D and a large splitting of the HD line with only the higher frequency line being observed. (We have searched for an additional HD line at lower frequency, but without success.)

Our uniaxial stress results provide new information about the symmetry of the H_2 molecule in Si and important clues about the direction of the molecular axis. In spite of the progress made, many of our observations have been unexpected and remain puzzling. The C_1 symmetry found in our experiments is lower than has been suggested by theoretical calculations [3,9–12] and by an analysis of the vibrational spectrum [11]. The absence of an ortho-para splitting of the H_2 vibrational line [8,11] and the lack of stress-induced alignment found here are consistent with a static center. All of these results for H_2 in Si are at variance with the theoretical expectation [9–12] that an *isolated* H_2 molecule will interact only weakly with its host cage (as seems to be the case for H_2 in GaAs [7]). Simple explanations, that the H_2 molecule is in the vicinity of another defect or is part of a larger complex of hydrogen atoms or molecules, conflict with strong evidence that the H_2 molecule is isolated [8,20]. An explanation of the low symmetry and substantial rotational barrier observed for H_2 in Si remains as a challenge.

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[20] Raman experiments on H_2 in Si (Ref. [7]) were performed with samples treated in an H_2 plasma. The high concentration of H_2 molecules expected in these samples ($>10^{18}$ cm^{-3}) makes it unlikely that there is an additional impurity present in float zone Si at comparable concentration.