Ortho and para O-H₂ complexes in silicon

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Interstitial H₂ becomes bound to interstitial O in silicon, forming an O-H₂ complex. Infrared absorption experiments performed for the O-HD complex in Si reveal HD vibrational lines that appear at elevated temperature (T > 10 K). These lines and their properties lead to the conclusion that the H₂ molecule in the O-H₂ complex is a nearly free rotor. Two near-lying lines seen for the oxygen mode of the O-H₂ complex are attributed to the ortho and para O-H₂ complexes. The ortho and para states of the O-H₂ complex also give rise to H₂ vibrational lines with distinct properties. These results may be understood in terms of a hindered-rotor model for the hydrogen molecule.

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I. INTRODUCTION

The microscopic properties of hydrogen molecules in semiconductors have been of interest since the early 1980s.¹⁻⁶ However, vibrational spectra for H₂, HD, and D₂ molecules in GaAs (Ref. 7) and Si (Refs. 8 and 9) were discovered only recently. In addition to the spectra of isolated interstitial hydrogen molecules, vibrational spectra of an O-H₂ complex in Si have been observed.¹⁰ In the present paper, results on the temperature dependence of the vibrational spectra of the O-H₂, O-HD, and O-D₂ complexes in Si are reported. These results lead to a model for O-H₂ in which the H₂ molecule in the complex is a nearly free rotor, giving rise to ortho and para O-H₂ complexes with distinct vibrational properties.

The O-H₂ complex in Si has been studied in a beautiful series of infrared (IR) absorption experiments by Markevich and co-workers^{11,12} and by Pritchard *et al.*¹⁰ An oxygen vibrational line near 1075 cm⁻¹ for an oxygen-hydrogen defect complex (shifted to 1076 cm^{-1} for oxygen-deuterium) was first reported by Markevich, Suezawa, and Sumino.¹¹ This line was produced by the introduction of hydrogen into Czochralski-grown (oxygen-rich) Si, and its reversible formation and dissociation kinetics were studied.^{8,10-12} It was later shown by Pritchard *et al.* that the 1075 cm^{-1} line is actually due to an O-H₂ complex.¹⁰ The oxygen modes of the $O-H_2$ and $O-D_2$ complexes at 1075 and 1076 cm⁻¹, respectively, were each found to consist of two components.¹⁰ In addition to the oxygen modes, the O-H₂ complex was found to give rise to a pair of high-frequency H₂ vibrational lines. Each of the O-HD and O-D₂ complexes also gives rise to a pair of high-frequency lines. Pritchard et al. concluded that there are two different O-H₂ complexes with similar structures, with each complex giving rise to one of the H₂ lines and one of the two near-lying O lines.¹⁰ Models for the O-H₂ complex with an interstitial H₂ molecule bound near an interstitial oxygen atom (located near the bond center between two nearest-neighbor Si atoms) have been considered theoretically.¹³

In addition to the vibrational modes of the O-H₂ complex, Pritchard *et al.* discovered an H₂ vibrational line at 3618.4 cm⁻¹ by IR spectroscopy¹⁰ that was later assigned to the isolated H₂ molecule located near a tetrahedral interstitial site in Si.⁸ HD and D₂ lines were also discovered at 3265.0 and 2642.6 cm⁻¹, respectively. (Independently, the vibrational lines of interstitial H₂ and D₂ in Si were also discovered by Raman spectroscopy.⁹)

In spite of the advances represented by these experiments, a number of observations have remained puzzling. The Raman band of the H₂ molecule in GaAs is split into two components, 8 cm⁻¹ apart, with an intensity ratio of \sim 3:1 (Ref. 7). These lines were assigned to ortho and para H_2 , whose frequencies differ because of rovibrational coupling. This interpretation leads naturally to the conclusion that H₂ in GaAs is freely rotating. In contrast to the situation in GaAs, the H₂ molecule in Si gives only a single, sharp, H₂-vibrational line at 3618.4 cm^{-1} and no evidence for an ortho-para splitting in its IR absorption spectrum.^{8,14} The absence of an ortho-para splitting was taken to be evidence for a substantial barrier to rotation.¹⁴ Theoretical calculations, however, find that the energy of the H₂ molecule at the tetrahedral interstitial site is insensitive to the orientation of the $defect^{14-17}$ and studies of the dynamics of H₂ in Si find that it should behave as a nearly free rotor.^{18,19} The position and intensity of the 3265.0 cm⁻¹ HD vibrational line are also anomalous.^{20–22}

In our recently reported experiments, a vibrational line at 3191.1 cm⁻¹ was discovered for the HD molecule in Si.²² This line appears for sample temperatures above T > 20 K and lies 73.9 cm^{-1} below the 3265.0 cm^{-1} line previously observed for HD by Pritchard et al.8 An energy-level diagram is shown in Fig. 1(a) that is consistent with the transition energies of the 3265.0 and 3191.1 cm⁻¹ lines and the activation energy (74 cm^{-1}) for the thermally populated state from which the 3191.1 cm^{-1} line originates. 74 cm^{-1} is in fact close to the J=0 to J=1 rotational transition energy for a free HD molecule. It was concluded that the 3191.1 cm^{-1} line is due to a purely vibrational transition of the HD molecule and that the 3618.4, 3191.1, and 2642.6 cm^{-1} lines are due to the corresponding vibrational transitions of the H₂, HD and D_2 molecules.²² The 3265.0 cm⁻¹ HD line is due to a rovibrational transition in which the rotational quantum number J changes from 0 to 1. Such a transition, with ΔJ = 1, is not possible for the *homonuclear* diatomic H_2 molecule because para H₂ must have only rotational states with (a) HD

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FIG. 1. Energy-level diagrams for the rovibrational states of (a) interstitial HD and (b) the O-HD complex in Si. The level spacings and the frequencies of the transitions are given in cm^{-1} .

even J while ortho H₂ must have only states with odd J^{23} . The situation is similar for D₂. Furthermore, it was found experimentally that there is no IR transition for HD in Si with the molecule in the J=0 rotational state.²² The absence of an IR transition between states with J=0, when applied to H₂ and D₂, explains the puzzling absence of an ortho-para splitting for the H₂ and D₂ IR absorption lines, i.e., para H₂ and ortho D₂ have ground rotational states with J=0 and do not give rise to vibrational absorption. However, IR transitions between states with J=1 are possible in tetrahedral symmetry for H₂ and D₂, i.e., for ortho H₂ and para D₂.

In the present paper, experimental results are presented and analyzed for the O-HD complex in Si. The recognition that the H₂ molecule in Si is a nearly free rotor^{19,22} suggests that the two near-lying oxygen lines seen for O-H₂ are due to ortho and para O-H₂ complexes. Additional high-frequency vibrational lines have also been found for O-HD in Si at elevated temperature, similar to the line observed for isolated HD in Si at elevated temperature.²² The model developed previously^{19,22} for the interstitial H₂ molecule in Si is extended to explain the properties of the O-H₂ complex.

II. EXPERIMENTAL PROCEDURE

For our experiments on the O-H₂, O-HD, and O-D₂ complexes, lightly doped, Czochralski-grown (Cz), Si samples (typical oxygen concentration $[O] \approx 10^{18} \text{ cm}^{-3}$) were used. Samples were cut with dimensions $6 \times 6 \times 15 \text{ mm}^3$ and with the optical viewing direction along the long axis of the sample. H and/or D were introduced by annealing the samples in sealed quartz ampoules that contained 0.7 atm of H₂, D₂, or mixtures of both for 30 min at 1250 °C. The samples were then quenched to room temperature in water. To form O-H₂ complexes, the hydrogenated samples were annealed for at least one week at room temperature. IR absorption measurements showed that primarily isolated H₂ molecules were produced immediately following hydrogenation. Following the week-long anneal at room temperature, $\approx 60\%$ of the H₂ molecules had formed O-H₂ complexes,



FIG. 2. Spectra measured as a function of temperature for the 3282.2-, 3285.4-, 3304.4-, and 3340.8-cm⁻¹ absorption lines assigned to the O-HD complex in Si. The vibrational lines present at 4.2 K are indicated with the dotted vertical lines. The lines that appear at elevated temperature are indicated with the dashed vertical lines. The sample is Cz Si into which both H and D had been introduced, followed by an anneal at room temperature for at least 1 week.

consistent with previous studies of the formation kinetics of $O-H_2$ in Si.¹²

IR absorption spectra with a resolution of 0.1 cm⁻¹ were measured with a Bomem DA 3.16 Fourier-transform spectrometer equipped with InSb and HgCdTe detectors. Samples were cooled in an Air Products variable-temperature 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.

III. ORTHO AND PARA O-H2 AND O-D2 COMPLEXES

A. The hydrogen modes of the O-HD complex

In our recent work on interstitial HD in Si,²² we found an additional vibrational absorption line that appeared at elevated temperature (T>20 K). In the experiments reported here, vibrational spectra were measured as a function of temperature for Cz Si into which H and D had been introduced, followed by a week-long anneal at room temperature, to search for lines that might be associated with the O-HD complex. Figure 2 shows spectra for the O-HD complex. As the temperature is increased above 4.2 K the 3285.4 and 3304.4 cm⁻¹ lines previously assigned to O-HD (Ref. 10) become weaker while two lines at 3282.2 and 3340.8 cm⁻¹ grow in. The joint appearance of the two lines of O-HD at 3282.2 and 3340.8 cm⁻¹ as the temperature increases, while the two lines at 3285.4 and 3304.4 cm⁻¹ both weaken, shows that all of these lines are due to the same defect complex.



FIG. 3. Plot of I(3282)/I(3285) vs 1/T for the O-HD complex in S. The line is the result of a least-squares fit to the data and yields the activation energy shown.

Figure 3 shows a plot of the logarithm of the ratio of the intensities of the 3282.2 and 3285.4 cm⁻¹ lines, $\ln[l(3282)/l(3285)]$, vs T^{-1} . The slope of this plot gives an activation energy of (19 ± 1) cm⁻¹ for the thermal population of a state that lies above the ground vibrational state. (The error quoted here is estimated from the scatter of the data around the fit line in Fig. 3.)

Figure 1(b) shows an energy-level diagram that is consistent with the data for the HD lines of O-HD in Si. The origins of these levels will be discussed in Sec. IV. At low temperature [diagram (i)], the 3285.4 and 3304.4 cm⁻¹ lines are seen. These must correspond to transitions to final-state levels that are split by 19 cm⁻¹. At elevated temperature [diagram (ii)], a state 19 cm⁻¹ above the ground state is thermally populated. Two additional vibrational lines at 3282.2 and 3340.8 cm⁻¹ appear that correspond to transitions to final-state levels that differ in energy by 58.6 cm⁻¹.

We have also carefully examined the vibrational spectra of the O-H₂ and O-D₂ complexes for temperatures from 4.2 K up to 70 K. The energies of the high-frequency modes of the O-H₂, O-HD, and O-D₂ complexes in Si are given in Table I. The results for the lines seen at 4.2 K are in excellent agreement with the previous results of Pritchard *et al.*¹⁰ [Pritchard *et al.* found that the O-D₂ line near 2715 cm⁻¹ is split into a closely spaced doublet. Furthermore, we have discovered a very weak line at 3737.1 cm⁻¹ (4.2 K) for the O-H₂ complex. Discussion of the 1.1 cm⁻¹ splitting of the O-D₂ lines near 2715 cm⁻¹ and the weak 3737.1 cm⁻¹ line for O-H₂ will be deferred until Sec. IV D]. We have found that the O-H₂ and O-D₂ lines that are present at 4.2 K simply

TABLE I. Vibrational frequencies of the O-H₂, O-HD, and O-D₂ complexes in Si. The frequencies of the O-HD lines seen at low temperature [O-HD (4.2 K)] and of the O-HD lines that appear at elevated temperatures [O-HD (25 K)] are both given. The assignments of the O-H₂ and O-D₂ lines to ortho (*O*) and para (*P*) complexes are also given. The frequencies have units cm⁻¹.

О-Н ₂	O-D ₂	O-HD	O-HD
(4.2 К)	(4.2 K)	(4.2 K)	(25 K)
3788.9 (<i>O</i>)	2775.5 (P)	3304.4	3340.8
3731.0 (<i>O</i>)–3737.1 (<i>P</i>)	2715.0 (P)–2716.1 (O)	3285.4	3282.2

shift and broaden without the appearance of any additional lines or line structure as the temperature is increased.

The differences in frequency for the two high-frequency lines for $O-H_2$ and $O-D_2$ are 58 and 60 cm⁻¹, respectively (ignoring the weak 3737.1 cm⁻¹ line of O-H₂ until later). The two O-HD lines seen at low temperature are spaced by 19 cm^{-1} , while the O-HD lines that appear at elevated temperature are spaced by 59 cm^{-1} , i.e., with essentially the same spacing as for O-H₂ and O-D₂. Therefore, we conclude that it is the O-HD lines at 3282.2 and 3340.8 cm^{-1} that are due to transitions similar to those seen for O-H₂ and O-D₂ (Ref. 24). Furthermore, this suggests that the 3731.0 and 3788.9 cm^{-1} lines seen for O-H₂ (and similarly for the corresponding lines seen for $O-D_2$) are due to the same defect complex because the corresponding lines of the O-HD complex at 3282.2 and 3340.8 cm⁻¹ are associated with one defect. These conclusions are an important departure from the previous interpretation of Pritchard et al., who associated the two high-frequency lines of O-H₂ (and also of O-D₂) with two defects with different structures.¹⁰

B. The oxygen modes of the ortho and para O-H₂ and O-D₂ complexes

Our conclusion that one O-H₂ complex gives rise to both H₂ vibrational lines suggests that the two near-lying oxygen lines observed for O-H₂ are due to the ortho and para states of the complex, and similarly for O-D₂. This possibility was originally considered by Pritchard et al., but was rejected in favor of an alternative model.¹⁰ We have repeated the measurement of the oxygen modes of the O-H₂ and O-D₂ complexes because the results are critical to our conclusion that the oxygen modes of the ortho and para complexes are being seen. Figure 4 shows absorption spectra of Cz-Si samples measured after the indiffusion of (a) H_2 and (b) D_2 and an anneal at room temperature for ~ 1 week. In spectra (a) and (b), two strong near-lying oxygen lines are seen. [Pritchard et al. assigned the two weak lines seen at lower frequency (1073 and 1075 cm^{-1} for O-D₂, for example) to the isotopic configurations ³⁰Si-O-²⁸Si and ²⁹Si-O-²⁸Si bonded to (a) H₂ or (b) D_2 , confirming the role of interstitial O in the O-H₂ and O-D₂ complexes.¹⁰] For the O-H₂ complex, spectrum (a) was fit by two lines with Voigt shapes with a separation of 1.0 cm⁻¹ and a full width at half maximum (FWHM) of $\Delta = 0.8 \text{ cm}^{-1}$. The ratio of the intensities of the two components was found to be 3:1. For the O-D₂ complex, spectrum



FIG. 4. IR absorption spectra (4.2 K) of the oxygen modes of (a) the O-H₂ and (b) the O-D₂ complexes in Si. Fits to the line shapes are shown. The samples are Cz Si into which H or D had been introduced, followed by an anneal at room temperature for at least 1 week.

(b) was again fit by two lines with Voigt shapes, but with a separation of 0.5 cm⁻¹ and a FWHM of $\Delta = 0.7$ cm⁻¹. The ratio of the intensities of the two components was found to be 2:1. The above analysis of the oxygen modes of the O-H₂, and O-D₂ complexes gives results that are in excellent agreement with the results of Pritchard *et al.*^{10,25}

The relative intensities of the two oxygen modes, 3:1 for O-H₂ and 2:1 for O-D₂, are consistent with the ratios expected for ortho to para complexes, where the ratios of the intensities are given by the ratios of the degeneracies of the ortho and para nuclear-spin states.²³ These results, and the knowledge that isolated, interstitial H₂ and D₂ in Si exhibit rotational motion,²² lead us to conclude that the two nearlying oxygen lines are indeed due to ortho and para O-H₂ and O-D₂ complexes. We note that para O-H₂ and ortho O-D₂ (i.e., the species with rotational ground states with *J* = 0) have the higher vibrational frequency for each pair of near-lying oxygen lines.

IV. MODEL FOR THE HIGH-FREQUENCY MODES OF THE O-H₂, O-HD, AND O-D₂ COMPLEXES

Pritchard *et al.* assigned the 3788.9- and 3731.0-cm⁻¹ lines of the O-H₂ complex to two different defects with similar structures, because the 57.9 cm⁻¹ splitting seen for these lines is too large to be an ortho-para splitting.¹⁰ Here, a model that explains the ~59 cm⁻¹ splitting for the high-frequency vibrational lines of the O-H₂, O-HD, and O-D₂



FIG. 5. Spectra of interstitial ¹⁸O and of the ¹⁶O modes of the $O-D_2$ complex in Si measured at different temperatures. For the three lower spectra, a reference spectrum was measured without a Si sample in the cryostat. For the top spectrum, a reference spectrum was measured at 40 K for a Cz Si sample that did not contain H or D.

complexes in Si is proposed. Furthermore, the H_2 and D_2 lines of the complexes are assigned to vibrational transitions of ortho and para O-H₂ and O-D₂.

A. The \sim 59-cm⁻¹ energy

Surprisingly, the high-frequency vibrational lines of the O-H₂, O-HD, and O-D₂ complexes are all split by \sim 59 cm^{-1} . Isolated interstitial oxygen has a low-frequency mode at 29 cm^{-1} that gives rise to thermally activated side bands that are associated with oxygen's antisymmetric stretching mode at 1136 cm⁻¹ (4.2 K).^{26–28} Therefore, an obvious candidate for the \sim 59-cm⁻¹ energy difference that is nearly independent of the hydrogen isotope is an oxygen mode. We have studied the oxygen-stretching modes of the O-H₂, O-HD, and O-D₂ complexes to see whether they provide evidence for low-frequency excitations that might be similar to the 29-cm⁻¹ mode of isolated interstitial oxygen. Figure 5 shows spectra of the oxygen-stretching modes of interstitial ¹⁸O (1085 cm⁻¹), present here because of its 0.2% natural abundance, and of the O-D₂ complex (1076 cm⁻¹). (The $O-D_2$ complex is shown as an example because it has the sharpest O line shape.) As the temperature is increased, a line at 1078 cm⁻¹ that is known to be a thermally activated sideband associated with the isolated, interstitial-¹⁸O line appears.²⁶⁻²⁸ (Reference spectra were measured at temperatures corresponding to those of Fig. 5 for a Cz-Si sample but without H or D. When these reference spectra were used, the 1078- and 1085-cm⁻¹ lines were eliminated together, confirming that both are associated with interstitial ¹⁸O. See, for example, the 40 K spectrum in Fig. 5.) There are no corresponding thermally activated sidebands associated with the O-stretching mode of the $O-D_2$ complex. Similarly, there were no thermally activated O lines seen in spectra measured for the O-HD complex. It is for the same range of temperatures that the O-HD complex gives rise to thermally activated HD lines. These results suggest that the ~59-cm⁻¹ energy difference is not due to a low-frequency excitation of the oxygen atom in the defect. (Similarly, there is no evidence for a 19-cm⁻¹ excitation corresponding to the 19-cm⁻¹ energy seen for O-HD.)

Another possibility for the origin of the \sim 59-cm⁻¹ splitting is now considered. The behavior of the 3618.4- and 2642.6-cm⁻¹ vibrational lines of *isolated*, interstitial H₂ and D_2 has been studied for applied uniaxial stresses.^{29,30} (The stress splittings of the weaker IR lines due to isolated HD in Si have not been investigated.) The 3618.4- and 2642.6-cm⁻¹ transitions both show sizable stress splittings, with the remarkable characteristic that the line splittings seen for H_2 and D_2 are identical in magnitude, within experimen-tal error.^{29,30} The absence of an isotope effect for both the isolated molecules and the oxygen-hydrogen complexes is compelling evidence that in both cases the H_2 , D_2 , and HD molecules are undergoing hindered rotation and that what is observed is the splitting of the J=1 rotational level either by applied stress or by internal fields (in the case of the oxygenrelated defects).³⁰ This field-induced splitting also leads to the 19-cm⁻¹ difference between the J=0 level and the lower component of the J=1 level for both the ground and excited vibrational states of O-HD [Fig. 1(b)]. The L=2 potentialenergy perturbation associated with the presence of the oxygen will split the J=1 rotational level. Most significantly, the *magnitude* of the rotational splitting is independent of the isotope since it involves matrix elements of the perturbation with respect to rotational wave functions, and both the perturbation and wave functions are independent of the isotope. Conversely, if the splitting were due to shifts of vibrational levels, it would depend on isotopic mass since the matrix elements of the perturbation would involve vibrational wave functions that depend on the mass of the oscillator. Results of this hindered-rotor model are discussed in more detail in Sec. IVF.

B. Rovibrational transitions of the O-HD complex

An energy-level diagram for the HD lines of the O-HD complex is shown in Fig. 1(b). At low temperature [diagram (i)], rovibrational transitions are seen in which the rotational quantum numbers associated with the initial and final states are J=0 to J=0 and J=0 to J=1, with the former transition being stronger. (Here, we continue to use the rotational quantum numbers of the unsplit states as labels.) When the temperature is increased [diagram (ii)], the lower component of the J=1 state, 19 cm⁻¹ above the ground rotational state, is thermally populated. Here, vibrational transitions between the lower component of the J=1 initial state to both J=1 components associated with the excited vibrational state are seen. The frequencies of the 3285.4- and 3282.2-cm⁻¹ lines are similar in this model because the rotational states (J=0 for the former and J=1 for the latter) are not changed during



FIG. 6. Energy-level diagrams for the rovibrational states of (a) isolated interstitial H_2 and (b) the O-H₂ complex in Si. Diagrams (i) and (ii) show the transitions for the ortho and para O-H₂ complexes, respectively. The level spacings and the frequencies of the transitions are given in cm⁻¹.

these transitions. The frequencies then differ (by 3.2 cm^{-1}) only because of rovibrational coupling.

For isolated HD [Fig. 1(a)], only the rovibrational transition in which the rotational state changes from J=0 to J =1 was observed at low temperature.²² At elevated temperature, a $\Delta J = 0$ transition was observed with the molecule in its J=1 rotational state. There is no $\Delta J=0$ transition seen when the isolated HD molecule is in its J=0 rotational state. The model proposed here for the O-HD complex is similar to the model for isolated interstitial HD in Si, except that the J=1 rotational states associated with the ground and excited vibrational states are split by the presence of the oxygen atom [Fig. 1(b)]. Furthermore, the presence of the O atom has affected the selection rules for the rotational quantum number. A $\Delta J=0$ vibrational transition can now be seen when the O-HD complex is in the J=0 state. One possible explanation is that the presence of the oxygen atom mixes the J=0 and J=1 states, making transitions from the lowest state in Fig. 1(b) allowed. A second possibility (for which we find evidence in the following sections) is that vibrational transitions become allowed in the J=0 state without the mixing of J=0 with J=1.

C. Ortho $O-H_2$ and para $O-D_2$: Vibrational transitions in the J=1 rotational state

A comparison of the transitions seen for the O-H₂ complex with those seen for O-HD leads to interesting conclusions. For O-H₂, the two dominant high-frequency vibrational lines at 3788.9 and 3731.0 cm⁻¹ are due to transitions similar to those seen for O-HD at elevated temperature [Fig. 1(b), diagram (ii)], where the complex is in the J=1 rotational state. These O-H₂ transitions are shown in Fig. 6(b), diagram (i), along with the corresponding transition of isolated H₂ [Fig. 6(a)]. Transitions with $\Delta J=1$ occur only for O-HD. There are no transitions seen for O-H₂ with $\Delta J = 1$, suggesting that rotational states with J=0 and with J=1occur at different defects, ortho O-H₂ for J=1 and para O-H₂ for J=0. This conclusion is consistent with the assignment of the two near-lying oxygen lines to distinct ortho and para O-H₂ complexes (Sec. III B). Therefore, the IR absorption lines at 3731.0 and 3788.9 cm⁻¹ are assigned to ortho O-H₂, where the transitions are between rovibrational states with rotational quantum number J=1.

We have also searched for additional vibrational lines for the O-H₂ complex that are suggested by our model. For example, our model suggests that there might be transitions originating from the upper J=1 state, shown dashed in Fig. 6(b). We have carefully examined the spectra of the O-H₂ complex for temperatures up to 70 K and have found no additional lines that might correspond to such transitions.

Similar considerations apply to O-D₂ except that it is para O-D₂ that has a rotational state with J=1. For O-D₂ there are two closely spaced lines near 2715 cm⁻¹ and another line ~60 cm⁻¹ toward higher frequency (Table I). In the following section, we will argue that the 2716.1-cm⁻¹ line is due to ortho O-D₂. The 2715.0- and 2775.5-cm⁻¹ lines are then due to vibrational transitions of para O-D₂ that are similar to those shown in Fig. 6(b), diagram (i), with the complex in its J=1 rotational state.

D. Para O-H₂ and ortho O-D₂: Vibrational transitions in the J=0 rotational state

Pritchard *et al.* observed two closely spaced vibrational lines at 2715.0 and 2716.1 cm⁻¹ with nearly equal intensities for the O-D₂ complex.¹⁰ In our experiments, we have discovered that the O-H₂ complex has a similar pair of closely spaced lines. Figure 7 shows vibrational spectra of Cz Si into which H had been introduced. A weak line at 3737.1 cm⁻¹ (marked by an arrow in Fig. 7) can be seen 6.7 cm⁻¹ toward higher frequency than the 3731.0-cm⁻¹ line of the O-H₂ complex. This weak line shows qualitatively the same behavior upon the dissociation of the O-H₂ complex by an anneal at 100 °C, followed by reformation at room temperature, as the stronger O-H₂ lines.¹⁰⁻¹² Thus, it appears that there are two closely spaced high-frequency lines for both the O-H₂ and O-D₂ complexes. The ratio of the intensities of the 3731.0- and 3737.1-cm⁻¹ O-H₂ lines is 8.5 to 1.

The splittings of the O-H₂ and O-D₂ lines near 3731 and 2715 cm⁻¹ by a few cm⁻¹ are consistent with the small ortho-para line splittings caused by rovibrational coupling. The O-HD complex also has transitions at 3282.2 and 3285.4 cm⁻¹ [Fig. 1(b)] that are split by rovibrational coupling, where the vibrational transition in the J=0 rotational state has a higher frequency. For O-H₂ and O-D₂, we assign the higher-frequency line of each closely spaced pair to the vibrational transition in the J=0 rotational state, the 3737.1-cm⁻¹ line to para O-H₂ and the 2716.1-cm⁻¹ line to ortho O-D₂. The energy differences between the vibrational transitions taking place in the J=0 and J=1 rotational states for the O-D₂, O-HD, and O-H₂ lines are 1.1, 3.2, and 6.1 cm⁻¹, where the line splitting is seen to increase in size as the frequency increases.³¹ This trend is consistent with



FIG. 7. Spectra (4.2 K) of the interstitial H_2 (left panel) and O-H₂ defects (center and right panels) in Cz Si that contained hydrogen. A weak line at 3737.1 cm⁻¹ is indicated by an arrow. The sample was annealed at 100 °C for 30 min to dissociate O-H₂ complexes and cooled promptly for the measurement shown in the lower spectrum. The sample was then annealed at room temperature for 1 week to produce O-H₂ prior to the final measurement shown in the upper spectrum.

a splitting caused by rovibrational coupling because the anharmonicity of the vibrational potential increases as the frequency increases and supports our assignment of the lines. The assignments of the high-frequency vibrational lines of O-H₂ and O-D₂ to ortho and para defects are given in Table I.

E. Intensities of the high-frequency lines

1. General considerations

The strengths of the absorption lines due to H_2 , HD, and D_2 , and also $O-H_2$, O-HD, and $O-D_2$ were reported in a previous study by Newman *et al.*²¹ The HD and O-HD lines were found to be surprisingly weak relative to the strengths of the lines associated with their isotopic siblings. In our previous work on HD in Si, it was found that the 3191.1-cm⁻¹ HD line that appears at elevated temperature is stronger than the 3265.0-cm⁻¹ line present at 4.2 K and that the 3191.1-cm⁻¹ line has an absorption strength that is consistent with the strengths of the H_2 and D_2 lines.²² The situation is similar for the O-H₂, O-HD, and O-D₂ complexes in Si.

For equal concentrations of H and D in a Si sample, the ratio of the concentrations of $O-H_2$, O-HD, and $O-D_2$ would be 1:2:1 for a random distribution of H and D. However, this ignores the separation of $O-H_2$ and $O-D_2$ into distinct ortho and para species and that vibrational transitions occurring in the J=0 and J=1 rotational states can have different absorption strengths. Here we calculate the ratios of the concentrations of $O-H_2$, O-HD, and $O-D_2$ complexes in the J

=1 and J=0 rotational states. These ratios are then compared with the ratios of concentrations determined from IR absorption measurements to determine whether the separation of O-H₂ and O-D₂ complexes into ortho and para species can explain the isotope dependence of the line intensities.

The ratio of the intensities of the O-H₂, O-HD, and O-D₂ lines in Si that contained equal concentrations of H and D was found to be 1:0.4:0.4 by Newman *et al.*,²¹ where the O-HD lines seen at 4.2 K (3285.4 and 3304.4 cm⁻¹) were considered. The intensities of the IR lines are proportional to η^2/μ times the concentration of absorbing species, where η is an effective charge and μ is the reduced mass of the oscillator.^{21,32} If the effective charge η is assumed to be similar for O-H₂, O-HD, and O-D₂, then the ratio of the concentrations implied by the intensity ratio reported by Newman *et al.*²¹ would be 1:0.53:0.8. This ratio provides a starting point for a comparison of the concentrations determined from absorption measurements for a sample containing equal concentrations of H and D with the predictions of our model for the transitions.

2. Intensities of the vibrational transitions in the J=1 rotational state

We consider first the IR transitions that occur between rovibrational states with J=1. Thus only ortho O-H₂, para O-D₂, and O-HD contribute. If we assume that the ratio of para to ortho species is given by the ratio of the degeneracies of the nuclear-spin states, then the para:ortho ratio will be 1:3 for O-H₂ and 1:2 for O-D₂. Therefore, 0.75 of the total O-H₂ concentration is ortho O-H₂ and 0.33 of the total O-D₂ concentration is para O-D₂. For the O-HD complex, there is no corresponding restriction. Therefore, for equal concentrations of H and D, the ratio of O-H₂, O-HD, and O-D₂ complexes that can be in the J=1 rotational state would be 0.75:2:0.33, or, if we scale to bring the O-H₂ concentration to unity, 1:2.7:0.44.

A first comparison with the experimental ratio of concentrations given above finds the O-HD concentration predicted by our model to be a factor of 5 too large and the predicted $O-D_2$ concentration to be a factor of 1.8 too small. However, the comparison with experiment requires that the ratio of concentrations determined from the line intensities be modified so as to be consistent with the new assignments of the lines. For O-H₂, the absorption intensity observed by Newman et al.²¹ is due to ortho O-H₂ and does not require modification. However, similar to the case of isolated HD in Si,²² it is the O-HD lines that appear at elevated temperature that result from transitions in the J=1 rotational state. The prefactor, 3.7 ± 1 , determined from the fit shown in Fig. 3, is approximately equal to the ratio of the strengths of O-HD absorption lines observed at elevated temperature and the lines observed at 4.2 K.³³ Furthermore, we have assigned the 2715.0- and 2775.5-cm⁻¹ lines to para O-D₂ and find that these lines represent 68% of the total intensity of the highfrequency O-D₂ lines. We use these factors, 3.7 for O-HD and 0.68 for O-D₂, to determine the relative concentrations of $O-H_2$, O-HD, and $O-D_2$ seen by IR absorption in the J =1 rotational state to obtain 1:2.0:0.54. These relative concentrations found from experiment differ from their predicted values, given in the paragraph above, only by small factors <1.5. Given the uncertainties in our estimate of the experimental ratio of concentrations, we take the agreement of experiment with our model for the transitions to be excellent.

3. Intensities of the vibrational transitions in the J=0 rotational state

The ratios of concentrations of O-H₂, O-HD, and O-D₂ in the J=0 rotational state are predicted to be 0.25:2:0.66, where para O-H₂, ortho O-D₂, and the entire O-HD population are considered. If these values are scaled to make the O-H₂ concentration unity, the ratio 1:8:2.6 is obtained.

Again, the concentration ratio derived from the intensities of the absorption lines must be modified to account for the assignments of the vibrational lines. Here, the intensity of the O-HD lines seen at low temperature is for the complex in its J=0 state, so this intensity does not require correction. We have found that the 3737.1-cm⁻¹ line (the transition of para O-H₂ with J=0) represents 7% of the total intensity of the high-frequency O-H₂ lines. Similarly, we have assigned the 2716.1-cm⁻¹ line to ortho O-D₂ and find that this line represents 32% of the total intensity of the high-frequency $O-D_2$ lines. We use these factors to modify the ratio of concentrations determined from the absorption intensities to obtain 0.07:0.53:0.26 for the relative concentrations of the O-H₂, O-HD, and O-D₂ complexes in the J=0 rotational state. If we scale these values to bring the O-H₂ concentration to unity, the ratio 1:7.6:3.7 is obtained. Again, the agreement of these experimental values with the values predicted by our model for the transitions is excellent.

For the isolated H₂, HD, and D₂ molecules in Si, vibrational transitions in the J=0 rotational state were found to be forbidden. Here, for O-H₂, O-HD and O-D₂, the oscillator strengths for transitions with the complexes in the J=0rotational state are found to be a factor of ~4 times weaker than for transitions with the complexes in the J=1 state. (This estimate is made most easily from the intensities of the 3285.4- and 3282.2-cm⁻¹ lines of O-HD.) The result that the high-frequency transitions of O-H₂, O-HD, and O-D₂ in the J=0 rotational state have similar oscillator strengths indicates that these transitions are not made allowed by the mixing of J=0 and J=1 states. If this were the case, one should expect a greater absorption strength for O-HD, where rotational states with odd J and even J can occur for the same defect.

F. Calculations for a hindered-rotor model

How reasonable are these arguments? How, for example, can one have J=0 to J=0 transitions without mixing J = 1 states into J=0? How can an internal perturbation lead to a difference of only 19 cm⁻¹ between J=0 and J=1 states when the corresponding difference for the free HD molecule is ~80 cm⁻¹?

We have used a simple hindered-rotor model to test numerically many of the ideas discussed here. Details of this model and results will be presented elsewhere.¹⁹ Here we briefly summarize some essential points. We have constructed a potential-energy function to treat the dynamics of the interstitial H₂ molecule in terms of a potential-energy function for the interstitial hydrogen atom computed from first principles by Porter, Towler, and Needs.³⁴ Using this molecular potential-energy function, including L=3, 4, and 6 terms, we then calculated both center-of-mass motion and rotational motion of the molecule, the latter using a Devonshire-type code of Martin and Fowler.³⁵ In the case of isolated interstitial H₂ and D₂, the *existence* of a dipole moment comes about from the zero-point displacement of the molecule from the tetrahedral site. Ortho-para separations persist for H₂ and D₂, and the rotational quanta are only slightly reduced from the free-molecule values. Selection rules for rovibrational transitions for the various isotopes follow from these considerations.²²

In the present case the existence of an oxygen atom at an adjacent bond-centered site leads to additional potential terms of L=2 symmetry. The low symmetry of the bond-centered site with respect to the tetrahedral site splits the J = 1 rotational level into three distinct states. The resulting rotational motion will resemble that of a propeller; the potential energy (with respect to the H₂-oxygen axis) may be taken as the sum of a large $\cos^2 \theta$ term plus a smaller $\sin^2 \theta [1-\cos(2\phi)]$ term. Similar potentials have been used to simulate H₂ rotation near surfaces.³⁶⁻³⁸

It is then the two lowest states derived from J=1 that are responsible for the two observed J=1 states discussed earlier. By varying the strength of the L=2 terms it is possible to simulate all the features seen experimentally. Namely, we can generate one split level that is close to the ground state (the 19-cm⁻¹ level of HD) and a second level whose splitting from the first split level is large and is independent of the isotope (the 59-cm⁻¹ splitting). The finite J=0 to J=0 oscillator strength comes not from mixing of J=0 and J=1, but rather from the *E*-field³⁹ associated with the presence of the oxygen atom.

V. CONCLUSION

The recent discovery of vibrational lines for the interstitial HD molecule in Si, and the conclusion that the isolated H_2 molecule in Si exhibits rotational motion,²² have led us to perform experiments for the O-H₂, O-HD, and O-D₂ complexes in Si. We have found vibrational lines for the O-HD complex that appear at elevated temperature (T > 10 K). Based on these observations, a model for the behavior of the O-H₂ complex in Si has been proposed. The most important feature of this model is that the interstitial H₂ molecule in the

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complex acts as a rotor, leading to distinct ortho and para $O-H_2$ defects. Furthermore, the interstitial H_2 molecule is perturbed by the interstitial oxygen atom to which it is weakly bound. The O modes of both the ortho and para $O-H_2$ complexes are seen, giving rise to the two near-lying O lines seen by IR spectroscopy. The ortho and para $O-H_2$ complexes also give rise to distinct H_2 vibrational lines. The situation is similar for $O-D_2$ except that the roles of the ortho and para complexes are reversed. The isotope dependence of the intensities of the high-frequency lines of the $O-H_2$, O-HD, and $O-D_2$ complexes are explained naturally by the concentrations of the ortho and para species with their different vibrational properties, providing a strong confirmation of our model for the complexes.

We note that the selection rules used to explain the differences between the transitions that can be seen for O-HD and O-H₂ depend on there being distinct ortho and para O-H₂ complexes, each with its own manifold of rotational states. Rotational states with both even and odd *J* are possible for the same defect only for O-HD. These distinguishing properties of the ortho and para complexes argue against other low-frequency excitations, for example, silicon resonance modes or oxygen modes, being involved in the transitions we have seen.

The O-H₂, O-D₂, and O-HD complexes all give highfrequency vibrational lines split by an energy of ~59 cm⁻¹. We have proposed that these ~59-cm⁻¹ splittings are produced by the perturbation arising from the oxygen atom in the complexes, which splits the J=1 rotational state of the nearby hydrogen molecule. Related to this explanation for the nearly identical splittings of the high-frequency lines of the O-H₂, O-HD, and O-D₂ complexes is the experimental finding that the H₂ and D₂ molecules show splittings for externally applied stresses that are identical in magnitude, within experimental error.³⁰ The independence of these splittings with isotopic mass is compelling evidence for hindered rotation of the hydrogen molecules.

Our model explains essentially all of the experimentally observed features of the $O-H_2$, O-HD, and $O-D_2$ complexes Si and is pleasantly consistent with the properties of the isolated H_2 , HD, and D_2 defects.

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