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Ortho-para transition of interstitial H_2 and D_2 in Si

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The ortho-para transition of interstitial H_2 in Si has been observed in a recent Raman study [M. Hiller *et al.*, Phys. Rev. Lett. **98**, 055504 (2007); **99**, 209901 (2007)]. In order to address issues that are difficult to study by Raman spectroscopy, we have performed IR-absorption experiments to further investigate this ortho-para transition. We find that when a Si sample containing H_2 that has been equilibrated at room temperature is subsequently held at 77 K, the 3618.4 cm^{-1} IR line assigned to ortho-H_2 is reduced in intensity with a single *exponential* time constant of 229 h as the system relaxes to the para-H_2 state. The previous Raman data had been analyzed by a model in which the ortho-para transition is caused by an interaction with the nuclear magnetic moment of ^{29}Si (4.7% abundant) that is present in natural Si. However, in order for every H_2 molecule to interact with a ^{29}Si, at least six shells of Si neighbors must be considered. Because of the strong dependence of the transition rate on the ^{29}Si-H_2 distance, the kinetics of such a transition should be highly *nonexponential*. Thus, our IR data are not consistent with this mechanism. We have also investigated the para-ortho transition of interstitial D_2 and have found decay rates similar to those for the ortho-para transition of H_2. We have considered two possible mechanisms for this transition: H_2 or D_2 tunneling, which would allow the molecule to sample tetrahedral sites adjacent to ^{29}Si, and spin-rotation coupling that can act while the molecule is dynamically off-center. Consideration of a possible tunneling rate by theory and the similarity of the H_2 and D_2 results seem to rule out the tunneling mechanism but not the spin-rotation mechanism. These results clearly show that the mechanism of the ortho-para transition for H_2 and D_2 in Si remains an experimental and a theoretical challenge.

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I. INTRODUCTION

The H_2 molecule was suggested to be an important defect in semiconductors in the early 1980s.[1,2] Nonetheless, it was more than a dozen years before H_2 was observed directly by vibrational spectroscopy.[3–5] The H_2 stretching line for molecular H_2 in GaAs was discovered by Raman spectroscopy and was found to be split into two components 8 cm^{-1} apart.[3] These lines were assigned to ortho- and para-H_2. This interpretation led to the conclusion that H_2 in GaAs is rotating freely. However, the path to understanding H_2 in Si was not so direct.[6,7] A vibrational line for H_2 in Si at 3618.4 cm^{-1} was found but an ortho-para splitting was not detected initially.[4,5,8] It required several years of study[6,7,9–11] before the experimental properties of H_2 in Si could be reconciled with the prediction of theory that molecular H_2 in Si is located within the tetrahedral interstitial site [Fig. 1(a)] and is a nearly free rotator whose center of mass is also in motion.[8,10,12–15]

The H_2 molecule has ortho and para states with the nuclear spins of the two protons aligned either parallel (ortho) or antiparallel (para).[16,17] Because the total molecular wave function of H_2 must be antisymmetric upon exchange of the two identical protons, ortho-H_2 has rotational states with odd values of the rotational quantum number J, whereas para-H_2 has rotational states with even J. The lowest energy state of para-H_2 has rotational quantum number $J=0$ and the lowest energy state of ortho-H_2 has rotational quantum number $J=1$. In most practical circumstances, these behave as two distinct molecular species, each with its own rotational spectrum. However, if one waits a sufficiently long time at low temperature, H_2 can relax to its lower energy para state. This transition rate can be remarkably slow because the nuclear spin of the proton interacts only weakly with its environment.

The observation by Raman spectroscopy of the ortho-para transition of interstitial H_2 in Si has been reported recently.[18,19] Raman scattering may be used to probe the stretching mode of a free H_2 molecule because, while an electric-dipole transition is forbidden for a homonuclear diatomic molecule, Raman spectroscopy is subject to different selection rules.[17] For interstitial H_2 in Si, a Raman line at 3618 cm^{-1} (10 K) was discovered and assigned to the H_2 stretching mode.[4] An ortho-para splitting was not seen in these early experiments because laser heating problems caused para-H_2 to be promoted to its rotational excited states, which apparently broadened and weakened the H_2 stretching, Raman line.[20] Once this confusing issue was resolved, both the ortho and para states could be studied by Raman spectroscopy.

Surprisingly, infrared (IR)-absorption experiments found that the stretching mode for H_2 in Si is weakly IR allowed and gives rise to a single sharp line at 3618.4 cm^{-1} (Ref. 5).

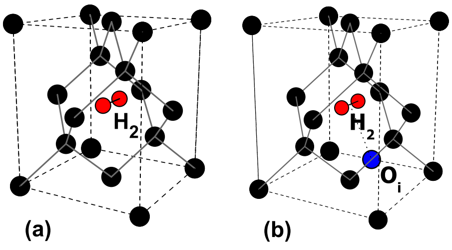

FIG. 1. (Color online) (a) Interstitial H_2 in Si. (b) The O-H_2 complex in Si.

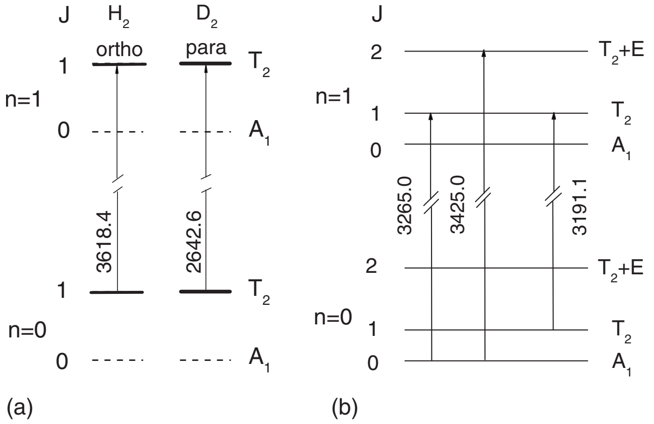

FIG. 2. (a) Energy levels of interstitial H_2 and D_2 in Si. (b) Energy levels of HD in Si.

In this case, the para line is not observed because of selection rules for transitions of the H_2 molecule in the tetrahedral crystal field.[6,9,10] Figure 2(a) is an energy-level diagram showing the rotational-vibrational levels of H_2 in Si and the 3618.4 cm^{-1} transition. In tetrahedral symmetry, the $J=0$ rotational state of para-H_2 becomes A_1 and the $J=1$ rotational state of ortho-H_2 becomes T_2. A purely vibrational transition with the molecule in its $J=0$ rotational state is an $A_1 \rightarrow A_1$ transition and is electric-dipole forbidden in tetrahedral symmetry. A vibrational transition with the molecule in its $J=1$ rotational state is a $T_2 \rightarrow T_2$ transition and is allowed by symmetry. Therefore, the line at 3618.4 cm^{-1} has been assigned to a $T_2 \rightarrow T_2$ transition of ortho-H_2, and para-H_2 cannot be seen by IR-absorption spectroscopy. These assignments have been confirmed in detail by the splitting of the rotational states under uniaxial stress.[21,22]

When a Si sample containing H_2 molecules is stored at elevated temperature (room temperature is sufficient), the ratio of the populations of ortho- and para-H_2 is 3 to 1 because of the degeneracies of the nuclear-spin states, a fact that has been verified by Raman measurements.[18–20] When a sample was stored at 77 K for a long time, the relative intensity of the para line was found to increase as ortho-H_2 made a transition to the lower energy para-H_2 state. The time scale for the ortho-para transition at 77 K was found to be of order 200 h.[18,19]

These observations of the ortho-para transition of H_2 in Si have been interpreted in terms of the following transition probability for a catalytically induced collision process derived by Wigner[23]

$$W = \frac{2\mu_a^2 \mu_P^2 J_m}{3\hbar^2 d^6 M v^2}. \tag{1}$$

Here, μ_a is the magnetic moment of the paramagnetic species inducing the transition at distance d from the H_2 molecule and μ_P is the magnetic moment of the proton. J_m, M, and v are the moment of inertia, mass, and thermal velocity of H_2. It was suggested that the ^{29}Si isotope (4.7% abundant), with its unpaired nuclear spin, causes the ortho-para transition.[18,19] If a near-lying ^{29}Si nucleus is responsible for the transition, then several shells of Si neighbors must be involved for every H_2 molecule to interact with a ^{29}Si. Hiller *et al.*[18,19] constructed a model for the ortho-para transition of interstitial H_2 in which a sum of exponential functions with different time constants was used to fit the observed kinetics at 77 K. That is, the d^{-6} dependence in Eq. (1) means that H_2 molecules with near-lying ^{29}Si nuclei in different neighbor shells will show very different transition rates in this model.

Conclusions about the mechanism for the ortho-para transition depend strongly on the accuracy of the measurements of the ortho-para ratio, and such experiments are especially difficult by Raman spectroscopy because laser heating problems are an important source of error in the measurement of the ortho/para ratio.[20] In the present work, we have measured the ortho-para transition for interstitial H_2 in Si with increased accuracy by IR spectroscopy so that the behavior of the transition rate can be tested to shed light on the transition mechanism. We have also refined the data analysis and have investigated alternative mechanisms for the ortho-para transition.

Because IR-absorption experiments that probe the ortho-para transition of H_2 in Si see only the ortho state,[6,9,10] the population change in the para state must be inferred. We have addressed this problem by investigating the O-H_2 defect in Si [Fig. 1(b)].[20,24–27] The frequency of the oxygen mode of the O-H_2 complex near 1075 cm^{-1} depends slightly on whether its H_2 neighbor is ortho-H_2 or para-H_2 (Ref. 27), giving two components that have made it possible for us to probe changes in both the ortho and para populations. In addition to probing the ortho-para transition, these experiments test the assignment of the O-H_2 defect's oxygen modes. The O-H_2 defect also has H_2 stretching modes[20,24,27] that were studied previously by Raman spectroscopy to reveal the ortho-para transition.[19,28] The H_2 stretching mode at 3731.1 cm^{-1} of O-ortho-H_2 in Si has been investigated in the present work by IR absorption to complement results for the defect's oxygen mode. Finally, we have also studied the ortho-para transition for D_2 in Si to obtain further clues about the ortho-para transition mechanism.

II. EXPERIMENT

For our experiments on the interstitial H_2 and D_2 molecules, lightly doped Si samples grown by the floating-zone method were used. Sample dimensions were typically $6 \times 6 \times 15$ mm^3 with the optical viewing direction being along the long axis of the sample. H or D was introduced by annealing the samples for 1 h at 1250 °C in sealed quartz ampoules that contained 0.7 atm of H_2 or D_2 gas. The anneals were terminated by a rapid quench in water to room temperature. Samples that were selected for our experiments typically had a concentration of H_2 or D_2 molecules near 5×10^{15} cm^{-3} (Ref. 29). For experiments on the O-H_2 complex, lightly doped, Czochralski-grown Si samples (typical oxygen concentration $[\text{O}] \approx 10^{18}$ cm^{-3}) were used. To form O-H_2 complexes, samples were hydrogenated as above and then annealed for longer than 1 week at room temperature.[24–27] Following the long anneal at room temperature, approximately 60% of the H_2 molecules had become bound to interstitial oxygen to form O-H_2 complexes.

IR-absorption spectra were measured with a Bomem DA3.16 Fourier-transform spectrometer equipped with a KBr beamsplitter and InSb and HgCdTe detectors. Interference filters were used to narrow the spectral range that was examined in order to increase the signal-to-noise ratio of our absorption measurements.

For many of our experiments, samples were transferred rapidly from a liquid N_2 storage container to an optical cryostat for absorption measurements at 4 K and then back again into liquid N_2. To perform the transfer, a sample was removed from liquid N_2 and warmed to room temperature by immersion in water. The sample at room temperature was then inserted into a top-loading cryostat that had been precooled to less than 80 K. The sample was then cooled to 4 K for measurement. After IR measurements were made at 4 K, the sample was then quickly transferred back to the liquid N_2 storage container. An Oxford CF 1204 cryostat with He contact gas was used for this procedure. Temperature was measured with a RhFe resistance sensor mounted on the heat exchanger of the cryostat. With practice, the transfer of the sample from liquid N_2 into the cold optical cryostat could be performed in less than 10 min, which is much shorter than the time scale for the ortho-para transition at room temperature found previously by Raman spectroscopy[18,19] or in the present work.

III. EXPERIMENTAL RESULTS

A. H_2

To investigate the ortho-para transition at 77 K, a Si sample which contained H_2 molecules throughout the Si bulk was prepared initially by storage for a long time (>2 weeks) at room temperature to achieve thermal equilibrium. (Results for the ortho-para transition reported in Refs. 18 and 19 were used initially to determine appropriate time scales for preparing samples at room temperature and at 77 K.) This sample was then placed in liquid N_2 so that the ortho-para transition at 77 K could be probed. The inset to Fig. 3 shows the IR-absorption line at 3618.4 cm^{-1} due to ortho-H_2 for the times at 77 K that are indicated. The 3618.4 cm^{-1} line was found to decrease in intensity as the annealing time at 77 K was increased. The open squares in Fig. 3 show the peak absorbance of the 3618.4 cm^{-1} line as a function of the time the sample was held at 77 K. For each data point in these experiments, the sample was removed from liquid N_2 and warmed quickly to room temperature so that it could then be transferred to a precooled optical cryostat for an IR measurement at 4 K as was described in Sec. II.

To investigate the ortho-para transition at room temperature, a Si sample containing H_2 molecules was stored in liquid N_2 for 2 months to produce a thermal equilibrium distribution of ortho- and para-H_2 at 77 K. This sample was then annealed at room temperature and the intensity of the 3618.4 cm^{-1} line was measured as a function of the annealing time. The inset in Fig. 4 shows the IR line at 3618.4 cm^{-1} for the annealing times at room temperature that are indicated. The open squares in Fig. 4 show the peak absorbance of the 3618.4 cm^{-1} line as a function of the time the sample prepared at 77 K was subsequently held at room temperature.

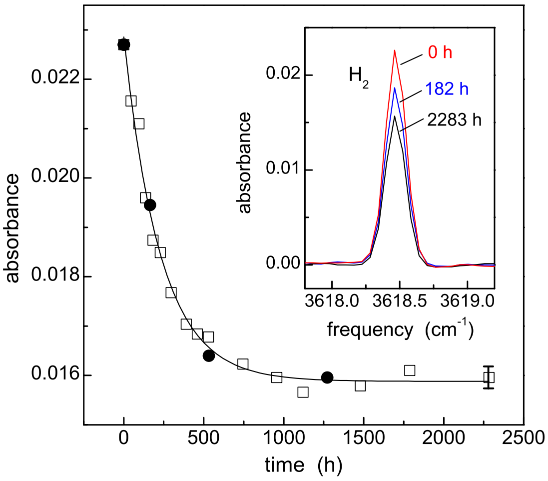

FIG. 3. (Color online) The peak absorbance of the 3618.4 cm^{-1} line due to H_2 in Si as a function of time held at 77 K. The sample was initially equilibrated at room temperature. A typical error bar estimated from the noise in the baseline of the IR spectrum is shown for the data point at highest frequency. The data are fit by the relationship $(1.59\pm0.01)\times10^{-2}+(7.0\pm0.02)\times10^{-3}\exp[-t/(229\pm14)\ \text{h}]$. The inset shows the 3618.4 cm^{-1} line for the times at 77 K that are indicated.

B. O-H_2

Spectra for the oxygen mode of the O-H_2 complex in Si are shown in Fig. 5. There are two near-lying lines because the frequency of the O mode of the complex depends on

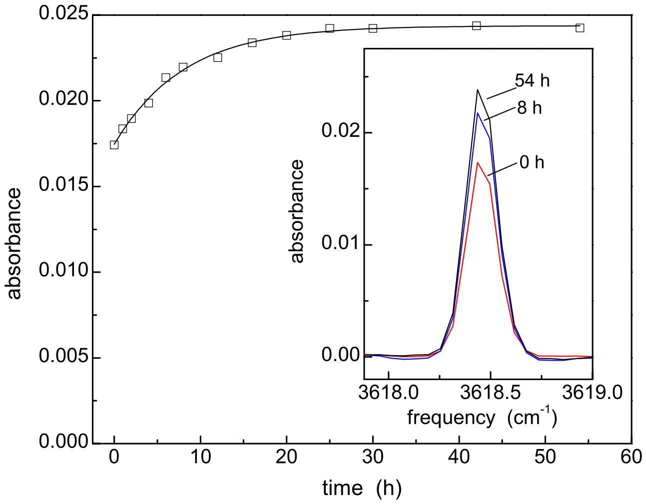

FIG. 4. (Color online) The peak absorbance of the 3618.4 cm^{-1} line due to H_2 in Si as a function of time held at room temperature. The sample was initially equilibrated at 77 K. The height of a curve symbol is typical of the uncertainty in the measured absorbance. The data are fit by the relationship $(2.44\pm0.01)\times10^{-2}-(6.9\pm0.14)\times10^{-3}\exp[-t/(8.1\pm0.5)\ \text{h}]$. The inset shows the 3618.4 cm^{-1} line for the times annealed at room temperature that are indicated.

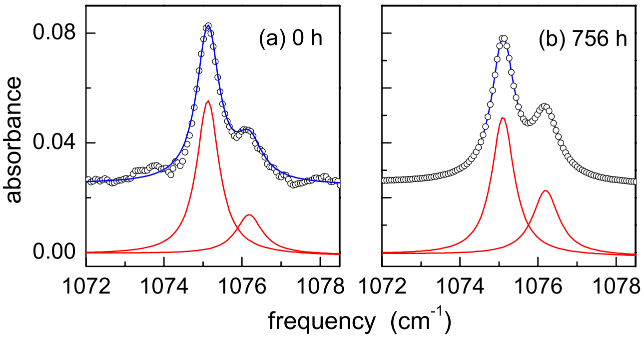

FIG. 5. (Color online) IR-absorption spectra (4.2 K) of the oxygen mode of the O-H_2 complex in Si. (a) Sample equilibrated initially at room temperature and (b) held subsequently at 77 K for 756 h. The line shapes are fit by the sum of two Lorentzian functions.

whether ortho-H_2 or para-H_2 is trapped nearby.[27] To investigate the ortho-para transition for H_2 in the O-H_2 complex, a Si sample containing O-H_2 complexes was held at room temperature for a long time (>2 weeks) to achieve thermal equilibrium. This sample was then placed in liquid N_2 so the ortho-para transition at 77 K could be examined. In this case, both the O band and the H_2 stretching line of the complex at 3731.1 cm^{-1} were examined.

Figure 5(a) shows the O band for the sample equilibrated at room temperature and Fig. 5(b) shows the O band after the sample was held at 77 K for 756 h. As the "annealing" time at 77 K is increased, the component due to O-ortho-H_2 is seen to decrease in intensity while the component due to O-para-H_2 is seen to increase in intensity. To analyze the IR spectra, the O-band's line shape was fit with the sum of two Lorentzian components (see Fig. 5). Spectra measured over the entire range of annealing times could be fit well with the sum of two Lorentzian line shapes with center frequencies 1075.1 and 1076.2 cm^{-1} and with full widths at half maximum of 0.70 and 0.82 cm^{-1}, respectively. From these fits, the areas of the O-ortho-H_2 line at 1075.1 cm^{-1} [$I_o(t)$] and the O-para-H_2 line at 1076.2 cm^{-1} [$I_p(t)$] were determined. Figure 6 shows plots of the total area of the O band, $I_o(t)+I_p(t)$, and the difference of the areas of the ortho and para components, $I_o(t)-I_p(t)$, as a function of the time at 77 K. Similar to the experiments performed to probe the ortho-para transition at 77 K for isolated interstitial H_2, the Si sample containing O-H_2 complexes was transferred from liquid N_2 to a precooled optical cryostat for IR measurements at 4 K by warming quickly to room temperature to effect the transfer.

The H_2 stretching lines at 3731.1 and 3788.9 cm^{-1} have been assigned to the O-ortho-H_2 complex.[27] Here, we focus on the stronger of these lines at 3731.1 cm^{-1}. Spectra of the 3731.1 cm^{-1} line were measured in the same experiment in which the data shown in Fig. 6 for the O band of the O-H_2 complex were measured. The inset to Fig. 7 shows the 3731.1 cm^{-1} line for the times at 77 K that are indicated. The open circles in Fig. 7 show the peak absorbance of the 3731.1 cm^{-1} line as a function of the time the sample was held at 77 K.

To investigate the ortho-para transition of the O-H_2 complex at room temperature, a Si sample containing O-H_2 centers was stored in liquid N_2 for 2 months to produce a thermal equilibrium distribution of O-ortho-H_2 and O-para-H_2 at 77 K. This sample was then annealed at room temperature and the intensity of the 3731.1 cm^{-1} line was measured as a function of the annealing time. Figure 8 shows the peak absorbance of the 3731.1 cm^{-1} line as a function of the time the sample initially equilibrated at 77 K was subsequently held at room temperature.

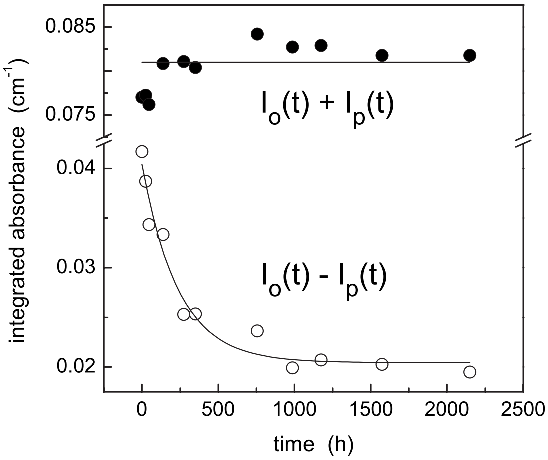

FIG. 6. $I_o(t)$ and $I_p(t)$ are the areas of the oxygen modes of O-ortho-H_2 and O-para-H_2, respectively. $I_o(t)+I_p(t)$ is shown by solid circles and $I_o(t)-I_p(t)$ is shown by open circles as a function of time the sample was held at 77 K. The sample was equilibrated initially at room temperature. The data points shown by the solid circles are fit by the constant $(8.06\pm0.08)\times10^{-2}$ cm^{-1}. The data points shown by the open circles are fit by the relationship $(2.04\pm0.08)\times10^{-2}$ cm^{-1}$+(2.00\pm0.13)\times10^{-2}$cm^{-1} $\exp[-t/(238\pm43)\ \mathrm{h}]$.

The intensity of the 3618.4 cm^{-1} line due to interstitial H_2 was also examined in oxygen-rich Si grown by the Czochralski method. Results for the ortho-para transition monitored at 77 K and at room temperature were found to be

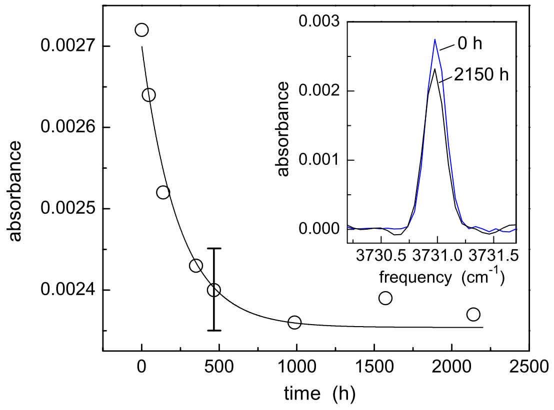

FIG. 7. (Color online) The peak absorbance of the 3731.1 cm^{-1} line due to the H_2 stretching mode of the O-ortho-H_2 complex in Si as a function of time held at 77 K. The sample was initially equilibrated at room temperature. A fit to the data is shown with the exponential time constant (238 h) determined from data for the oxygen mode. The inset shows the 3731.1 cm^{-1} line for the times annealed at 77 K that are indicated.

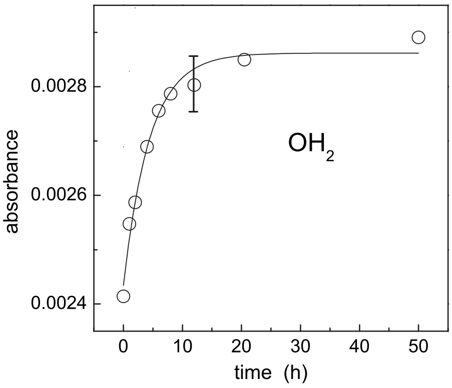

FIG. 8. The peak absorbance of the 3731.1 cm^{-1} line due to the H_2 stretching mode of the O-ortho-H_2 complex in Si as a function of time held at room temperature. The sample was initially equilibrated at 77 K. The data points shown by solid circles for O-H_2 are fit by the relationship $(2.86\pm0.02)\times10^{-3}-(4.3\pm0.2)\times10^{-4}\exp[-t/(4.5\pm0.5)\ \text{h}]$.

similar to those shown in Figs. 3 and 4 for H_2 in a Si sample grown by the floating-zone method.

IV. EQUILIBRIUM ORTHO/PARA RATIO AT ROOM TEMPERATURE AND AT 77 K

A. H_2

In the present paper, $n_o(t)$ is taken to be the concentration of the ortho species and $n_p(t)$ is taken to be the concentration of the para species at time t. Concentrations at thermal equilibrium at temperature T are denoted $n_o^{T(K)}$ and $n_p^{T(K)}$. If a sample is held at a given temperature for a time sufficient for thermal equilibrium to be established, the ortho/para ratio for an H_2 molecule is given by,[16]

$$\frac{n_o^{T(K)}}{n_p^{T(K)}} = \frac{3\sum_{J=\text{odd}}(2J+1)\exp[-E(J)/kT]}{\sum_{J=\text{even}}(2J+1)\exp[-E(J)/kT]}. \tag{2}$$

The factor of 3 accounts for the degeneracies of the nuclear-spin states and $(2J+1)$ is the degeneracy of a rotational state. The rotational energy levels are given by

$$E(J) = \hbar^2 J(J+1)/(2\mu R^2), \tag{3}$$

where R is the interatomic separation and μ is the reduced mass of the molecule.

The rotational energies for interstitial H_2 in Si have not been measured directly but can be determined from the rotational levels observed for interstitial HD that are shown in Fig. 2(b).[22] The spacing between the $J=0$ and $J=1$ levels was found to be 74 cm^{-1} (Ref. 9) and the spacing between the $J=1$ and $J=2$ levels was found to be 160 cm^{-1} (Ref. 22). These results are consistent with an interatomic separation of $R=0.788$ Å (i.e., with a theoretically predicted extension of 0.04 Å from the free molecule value[14]) and a corresponding rotational constant for HD of $\hbar^2/(2\mu R^2)=40.3\ \text{cm}^{-1}$. From the dependence of the rotational constant on the reduced mass, the value $\hbar^2/(2\mu R^2)=54\ \text{cm}^{-1}$ for interstitial H_2 is obtained. Equation (2) gives an equilibrium ortho/para ratio for interstitial H_2 of 3.0 at room temperature and of 1.18 at 77 K.

The changes in the intensity of the 3618.4 cm^{-1} line shown in Figs. 3 and 4 are attributed to the ortho-para transition of the interstitial H_2 molecule. When a sample prepared with an equilibrium distribution of ortho- and para-H_2 at room temperature is subsequently held at 77 K, the ortho-H_2 line decreases in intensity to eventually produce the equilibrium distribution of ortho- and para-H_2 characteristic of 77 K. When a sample prepared by storage for a long time at 77 K is subsequently annealed at room temperature, the ortho-H_2 line grows in intensity to eventually produce the equilibrium distribution of ortho- and para-H_2 characteristic of room temperature.

While only the intensity of the line due to ortho-H_2 can be observed directly in IR-absorption experiments to monitor changes in the ortho population,[9] changes in the population of para-H_2 can be inferred if reasonable assumptions are made. First, the ortho/para ratio at elevated temperature is taken to be $n_o^{295}/n_p^{295}=3$. Second, the change in the ortho population is assumed to be equal to the negative of the change in the para population, that is, $[n_o(t)-n_o(0)]=-[n_p(t)-n_p(0)]$. With these assumptions, the para concentration can be determined from the ortho concentration with the relationship $n_p(t)=4/3n_o^{295}-n_o(t)$ and the ortho/para ratio can be determined with the relationship,

$$\frac{n_o(t)}{n_p(t)} = \left[4/3\frac{n_o^{295}}{n_o(t)} - 1\right]^{-1}. \tag{4}$$

The kinetics for the change in the ortho/para ratio at 77 K for the sample initially equilibrated at room temperature (Fig. 3) could be fit well by a single exponential function. For this experiment, n_o^{295}/n_o^{77} is equal to the ratio of the intensity of the 3618.4 cm^{-1} line at $t=0$ (characteristic of room temperature) to the intensity at $t=\infty$ (characteristic of 77 K). From the parameters of the fit shown in Fig. 3, n_o^{295}/n_o^{77} is determined, and from Eq. (4), the ortho/para ratio at 77 K is found to be $n_o^{77}/n_p^{77}=1.08\pm0.05$ (Ref. 30).

A similar analysis can be performed for the data shown in Fig. 4. For this experiment, n_o^{295}/n_o^{77} is equal to the ratio of the intensity of the 3618.4 cm^{-1} line at $t=\infty$ (characteristic of room temperature) to the intensity at $t=0$ (characteristic of 77 K). From the parameters of the fit shown in Fig. 4 and from Eq. (4), the ortho/para ratio at 77 K is found to be $n_o^{77}/n_p^{77}=1.16\pm0.05$.

The ortho/para ratios characteristic of 77 K found from the data in Figs. 3 and 4 are equal, within error, and are consistent with 100% of the interstitial H_2 molecules achieving the equilibrium ortho/para ratio calculated from Eq. (2) with the rotational energy for H_2 determined from spectroscopic results for HD and theory. These results are also consistent with the ortho/para ratio at 77 K determined previously by Raman spectroscopy[18] of 1.22 ± 0.26.

B. O-H_2

The spectrum of the oxygen mode of the O-H_2 complex reveals both the ortho- and para-H_2 components. These IR data permit the ortho/para ratio to be determined without the assumptions that were necessary to analyze the data for the 3618.4 cm^{-1} line of ortho-H_2.

The changes in the intensities of the 1075.1 and 1076.2 cm^{-1} components of the oxygen mode shown in Fig. 5 are attributed to the ortho-para transition of the interstitial H_2 molecule in the O-H_2 complex. When a sample prepared with an equilibrium distribution of ortho- and para-H_2 at room temperature is subsequently held at 77 K, the O-ortho-H_2 component at 1075.1 cm^{-1} decreases in intensity while the O-para-H_2 component at 1076.2 cm^{-1} increases in intensity as an equilibrium distribution of ortho- and para-H_2 in the complex characteristic of 77 K is eventually produced. At the same time, the H_2 stretching line at 3731.1 cm^{-1} assigned to the O-ortho-H_2 complex decreases in intensity (Fig. 7). These intensity changes provide a strong confirmation of the assignment[27] of the oxygen-mode components at 1075.1 and 1076.2 cm^{-1} to the O-ortho-H_2 and O-para-H_2 complexes, respectively. Furthermore, the assignment of the 3731.1 cm^{-1} line to the H_2 stretching mode of the O-ortho-H_2 complex[27] is similarly confirmed.

The ortho/para ratio can be determined from the parameters for the fit to the data shown in Fig. 6 from the relationship,

$$\frac{n_o(t)}{n_p(t)} = \frac{[I_o(t)+I_p(t)]+[I_o(t)-I_p(t)]}{[I_o(t)+I_p(t)]-[I_o(t)-I_p(t)]}. \tag{5}$$

The ortho/para ratio at room temperature is found to be $n_o^{295}/n_p^{295}=3.0\pm 0.3$. This result is consistent with the assumption made above that the ortho/para ratio for the interstitial H_2 molecule is 3 at room temperature. The ortho/para ratio at 77 K is found to be $n_o^{77}/n_p^{77}=1.68\pm 0.07$ (Ref. 30).

Previous measurements of the ortho-para ratio for the O-H_2 complex made by Raman spectroscopy have substantial error bars.[28] Nonetheless, the ortho-para ratios determined at 77 K and at room temperature by Raman spectroscopy are consistent, within error, with the results we have obtained by IR spectroscopy.

The rotational levels of the H_2 molecule in the O-H_2 complex are split by the field of the nearby O atom.[27,28,31] The splitting of the $J=1$ level in the first excited vibrational state has been observed to be 58 cm^{-1}.[27] If we assume that the splitting of the $J=1$ level in the ground vibrational state is similar, then the first excited rotational level of O-H_2 is estimated to be ≈ 50 cm^{-1} above the ground rotational state. Therefore, the ortho/para ratio at 77 K should be larger for the O-H_2 complex than for interstitial H_2, consistent with experiment. However, the splittings of the other rotational states of O-H_2 have not been determined experimentally.[20,27] Therefore, we do not attempt to calculate an equilibrium ortho/para ratio from a relationship like Eq. (2).

V. KINETICS OF THE ORTHO-PARA TRANSITION

The intensity changes for interstitial ortho- and para-H_2 in Si when the temperature of a sample is changed between room temperature and 77 K are consistent with all of the interstitial H_2 molecules obtaining their thermal equilibrium distribution if sufficient time is allowed for equilibrium to be established. The time scales for the ortho-para transition that we have found at room temperature and at 77 K are in agreement with those found in recent Raman experiments.[18,28] However, the interpretation of the data for the kinetics of the ortho-para transition strongly affects the model for the transition mechanism and the ortho-para transition rate that is inferred.

What is the mechanism for the ortho-para transition of H_2 in Si? In previous Raman experiments performed by Hiller *et al.*,[18] the transition rate was found not to depend on the concentration of dopants in the Si sample. Interstitial H_2 in Si grown by the floating-zone method with a low oxygen content and in Si grown by the Czochralski method with $[\text{O}]\approx 10^{18}$ cm^{-3} also show similar transition rates.[18,28] These results suggest that oxygen and dopant impurities do not play a role in the ortho-para transition. Hiller *et al.*[18,19] proposed a mechanism for the ortho-para transition of interstitial H_2 in which the interaction with the nuclear magnetic moment of ^{29}Si atoms (4.7% natural abundance) in the shells of Si neighbors surrounding the interstitial molecule causes the transition.

Experiments reported in the present paper also find similar transition rates for H_2 in Si with high and low oxygen concentrations, supporting the conclusion that the oxygen impurities do not affect the ortho-para transition rate. Furthermore, samples for Raman studies[18] were hydrogenated with an H_2 plasma and have a high local H_2 concentration, near $[H_2]\approx 10^{20}$ cm^{-3}, in a thin layer at the sample surface. Samples for our IR experiments have interstitial H_2 distributed throughout the Si bulk with a concentration near $[H_2]\approx 5\times 10^{15}$ cm^{-3}. Because Raman and IR experiments find similar transition rates, the interaction between interstitial H_2 molecules is unlikely to play a role in the ortho-para transition mechanism that has been observed.

In the remainder of this section, we consider whether the mechanism suggested by Hiller *et al.*[18,19] in which the ortho-para transition of interstitial H_2 is caused by the interaction with the nuclear magnetic moment of its ^{29}Si neighbors is consistent with the kinetics for the transition that have been observed.

A. Kinetics for the ortho-para transition described by a single time constant

The time evolution of the ortho- and para-H_2 populations is determined by the following rate equations when the transition mechanism involves a single time constant[19]

$$\frac{dn_o(t)}{dt} = -kn_o(t) + k^* n_p(t), \tag{6a}$$

$$\frac{dn_p(t)}{dt} = kn_o(t) - k^* n_p(t). \tag{6b}$$

In thermal equilibrium, $dn_o(t)/dt=0$, so that $k^* = (n_o^{T(K)}/n_p^{T(K)})k$, where the ortho/para ratio in thermal equilibrium at temperature T is given by Eq. (2). The following are the solutions to Eqs. (6a) and (6b),

TABLE I. Shells of Si neighbors surrounding a tetrahedral interstitial site. The number of atoms in each shell and its distance d from the interstitial site at the center are given. The lifetimes for transitions with distance dependences of d^{-6} and d^{-8} are given in terms of the lifetime τ_1 caused by a Si atom in shell 1.

Shell	n	d	Lifetime (d^{-6})	Lifetime (d^{-8})
1	4	2.350	τ_1	τ_1
2	6	2.714	$2.37\tau_1$	$3.13\tau_1$
3	12	4.499	$49.3\tau_1$	$178\tau_1$
4	8	4.700	$64\tau_1$	$256\tau_1$
5	12	5.914	$254\tau_1$	$1609\tau_1$
6	24	6.068	$296\tau_1$	$1976\tau_1$

$$n_o(t) - n_o^{T(K)} = [n_o(0) - n_o^{T(K)}]\exp - (t/\tau), \tag{7a}$$

$$n_p(t) - n_p^{T(K)} = [n_p(0) - n_p^{T(K)}]\exp(- t/\tau), \tag{7b}$$

where $\tau^{-1} = (k + k^*)$.

We have found that our data for the time evolution of the ortho- and para-H_2 populations can be fit well by single exponential functions with the parameters given in the captions to Figs. 3, 4, 6, and 8. The time constant for the ortho-para transition of interstitial H_2 at 77 K is 229 ± 14 h. The time constant at room temperature is 8.1 ± 0.5 h. The time constants for the ortho-para transition of the H_2 molecule in the O-H_2 complex at 77 K and at room temperature are very similar to those seen for isolated interstitial H_2.

B. ^{29}Si in shells of Si neighbors surrounding interstitial H_2

Hiller *et al.*[18,19] have proposed that the ortho-para transition of interstitial H_2 in Si is caused by its interaction with the nuclear magnetic moment of a near-lying ^{29}Si atom (4.7% natural abundance) and that it follows the theory of catalytically induced transitions derived by Wigner[23] [Eq. (1)]. It has been determined experimentally that all interstitial H_2 molecules can undergo an ortho-para transition to achieve thermal equilibrium. For all H_2 molecules to interact with a ^{29}Si, six or more shells of Si neighbors must be considered. The numbers of atoms in the shells of Si atoms that surround a tetrahedral interstitial site are given in Table I along with their distance d. If ^{29}Si neighbors are indeed the cause of the ortho-para transition, the kinetics of the transition should reflect the summation of exponential functions with different transition rates (Table I) that arise from H_2 molecules with ^{29}Si atoms in different neighbor shells. We have seen that the kinetics of the ortho-para transition can be fit well with a single exponential function. Can these experimental data also be fit satisfactorily by a model in which the different rates associated with H_2 molecules with different ^{29}Si neighbor environments are considered?

Hiller *et al.*[18,19,28] constructed a model with different exponential rates for H_2 molecules with ^{29}Si atoms in different neighbor shells. This model was found to be consistent with Raman data for the time dependence of the ortho-para ratio at 77 K within the associated error bars. The IR data reported here have a smaller uncertainty and provide a more stringent test of models for the transition kinetics.

In the spirit of the work of Hiller *et al.*,[18,19] we have constructed a model for the kinetics of the ortho-para transition of interstitial H_2 (77 K) that includes ^{29}Si atoms distributed among six shells of Si neighbors.[32] Six shells include 66 Si atoms and the probability that these six shells contain one or more ^{29}Si atoms is $1-(1-0.047)^{66}=95.8\%$. To fit the decay kinetics of the ortho population, $n_o(t)-n_o^{T(K)}$, we sum the contributions from H_2 molecules with ^{29}Si atoms in different neighbor shells.

Hiller *et al.*[18,19] fit their results to Eq. (1), first presented by Wigner.[23] This equation was derived for the case of gaseous H_2 molecules interacting with paramagnetic molecules. A "sudden approximation" was made by Wigner and an interaction time interval was estimated from the velocity of the H_2 molecules and the distance of closest approach to the paramagnetic molecule. In fact, as noted by Ilisca,[33] the Wigner mechanism predicts a distance variation as d^{-8}; the d^{-6} in Eq. (1) comes from the estimation of the interaction time for the collision mechanism. If only ^{29}Si adjacent to the interstitial H_2 participated in the ortho-para transition, such an approach might be valid; it clearly is not when more distant ^{29}Si are included in the interaction. Hence proper application of the Wigner mechanism in the present situation requires a d^{-8} dependence.

We have carried out the fit to the data using both distance dependences. In each case, because the transition rate is proportional to d^{-n}, a single parameter τ_1 can be used to describe the decay rates arising from shells with different d (Table I).

The binomial distribution function,

$$P_N(n) = \frac{N!}{n\,!\,(N-n)!}(0.047)^n(1-0.047)^{N-n}, \tag{8}$$

gives the probability that a neighboring shell of N atoms contains n atoms of ^{29}Si. Furthermore, we take the rate contributed by a particular shell to be proportional to the number of ^{29}Si atoms in that shell. If we consider the 12 Si atoms in shell 3 as an example, its contribution to the decay kinetics is proportional to

$$\sum_{n=1} P_{12}(n)\exp(-nt/\tau_3). \tag{9}$$

Furthermore, we note that ^{29}Si atoms in neighbor shell j contribute significantly to the decay rate only if there is not a ^{29}Si atom(s) in a nearer shell. In our model, the contribution of the H_2 molecules with ^{29}Si in shell j is weighted by the probability that shells with smaller j do not contain any ^{29}Si atoms.[32] Again, using shell 3 as an example, Eq. (9) is multiplied by the factor $(1-0.047)^{10}=0.618$ to account for the probability that the ten Si atoms in shells 1 and 2 should not include a ^{29}Si atom.

In the following discussion of the kinetics of the ortho-para transition, we focus on the data shown in Fig. 3 because, of the different experiments reported here, these data have the smallest error bars. Figure 9 shows both a d^{-6} fit and a d^{-8} fit of the shell model just described to the IR data

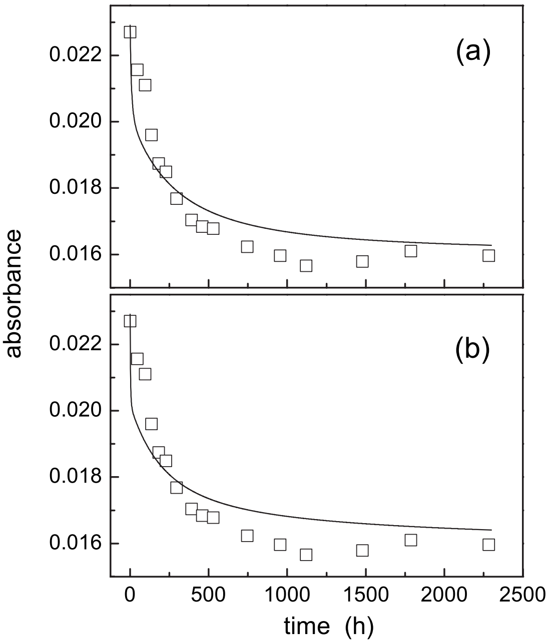

FIG. 9. The peak absorbance of the 3618.4 cm^{-1} line due to H_2 in Si as a function of time held at 77 K. The sample was initially equilibrated at room temperature. The data are fit by a model in which ^{29}Si atoms in six shells of Si neighbors are taken to be responsible for the ortho-para transition. In (a), the distance dependence of the transition rate is taken to be d^{-6}. In (b), the distance dependence of the transition rate is taken to be d^{-8}.

of Fig. 3 in which τ_1 was adjusted to minimize the mean-square error per data point. The d^{-6} fit shown in Fig. 9(a) yields a decay rate of $\tau_1 = 6.09$ h; the associated value of τ_6 is 1803 h. The corresponding values for the d^{-8} fit shown in Fig. 9(b) are $\tau_1 = 1.36$ h; the associated value of τ_6 is 2688 h. In these fits, the change in the ortho-para ratio is constrained to be consistent with the equilibrium values at room temperature and at 77 K given by Eq. (2).

To compare the quality of the fits shown in Fig. 3 (single exponential) and in Fig. 9 (shell model), the root-mean-square (rms) error per data point has been determined. For the fit shown in Fig. 3, the rms error per data point is 2.1×10^{-4}. This value is comparable to the error in the intensity of the 3618.4 cm^{-1} line that has been estimated from the noise in the IR spectrum, $\pm 2 \times 10^{-4}$. The rms error per data point for the d^{-6} fit shown in Fig. 9(a) is 8.5×10^{-4} or 4.1 times larger than the fit of $n_o(t) - n_o^{T(K)}$ at 77 K with a single exponential function; that for the d^{-8} fit shown in Fig. 9(b) is slightly worse, 9.3×10^{-4}. These results show that a single exponential provides a substantially better fit to the kinetics of the ortho-para transition than a model in which ^{29}Si atoms in different Si shells surrounding an H_2 molecule located at a specific interstitial site contribute different rates.

C. Thermally activated motion of interstitial H_2

The model presented in Sec. V B. assumes that the H_2 molecule is fixed at a particular interstitial site with ^{29}Si atoms distributed randomly in neighbor shells. We consider the possibility of thermally activated motion of H_2 between interstitial sites under the conditions in which our experiments were performed.

The diffusion constant of H_2 in Si was reported to be,[25,26]

$$D = 2.6 \times 10^{-4} \text{ cm}^2/\text{s} \exp(-0.78 \text{ eV/kT}). \qquad (10)$$

At 295 K, Eq. (10) yields an interstitial H_2 diffusivity of $D_{295} = 1.2 \times 10^{-17}$ cm^2/s. On the time scale of the ortho-para transition at room temperature of 8 h, the $\sqrt{Dt}$ diffusion length of interstitial H_2 is 60 Å, making it clear that the H_2 molecule will move between many interstitial sites so that the consideration of a static ^{29}Si environment is not appropriate at room temperature. In this case, the kinetics of a ^{29}Si-catalyzed ortho-para transition would be expected to be fit by a single exponential function with a rate dominated by the time the H_2 molecule has a ^{29}Si first or second neighbor.

At 77 K, the diffusivity of interstitial H_2 given by Eq. (10) is $D = 2.5 \times 10^{-55}$ cm^2/s. This small diffusivity suggests that the H_2 molecule remains fixed at a particular interstitial site on the time scale of the ortho-para transition at 77 K, i.e., 229 h. However, we must consider how our experiments were done. To transfer a Si sample from liquid N_2 to a cold optical cryostat, the sample was warmed briefly (10 min) to room temperature. During this time the diffusivity of interstitial H_2 at room temperature predicts a $\sqrt{Dt}$ diffusion length of ~8 Å. Therefore, H_2 is expected to sample several different interstitial sites over the course of experiments where several measurements are made to probe the ortho-para transition at 77 K. In this case, a fit to the kinetics of a ^{29}Si-catalyzed transition with a single exponential function would reflect the effect of a partially averaged environment, one with a higher probability of containing a ^{29}Si next neighbor than would be the case if the warming had not occurred.

To eliminate the effect of the thermally activated diffusion of interstitial H_2 on the ortho-para transition rate, we have performed a series of experiments in which a Si:H_2 sample, equilibrated initially at room temperature, was held at 77 K for the full duration of the subsequent anneal. After the time held at 77 K, the sample was warmed to room temperature just once so that it could be transferred to a cold optical cryostat for a measurement of the intensity of the 3618.4 cm^{-1} line. This entire process, beginning with an initial equilibration at room temperature, was repeated for each data point with different anneal times at 77 K. The data points resulting from these experiments are shown by the filled circles in Fig. 3. The results of these more time-consuming experiments are in good agreement with the kinetics of the ortho-para transition measured in our experiment in which a sample was warmed to room temperature several times as the ortho-para transition was monitored at 77 K. Thus, thermally activated diffusion of the H_2 molecule at room temperature does not appear to explain the kinetics observed for the 77 K ortho-para transition.

D. Alternative mechanisms for the ortho-para transition

The fit of the kinetics of the ortho-para transition at 77 K with a single exponential function has caused us to question the mechanism for the transition involving ^{29}Si proposed by

Hiller *et al.*[18,19] In the following, we discuss possible alternative mechanisms for the ortho-para transition that would give a single time constant for the transition. Experiments with isotopically controlled Si will be important to completely resolve these issues.

1. "Coherent" tunneling motion of interstitial H_2

There is another way that ^{29}Si could be involved in the ortho-para transition. If during the time of the experiment the hydrogen molecule could move among different interstitial sites, it could in the process sample sites in which it has one or more ^{29}Si neighbors. A rough calculation suggests that in sampling 15–20 interstitial sites the H_2 would have more than a 90% chance of having a ^{29}Si neighbor along the way.

Is the site-to-site motion of H_2 at all reasonable at 77 K? At first sight, no: thermally activated diffusive motion [Eq. (10)] would be many orders of magnitude too slow to explain the present data. There is another possibility, however, that bears consideration, at least, in principle: quantum-mechanical tunneling. There is evidence for atomic and molecular hydrogen tunneling in a number of systems, and a considerable experimental and theoretical literature has emerged on this topic.[34–37]

Theoretical investigation of this possibility involves several steps. First we have constructed a potential-energy curve for the tunneling process along the (111) direction using the CRYSTAL2006 code[38] with density functional theory. In the process we find that the silicon relaxation energy is only ~0.035 eV (e.g., the H_2 couples only weakly to its surroundings). We then consider a motion in which the silicons are fixed at their equilibrium positions corresponding to H_2 being in the transition state, that is, halfway between interstitial sites along the (111) axis. This makes some sense in that it can be thought of as "opening a gate" for the H_2 to tunnel through,[39] that is, we imagine that the H_2 rattles within its interstitial cage until the silicons near the transition point vibrate to a location that equates the energies for H_2 on both sides of the barrier.

We then fit the computed energies to a sixth order polynomial[40] of the form

$$V(x) = (x^2 - a^2)^2[(ka^2 - 8V_0)x^2 + 8V_0a^2]/(8a^6) \qquad (11)$$

with three parameters: V_0, the height of the potential barrier; a, the distance from the potential minimum to the transition point; and $k=m\omega^2$, the force constant about the potential minimum, where m is the mass of H_2. This fit yields the following values of the parameters: $V_0=0.964$ eV, $a=1.077$ Å, and $k=5.077$ eV/Å^2. We then use this potential in a modified Wentzel-Kramers-Brillouin (WKB) approach[41] to calculate[42] the coherent tunneling splitting Δ and from that the tunneling time constant τ,

$$\Delta = 2\hbar\omega\sqrt{\frac{m\omega a^2}{\pi\hbar}}e^{-S_0/\hbar}e^A, \qquad (12)$$

where

$$S_0 = \int_{-a}^{a}\sqrt{2mV(x)}dx, \qquad (13)$$

$$A = \int_0^a\left[\frac{m\omega}{\sqrt{2mV(x)}} - \frac{1}{a-x}\right]dx, \qquad (14)$$

$$\tau = \hbar/\Delta. \qquad (15)$$

This yields the results $\Delta=3.72\times10^{-19}$ eV and $\tau=0.49$ h.

If we repeat the tunneling calculation but replace V_0 by the experimental value of 0.78 eV (Refs. 25 and 26), the tunneling rate increases dramatically: now $\Delta=1.61\times10^{-17}$ eV and $\tau=0.01$ h. The result is also rather insensitive to the value of k; for example, if k is reduced from 5.077 to 1.0 eV/Å^2, the tunneling time decreases by only about a factor of 2.

It is important to emphasize that the tunneling system has been treated as isolated; no interactions with phonons have been included. There are various ways to include such effects as, for example, by using a spin-boson approach.[43] The general effect of such coupling is to change the physics from coherent to incoherent tunneling at some critical temperature. One widely cited result is that of Flynn and Stoneham.[44] They considered incoherent tunneling and found a thermally activated tunneling in which the thermal "activation energy" is not the activation barrier but the energy required to bring the initial and final states into degeneracy. (As noted above, in our calculations this energy would be ~0.035 eV, as opposed to the experimental activation barrier of 0.78 eV.) However, the tunneling matrix element in our case is so small that any incoherent tunneling process will be many orders of magnitude too slow to be in agreement with experiment. Hence if tunneling is to occur, it must in some respect be coherent.

We can imagine a modified "coherent" tunneling process to take place as follows. First, the calculated tunneling rate must be reduced by a Boltzmann factor representing the probability of the system energy increasing by, say, 0.035 eV at 77 K. This would reduce a tunneling rate of 100 h^{-1} by a factor of 200 to 0.5 h^{-1}. The tunneling rate would be reduced further by an entropy factor that would reflect the probability that the thermal fluctuation of 0.035 eV would yield the proper atomic configuration. If this factor was 100 the resulting time constant would be 200 h, as measured; however, given the many degrees of freedom of the thermally fluctuating system, it is likely that the entropy factor would be much larger than this, so we conclude that such a coherent tunneling mechanism would be unlikely.

2. Spin-rotation coupling within H_2

While a number of alternative ortho-para decay mechanisms have been suggested,[33,45–49] nearly all involve a nearby paramagnetic species, either electronic or nuclear. As discussed, most of these have been ruled out as possible perturbations in the present case. If in addition ^{29}Si is ruled out, we must consider H_2 rotating, vibrating, and "bouncing" within its tetrahedral cage.

"Caged" H_2 has in fact been the object of considerable recent attention in different contexts, namely, a single H_2 molecule trapped within a buckyball, C_{60} (Refs. 49–52), or within clathrate hydrates.[53,54] In these cases as well, ortho-para transitions have been studied, but generally these have been associated with a paramagnetic perturbation and have had relatively short decay times. Still, this work has provided interesting insights into the general properties of confined H_2 with parallels to the present case.

For an ortho-para transition to take place, the magnetic fields at the two proton sites must be different. For a freely rotating H_2, or for H_2 rotating about the center of a tetrahedral interstitial site, this condition will not be achieved. However, the motion of the center of mass of H_2 is quantum mechanical, and in fact the molecule spends very little time at the exact center; the expectation value of its displacement has been estimated to be from 0.04 to 0.13 Å.[10,15] Furthermore, the nominally neutral molecule has some net charge associated with the electron density from the neighboring silicons. When the molecule is off-center, the net charge on the two atoms will be different, and because of its interaction with the neighboring silicons the instantaneous center of rotation may be displaced from the molecule's center of mass. These features will conspire to create different magnetic fields on the two atoms generated by the rotating molecule and thus allow the mixing of ortho and para states. Such a dynamical mechanism might also explain the large observed increase in transition rate in going from 77 K to room temperature, since the dynamics of the system changes radically between 77 K and room temperature, from being confined at one site to hopping to adjacent sites.

While these hand-waving arguments do not yield an estimate of the magnitude of the effect, they constitute an "existence theorem" to demonstrate that dynamical effects could conspire to cause the ortho-para transition, much as dynamical effects allow the nominally forbidden IR transitions to take place. Such mechanisms may be very weak, but the transition time is very long, so very weak mechanisms must be considered.

VI. INTERSTITIAL D_2

In the sections above, infrared-absorption spectroscopy and theory have been used to investigate the ortho-para transition of interstitial H_2 in Si and its mechanism. D_2 also has ortho and para states with different rotational spectra.[16,17] However, the nuclear spin of the deuteron is 1 and, therefore, the total molecular wave function of D_2 must be symmetric. The rotational states with odd rotational quantum numbers are associated with para-D_2 and those with even rotational quantum numbers are associated with ortho-D_2.

For the interstitial D_2 molecule in Si, the D_2 stretching line at 2642.6 cm^{-1} has been assigned to a purely vibrational transition with the molecule in its $J=1$ rotational state (a $T_2 \rightarrow T_2$ transition in tetrahedral symmetry), similar to interstitial H_2 [Fig. 2(a)].[9,10] For interstitial D_2, it is the higher-energy para species with $J=1$ that is seen by IR absorption at 4.2 K, and the lower-energy ortho species with $J=0$ is not seen.

A. Experimental results

In the present section we investigate the properties of the para-ortho transition of interstitial D_2 in Si. In this case, Raman experiments had not been performed and would prove difficult because the Raman lines for the para- and ortho-D_2 species are not cleanly resolved[20] and the changes in their intensities would be smaller than for interstitial H_2.

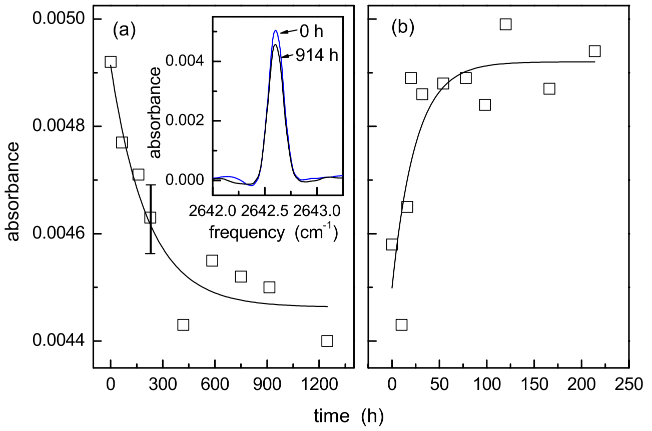

FIG. 10. (Color online) (a) The peak absorbance of the 2642.6 cm^{-1} line due to D_2 in Si as a function of time held at 77 K. The sample was initially equilibrated at room temperature. A typical error bar estimated from the noise in the baseline of the IR spectrum is shown. The data are fit by the relationship $(4.46\pm0.04)\times10^{-3}+(4.5\pm0.6)\times10^{-4}\exp[-t/(213\pm72)\ \mathrm{h}]$. The inset shows the 2642.6 cm^{-1} line for the times at 77 K that are indicated. (b) The peak absorbance of the 2642.6 cm^{-1} line due to D_2 in Si as a function of time held at room temperature. The sample was initially equilibrated at 77 K. The data are fit by the relationship $(4.92\pm0.05)\times10^{-3}-(4.2\pm1.1)\times10^{-4}\exp[-t/(25\pm20)\ \mathrm{h}]$.

To investigate the para-ortho transition at 77 K, a Si sample which contained D_2 molecules throughout the Si bulk was prepared initially by storage for a long time (>4 weeks) at room temperature to achieve thermal equilibrium. This sample was then placed in liquid N_2 so that the para-ortho transition at 77 K could be probed. The inset to Fig. 10(a) shows the IR-absorption line at 2642.6 cm^{-1} due to para-D_2 for the times at 77 K that are indicated. The 2642.6 cm^{-1} line was found to decrease in intensity as the annealing time at 77 K was increased. The open squares in Fig. 10(a) show the peak absorbance of the 2642.6 cm^{-1} line as a function of the time the sample was held at 77 K.

To investigate the para-ortho transition at room temperature, a Si sample containing D_2 molecules was stored in liquid N_2 for 1 year to produce a thermal equilibrium distribution of para- and ortho-D_2 at 77 K. This sample was then annealed at room temperature and the intensity of the 2642.6 cm^{-1} line due to para-D_2 was measured as a function of the annealing time. The open squares in Fig. 10(b) show the peak absorbance of the 2642.6 cm^{-1} line as a function of the time the sample prepared at 77 K was subsequently held at room temperature.

B. Equilibrium para-ortho ratio

If a sample containing interstitial D_2 molecules is held at a given temperature for a time sufficient for thermal equilibrium to be established, the para/ortho ratio for a D_2 molecule is given by[16,17]

$$\frac{n_p^{T(K)}}{n_o^{T(K)}} = \frac{\sum_{J=\text{odd}} (2J+1)\exp[-E(J)/kT]}{2\sum_{J=\text{even}} (2J+1)\exp[-E(J)/kT]}. \tag{16}$$

The factor of 2 in the denominator accounts for the degeneracies of the nuclear-spin states of D_2. The rotational energies of interstitial D_2 can be determined from the energy levels of HD shown in Fig. 2(b). From the dependence of the rotational constant on the reduced mass, the value $\hbar^2/(2\mu R^2)=27\ \text{cm}^{-1}$ for interstitial D_2 is obtained. Equation (16) gives an equilibrium para/ortho ratio for interstitial D_2 of 0.5 at room temperature and of 0.446 at 77 K.

The changes in the intensity of the $2642.6\ \text{cm}^{-1}$ line shown in Fig. 10 are attributed to the para-ortho transition of the interstitial D_2 molecule. When a sample prepared with an equilibrium distribution of para- and ortho-D_2 at room temperature is subsequently held at 77 K [Fig. 10(a)], the para-D_2 line decreases in intensity to eventually produce the equilibrium distribution of para- and ortho-D_2 characteristic of 77 K. When a sample prepared by storage for a long time at 77 K is subsequently annealed at room temperature [Fig. 10(b)], the para line grows in intensity to produce an equilibrium distribution of para- and ortho-D_2 characteristic of room temperature.

With the assumptions that the para/ortho ratio is 0.5 at room temperature and that, upon annealing, the change in the para concentration is equal and opposite to the change in the ortho concentration, the following relationship between the para/ortho ratio and the concentration of para-D_2 is obtained,

$$\frac{n_p(t)}{n_o(t)} = \left[3\frac{n_p^{295}}{n_p(t)} - 1\right]^{-1}. \tag{17}$$

For the results shown in Fig. 10(a), n_p^{295}/n_p^{77} is equal to the ratio of the intensity of the $2642.6\ \text{cm}^{-1}$ line at $t=0$ (characteristic of room temperature) to the intensity at $t=\infty$ (characteristic of 77 K). Similar to the situation for H_2, we presume that kinetics of the para-ortho transition of interstitial D_2 can be fit with a single exponential time constant. From the parameters of the fit shown in Fig. 10(a) and from Eq. (17), the para/ortho ratio at 77 K is found to be $n_p^{77}/n_o^{77}=0.43\pm0.02$. The data shown in Fig. 10(b) give a similar result for n_p^{77}/n_o^{77}. The para/ortho ratio characteristic of 77 K found from the data in Fig. 10 is consistent with 100% of the interstitial D_2 molecules achieving the equilibrium para/ortho ratio calculated from Eq. (16) with the rotational energy for D_2 determined from spectroscopic results for HD [Fig. 2(b)].

C. Kinetics of the para-ortho transition

The time constants for the para-ortho transition of D_2 at 77 K and at room temperature are 213 ± 72 and 25 ± 20 h, respectively. For the data shown in Fig. 10(a), the sample containing D_2 was warmed quickly from 77 K to room temperature to effect the transfer of the sample to a precooled optical cryostat for each succeeding time interval at 77 K for the sequence of measurements that is shown. The more time-consuming experiments, similar to those performed for interstitial H_2 with each time interval at 77 K measured separately, were not attempted because the large size of the experimental error bars compared to the change in the para/ortho ratio did not justify such experiments. Thermally activated motion of D_2 during the brief intervals at room temperature is possible similar to the situation for H_2. However, the possible tunneling motion of D_2 is greatly suppressed compared to H_2.

The rates of the para-ortho transition of interstitial D_2 in Si at 77 K and at room temperature are found to be remarkably similar to the rates found for H_2. The nuclear magnetic moment of the deuteron (0.43307×10^{-26} J/T) is approximately one third that of the proton (1.4106×10^{-26} J/T).[55] A simple application of a mechanism like that of Wigner [Eq. (1)],[23] would predict an ortho-para transition rate that is proportional to the square of the nuclear magnetic moment of the proton or deuteron so that the transition rate for D_2 would be ten times smaller than that for H_2.

The surprising similarity of the ortho-para transition rates for H_2 and D_2 may provide a further clue about the mechanism for the transition. In particular, it effectively rules out the coherent tunneling mechanism explored in Sec. V D 1 since that process would be exponentially quenched in going from H_2 to D_2. On the other hand, while the spin-rotation mechanism suggested in Sec. V D 2 might be isotope dependent, that dependence would not be exponential as would be the tunneling mechanism.

VII. CONCLUSIONS

The approximate time scales for the ortho-para transition of interstitial H_2 in Si at room temperature and at 77 K observed in the present study are in good agreement with results obtained in previous Raman-scattering experiments.[18,19,28] However, the detailed kinetic results strongly affect the possible mechanisms for the transition.

The previous Raman experiments had been analyzed by a mechanism originally proposed by Wigner[23] in which the ortho-para transition is caused by a catalytic interaction with the nuclear magnetic moment of ^{29}Si (4.7% abundant). In this case, at least six shells of Si neighbors had to be considered in order for every H_2 molecule to be able to interact with a ^{29}Si nucleus. This led to a predicted *nonexponential* decay rate, which was consistent with the experimental uncertainty of the Raman data.

On the contrary, our present IR studies find that the kinetics of the ortho-para transition, with a larger signal-to-noise ratio than in the Raman data, are well described by single *exponential* functions with time constants of 229 h at 77 K and 8.1 h at room temperature. A fit of the IR data with a single exponential function yields an rms error that is four times smaller than that for a model involving shells of ^{29}Si neighbors with different transition rates. Thus, our IR results are not consistent with the suggested mechanism for the ortho-para transition that involves the interaction of an interstitial H_2 molecule with a static environment containing ^{29}Si. To obtain further clues about the mechanism for the transition, we have also investigated by IR spectroscopy the ortho-para transition of interstitial D_2 in Si and have found that the corresponding transition rates for interstitial D_2, 213 h at 77

K and 25 h at room temperature, are similar to those of interstitial H_2 (but with greater experimental uncertainty).

We have considered alternative mechanisms that would give a single exponential time constant. These mechanisms include a tunneling motion of interstitial H_2 or D_2 so that every molecule might have a ^{29}Si first neighbor during a portion of the transition time and a spin-rotation coupling within the molecule that can act while the molecule is dynamically off-center. Consideration of a possible tunneling rate by theory and the similarity of the H_2 and D_2 results are in opposition to the tunneling mechanism, which if occurring for H_2 would certainly be exponentially quenched for D_2, but not the spin-rotation mechanism, which might well be of similar order in both cases.

The interstitial H_2 molecule in Si is a fascinating defect because of the important role played by quantum mechanics in determining its microscopic properties. The ortho-para interaction is very weak in contrast to the situation in many other hosts. An explanation of the mechanism for this slow transition remains as a challenge. Experiments for interstitial H_2 in isotopically controlled Si would help to determine the role, if any, that ^{29}Si might play in the ortho-para transition.

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