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Theory of anharmonicity on bond-centered hydrogen oscillators in silicon

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Abstract

An *anomalous* positive shift when the mass of the Si host isotope is increased has been observed recently [Pereira et al., Physica B 340-342 (2003) 697] for the asymmetric stretch frequency of the bond-centered proton in Si ($\mathrm{H}_{\mathrm{BC}}^{+}$). On the other hand, the usual downward isotope shift was observed for the analogous bond-centered deuteron ($\mathrm{D}_{\mathrm{BC}}^{+}$). Based on phenomenological and ab initio modeling studies, we explain the observed puzzling effect. We introduce a Si–H–Si linear model that accounts well for the observations when anharmonicity, volumetric effects due to the host-isotope mass change, and the coupling of the Si–H–Si unit to the lattice are taken into account. The positive isotope shift for $\mathrm{H}_{\mathrm{BC}}^{+}$ results from anharmonic $A_{2u}+A_{1g}$ mode mixing and volumetric effects.

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1. Introduction

Local vibrational mode (LVM) infrared absorption spectroscopy is among the most powerful techniques to extract information concerning the atomic identity and structural arrangement of light defects in solids (see for example Refs. [1,2] and references therein). These include many dopants and common contaminants in semiconductors. Defect LVM frequencies are usually described within the harmonic approximation by reducing the defect-host system to a diatomic (molecular) oscillator. In such approach, a light mass m, representing the impurity, vibrates against a heavy species of mass M, which represents the host ligands whose mass is scaled by an empirical parameter χ. This is usually referred as the *defect-lattice coupling parameter* [3] and corrects the oscillator effective mass to account for the essentially different *defect-in-a-crystal* problem. According to the molecular approach, the LVM frequency ω_{mol} is

$$\omega_{\mathrm{mol}}^{2}=f_{\mathrm{mol}}\left(\frac{1}{m}+\frac{1}{\chi M}\right), \tag{1}$$

where f_{mol} is the effective force constant for the oscillator. Both f_{mol} and χ may be obtained from a fit to experimental frequencies. Eq. (1) has been successful in characterizing many centers like substitutional impurities in silicon [4].

Difficulties arise when χ and f_{mol} are fitted to data which are strongly affected by anharmonicity. For example, the hydroxyl free radical has an O–H stretch mode frequency at $3568.0\,\mathrm{cm}^{-1}$ (for OH^{-}) and at $2632.1\,\mathrm{cm}^{-1}$ (for OD^{-}), leading to $f_{\mathrm{mol}}=42.68\,\mathrm{eV\,Å}^{-2}$ and $\chi=0.6446$. The latter value is well far from the expected value $\chi=1.0$ for a free diatomic molecule. Moreover, measurements of the second harmonic of the stretch fundamental yield the determination of the harmonic frequencies at $3735.2\,\mathrm{cm}^{-1}$ for OH^{-} and $2720.9\,\mathrm{cm}^{-1}$ for OD^{-}. These correspond now to rather different values of $f_{\mathrm{mol}}=48.16\,\mathrm{eV\,Å}^{-2}$ and $\chi=0.9576$, which is now close to 1.

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The recent availability of quasi-monoisotopic Si crystals [5] opened new prospects for the investigation of the host-mass dependence of defect-related vibrations in this material. In one of such studies, infrared bands at 1998 and 1448 cm^{-1} in natural Si, arising from the A_{2u} vibration of bond-centered protons ($\mathrm{H}^{+}_{\mathrm{BC}}$) and deuterons ($\mathrm{D}^{+}_{\mathrm{BC}}$), respectively, have been monitored in ^{28}Si, ^{29}Si and ^{30}Si enriched crystals [6]. While the 1448 cm^{-1} band shifted towards lower energies at a rate $\Delta\omega/\Delta m_{\mathrm{Si}} \approx -0.17\,\mathrm{cm}^{-1}/\mathrm{amu}$ with increasing the Si isotope mass, the 1998 cm^{-1} band showed an *anomalous* blue-shift ($\sim$0.1 cm^{-1}/amu). This behavior cannot be accounted for by the above mentioned harmonic molecular model. In a preliminary study [6], a three-body model, where the two bonds are represented by the simple Morse potential, has been used to describe the *anomalous* isotope effect in a fairly accurate way. However, (i) the χ parameter was assumed to be that of an isolated molecule ($\chi = 1$), which may have affected the values obtained for the force constants and (ii) changes in the crystal volume due to the small variations in zero-point motion that result from the mass change of the host atoms were not considered. The volumetric effect (ii) leads to changes in LVM frequencies and, as we shall see, for $\mathrm{H}^{+}_{\mathrm{BC}}$ in silicon they are of the same order of magnitude of the observed shifts.

State-of-the-art density functional modeling studies are able to account for several hundreds of ligand atoms around impurities to calculate accurate LVM frequencies and, above all, to separate the harmonic, anharmonic, volumetric, and defect-lattice coupling contributions to an LVM frequency. Here we take a look at this problem, in particular at the A_{2u} vibrational frequency of $\mathrm{H}^{+}_{\mathrm{BC}}$ and $\mathrm{D}^{+}_{\mathrm{BC}}$ centers in Si. Firstly, we estimate the defect-lattice parameter for this mode. Secondly, we use experimental data to estimate the isotope-induced volumetric contribution to the frequency shift. Finally, we calculate the harmonic, anharmonic, and mode-mixing frequency contributions to the LVM frequency.

2. Method

Energetics and vibrational properties of $\mathrm{H}^{+}_{\mathrm{BC}}$ in Si are calculated using a pseudopotential [7] density functional code (AIMPRO) [8], along with the Padé parameterization for the local density approximation [9]. Defects were embedded in 216 atom cubic supercells, the Brillouin-zone was sampled at 8 (MP-2^3) special **k**-points [10], and the basis consisted in sets of atom-centered spd-like Cartesian–Gaussian orbitals. Specifically, a total of 4, 12, and 12 s, p, and d-like functions were used for each Si atom, respectively, whereas 4 s and 12 p functions were used on the H site. The charge density and potential terms were dealt in reciprocal space with plane-waves of up to 200 Ry.

Now, we introduce an analytical vibrational model for $\mathrm{H}^{+}_{\mathrm{BC}}$ in Si that is based on the three-atom Si–H–Si unit shown in Fig. 1. We write the potential energy U in terms of the $Q_{A_{1g}}$ and $Q_{A_{2u}}$ normal coordinates of the two modes of this D_{3d} center. The potential energy considers quadratic (U_2), cubic (U_3), and quartic (U_4) terms and reads

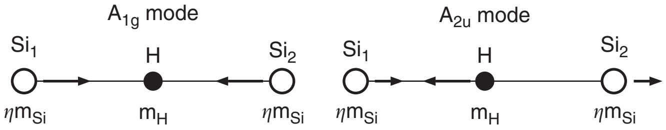

Fig. 1. A sketch of the normal modes in the Si–H–Si three-atom model for H_{BC} in Si. Si and H atoms are represented as large white and small black circles, respectively.

$$U(Q_{A_{1g}}, Q_{A_{2u}}) = U_2 + U_3 + U_4, \tag{2}$$

where

$$U_2 = a^2 f_{A^2_{1g}} Q^2_{A_{1g}} + b^2 f_{A^2_{2u}} Q^2_{A_{2u}}, \tag{3}$$

$$U_3 = 2a^3 f_{A^3_{1g}} Q^3_{A_{1g}} + 2ab^2 f_{A^1_{1g}A^2_{2u}} Q_{A_{1g}} Q^2_{A_{2u}}, \tag{4}$$

$$U_4 = a^4 f_{A^4_{1g}} Q^4_{A_{1g}} + b^4 f_{A^4_{2u}} Q^4_{A_{2u}} + 2a^2b^2 f_{A^2_{1g}A^2_{2u}} Q^2_{A_{1g}} Q^2_{A_{2u}}, \tag{5}$$

and $f_{A^i_{1g}A^j_{2u}}$ are force constants. Other parameters are $a = 1/\sqrt{2\eta m_{\mathrm{Si}}}, b = 1/\sqrt{2\eta m_{\mathrm{eff}}}$, $1/m_{\mathrm{eff}} = 2/m_{\mathrm{H}} + 1/\eta m_{\mathrm{Si}}$, and η is the three-atom analogous of the defect-lattice coupling parameter χ, which is introduced in an ad hoc manner, such that the mass of each Si atom neighboring the proton is ηm_{Si}. Within the harmonic approximation, symmetric and asymmetric stretching frequencies are

$$\omega^{A_{1g}}_{\mathrm{harm}} = \sqrt{f_{A^2_{1g}}/\eta m_{\mathrm{Si}}} \quad \text{and} \quad \omega^{A_{2u}}_{\mathrm{harm}} = \sqrt{f_{A^2_{2u}}/m_{\mathrm{eff}}}, \tag{6}$$

respectively. We now drop the symmetry labeling of frequencies, and hereafter any frequency refers to the A_{2u} mode, unless otherwise stated.

We obtain the anharmonic contribution to the asymmetric frequency $\omega_{\mathrm{anharm}} = \omega^{\mathrm{A}}_{\mathrm{anharm}} + \omega^{\mathrm{B}}_{\mathrm{anharm}} + \omega^{\mathrm{C}}_{\mathrm{anharm}}$ from the sum of the second-order and first-order corrections to the cubic (U_3) and quartic (U_4) potentials, respectively. Hence [11],

$$\omega^{A}_{\mathrm{anharm}} = -\frac{3\hbar}{2m_{\mathrm{eff}}}\left(\frac{f^2_{A^1_{1g}A^2_{2u}}}{3f_{A^2_{1g}} f_{A^2_{2u}}} - \frac{f_{A^4_{2u}}}{2f_{A^2_{2u}}}\right), \tag{7}$$

$$\omega^{B}_{\mathrm{anharm}} = -\frac{3\hbar}{4\sqrt{\eta m_{\mathrm{Si}} m_{\mathrm{eff}}}}\left(\frac{f_{A^3_{1g}} f_{A^1_{1g}A^2_{2u}}}{f_{A^2_{1g}}\sqrt{f_{A^2_{1g}} f_{A^2_{2u}}}} - \frac{f^2_{A^1_{1g}A^2_{2u}}}{6f_{A^2_{1g}}\sqrt{f_{A^2_{1g}} f_{A^2_{2u}}}} - \frac{f_{A^2_{1g}A^2_{2u}}}{3\sqrt{f_{A^2_{1g}} f_{A^2_{2u}}}}\right), \tag{8}$$

$$\omega^{C}_{\mathrm{anharm}} = \frac{\hbar}{16\eta m_{\mathrm{Si}}} \frac{f^2_{A^1_{1g}A^2_{2u}}}{f^2_{A^2_{2u}}}. \tag{9}$$

The potential energy represented in Eq. (2) may be estimated from ab initio calculations. Such ab initio