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Force constant change upon isotopic substitution of hydrogen for deuterium

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It is shown that more accurate calculations of the hydrogen vibrational frequencies require more precise calculations of corrections of the zero-temperature vibration. Using, as an example, the silane molecule, we interpret the isotope frequency shift of the H(D)-stretch modes in terms of both the bond length change upon isotopic substitution (due to cubic anharmonicity), as well as of cubic and quartic anharmonic corrections to vibrations. The Si-H bond length is always longer than that of Si-D. The harmonic force constant and anharmonic parameters depend not only on the electronic structure but also, indirectly, on the masses of the atoms involved. The importance of intermode mixing by anharmonic terms is demonstrated.

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I. INTRODUCTION

Among the various possible isotopic substitutions, by far the most important in vibrational spectroscopy is the substitution of hydrogen (H) with deuterium (D). During the past few years, H has been widely investigated in semiconductors[1] and molecules,[2,3] and experiments with both H and D have been performed. As the mass of D is twice that of H a very large frequency shift occurs for the modes that mainly involve the displacement of the H (D) atom. It is usually assumed that the theoretical values of the vibrational mode frequencies depend upon the force constants determined at the minimum of the adiabatic potential energy surface. This leads to a theoretical ratio $\omega(\mathrm{H})/\omega(\mathrm{D})$ of the angular frequencies of the stretching H (D) modes that always exceed the experimental data.[1] Anharmonicity[4,5] has been proposed to be responsible for the lower value of this ratio. However, the residual persistent disagreement between the calculations and observations most likely arises from approximations made in the estimation of the zero-point motion and from the neglect of the intermode mixing by anharmonicity. The aim of this paper is to calculate more accurately the dependence of the bond length on masses due to zero-point motion (and, consequently, to investigate the indirect dependence of the force constants on the atomic masses) and to assess how this influences the $\omega(\mathrm{H})/\omega(\mathrm{D})$ ratio. By exploring the influence of various anharmonic corrections to vibrational frequencies, we gain additional insight into the nature of anharmonicity.

Many properties of solids and molecules can be determined by calculating the bond energy. Using tight-binding theory and some results coming out from density-functional theory, Harrison[6–8] simplified the calculations showing that the bond energy can be expressed in terms of one-electron atomic energies and some ''universal'' parameters. These ''universal'' parameters replace the complicated interaction integrals and are similar for many covalent crystals. In this work, we apply Harrison's theory to study the silane molecule, which is a prototype for investigations of the local vibrational modes due to light impurities in tetrahedrally coordinated semiconductors. The vibrational modes of this molecule have been investigated both theoretically and experimentally.[2,3,9] The aim of this paper is to show that it is more appropriate to determine the bond length from the nonperturbative minimization of the Helmholz energy rather than from the minimization of the adiabatic potential energy only with the perturbative account of the zero-point motion. In this respect, the use of Harrison's simple formalism is sufficient for reaching this goal. The interaction between H (D) atoms is remarkably weaker as compared to that of Si-H and Si-D and will be ignored. Therefore the model used will not describe the bending modes of vibration. We demonstrate that corrections to vibrational frequencies due to intermode mixing are important.

II. THEORETICAL BACKGROUND

In the tight-binding theory for tetrahedrally coordinated crystals, four orthogonal and normalized sp^3 hybrids are chosen on each atom as basis wave functions. The electronic bond energies are given by[6–8]

$$\varepsilon=\frac{1}{2}(\varepsilon_h^a+\varepsilon_h^b)\pm q\sqrt{V_2^2+V_3^2}+\frac{qV_2^2}{k|\overline{\varepsilon_h}|}. \tag{1}$$

In this formula, a and b represent the two atoms involved in the bond, $\varepsilon_h^{a,b}=(\varepsilon_s^{a,b}+3\varepsilon_p^{a,b})/4$, where ε_s and ε_p are the free-atom energies for s and p states;[10] $V_3=(\varepsilon_h^a-\varepsilon_h^b)/2$ and $V_2=f(\eta)\hbar^2/md^2$, m being the electron mass. V_2 represents the coupling between the two atoms and the function $f(\eta)$ is expressed in terms of the four ''universal'' coefficients: $\eta_{ss\sigma}=-1.40$, $\eta_{sp\sigma}=1.84$, $\eta_{pp\sigma}=3.24$, and $\eta_{pp\pi}=-0.81$. For example, in the perfect silicon lattice, for two sp^3-sp^3 hybrids pointing towards each other, $f_{sp^3-sp^3}(\eta)=\eta_{ss\sigma}/4-2\sqrt{3}\eta_{sp\sigma}/4-3\eta_{pp\sigma}/4=-4.373$. q is the electron occupancy of the bond in units of the electron charge and $\overline{\varepsilon_h}$ is the average of ε_h^a and ε_h^b. k is the only adjustable parameter of this theory. It is determined from the requirement that the calculated bond lengths for the C, Si, and Ge crystals is equal to the experimental ones. The value of k is the same for all crystals built from the elements entering the same row of the periodic table. For instance,[11] for the C row $k=2.5$, for the Si row $k=1.445$, and for the Ge row $k=1.33$.

The effect of isotopic substitutions on the vibrational frequency can be used for the identification of the chemical species that are involved in a complex. In particular, the large frequency shift that results from the substitution of H by D leads to an unambiguous identification of the H defects in crystals. In the limit of the Born-Oppenheimer approximation the force constant calculated at the minimum of the total energy depends upon the electronic structure and not upon the masses of the atoms. Two different isotopic species of the same atom will have different vibrational frequencies only because of the difference in isotopic masses. For example, the ratio r of the vibrational frequencies of the stretching A_1 mode for SiH_4 and SiD_4 molecules is given in harmonic approximation by

$$r \equiv \frac{\omega(\mathrm{H})}{\omega(\mathrm{D})} = \sqrt{\frac{M_{\mathrm{D}}}{M_{\mathrm{H}}}} = \sqrt{2} = 1.4142, \tag{2}$$

while the experimental value (which includes anharmonics effects) is ≈ 1.3988 (see Table II). Equation (2) is a particular case of a more general statement, known as the Teller and Redlich rule.[12] However, this rule is never exactly satisfied by experimental vibrational frequencies of isotopic substitution. The observed frequency ratio is always some percent smaller than the theoretical ratio. The source of this disagreement between theory and experiment is usually thought to be entirely due to anharmonic corrections to the vibrational frequency determined in the harmonic approximation.[4,5] However, the indirect isotope dependence of the force constant was never taken into account.

The determination of the bond length from the minimum of the bond energy (or from the minimum of the total energy in *ab initio* theories) is only an approximation since the kinetic vibration energy is neglected (it is assumed that the atoms possess an infinite mass). More accurately,[13–15] the equilibrium interatomic distance can be determined from the minimum of the Helmholz free energy F,

$$F(d,T;M) = \varepsilon(d) + \frac{1}{2}\hbar\omega + k_B T \ln\left[1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right], \tag{3}$$

where k_B is the Boltzman constant and ε is the bond energy (1) for atoms interacting through Coulomb forces. ω is the stretching angular frequency for the given bond. The frequency of the stretching mode is $\omega = \sqrt{k_h/\mu}$, where $k_h = \partial^2\varepsilon/\partial d^2$ is the harmonic force constant and $\mu = M_{\mathrm{Si}}M_{\mathrm{H}}/(M_{\mathrm{Si}}+M_{\mathrm{H}})$ is the reduced mass of single bond. The second term in Eq. (3) is the energy of the zero-temperature vibration and it indirectly depends upon the atomic mass. We shall consider only the influence of this term on the bond length, i.e., we consider the situation at $T=0$ K.

The equilibrium distance d at zero temperature is determined from the minimum of the Helmholz free energy, i.e., from the bond energy (1) supplemented by the zero-point stretching mode vibration energy for the Si-H bond. Thus, the equation for the determination of d is given as

$$\frac{\partial\varepsilon}{\partial d} + \frac{\hbar}{4\sqrt{\mu}} \frac{\dfrac{\partial^3\varepsilon}{\partial d^3}}{\sqrt{\dfrac{\partial^2\varepsilon}{\partial d^2}}} = 0. \tag{4}$$

TABLE I. Influence of zero-temperature vibration energy on the interatomic distance d_0 and harmonic force constant k_h, cubic α, and quartic β anharmonic parameters.

Parameter		Minimization of ε	Minimization of F
d_0 (Å)	SiH_4	1.5262	1.5490
	SiD_4	1.5262	1.5425
k_h(eV/Å^2)	SiH_4	21.56	18.63
	SiD_4	21.56	19.43
α(eV/Å^3)	SiH_4		−20.1
	SiD_4		−20.8
β(eV/Å^4)	SiH_4		27.9
	SiD_4		28.9

The third derivative of ε accounts for the anharmonic effect and is usually negative. Therefore Eq. (4) will be fulfilled when $\partial\varepsilon/\partial d$ is positive. This means that taking into account anharmonicity one always gets a larger bond length than that obtained from the minimization of the adiabatic potential. It follows from Eq. (4) that the Si-H bond length is longer than that of Si-D (see Table I). The isotopic dependence of the bond length (the lattice constant) and other crystal parameters was studied experimentally and theoretically.[16,17] The theoretical estimations were based on the London theory,[15] which use, as a starting point, the expression for the Helmholz free energy. Using the first-order perturbation theory the effect of the zero-point motion on the bond length is expressed in terms of the Grüneisen parameter (which depends on the cubic anharmonicity) and the isothermal compressibility (or the bulk modulus). Usually, both parameters are calculated at the minimum of the total energy of the crystal. From this approximation follows that two chemically identical crystals formed by different isotopes possess the same isothermal compressibility at $T=0$ K. Generally, it is not true because of the zero-point motion of the atoms. The calculation utilizing Eq. (4) avoids this approximation and the three derivatives are calculated at the minimum of the free energy, i.e., at the appropriate equilibrium interatomic distance. It is seen from Table I that the account of the zero-point vibration influences noticeably the value of the harmonic force constant k_h. The influence of the zero-point motion on the harmonic, cubic, and quartic force constants is disproportionally larger than that on the equilibrium interatomic distance. However, in the case of the ^{28}Si substitution by ^{29}Si the value of the harmonic force constant calculated from minimization of the bond energy ε is close to that calculated from the free energy F.

III. HARMONIC APPROXIMATION AND ANHARMONIC CORRECTIONS

The bond energy can be expanded into a Taylor series over the stretching displacement u_i around the equilibrium position d_0 found in the harmonic approximation

$$\varepsilon_i=\varepsilon(d_0)+\frac{1}{2}k_h u_i^2+\alpha u_i^3+\beta u_i^4+\cdots. \tag{5}$$

If we express the positions of the 1, 2, 3, and 4 hydrogen atoms in the $\mathrm{SiH_4}$ molecule by their Cartesian coordinates in units of $d_0/\sqrt{3}$ as (1,1,1), (1,−1,−1), (−1,1,−1), and (−1,−1,1), respectively, the displacements u_i along the particular bonds are $u_1=[z_1-(x_c+y_c+z_c)/\sqrt{3}]$, $u_2=[z_2-(x_c-y_c-z_c)/\sqrt{3}]$, $u_3=[z_3-(-x_c+y_c-z_c)/\sqrt{3}]$, and $u_4=[z_4-(-x_c-y_c+z_c)/\sqrt{3}]$. To simplify the notation, the displacements x_c, y_c, z_c of the Si atom are given in Cartesian coordinates while the stretching displacements of the H atoms are given along their bond directions. The elastic energy of the $\mathrm{SiH_4}(\mathrm{SiD_4})$ molecule can be written as a superposition of the four bond energies $H=\Sigma_i^4\varepsilon_i$. Then, using the collective displacement coordinates Q and T given in the Appendix we can write in the harmonic approximation

$$H=4\varepsilon(d_0)+\frac{k_h}{2}\sum_i^4 u_i^2=H_0+\frac{k_h}{2}Q_1^2+\frac{k_h}{2}(T_4^2+T_5^2+T_6^2). \tag{6}$$

Q_1 involves only displacements of the H atoms. It has to be noted that in Eq. (6), the same force constants are employed for A_1 and T_2 stretching modes. The T_i's measure the relative displacement of the H atoms with respect to the Si atom from their equilibrium values. The eigenvalue of H_0 is $4\varepsilon(d_0)$. The equations of the motion of the $\mathrm{SiH_4}$ molecule in terms of these coordinates are $\mu_A d^2Q_1/dt^2=-k_hQ_1$ and $\mu_T d^2T_i/dt^2=-k_hT_i$, where the reduced masses are $\mu_A=M_H$ and $\mu_T=3M_{\mathrm{H}}M_{\mathrm{Si}}/(4M_{\mathrm{H}}+3M_{\mathrm{Si}})$, respectively. The corresponding harmonic vibrational frequencies are $\omega_{A_1}=\sqrt{k_h/\mu_A}$ and $\omega_{T_2}=\sqrt{k_h/\mu_T}$.

The harmonic treatment of vibrational frequencies, discussed above, implies that atoms are bounded inside a parabolic potential well. The atoms in this approximation cannot diffuse through a crystal and a molecule cannot dissociate. The anharmonic terms in the potential allow diffusion and dissociation. For vibrations involving the displacement of light atoms, such as hydrogen stretching motions that are of rather large amplitude, the anharmonic corrections can be quite important. The energy of the $\mathrm{SiH_4}(\mathrm{SiD_4})$ molecule can be written as

$$E=\sum_i^4\varepsilon_i=4\varepsilon(d_0)+\omega_{A_1}(n_{A_1}+\tfrac{1}{2})+\omega_{T_2}(n_{T_2}+\tfrac{3}{2})+E_{anh}, \tag{7}$$

where E_{anh} is the eigenvalue of the Hamiltonian (8) expressed in terms of the collective coordinates given in the Appendix:

$$\begin{aligned}H_{anh}=&\frac{\alpha}{2}Q_1^3+\frac{3\alpha}{2}Q_1(T_4^2+T_5^2+T_6^2)+3\alpha T_4T_5T_6\\&+\frac{\beta}{4}Q_1^4+\frac{3\beta}{2}Q_1^2(T_4^2+T_5^2+T_6^2)+\frac{\beta}{4}(T_4^4+T_5^4+T_6^4)\\&+\frac{3\beta}{2}(T_4^2T_5^2+T_5^2T_6^2+T_4^2T_6^2)+6\beta Q_1T_4T_5T_6.\end{aligned} \tag{8}$$

The Hamiltonian (8) contains anharmonic terms that involve the coupling between the A_1 and T_2 stretching modes of the molecule. At this point, one limitation of our model should be noted. Neither does it include the interaction between the hydrogen (deuterium) atoms, nor does it describe the E and T_2 bending modes of vibration of the molecule. Reference 18 gives the anharmonic oscillator potential for the investigation of the T_2 local impurity modes in tetrahedrally coordinated crystals. Equation (8) expresses the constants imposed by symmetry in Eq. (3.6) of Ref. 18 in terms of the single anharmonic parameters α and β. Moreover, Eq. (8) contains coupling terms not included in Eq. (3.6) of Ref. 18 since this latter equation does not involve coupling to the A_1 mode.

Contrary to all previous calculations of the H (D) vibrational frequencies, we account self-consistently, by using Eq. (4), for the influence of zero-temperature vibrations on the bond length. The account of zero-temperature motion energy increases the calculated equilibrium distance and decreases the vibrational frequency. Consequently, the force constants depend indirectly on masses. Since in the $\mathrm{SiH_4}(\mathrm{SiD_4})$ molecule the reduced mass of the A_1 mode depends only on the H (D) mass, the deviation of the ratio r from $\sqrt{2}$ is due to the mass dependence of the corresponding force constants as well as due to anharmonic corrections to frequency.

IV. RESULTS AND DISCUSSION

A. Harmonic approximation

In the $\mathrm{SiH_4}$ molecule there are four $\mathrm{Si}(sp^3)$-$\mathrm{H}(s)$ bonds $[f_{sp^3-s}(\eta)=-2.293,\ k=1.445]$, each bond being occupied by two electrons, i.e., $q=2$. Without taking into account zero-temperature vibration, the calculation yields $d_0=1.5262$ Å, $k_h=21.56$ eV/Å (see Table I). In this case, the Si-H (D) pairs have the same bond length and the r factor for the A_1 mode is $\sqrt{2}=1.4142$ (see Table II). The harmonic frequencies are 2412 cm^{-1} for the A_1 mode and 2469 cm^{-1} for the T_2 mode.

We repeated the calculations of vibrational frequencies in the harmonic approximation employing Eq. (4). From the results given in Table I it is seen that the Si-D bond is shorter by 0.0065 Å than the Si-H bond. As a consequence, the force constant k_h for the Si-D bond is about 5% larger than the Si-H one. Columns 3 and 4 of Table II clearly show that, staying in the framework of the harmonic approximation for frequencies and taking into account the different force constants for Si-H and Si-D (because of the different equilibrium bond lengths), one obtains r factors for both A_1 and T_2 modes clearly smaller than those expected usually without account of the zero-point motion. This is due to the com-

TABLE II. Fundamental transition energies calculated using minimization of the bond energy ε and of the Helmholz free energy F. The ratio $r=\omega(\mathrm{SiH}_4)/\omega(\mathrm{SiD}_4)$ for each case is indicated.

Parameter		Minimization of ε	Minimization of F	Minimization of F with anharmonic corrections	Experiment (Ref. 9)
ω_{A_1} (cm^{-1})	SiH_4	2412	2243	2234.6	2186.87
	SiD_4	1706	1619.6	1617.2	1563.3
r		1.4142	1.3849	1.3818	1.3988
ω_{T_2} (cm^{-1})	SiH_4	2469	2295.9	2193.9	2189.19
	SiD_4	1785	1695.0	1642.6	1598.40
r		1.3831	1.3544	1.3356	1.3695

bined effects of the anharmonicity of the potential [$\partial^3\varepsilon/\partial d^3$ in Eq. (4)] and the difference in masses of H and D.

B. Anharmonic corrections

The anharmonic corrections have been obtained by perturbation theory treating the cubic part of the anharmonic Hamiltonian (8) in second order and the quartic part in the first order. The analytical corrections for the three lowest vibrational levels are given in the Appendix. Table III gives the numerical values for the corrections $\Delta\omega_{A_1}$ and $\Delta\omega_{T_2}$ for the two fundamental transitions and Table II gives the resulting wave numbers ω_{A_1} and ω_{T_2} of these transitions for both SiH_4 and SiD_4. The inclusion of anharmonic corrections decreases again the r factors. It turns out that the decrease of r due to the indirect dependence of the harmonic force constant on masses is of the same order of magnitude as that due to anharmonic corrections to frequency.

It is of interest to look at the detail of the anharmonic corrections. In Table III, together with the total contribution, the contributions of the terms involving only Q_1 or T_i's (''intrinsic'' contribution) on the one hand and those involving both Q_1 and T_i's on the other hand, are given. It clearly appears that the contribution of the anharmonic coupling between the A_1 and T_2 modes is most important. For the transition towards the first excited T_2 level, these terms even change the sign of the anharmonic correction. It has to be noted that the anharmonic coupling between the different modes is very often ignored (because it is difficult to determine it theoretically) and obviously this leads to very important errors in the anharmonic contributions. As already pointed out previously, our calculations ignore the bending modes and therefore, the total anharmonic contribution given in Table III does not intend to be very accurate.

TABLE III. Anharmonic correction $\Delta\omega$ (in unit of cm^{-1}) to fundamental transitions.

	Mode	Total	''Intrinsic'' contribution	A_1-T_2 coupling contribution
SiH_4	A_1	-7.7	-35	27.3
	T_2	-101.9	57	-158.9
SiD_4	A_1	-2.4	-17.2	14.8
	T_2	-52.4	29.9	-82.3

V. DISCUSSION

Due to the asymmetric form of the interatomic potential arising from the cubic anharmonic term αu^3 in Eq. (5), the equilibrium bond length depends both on the atomic masses and the atomic vibrational state occupied. The mean position shift due to anharmonicity is well known in the classical theory of vibrations.[19] The quantum and classical theories of vibrations differ in the limit $T\rightarrow 0$ K. According to the classical theory the amplitude of vibration approaches zero when $T\rightarrow 0$ K. At enough low temperature the anharmonic terms in Eq. (5) can be neglected as compared to the harmonic term. Therefore, below this temperature the bond length and the harmonic force constant do not depend on the isotopic substitution. The classical calculations of the bond length shift upon isotopic substitution use the force constants determined at the minimum of the adiabatic potential. These estimations are sufficiently accurate for the heavy atoms which have the relatively small amplitude of vibrations. In such a case the calculations based on Eq. (4) give the similar result. However, there is a different situation for the light atoms where the anharmonic effects are large. For example, the amplitude of the vibration of the hydrogen atom is ≈0.1 Å, i.e., it includes a region which is outside of the harmonic regime.

The different description is given by the quantum theory of vibrations from which the classical limit of $T\rightarrow 0$ K is obtained taking the Planck constant $\hbar\rightarrow 0$. According to the quantum theory the atoms vibrate even at $T=0$ K. This is consequence of the Heisenberg uncertainty principle for position and momentum. Therefore, due to the anharmonic terms in the potential, the isotopic mass substitution changes the bond length even at $T=0$ K. Due to zero-temperature vibrations the H-Si and D-Si bond lengths differ at $T=0$ K. The H-Si iteratomic potential is a steep function of the distance and the force constants change with the bond length. Therefore it is reasonable to calculate the force constants at the bond length determined by the minimum of the free energy. Though the bond length determined from the minimization of ε or F differs slightly, this leads to the disproportional change in the harmonic force constant and hence modifies the fundamental frequency.

The results for the fundamental transitions obtained by minimizing the free energy in the ''harmonic'' approximation are in reasonable agreement with the experimental data. In particular, the first T_2 level is calculated to be above the first excited A_1 level. The r factors obtained are clearly smaller than those obtained by minimizing the total energy. The inclusion of the anharmonic contribution further decreases the r factors. It does not improve the agreement with experiment. This is not surprising because our model, ignoring the interaction between bonds, cannot take into account the bending modes and their anharmonic coupling with the stretching modes. The theoretical expressions can be used for the analysis of the observed stretching vibrational modes (the bending modes usually fall out into phonon spectrum and they are difficult to observe) due to the light impurities in semiconductors. An important point to be noted is that the anharmonic contribution arising from the coupling between the A_1 and T_2 modes is quite large and comparable with the ''intrinsic'' contributions for each mode.

As a matter of fact, the effect reported in the ''harmonic'' approximation resulting from the minimization of the free energy involves, according to Eq. (4), the third derivative of ε with respect to d. The anharmonicity parameter α also involves this third derivative of ε. In this respect, what we call ''harmonic'' approximation in this paper is not really fully harmonic, but the important conclusion is that, in order to have a homogeneous description of the problem, *one should take into account the difference in bond length for the different isotopes together with the anharmonic corrections to frequency.*

A semiempirical model has been developed for fitting the stretching modes of experimental data including a large number of overtones.[2,3,9] This model is also based on the superposition of single bonds, but includes bond-bond interactions. Indeed, it would be of interest to compare the results coming out from both models. Unfortunately, the comparison is not easy as Refs. 2, 3, and 9 work in the framework of a local mode model whilst the present work is performed in the frame work of a normal mode model; this leads to big differences. For instance, in the framework of the local mode model the A_1 and T_2 modes have the same frequencies in the harmonic approximation if one ignores the bond-bond interactions; it is still the case when anharmonic corrections are included.

The accurate determination of the bond length and the fundamental frequency is the difficult task. In the past few years the molecular dynamics[20] is playing increasingly important role in the study of materials. In this context, it is interesting to compare the principal results obtained from molecular dynamics simulation and the present semiempirical calculation. Molecular dynamics simulation needs no empirical input. The motion of the atoms is described by equations of classical mechanics. In a ''start-up'' configuration the positions and velocities of atoms are assigned. The temperature of the system is varied by changing the magnitude of velocities that correspond to the kinetic energy appropriate to the temperature used in the simulation. Reducing the velocities, the system is set to its equilibrium state at $T = 0$ K. The molecular dynamics simulations provide information on anharmonicity of the interatomic potential. The vibrational modes are determined by the Fourier transform of the velocity-velocity autocorrelation function. Since the molecular dynamics is based on the Newtonian equations of motion, it gives the same results as the classical theory of vibrations in the limit of $T \rightarrow 0$ K. At some higher temperatures the results of the molecular dynamics simulation should approach the quantum theory prediction because it explicitly includes the kinetic energy of atoms.

First-principle calculations based on the density-functional theory determine the interatomic distance (assuming that they are determined by the first derivative of the total energy) with an accuracy of about 1%. In our calculations we need the third and fourth derivatives; it is clear that they cannot be determined as precisely as the first one. Errors of the order of 50–100 % on the third and fourth derivatives are plausible. The anharmonic parameters α and β used in this work are determined by the accuracy of expression (1) for the bond energy. It is seen from Table II that calculated frequencies (at the equilibrium distance derived from the free energy) are in reasonable agreement with the experimental ones. Since the anharmonic cubic and quartic contributions to vibrational frequencies partially cancel each other, it is impossible to conclude how accurate the calculated force constants are even if the calculated frequencies are in reasonable agreement with experimental ones.

VI. SUMMARY

Contrary to all previous calculations of the H (D) vibrational frequencies we directly account for the influence of zero-temperature vibrations on the bond length by using Eqs. (3) and (4). The inclusion of the zero-temperature vibration energy increases the calculated equilibrium distance and decreases the vibrational frequency. Consequently, the harmonic force constant depends indirectly on isotope mass because it is calculated at the distance where Eq. (4) is fulfilled. Equation (4) links self-consistently the first, second, and third (anharmonicity) derivatives of the adiabatic potential. We described the stretching modes of $\mathrm{SiH_4(SiD_4)}$ with full account of third- and fourth-order anharmonic corrections involving the stretching modes.

It is seen from Table II that the calculated ratio r of the isotopic frequencies is closer to the experimental values in the ''harmonic'' approximation. It has been shown that the anharmonic corrections involving the coupling between modes give strong corrections to the vibrational levels and should definitively to be taken into account together with the ''intrinsic'' harmonic corrections to the modes.

The effect of mass on the force constant considered in this paper is especially important in the case of substitution of hydrogen by deuterium because of the factor 2 in mass between the two isotopes; this does not mean that it should be ignored in other cases. For instance, the described consideration can be applied for the studies of the local frequencies due to the light impurities in tetrahedrally coordinated semiconductors.

APPENDIX

The orthogonal transformations between the displacements z_i along the bonds and the collective displacements coordinate Q_1 and Q_4, Q_5, Q_6, which transform according to the representations A_1 and T_2, respectively:

$$Q_1=(z_1+z_2+z_3+z_4)/2,$$

$$Q_4=(z_1+z_2-z_3-z_4)/2, \quad T_4=Q_4-4x_c/\sqrt{3},$$

$$Q_5=(z_1-z_2+z_3-z_4)/2, \quad T_5=Q_5-4y_c/\sqrt{3},$$

$$Q_6=(z_1-z_2-z_3+z_4)/2, \quad T_6=Q_6-4z_c/\sqrt{3}.$$

Q_1 is the breathing type distortion in which the Si atom does not participate. Each component of the T_2 displacement corresponds to a situation where two H (D) atoms move inward while the two other move outward from the molecule. The Si atom moves in antiphase with all H (D) atoms.

$$z_1=(Q_1+Q_4+Q_5+Q_6)/2,$$

$$z_2=(Q_1+Q_4-Q_5-Q_6)/2,$$

$$z_3=(Q_1-Q_4+Q_5-Q_6)/2,$$

$$z_4=(Q_1-Q_4-Q_5+Q_6)/2.$$

Below we list the corrections calculated using ΔH_{anh} of Eq. (8) as the perturbation and the product of the oscillator wave functions as given in the harmonic approximation. The ground state correction is

$$\begin{aligned}\varepsilon_g=&-\alpha^2\left[\frac{11}{32}\frac{1}{\hbar\omega_A}\left(\frac{\hbar}{\mu_A\omega_A}\right)^3+\frac{27}{32}\left(\frac{3}{\hbar\omega_A}+\frac{2}{\hbar(\omega_A+2\omega_T)}\right)\right.\\&\left.\times\frac{\hbar}{\mu_A\omega_A}\left(\frac{\hbar}{\mu_T\omega_T}\right)^2+\frac{3}{8}\frac{1}{\hbar\omega_T}\left(\frac{\hbar}{\mu_T\omega_T}\right)^3\right]\\&+\beta\left[\frac{3}{16}\left(\frac{\hbar}{\mu_A\omega_A}\right)^2+\frac{9}{8}\frac{\hbar}{\mu_A\omega_A}\frac{\hbar}{\mu_T\omega_T}+\frac{27}{16}\left(\frac{\hbar}{\mu_T\omega_T}\right)^2\right].\end{aligned}$$

The correction to the first excited A_1 state is

$$\begin{aligned}\varepsilon_A=&-\alpha^2\left[\frac{71}{32}\frac{1}{\hbar\omega_A}\left(\frac{\hbar}{\mu_A\omega_A}\right)^3\right.\\&+\frac{27}{32}\left(\frac{3}{\hbar\omega_A}+\frac{2}{\hbar(-\omega_A+2\omega_T)}+\frac{4}{\hbar(\omega_A+2\omega_T)}\right)\\&\left.\times\frac{\hbar}{\mu_A\omega_A}\left(\frac{\hbar}{\mu_T\omega_T}\right)^2+\frac{3}{8}\frac{1}{\hbar\omega_T}\left(\frac{h}{\mu_T\omega_T}\right)^3\right]\\&+\beta\left[\frac{15}{16}\left(\frac{\hbar}{\mu_A\omega_A}\right)^2+\frac{27}{8}\frac{\hbar}{\mu_A\omega_A}\frac{\hbar}{\mu_T\omega_T}+\frac{27}{16}\left(\frac{\hbar}{\mu_T\omega_T}\right)^2\right].\end{aligned}$$

The correction to the first excited T_2 state is

$$\begin{aligned}\varepsilon_T=&-\alpha^2\left[\frac{11}{32}\frac{1}{\hbar\omega_A}\left(\frac{\hbar}{\mu_A\omega_A}\right)^3+\frac{45}{32}\left(\frac{5}{\hbar\omega_A}+\frac{2}{\hbar(\omega_A+2\omega_T)}\right)\right.\\&\left.\times\frac{\hbar}{\mu_A\omega_A}\left(\frac{\hbar}{\mu_T\omega_T}\right)^2+\frac{15}{8}\frac{1}{\hbar\omega_T}\left(\frac{\hbar}{\mu_T\omega_T}\right)^3\right]\\&+\beta\left[\frac{3}{16}\left(\frac{\hbar}{\mu_A\omega_A}\right)^2+\frac{15}{8}\frac{\hbar}{\mu_A\omega_A}\frac{\hbar}{\mu_T\omega_T}+\frac{63}{16}\left(\frac{\hbar}{\mu_T\omega_T}\right)^2\right].\end{aligned}$$

The anharmonic corrections to fundamental transitions are $\Delta\hbar\omega_{A_1}=\varepsilon_A-\varepsilon_g$ and $\Delta\hbar\omega_{T_2}=\varepsilon_T-\varepsilon_g$.

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