Quantum effects of translational motions in solid para-hydrogen and ortho-deuterium:

anharmonic extension of the Einstein model

Quantum effects of translational motions in solid para-hydrogen and ortho-deuterium: anharmonic extension of the Einstein model

O Kühn[1], J Manz[2] and A Schild[2]

[1] Institut für Physik, Universität Rostock, D-18051 Rostock, Germany
[2] Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, D-14195 Berlin, Germany

E-mail: jmanz@chemie.fu-berlin.de

Abstract

An anharmonic extension of the Einstein model is developed in order to describe the effect of translational zero point motion on structural and thermodynamic properties of para-H_2 and ortho-D_2 crystals in the zero temperature limit. Accordingly, the molecules carry out large amplitude translational motions in their matrix cage, which are formed by the frozen environment of all other molecules. These translations lead from the molecular equilibrium positions via the harmonic to the anharmonic domain of the potential energy surface. The resulting translational distributions are roughly isotropic, and they have approximately Gaussian shapes, with rather broad full widths at half-maximum, FWHM(para-H_2/ortho-D_2) = 1.36/1.02 Å. The translational zero point energies induce expansions of the crystals, in nearly quantitative agreement with experimental results. Furthermore, they make significant contributions to the sublimation energies and zero pressure bulk moduli. These quantum effects decrease with heavier molecular masses. The corresponding isotope effects for ortho-D_2 compared to para-H_2 are confirmed by application of the model to Ar crystals. The results imply consequences for laser induced reaction dynamics of dopants with their host crystals.

1. Introduction

As a consequence of the light mass of the constituent particles and their weak interaction molecular para-hydrogen (p-H_2) and ortho-deuterium (o-D_2) form translational quantum solids and many of their properties are determined by zero point energy (ZPE) effects. Most of the previous research has been focused on the structural and thermodynamic properties (for an early review, see [1]). Moreover, recent detailed spectroscopic investigations of dopant molecules revealed a host of quantum dynamical effects including chemical reactions triggered by laser excitation [2, 3]. For instance, photo-dissociation of Cl_2 at 355 nm can lead to the formation of HCl provided that H_2 is vibrationally excited [4–6]. Due to the exponential scaling of quantum dynamics simulations with the number of degrees of freedom, simulation of such reaction dynamics requires approximation schemes such as quantum-classical ones [7] or models in reduced dimensionalities. For reactive collisions between Cl and H_2 in p-H_2 crystals, or Cl+D_2 in o-D_2 crystals, this should include information on the center of mass (c.o.m.) motions which are determined by the ZPE effects. The present anharmonic extension of the Einstein model provides this information; in fact, the resulting values of the mean zero point amplitudes have already been applied as input to our previous quantum dynamics simulations of the Cl + H_2 reaction in solid p-H_2 [6]. The respective experimental studies [3–5] motivate not only the previous [6] but also the present investigation.

Our model considers single p-H_2 or o-D_2 molecules moving in the frozen environment of all other p-H_2 or o-D_2 molecules of the crystals, respectively. Provided that the particle motions with respect to the equilibrium lattice site were harmonic, this situation would correspond to the Einstein model [8]. In fact, the Einstein model has been applied to solid p-H_2 before in the context of a path integral simulation

of structural and thermodynamic properties [9] (for extended simulations of p-H$_2$ quantum fluid behavior see, e.g. [10]). Providing an analytically solvable reference system within a variational procedure, it was shown to give rather good results e.g., for the pair distribution function and for the expansion of the crystal due to zero point motion. Therefore, it represents an interesting alternative to the more elaborate variational approaches starting from the Jastrow ansatz for the wavefunction [1, 11] such as the recent diffusion Monte Carlo (DMC) study in [12].

Our description of the translational quantum effects of p-H$_2$ versus o-D$_2$ crystals in frozen environment will, however, go beyond the traditional Einstein model: we shall consider translational motions in matrix cages, which will be referred to as 'Einstein cells' (ECs), with anharmonic potentials V_{EC}. A derivation of the model with the underlying assumptions is presented in appendix. Essentially, this is a quantum mechanical extension of the classical separable potential (CSP) method of Gerber and co-workers [7, 13]. The important role of anharmonicity is motivated by the fact that—as we shall demonstrate below—the translational motions in the quantum crystal have rather large amplitudes, compared to small amplitude motions in 'classical' crystals such as solid Ar. As a consequence, the translational motions are not confined to small domains close to the equilibrium positions, where V_{EC} is nearly harmonic. Instead, they penetrate into wider domains where anharmonicities are significant. These anharmonicities are caused by the interaction potentials between the moving molecule and all other ones in the frozen environment of the quantum crystals. For an adequate description of these interactions, we employ the widely used empirical potential of Buck *et al* [14, 15]. It has been derived from scattering data supplemented by feedback from variational calculations of solid state properties. For comparison, we have also applied the empirical H$_2$–H$_2$ potential due to Silvera and Goldman [16], which accounts for three-body interactions which are usually deemed unimportant for the spherically symmetric $J = 0$ p-H$_2$. Recently, the influence of the potential on structural and thermodynamical properties was explored in a DMC study [12]. Interestingly it was found that adding a triple dipole interaction term to the original Buck potential gives a slight improvement e.g. for the heat of sublimation. On the other hand, the pair distribution function at equilibrium density was not noticeably affected by the choice among these potentials. There have been efforts to determine the full anisotropic interaction potentials using *ab initio* quantum chemical methods. A benchmark coupled cluster calculation has been reported in [17]. Comparing the isotropic part with the Silvera–Goldman potential it is found, for instance, that the latter is slightly too attractive. However, as the authors noted the comparison of gas phase *ab initio* and condensed phase empirical potentials has to be taken with care as the latter implicitly account for certain condensed phase effects. To summarize, all the results which are presented below have been obtained using the empirical potential of Buck *et al* [14, 15]. Suffice it here to say that we have confirmed that the results based on the potential of Silvera and Goldman [16] are very similar.

The specific goals of the present investigation call for several tasks, starting from the determination of the anharmonic potential energy surfaces V_{EC} for translational motion in the ECs, as outlined above. Next we shall evaluate the corresponding ground state wavefunctions, together with the corresponding rather broad translational distributions which penetrate into the anharmonic domains of V_{EC}, and the translational ZPEs. Then we shall consider the consequences for the structural and thermodynamic properties of the quantum crystals. These include the lattice expansion from the classical reference $R_{0,\text{class}}$ to the quantum mean values R_{0,H_2} or R_{0,D_2} of the nearest neighbor (NN) distances and the corresponding distributions, the sublimation energies, and the bulk moduli, focusing on isotope effects. In order to confirm the latter, we shall apply our model also to solid Ar.

The paper is organized as follows: in section 2 we will outline the extended Einstein model, see the appendix for further details. Results for the translational motions of the p-H$_2$ and o-D$_2$ molecules in ECs of solid p-H$_2$ or o-D$_2$ crystals, respectively, with anharmonic potentials V_{EC}, and a discussion of quantum effects on the geometric structures, pair distribution functions, sublimation energies, and bulk moduli are given in section 3. For comparison and demonstration of ZPE effects this section also includes results for solid Ar. Section 4 summarizes and gives some perspectives on the consequences of the present model for simulations of laser induced reactions of dopants in solid p-H$_2$ or o-D$_2$.

2. Model

Depending on the growth conditions solid para-H$_2$ exhibits either a face-centered cubic (fcc) or a hexagonal closed packing (hcp) lattice [1]; here we will use the fcc form shown in cuboctahedral representation in figure 1. Further, we will assume that for the $J = 0$ spherical X$_2$ = p-H$_2$ or o-D$_2$ molecules, it will be sufficient to account for the isotropic part of the interaction potential $V(R_{ij})$, where $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ is the c.o.m. distance between the pair of molecules labeled i and j with centers of masses located at $\mathbf{R}_i(R_0)$ and $\mathbf{R}_j(R_0)$, respectively. The notation $\mathbf{R}_i(R_0)$ indicates that the positions $\mathbf{R}_i$ of the molecules in the fcc lattice depend on the nearest neighbor (NN) distance R_0. For $V(R)$, we use the empirical interaction potential provided by Buck *et al* [14, 15] (in units of k_b K, abbreviated K)

$$V(R) = A \exp(-\beta R - \gamma R^2) - \left(\frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} \right) F(R) \quad (1)$$

with $A = 1177 \times 10^3$ K, $\beta = 2.779$ Å^{-1}, $\gamma = 0.08$ Å^{-2}, $C_6 = 84.18 \times 10^3$ K, $C_8 = 417.86 \times 10^3$ K, and $C_{10} = 2617.5 \times 10^3$ K. Further, we have

$$F(R) = \exp(-(R_c/R - 1)^2)\theta(R_c - R) + \theta(R - R_c) \quad (2)$$

which switches-off the long-range interaction at the cut-off distance $R_c = 5.102$ Å. Using the interaction potential between individual X$_2$ molecules, the classical potential energy

per molecule of the fcc lattice

$$V_{\mathrm{fcc}}(R_0) = 0.5 \sum_{j>1} V(|\mathbf{R}_1(R_0) - \mathbf{R}_j(R_0)|) \qquad (3)$$

(cf appendix) has been minimized by varying the NN distance, R_0. The value of R_0 which yields the minimum value of $V_{\mathrm{fcc}}(R_0)$ is called the 'classical NN distance', $R_{0,\mathrm{class}}$. Likewise, the value of $V_{\mathrm{fcc}}(R_{0,\mathrm{class}})$ at $R_0 = R_{0,\mathrm{class}}$ is called the 'classical sublimation energy'. Periodic boundary conditions were employed and the convergence with respect to the size of the cubic simulation box has been investigated. It turned out that convergence of $R_{0,\mathrm{class}}$ in the third digit is reached with a simulation box including 4000 molecules.

The extended Einstein model considers anharmonic translational motions of a single molecule in its EC. Exemplarily we focus on motions of the central molecule, with the coordinates of its c.o.m. labeled $\mathbf{R}_1$. Its EC consists of all other molecules frozen at their mean fcc lattice positions $\langle \mathbf{R}_2(R_0)\rangle, \langle \mathbf{R}_3(R_0)\rangle, \ldots$ depending on the NN distance R_0. The position of the c.o.m. of the central molecule is written as $\mathbf{R}_1 = \delta R \mathbf{e}$, where δR is the distance from the origin, and $\mathbf{e}$ is a unit vector along the direction of the displacement. The potential V_{EC} for translational motions of the central p-H_2 or o-D_2 molecules from $\mathbf{R}_1 = \mathbf{0}$ to $\delta R \mathbf{e}$ in the fcc lattice characterized by the NN distance R_0 is

$$V_{\mathrm{EC}}(\delta R; \mathbf{e}|R_0) = 0.5 \sum_{j>1} V(|\delta R \mathbf{e} - \langle \mathbf{R}_j(R_0)\rangle|) - V_{\mathrm{fcc}}(R_0). \qquad (4)$$

Here, the notation $(\cdots|R_0)$ indicates that V_{EC} depends on the NN distance R_0. Further, subtraction of the fcc lattice potential energy per molecule $V_{\mathrm{fcc}}(R_0)$ implies the normalization of V_{EC} such that $V_{\mathrm{EC}}(\delta R = 0; \mathbf{e}|R_0) = 0$ at the center of the EC.

Exemplarily, we consider the cases where the unit vector $\mathbf{e}$ points along the crystallographic $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ directions of the otherwise frozen lattices (cf figure 1). The resulting wavefunctions $\Psi_0(\delta R; \mathbf{e}|R_0)$ describing one-dimensional (1d) translational motions of the $X_2 =$ p-H_2 or o-D_2 molecules with masses $M_{X_2} = 2m_H = 2.0158$ u or $M_{X_2} = 2m_D = 4.0028$ u, respectively, along δR, in the ground state (Ψ_0), for the given orientation $\mathbf{e}$ and NN distance R_0, are evaluated as solutions of the corresponding 1d Schrödinger equations (cf appendix),

$$\left[-\frac{\hbar^2}{2M_{X_2}} \frac{d^2}{d\delta R^2} + V_{\mathrm{EC}}(\delta R; \mathbf{e}|R_0) \right] \Psi_{0,X_2}(\delta R; \mathbf{e}|R_0)$$
$$= E_{0,X_2}(\mathbf{e}|R_0)\Psi_{0,X_2}(\delta R; \mathbf{e}|R_0), \qquad (5)$$

using the Fourier–Grid–Hamiltonian method [18]. This yields the ZPEs $E_{0,X_2}(\mathbf{e}|R_0)$ and the probability distributions

$$\rho_{0,X_2}(\delta R; \mathbf{e}|R_0) = |\Psi_{0,X_2}(\delta R; \mathbf{e}|R_0)|^2. \qquad (6)$$

The traditional Einstein model would yield isotropic Gaussian distributions corresponding to the ground state wavefunctions for the harmonic approximation to $V_{\mathrm{EC}}(\delta R; \mathbf{e}|R_0)$, with force constant $k_{\mathrm{EC}}(R_0)$. Accordingly, the ZPEs in harmonic approximation are $0.5\hbar\omega_{\mathrm{EC}}$, with frequency $\omega_{\mathrm{EC}} = \sqrt{k_{\mathrm{EC}}(R_0)/M_{X_2}}$. As we shall show in section 3, however, for increasing values of the NN distance R_0, significant

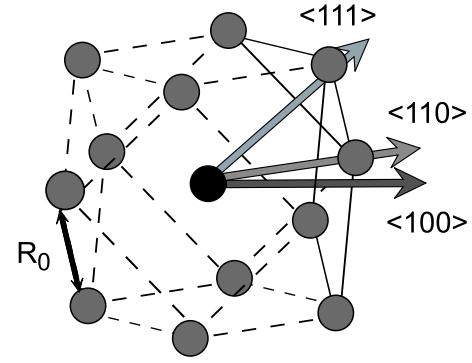**Figure 1.** Cuboctrahedral representation of the fcc $X_2 =$ p-H_2 or o-D_2 lattice with the three spatial directions along which the motion of the central X_2 molecule (black sphere) is considered. The nearest neighbor distance between the spherically symmetric X_2 molecules will be denoted by R_0.

anharmonicities change $V_{\mathrm{EC}}(\delta; \mathbf{e}|R_0)$ from single minimum to double minimum profiles implying negative force constants and, therefore, imaginary frequencies ω_{EC}, calling for the present anharmonic extension of the Einstein model. Nevertheless, it turns out that for values of R_0 close to the experimental ones, the ZPEs and the probability distributions depend only weakly on the direction $\mathbf{e}$ of the anharmonic potential cut $V_{\mathrm{EC}}(\delta R; \mathbf{e}|R_0)$. This near-isotropy is an empirical result which comes as a gift: it allows us to approximate the total translational ZPE of a single p-H_2 or o-D_2 molecule in their ECs by

$$E_{0,X_2,\mathrm{EC}}(R_0) \approx E_{0,X_2}(\mathbf{e}^{\langle 100\rangle}|R_0) + E_{0,X_2}(\mathbf{e}^{\langle 110\rangle}|R_0)$$
$$+ E_{0,X_2}(\mathbf{e}^{\langle 111\rangle}|R_0). \qquad (7)$$

Moreover, in spite of the anharmonicity of the nearly isotropic potentials $V_{\mathrm{EC}}(\delta R; \mathbf{e}|R_0)$, it turns out that the probability distributions are approximately Gaussian, in the domain of the experimental R_0,

$$\rho_{0,X_2}(\delta R; \mathbf{e}|R_0) \approx N_{0,X_2} e^{-(\delta R/\Delta R(X_2|R_0))^2} \qquad (8)$$

with widths parameter $\Delta R(X_2|R_0)$ depending on the isotope $X_2 =$ p-H_2 or o-D_2, and on the NN distance R_0. The corresponding FWHM is

$$\mathrm{FWHM}(X_2|R_0) = \sqrt{2\ln 2}\,\Delta R(X_2|R_0). \qquad (9)$$

3. Results

The classical equilibrium NN distance obtained with the Buck potential is $R_{0,\mathrm{class}} = 3.31$ Å whereas the experimental values are 3.79 Å for p-H_2 and 3.61 Å for o-D_2 [1]. Moreover, the classical sublimation energy is 283.6 K whereas the experimental values for the sublimation energies are 89.7 K for p-H_2 and 132.5 K for o-D_2. These discrepancies call for quantum corrections, in the frame of the present extended Einstein model.

The anharmonic potential energy surfaces $V_{EC}(\delta R; \mathbf{e}|R_0)$ for translational motions of p-H$_2$ or o-D$_2$ molecules versus δR, in their ECs along the direction $\mathbf{e} = \mathbf{e}^{\langle 100 \rangle}$, $\mathbf{e}^{\langle 110 \rangle}$, and $\mathbf{e}^{\langle 111 \rangle}$ are shown in figures 2(a)–(c), exemplarily for the NN distances $R_0 = R_{0,\text{class}} = 3.31$ Å, $R_0 = 3.79$ Å, and $R_0 = 4.2$ Å, respectively. Also shown are the ZPEs $E_{0,H_2}(\mathbf{e}|R_0)$ and the probability distributions $\rho_{0,X_2}(\delta R; \mathbf{e}|R_0)$. In panel (b) we also give the Gaussian approximation, equation (9). The corresponding value of the FWHM is FWHM(p-H$_2$|$R_0 = 3.79$ Å) = 1.36 Å. These rather broad FWHMs imply that the translational wavefunctions enter the anharmonic domains of $V_{EC}(\delta R; \mathbf{e}|R_0)$ as anticipated.

Apparently, expanding the lattice causes the potential to widen and at the same time to increase the anharmonicity. In general the potentials along the $\langle 110 \rangle$, and $\langle 111 \rangle$ directions are steeper as compared to the $\langle 100 \rangle$ case due to the configuration of the repulsive cage, cf figure 1. At 3.31 Å the differences between the distributions are hardly discernible; the average ZPE is 85.4 K. For the experimental value of 3.79 Å the ZPE drops to $E_{0,\text{cell}} = 30.2$ K and the differences in the distributions $\rho_{0,p-H_2}(\delta R; \mathbf{e}|R_0)$ depending on $\mathbf{e}$ are noticeable but not significant. For larger NN distances, the potential develops a double minimum character, giving clear evidence for the importance of anharmonicity, cf figure 2(c).

The lattice energy per X$_2$ = p-H$_2$ or o-D$_2$ molecule $V_{\text{fcc},X_2}(R_0)$ and the translational ZPEs $E_{0,X_2,EC}(R_0)$ in the ECs depend on the NN distance R_0 as shown in figure 3(a). The total quantum mechanical energy of that particle therefore is

$$V_{0,\text{crystal},X_2}(R_0) = V_{\text{fcc},X_2}(R_0) + E_{0,X_2,EC}(R_0). \qquad (10)$$

Plotting this function as in figure 3(a) we obtain the correction to the classical equilibrium NN distance due to translational zero point motion. For p-H$_2$, the value so obtained is $R_{0,\text{p-H}_2} = 3.86$ Å which is only 2% larger than the experimental value and thus a substantial improvement as compared to the classical case. The width of the ground state distribution at 3.86 Å is found to be FWHM(p-H$_2$|$R_0 = 3.86$ Å) = 1.46 Å. $V_{0,\text{crystal},X_2}(R_0 = R_{0,\text{p-H}_2})$ can also be used to calculate the sublimation energy which is 114.9 K, that is, 29% above the experimental value of 89.4 K [19]. It is interesting to compare the present values of equilibrium distance and sublimation energy with the values reported on the basis of DMC calculation for the same potential. In [12] the sublimation energy was found to be 93.4 K and $R_{0,\text{p-H}_2} = 3.78$ Å. This indicates that the error as compared with experiment is only partly due to the used interaction potential. In fact for the Silvera–Goldman potential [16] the DMC sublimation energy is 87.4 K at $R_{0,\text{p-H}_2} = 3.78$ Å. The Silvera–Goldman potential has been originally developed as an effective potential using the self-consistent phonon approximation [16]. Within this approximation it gives a sublimation energy of 85.5 K at $R_{0,\text{p-H}_2} = 3.77$ Å. Comparing the results of the various methods it is clear that the present anharmonic extension of the Einstein model accounts for most of the quantum corrections to the classical model, cf figure 3. It does not provide, however, an improvement as compared with the DMC or the self-consistent phonon approach. Besides its numerical simplicity, the main advantage of this method is
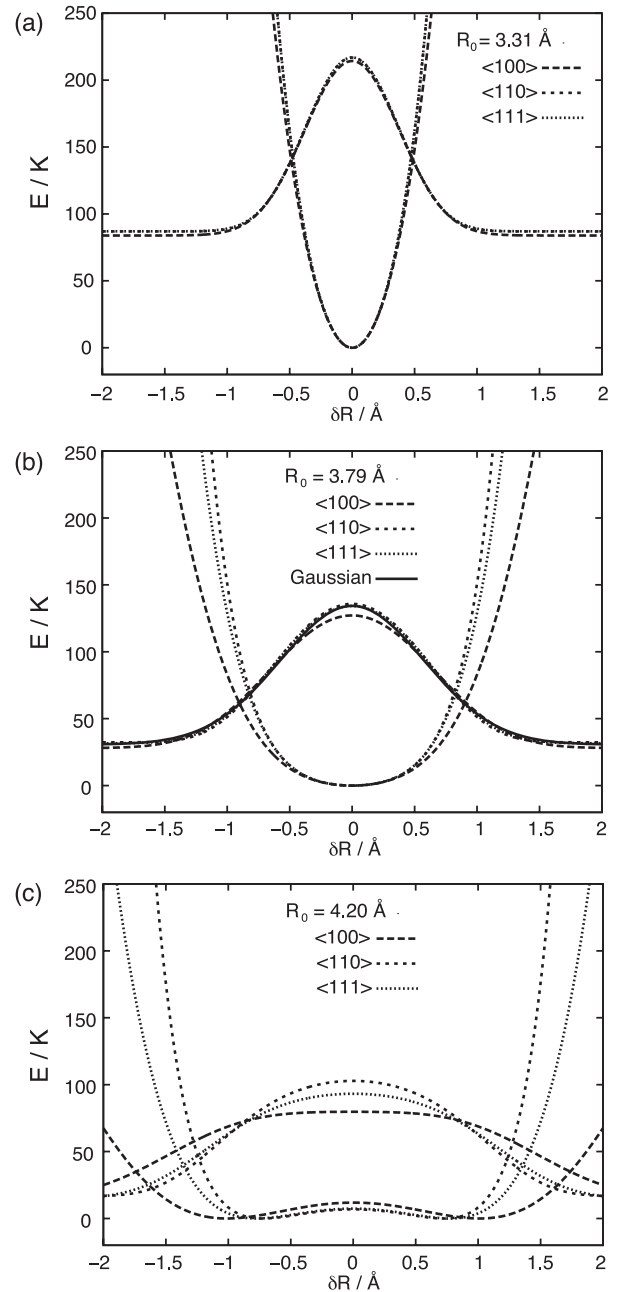

Figure 2. One-dimensional densities for the c.o.m. motion of a p-H$_2$ molecule in the matrix cage along the different spatial directions shown in figure 1. The NN distance corresponds to the classical minimum value, $R_{0,\text{class}}$, obtained for the Buck interaction potential (a), the experimental value of 3.79 Å (b), and $R_0 = 4.20$ Å (c). Panel (b) also shows the result of a Gaussian fit to the equally weighted average of the ground state for the three directions with FWHM(H$_2$|$R_0 = 3.79$) = 1.36 Å. The one-dimensional Schrödinger equations, equation (5), have been solved on a grid of 2000 points in the interval [−4: 4] Å.

that it can be applied to reactions in quantum solids as will be discussed in section 4.

The procedure can be adapted to o-D$_2$ solids as well, by merely changing the mass in the one-dimensional Schrödinger equation. Respective results are shown in figure 3(b). Here the zero point correction shifts the equilibrium NN distance to
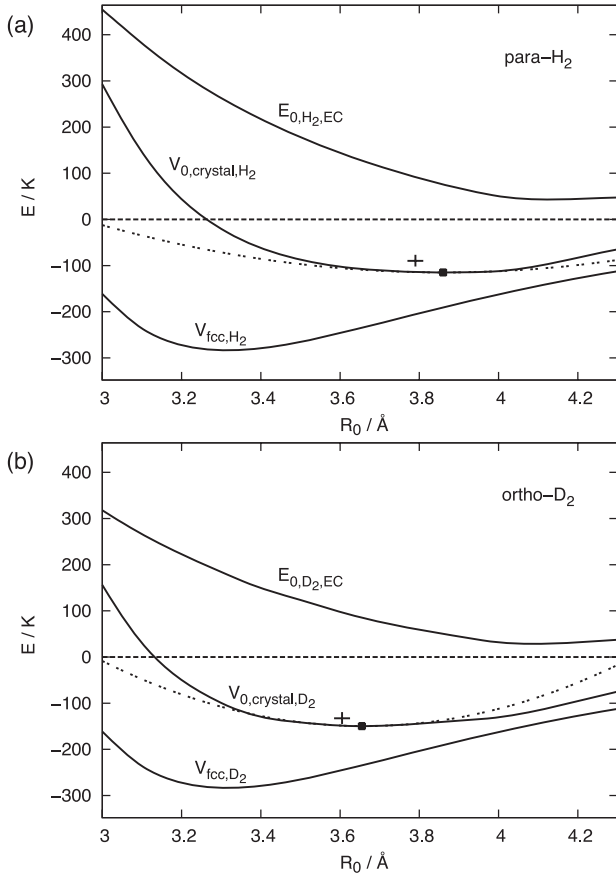
Figure 3. (a) Total interaction energy between the crystal and the p-H$_2$ molecule in the EC, $V_{\text{fcc,H}_2}$, ZPE of the tagged molecule, $E_{0,\text{P-H}_2,\text{EC}}$, and ZPE-corrected interaction energy $V_{0,\text{crystal,H}_2}$ as a function of the NN distance R_0. The cross marks the experimental equilibrium distance and the corresponding sublimation energy [1] and the square the minimum of $V_{0,\text{crystal,H}_2}(R_0)$. A harmonic expansion with respect to this equilibrium distance is shown as a dotted line. Panel (b) reports the results of an analogous calculation for o-D$_2$.

Figure 4. Total interaction energy between the argon crystal and a tagged Ar atom in the EC, $V_{\text{fcc,Ar}}$, ZPE of the tagged molecule, $E_{0,\text{Ar,EC}}$, and ZPE-corrected interaction energy $V_{0,\text{crystal,Ar}}$ as a function of the NN distance. The cross marks the experimental equilibrium distance and the corresponding sublimation energy, and the square the minimum of $V_{0,\text{crystal,H}_2}(R_0)$.

3.64 Å in excellent agreement with the experimental value of 3.61 Å [1]. Also the energy of sublimation which is found to be 148.5 K is in better agreement with the experimental value of 132.3 K [19] as compared to the p-H$_2$ case.

Having $V_{0,\text{crystal,X}_2}(R_0)$ for both isotopes at hand, one can determine the bulk moduli (i.e. the inverse compressibilities) which are calculated according to

$$B = -\Omega \frac{\partial p}{\partial \Omega} = \Omega \frac{\partial^2 V_{0,\text{crystal,X}_2}}{\partial \Omega^2}$$

$$= \Omega (R_0/3\Omega)^2 \frac{\partial^2 V_{0,\text{crystal,X}_2}}{\partial R_0^2}\bigg|_{R_0=R_{0,\text{X}_2}}$$

$$= \frac{\sqrt{2}}{9 R_0} \frac{\partial^2 V_{0,\text{crystal,X}_2}}{\partial R_0^2}\bigg|_{R_0=R_{0,\text{X}_2}} \qquad (11)$$

(Ω: volume of the elementary cell, here of the fcc lattice). The harmonic approximation to $V_{0,\text{crystal,X}_2}$ in the vicinity of the quantum mechanical equilibrium distance is shown in figure 3. Note that the range of the harmonic approximation is rather limited. Nevertheless, the extended Einstein model yields the values of $B = 1.6$ and 3.8 kbar for the p-H$_2$ and o-D$_2$ quantum
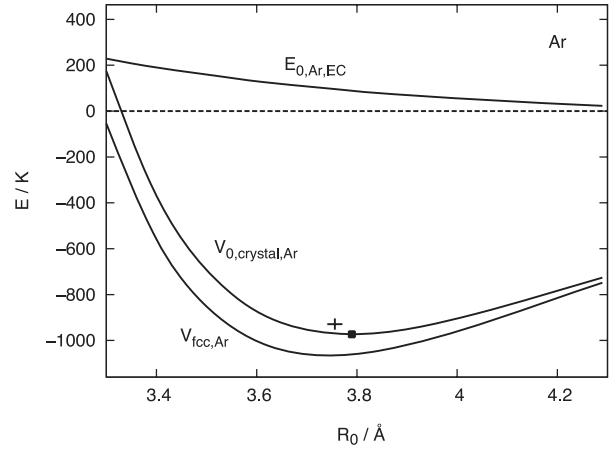
crystals, in satisfactory agreement with the experimental values, 1.7 and 3.2 kbar [20], respectively. Comparison of the results for p-H$_2$ and o-D$_2$ reveals the following additional isotope effects: the ZPEs decrease from the values of $E_{0,\text{p-H}_2,\text{EC}}(R_0)$ to $E_{0,\text{o-D}_2,\text{EC}}(R_0)$ as the mass increases from $M_{\text{p-H}_2}$ to $M_{\text{o-D}_2}$. As a consequence of this quantum isotope effect, the expansion of the p-H$_2$ crystal from $R_{0,\text{class}} = 3.31$ Å to $R_{0,\text{p-H}_2} = 3.86$ Å by 0.55 Å drops to the smaller value of $R_{0,\text{o-D}_2} = 3.65$ Å by only 0.34 Å. At the same time, the rather strong decrease of the sublimation energy, for the classical value $V_{\text{fcc,X}_2}(R_{0,\text{class}}) = 283.6$ K to $V_{0,\text{crystal,H}_2}(R_{0,\text{p-H}_2}) = 115$ K drops to just $V_{0,\text{crystal,D}_2}(R_{0,\text{o-D}_2}) = 150$ K. Thus in general, the quantum effects decrease with heavier masses of the isotopomer. In order to support this trend, we have also evaluated the corresponding quantum effects for an argon fcc lattice, based on the Ar–Ar interaction potential of [21]. The much larger mass $M_{\text{Ar}} = 39.95$ u compared to $M_{\text{o-D}_2}$ and $M_{\text{p-H}_2}$ implies that the quantum effects of the zero point translational motions should be almost negligible. This prediction is confirmed in figure 4 which shows the zero point corrected potential $V_{0,\text{crystal,Ar}}(R_0)$ as well as its classical and quantum contributions for the case of an argon fcc lattice. As expected, the zero point correction gives only a small shift of the equilibrium distance from 3.74 to 3.79 Å and for the sublimation energy a change from 1066 to 973 K. For comparison, the experimental values of the NN distance and sublimation energy are 3.759 Å [22] and 929 K [23], respectively. Overall, these values are in accord with the expectation that the importance of ZPE effects is significantly reduced due to the heavier mass of the argon atoms.

Finally, we have estimated the pair distribution function using the density calculated at the quantum corrected equilibrium distance. The pair distribution has been shown to be rather insensitive concerning the interaction potential [12]. In figure 5 we give as a reference the pair distribution function
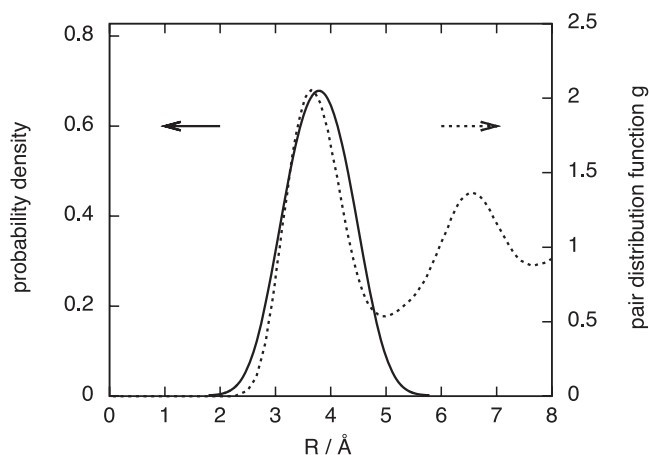
Figure 5. DMC (adopted from [12]) (dotted line) and present quantum mechanical (solid line) pair distribution function for p-H_2 at $R_0 = 3.79$ Å. The quantum mechanical distribution has been obtained from figure 2. Note that the two quantities are normalized in a different way, i.e. the absolute value of the first peak cannot be compared.

adopted from the DMC simulations of [12]. The first two peaks reflect the local shell structure of the lattice. Its emergence starting from clusters of different sizes has been investigated in [24, 25], for instance. The probability distribution for the translational motion of a given H_2 molecule taken at the quantum corrected equilibrium position can be used to estimate the position and width of the first peak in the pair distribution which is due to the NN molecules. This distribution function corresponds to the distribution of the central molecule in the crystal with respect to the mean value of the fixed nearest neighbors. Despite the simplicity of this approach, which does not take into account the zero point motion of the neighbors, the result is in rather good agreement with the more sophisticated DMC simulation, as can be seen in figure 5.

4. Conclusions

In summary we have presented an independent particle model which is an anharmonic extension of the Einstein model to simulate the effect of quantum mechanical translational zero point motion on structural and thermodynamic properties of solid p-H_2. Despite its apparent simplicity, the model performs surprisingly well in predicting the expansion of the quantum crystal due to translational delocalization of the H_2 molecules. Other quantities such as the sublimation energy and the bulk modulus are in qualitative agreement with experimental data. Results of comparable quality have been obtained for o-D_2 and argon where the importance of quantum effects diminishes due to the heavier mass. A possible improvement of the present model should include the effect of zero point motion of the nearest neighbors on the potential in the Einstein cell.

The utility of the present model lies, however, not in the quantitative prediction of bulk properties where it cannot compete with the DMC method or even the self-consistent phonon approximation or its anharmonic extension [11]. The

advantage of this model, which it shares with the CSP approach [7], is that it can be straightforwardly used for applications in reaction dynamics. Here, the present results imply important consequences for laser induced reactions of dopants with p-H_2 or o-D_2 molecules in the quantum crystals, quite different from corresponding reactions in the gas phase, or in 'classical' rare gas solids. As an example, consider the reaction

$$Cl(^2P_{3/2}) + H_2(v = 1) \rightarrow HCl + H \qquad (12)$$
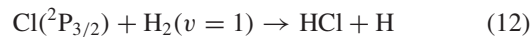
in solid p-H_2, which may be induced by ultraviolet (UV) and infrared (IR) co-irradiations causing electronic excitations of matrix-isolated Cl_2 molecules in the first excited $^1\Pi_u$ state and subsequent photo-dissociation to two $Cl(^2P_{3/2})$ atoms, and vibrational excitation of the molecular reactant $H_2(v = 1)$, respectively [5]. In the gas phase, the distribution of the distances between the reactants is quasi-infinite, implying sharp distributions in momentum space, at least in the case of continuous wave (cw) excitations. In contrast, 'classical' rare gas matrices constrain vibrational zero point motions to rather small amplitudes, implying large distributions of momenta which tend to wash out any sharp features of the reaction probabilities versus translational energy—this concerns e.g., the rather sudden onset of the reactivity at reaction thresholds as well as possible resonance phenomena, cf [26, 27]. Quantum solids provide an intermediate scenario, with zero point amplitudes that are much larger than for classical solids, yet much smaller than in the gas phase. Accordingly, one may predict that those sharp features which occur in gas phase reactions, such as resonances, should still be observable in quantum solids, entirely different from classical solids. Indeed, first signatures of resonances in the Cl + H_2 reaction in solid p-H_2 have already been predicted in [6]. Systematic analysis by means of quantum dynamics simulations is provided in [28]. The results in [6] and [28] are based, in part, on the present extended Einstein model for solid p-H_2. The complementary results for solid o-D_2 should allow comparative predictions and analyses of the Cl+H_2 and Cl+D_2 reactions in p-H_2 versus o-D_2 matrices; work along these lines is in progress. By extrapolation, the present model may also be extended to applications to dopants in quantum clusters, see e.g. [29].

Appendix

The present anharmonic extension of the Einstein model of the para-hydrogen (X_2 = p-H_2) or ortho-deuterium (X_2 = o-D_2) crystals aims at an approximate description of the ground state which is populated preferably at low temperature. This approach may also be considered as a quantum mechanical extension of the CSP method, which has been developed by Gerber and co-workers, starting from a variational ansatz [7, 13]. Accordingly, each X_2 molecule moves in the mean field of all others. Specifically, the CSP method provides an estimate of the mean field in terms of classical trajectories for the other particles. At very low temperatures (as in the present application), these trajectories accumulate close to local potential minima in the crystal. Our extension replaces those trajectories by the quantum mechanical mean values of the particle positions. By Ehrenfest's theorem, these mean values coincide with the potential minima. We anticipate corresponding fcc lattice symmetry of the crystal [1], with nearest neighbor distance R_0. Here, we assume that the X_2 molecules appear spherical, in accord with the properties of the X_2 molecules in their vibrotational ground state ($v, J, M = 0, 0, 0$). Neglecting intramolecular degrees of freedom, the Hamiltonian for the motions of the centers of masses $\mathbf{R}_j$ of N X_2 molecules labeled $j = 1, 2, \ldots, N$ in the crystal is

$$
\begin{aligned}
H &= \sum_{j=1}^{N} T_j + \sum_{i=1}^{N-1} \sum_{i<j}^{N} V_{ij} \\
&= \sum_{j=1}^{N} T_j + \tfrac{1}{2} \sum_{j=1}^{N} \sum_{i \neq j}^{N} V_{ij} \\
&= \sum_{j=1}^{N} (T_j + V_j)
\end{aligned}
\tag{A.1}
$$

where $T_j = -\hbar^2 \Delta_j / (2M_{X_2})$ describes the kinetic energy of the (center of mass of the) X_2 molecules labeled j, $V_{ij} = V(|\mathbf{R}_i - \mathbf{R}_j|)$ denotes the interaction energy between X_2 molecules i and j, and

$$
V_j = \tfrac{1}{2} \sum_{i \neq j} V_{ij}
\tag{A.2}
$$

is the interaction of the X_2 molecule labeled j with all others. For convenience, the 'central' X_2 molecule in the crystal is labeled $j = 1$. Assuming large crystals and neglecting effects of crystal boundaries, symmetry and periodicity imply that the ground state wavefunction of the crystal is translationally invariant with respect to the fcc lattice with mean nearest neighbor distance R_0. Accordingly, the wavefunction is invariant with respect to those permutations of the centers of masses of the p-H_2 molecules, which correspond to translations of the fcc lattice with nearest neighbor distance R_0. As a consequence, the ground state wavefunction yields the mean values of the coordinates $\langle \mathbf{R}_i(R_0) \rangle$ of the centers of masses of the X_2 molecules labeled i, which are located at periodic equilibrium positions of the fcc lattice, parametrized by the nearest neighbor distance R_0. Moreover, each of the X_2

molecules 'sees' the same environment. This is approximated by replacing equation (A.2) with

$$
V(\mathbf{R}_j | R_0) \approx \tfrac{1}{2} \sum_{i \neq j} V(|\mathbf{R}_j - \langle \mathbf{R}_i(R_0) \rangle|)
\tag{A.3}
$$

i.e. we consider the interaction of the X_2 molecule j at $\mathbf{R}_j$ with all other molecules i at their mean positions $\langle \mathbf{R}_i(R_0) \rangle$, neglecting effects of the distributions of probability densities of the X_2 molecules i around their mean values $\langle \mathbf{R}_i(R_0) \rangle$. Accordingly, the Hamiltonian of the extended Einstein model is approximated as

$$
H \approx \sum_{j=1}^{N} H_{\mathrm{EC},j},
\tag{A.4}
$$

with equivalent Hamiltonian operators $H_{\mathrm{EC},j}$ for the individual X_2 molecules j, in particular

$$
H_{\mathrm{EC},1} = -\frac{\hbar^2 \Delta_1}{2M_{X_2}} + V_{\mathrm{EC}}(\mathbf{R}_1 | R_0)
\tag{A.5}
$$

for the 'central' X_2 molecule, where

$$
V_{\mathrm{EC}}(\mathbf{R}_1 | R_0) = \tfrac{1}{2} \sum_{i \neq 1} V(|\mathbf{R}_1 - \langle \mathbf{R}_i(R_0) \rangle|)
\tag{A.6}
$$

is its effective potential energy in its 'Einstein cell' (EC). The ground state energy of the crystal is then equal to N times the ground state energy of the representative X_2 molecule labeled $j = 1$, or in other words, the mean ground state energy per molecule is obtained as solution of the Schrödinger equation

$$
H_{\mathrm{EC},1} \Psi_0(\mathbf{R}_1 | R_0) = E_{0,X_2,\mathrm{EC}}(R_0) \Psi_0(\mathbf{R}_1 | R_0),
\tag{A.7}
$$

depending parametrically on the nearest neighbor distance R_0, as indicated by the notation $(\cdots | R_0)$.

The interaction potential $V(|\mathbf{R}_i - \mathbf{R}_j|)$ between the individual molecules i and j is specified in section 2; note that the resulting potential $V_{\mathrm{EC}}(\mathbf{R}_1 | R_0)$ of the X_2 molecule in its Einstein cell may be anharmonic and anisotropic, calling for the present extension beyond the traditional Einstein model. In section 2, we consider additional approximations beyond (A.7); in particular, we explore corresponding uni-directional, one-dimensional motions of the central X_2 molecule in its Einstein cell, showing that the three-dimensional motion is nearly isotropic but anharmonic.

References

[1] Silvera I F 1980 *Rev. Mod. Phys.* **52** 393
[2] Momose T, Fushitani M and Hoshina H 2005 *Int. Rev. Phys. Chem.* **24** 533
[3] Yoshioka K, Raston P L and Anderson D T 2006 *Int. Rev. Phys. Chem.* **25** 469
[4] Raston P L and Anderson D T 2006 *Phys. Chem. Chem. Phys.* **8** 3124

[5] Kettwich S C, Raston P and Anderson D 2009 *J. Phys. Chem.* A **113** 7621
[6] Korolkov M V, Manz J and Schild A 2009 *J. Phys. Chem.* A **113** 7630
[7] Jungwirth P and Gerber R B 1999 *Chem. Rev.* **99** 1583
[8] Mahan G D 1981 *Many-Particle Physics* (New York: Plenum)
[9] Li D and Voth G A 1992 *J. Chem. Phys.* **96** 5340
[10] Nakayama A and Makri N 2006 *J. Chem. Phys.* **125** 024503
[11] Koehler T R and Werthamer N R 1971 *Phys. Rev.* A **3** 2074
[12] Operetto F and Pederiva F 2006 *Phys. Rev.* B **73** 184124
[13] Eshet E, Ratner M A and Gerber R B 2006 *Chem. Phys. Lett.* **431** 199
[14] Buck U, Huisken F, Kohlhase A, Otten D and Schaefer J 1983 *J. Chem. Phys.* **78** 4439
[15] Norman M J, Watts R O and Buck U 1984 *J. Chem. Phys.* **81** 3500
[16] Silvera I F and Goldman V V 1978 *J. Chem. Phys.* **69** 4209
[17] Diep P and Johnson J K 2000 *J. Chem. Phys.* **112** 4465
[18] Marston C C and Balint-Kurti G G 1989 *J. Chem. Phys.* **91** 3571
[19] Schnepp O 1970 *Phys. Rev.* A **2** 2574
[20] Anderson M S and Swenson C A 1974 *Phys. Rev.* B **10** 5184
[21] Manz J and Mirsky K 1980 *Chem. Phys.* **46** 457
[22] Linde D R (ed) 2006 *CRC Handbook of Chemistry and Physics* 87th edn (Boca Raton, FL: Taylor and Francis)
[23] Schwalbe L A, Crawford R K, Chen H H and Aziz R A 1977 *J. Chem. Phys.* **66** 4493
[24] Tejeda G, Fernández J M, Montero S, Blume D and Toennies J P 2004 *Phys. Rev. Lett.* **92** 223401
[25] Rabani E and Jortner J 2006 *J. Phys. Chem.* B **110** 18893
[26] Baer M 1974 *Mol. Phys.* **27** 1429
[27] Persky A and Baer M 1974 *J. Chem. Phys.* **60** 133
[28] Korolkov M V and Manz J 2010 *Chem. Phys.* at press (doi:10.1016/j.chemphys.2009.12.026)
[29] Toennies J P and Vilesov A F 2004 *Angew. Chem. Int. Edn* **43** 2622