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Thermodesorption of impurities from a transparent crystal surface

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Thermodesorption of impurities from a dielectric crystal surface can be stimulated by absorption of high-frequency phonons, e.g., Debye phonons. We study this process in the framework of a truncated-harmonic-oscillator model and find the desorption rate by methods of quantum statistics. In this paper, we present the estimates for the mean desorption rates that are simple, realistic, and at the same time allow us to predict a series of physical effects in thermodesorption processes.

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I. INTRODUCTION

Many of the modern high technologies are based upon the processes caused by intense external impacts in solids or on their surfaces. The effects of laser, plasma, and particle beam impacts are believed to be the most pertinent to this context. All such impacts lead to nonequilibrium transport processes whose physical description is often unclear or incomplete. The most typical examples of such processes are catalytic chemical reactions on solid surfaces, desorption and sublimation, generation of defects and surface (geometric) structures, surface and volume nonequilibrium diffusion, and others.

A physical description of these kinds of processes cannot be based on the standard quantum-mechanical methods. In most such problems, the variation of particles' energy and momentum distribution functions needs to be taken into account, which requires the use of more complex quantum-statistical or quantum-kinetic methods. Appropriate quantum-kinetic equations therefore need to be derived and solved for stimulated (nonthermal) processes, such as photodesorption or electron-beam sublimation, as well as for traditionally "thermal" processes taking place in the presence of intense external perturbations. For example, photostimulated processes are often accompanied by heating of the bulk material, which in turn causes various thermal but nonequilibrium processes.

The lucky exceptions from the above general trend are the processes of photodesorption and thermodesorption of impurities from a solid surface (as well as the sublimation of the solid's own atoms). The desorbed or sublimated particles usually depart into vacuum and do not have any "back action" on the initial system. This eliminates the need for a full quantum-statistical description and allows us to consider quasiequilibrium distribution functions for the initial system of particles. For the "heavy" atoms or ions we can adopt quasiclassical Boltzmann distribution. Yet a description of even these "simple" processes remains very complicated and is often carried out by phenomenological methods because of the difficulties in constructing the initial physical model for the nonequilibrium processes. Hence carrying out the quantum calculations in the analytical form all the way to the final results that can be compared to experiment is not usually possible. With that in mind, we study the process of thermal desorption of impurities from a transparent crystal surface (from a dielectric) as an extension of our earlier work [1]. We will utilize a simple model of a truncated harmonic oscillator, which is widely used for description of various processes involving bound atoms or molecules (e.g., see Refs. [2–4] and quotations therein). In this model, thermodesorption is caused by stochastic forces that arise from the phonon emission and absorption.

The truncated-oscillator model allows for an analytical description of an impurity bound on the crystal surface with very few parameters, all of which are well known [1]. This is one important aspect that contrasts the present work as well as Ref. [1] from Refs. [2,3], describing thermal desorption, and from Ref. [4] describing photodesorption. In Ref. [2], a mixed quantum-classical description is used, similar to the approach proposed in Ref. [5]. Its drawback is that the introduced friction kernel spectrum $\gamma(t)$ is not sufficiently well known. As a result, the final expressions of Ref. [2] depend on the absolute value square of this kernel's Fourier components, but the way these parameters can be estimated is not specified. The choice of functional forms for $\gamma(t)$ (exponential and Gaussian functions [2]) is not justified, and in any case does not provide the values of preexponential parameters. Therefore the estimates in Ref. [2] may be considered as mere illustrations. Another parameter that is not numerically determined is the oscillator frequency Ω (in our approach, this frequency and the number of levels in the potential well are derived from the size of the well and the dissociation energy).

An interesting and relevant work [3] reports the study of a variety of thermal processes on a metal surface, including thermal desorption. In Ref. [3], a very solid and complex theory is developed, that describes interaction of chemically adsorbed particles with the electron and phonon systems of the metal. The particle is assumed to be an impurity ion with some effective charge, some surface-binding energy, and with the equilibrium distance d_1 from the surface. The ion is bound in the surface-potential well that has a set of discrete energy levels. Transitions between these levels (not broadened) are studied in the harmonic approximations, with se-

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lection rules $\nu \to \nu \pm 1$. The anharmonic transitions $\nu \to \nu \pm 2$ that are 100 to 1000 times less probable than the harmonic transitions are also considered. The mean first passage time (after which the ion reaches the upper level, or the predissociation state) is then determined. This time is compared with the desorption rate. The analysis [3] largely reproduces and generalizes the results by Montroll and Shuler [6], and by Kim [7].

Calculations in Ref. [3] are carried out for two models: for the Morse-potential well, and for the truncated harmonic oscillator. The latter model is considered to be less accurate in Ref. [3]. However, analysis of the numerical results from Ref. [3] makes us take this statement carefully. The plots in Ref. [3] show that the results for these two models differ by less than an order of magnitude, and have the same temperature dependence (Boltzmann, or Arrhenius dependence of the form $\exp\{-\varepsilon_a/T\}$, where ε_a is the desorption activation energy and T is the temperature of the system in energy units). This reminds us of Feynman's remark [8] that constructing an evaporation or thermoemission theory, or chemical kinetic (we would like to add to this list other thermoactivated processes such as diffusion and desorption) never gives an exact preexponential temperature-dependent factor. One could have assumed other types of potentials for description of desorption, e.g., Slater potential [8], Lennard-Jones potential [8–10], and so on. Any of these potentials would lead to the same generic Arrhenius exponent but with different preexponential factors. Therefore the numerical variation of the results by a small factor could not make for a justified selection of the model for the potential. This selection requires more clear, functional distinctions. As for the results [3], it is clear from their Fig. 7 that one could make the "Morse" and "truncated oscillator" results to practically coincide (equally outstanding from the experimental data they are compared to) by only a small variation of the parameters.

Note that the kinetic equation (2.10) in Ref. [3] used for deriving the electron distribution function in metals does not account for the Pauli principle that is important for describing degenerate electron gas in metals. Linearization of the kinetic equation in Ref. [3] effectively makes the electron gas classical (despite involving the Fermi energy in the further consideration) by disregarding the prohibition for electron transitions into already occupied states. This is a purely classical approach known to lead to more than an order of magnitude errors, e.g., in the theory of metal conductivity.

Studying an ion in the immobile potential above the surface significantly simplifies the problem [3], but it is also important and interesting to determine the role of the potential's rotation degrees of freedom in the plane perpendicular to the metal surface (the "rotator" type oscillations). The "rotator" collisions with the surface cause additional transfer of energy and momentum from the lattice to the adsorbed particle. This transfer may noticeably affect the desorption rate. Considering these observations, the agreement of the theoretical results from Ref. [3] with the experimental data for an ion above a metal surface, when only phonon mechanism of stimulated transitions between the ion's levels in the well is considered, is strikingly surprising.

In the present work we carry out the study of thermal desorption of a particle replacing one of the surface's own atoms in terms of the truncated-harmonic-oscillator model. This is especially interesting because the model of the type given in Ref. [1] allows us to complete the calculations of matrix elements, transition probabilities, and desorption rate in a compact analytical form.

II. PHYSICAL MODEL AND ITS APPLICATION

A full description of the model is available in Refs. [2,1]. Let us briefly go over its main concepts and methods of application. We consider an impurity with mass M_0 bound in a surface-potential well. The spring constant K of this potential can be derived from the fact that the oscillator is truncated at the level of the binding energy ε_a, which is empirically known,

$$\frac{1}{2}Kl^2 = \varepsilon_a, \tag{1}$$

where $2l = a$, and a is about the lattice period, see Ref. [1].

In the above model, the energy spectrum of a bound impurity is [11]

$$\varepsilon_n = -\varepsilon_a + (n+1/2)\hbar\omega_0, \quad n = 0,1,2,\ldots, \tag{2}$$

with

$$\omega_0 = \sqrt{\frac{2\varepsilon_a}{M_0 l^2}}. \tag{3}$$

Coupling with phonons arises as a random displacement $\vec{\zeta}$ of the center of surface potential

$$U(x,\vec{\zeta}) = \frac{1}{2}K(\vec{i}x + \vec{\zeta})^2 \approx U(x) + Kx(\vec{i}\cdot\vec{\zeta}). \tag{4}$$

Displacement $\vec{\zeta}$ can be expressed in terms of phonon creation and annihilation operators $b^\dagger_{\vec{q},\mu}$ and $b_{\vec{q},\mu}$ with quasimomentum $\hbar\vec{q}$ and with the unitary polarization vector $\vec{e}_{\vec{q},\mu}$ [12],

$$\vec{\zeta} = \vec{i}\sum_{\vec{q}} \zeta^{(C)}(b_{\vec{q},\mu}e^{i\vec{q}\cdot\vec{r}} + b^\dagger_{\vec{q},\mu}e^{-i\vec{q}\cdot\vec{r}}). \tag{5}$$

The normalization constant $\zeta^{(C)}$ is

$$\zeta^{(C)} = \sqrt{\frac{\hbar}{3\rho V_0 \omega_{\vec{q},\mu}}}, \tag{6}$$

where ρ and V_0 are the crystal density and volume, respectively, and ω_q is the phonon frequency.

The complete Hamiltonian for the studied system,

$$\hat{H} = \hat{H}_{im} + \hat{H}_{ph} + \hat{H}_{int}, \tag{7}$$

includes the following terms: the unperturbed Hamiltonian with the kinetic-energy operator $\hat{K}$,

$$\hat{H}_{im} = \hat{K} + U(x), \tag{8}$$

the unperturbed energy operator for phonons,

$$\hat{H}_{ph}=\sum_{\vec{q}} \hbar\omega_q b_{\vec{q}}^{\dagger} b_{\vec{q}}; \tag{9}$$

and the interaction operator of the impurity with the random oscillations of the lattice,

$$\hat{H}_{int}=Kx(\vec{i}\cdot\vec{\zeta})=Kx\sum_{\vec{q}} \zeta^{(C)}(b_{\vec{q}}e^{i\vec{q}\cdot\vec{r}}+b_{\vec{q}}^{\dagger}e^{-i\vec{q}\cdot\vec{r}}). \tag{10}$$

In the following we will use the harmonic approximation for phonons. This means that we will neglect anharmonism resulting in multiphonon processes, e.g., broadening the oscillator energy levels. We will only consider the displacements along the x axis perpendicular to the crystal surface, i.e., the phonons with the wave vectors $\vec{q}=\vec{i}q$ and use the scalar index q in Eqs. (9) and (10). Operator (10) is considered to be small perturbations added to operators (8) and (9), which allows us to use perturbation theory.

Now we will introduce the second quantization representation for the impurity [1]. Let us define $\varepsilon_n=-\varepsilon_a+\varepsilon(n)<0$ as negative discrete energy levels and $\psi_n(x)$ as harmonic-oscillator eigenfunctions for a bound impurity. For a desorbed (free) particle, we define positive continuous energies $\varepsilon_k>0$,

$$\varepsilon_k=\frac{p_k^2}{2M_0}, \tag{11}$$

and the corresponding wave functions $\psi_k(x)$ that are plane waves.

The field operator for the impurity in this case is

$$\hat{\Psi}(x)=\sum_n \hat{A}_n\psi_n(x)+\sum_k \hat{B}_k\psi_k(x), \tag{12}$$

where $\hat{A}_n$ and $\hat{B}_k$ are the annihilation operators of the ion in the n and k states, respectively. For calculations, we assume that they have fermionic statistics. We will see in the following that this assumption will not affect the final results.

Carrying out second quantization with the field operator (12), we find from Eq. (8),

$$H_{im}=\sum_n \varepsilon_n\hat{A}_n^{\dagger}\hat{A}_n+\sum_k \varepsilon_k\hat{B}_k^{\dagger}\hat{B}_k, \tag{13}$$

and from Eq. (10),

$$\begin{aligned}H_{int}=&\sum_{n,k,q}\hat{B}_k^{\dagger}\hat{A}_n[\mu_{kn}(q)b_q+\mu_{kn}(-q)b_q^{\dagger}]\\&+\sum_{n,k,q}\hat{A}_n^{\dagger}\hat{B}_k[\mu_{kn}^*(-q)b_q+\mu_{kn}^*(q)b_q^{\dagger}]+\cdots,\end{aligned} \tag{14}$$

where we disregard all processes other than desorption and the reverse process. The transitions matrix elements in Eq. (14) are

$$\mu_{kn}(q)=K\zeta^{(c)}\int dx\,\psi_k^*(x)xe^{iqx}\psi_n(x). \tag{15}$$

Now we can write the Schrödinger equation with perturbation (14) in the interaction representation as

$$i\hbar\frac{\partial\psi}{\partial t}=V_{int}(t)\psi, \tag{16}$$

where

$$\begin{aligned}V_{int}(t)=\sum_{n,k,q}&[\mu_{kn}(q)\hat{B}_k^{\dagger}\hat{A}_nb_qe^{(i/\hbar)\beta t}\\&+\mu_{kn}^*(q)\hat{A}_n^{\dagger}\hat{B}_kb_q^{\dagger}e^{-(i/\hbar)\beta t}].\end{aligned} \tag{17}$$

In Eq. (17), we introduced

$$\beta=\varepsilon_k-\varepsilon_n-\hbar\omega_q \tag{18}$$

and retained only the terms representing desorption of an impurity with absorption of a phonon, discarding the terms representing desorption with emission of a phonon.

Substituting $\psi(t)=\hat{u}(t,t_0)\psi(t_0)$ into Schrödinger equation (16), we obtain for the evolution operator [13] the following equation:

$$i\hbar\frac{\partial\hat{u}(t,t_0)}{\partial t}=V_{int}(t)\hat{u}(t,t_0), \tag{19}$$

where $u(t_0,t_0)=1$.

Solving Eq. (19), we will be able to find the desorption rate and energy distribution of the desorbed particles. This and the following equations are formally similar to the ones that appear in Ref. [1], however, with a different interaction term $V_{int}(t)$, see Eq. (17). Note that this term was derived in the framework of the model [1], along with the term describing interaction of the impurity with light and photodesorption, which then was dominant. Now we study thermodesorption as the leading process, when light is not present.

The statistical operator found by solving Eq. (19),

$$\rho(t)=\hat{u}(t,t_0)\rho_0\hat{u}^{\dagger}(t,t_0), \tag{20}$$

where ρ_0 is the equilibrium (unperturbed) statistical operator, allows us to find the distribution function of the desorbed particles over the k states

$$\begin{aligned}f(k,t)&\equiv\langle\hat{B}_k^{\dagger}\hat{B}_k\rangle_t\\&=\mathrm{tr}\{\hat{u}^{\dagger}\hat{B}_k^{\dagger}\hat{B}_k\hat{u}\rho_0\}\\&\approx\mathrm{tr}\{(1+\hat{u}_1^{\dagger})\hat{B}_k^{\dagger}\hat{B}_k(1+\hat{u}_1)\rho_0\},\end{aligned} \tag{21}$$

as well as the desorption part of collision integral $J_d(k)$.

The total desorption rate R_d will be found by averaging the collision integral $J_d(k)$ over the initial states n and summation over the final states k. It will be sufficient to evaluate the evolution operator in the first order of perturbation theory,

$$\hat{u}(t,t_0)=1+\hat{u}_1(t,t_0),$$

$$\hat{u}_1(t,t_0)=-\frac{i}{\hbar}\int_{t_0}^{t}dtV_{int}(t). \tag{22}$$

To derive equations that are of practical use for an analytical study of the thermodesorption process, we need to know the transition-matrix elements and the initial distribution function $f_0(n)$ of the impurities. The energy spectrum of the bound particles is given by Eq. (2). We assume that the number of the potential-well levels $n_{max}\gg 1$, that the frequency ω_0 lies in the range of acoustical-phonon frequencies ω_q, and that the ratio $T_0/\hbar\omega_0$ is greater than, but close to 1 and the temperature T_0 is greater than, but close to 0.025 eV. Therefore the discrete character of ε_n should be taken into account, and one should take a sum over the initial distribution instead of integration. In this sum, we put $n_{max}\rightarrow\infty$ because of a large number of levels in the well, the strong inequality $\varepsilon_a\gg T_0$, and a rapid decrease of the $f_0(n)$ for large n. The initial distribution function of impurities is

$$f_0(n)=C\exp\left\{-\frac{\varepsilon_n}{T_0}\right\}, \tag{23}$$

where C is found from normalization to the number of the impurities N_{im} on the sample surface

$$\sum_{n=0}^{\infty}f_0(n)=N_{im}, \tag{24}$$

so taking Eq. (2) into account,

$$C=N_{im}\exp\left\{-\frac{1}{T_0}\left(\varepsilon_a-\frac{1}{2}\hbar\omega_0\right)\right\}\left\{1-\exp\left(-\frac{\hbar\omega_0}{T_0}\right)\right\}. \tag{25}$$

To calculate the matrix elements $\mu_{kn}(q)$, (15) we will take the initial states $\psi_n(x)$ in the form of the oscillator wave functions

$$\psi_n(x)=N^{(0)}H_n(\alpha x)\exp\left\{-\frac{1}{2}\alpha^2x^2\right\}, \tag{26}$$

where $H_n(\alpha x)$ are Hermitian polynomials, and

$$N^{(0)}=\sqrt{\frac{\alpha}{\sqrt{\pi}2^n n}},\quad \alpha=\sqrt[4]{\frac{M_0K}{\hbar^2}}. \tag{27}$$

The final states $\psi_k(x)$ are represented by plane waves,

$$\psi_k(x)=\exp\left\{\frac{i}{\hbar}p_kx\right\}. \tag{28}$$

We put the quantization volume to unity.

Now the matrix elements (15) can be evaluated,

$$\mu_{kn}(q)=K\zeta^{(c)}\frac{N^{(0)}}{\alpha^2}I_n, \tag{29}$$

where

$$I_n=\int_{-\infty}^{\infty}dy\,ye^{iyz}e^{-(1/2)y^2}H_n(y). \tag{30}$$

Using properties of Hermitian polynomials (e.g., Ref. [14]) we find

$$\mu_{kn}(q)=K\zeta^{(c)}\sqrt{2\pi}N^{(0)}\alpha^{-2}i^{n-1}e^{-(1/2)z^2}$$
$$\times[2nH_{n-1}(z)-zH_n(z)],$$
$$z=\frac{\hbar q-p_k}{\alpha\hbar}. \tag{31}$$

III. THERMODESORPTION RATE

Thermodesorption occurs as a result of energy transfer from the phonon ensemble to an impurity. Although thermodesorption is described in the framework of the same theoretical approach as photodesorption [1], it differs from the latter in two essential aspects. First, the thermodesorption rate does not depend on the impurity ion charge and is the same for neutral particles and for the charged ones. Second, the phonon-stimulated desorption can only occur from the highest levels of the truncated oscillator, that are close to the binding energy ε_a.

Let us find the first perturbation order $\hat{u}_1$ for the evolution operator $\hat{u}$ from Eq. (22),

$$\hat{u}_1=-2\pi i\sum_{n,q,k}\{\mu_{kn}(q)B_k^{\dagger}A_nb_q+\mu_{kn}^{*}(q)A_n^{\dagger}B_kb_q^{\dagger}\}\delta(\beta). \tag{32}$$

This operator allows us to evaluate expression (21) for the time-dependent distribution function $f(k,t)$. Separating the multiparticle distribution functions [15], we arrive at

$$f(k,t)=f(k,t_0)+\frac{2\pi}{\hbar}t[1-f(k,t_0)]\sum_{n,q}|\mu_{kn}(q)|^2$$
$$\times f(n,t)N_q(t)\delta(\beta). \tag{33}$$

In Eq. (33), the minus sign in front of the $f(k,t_0)$ corresponds to Fermi statistics. Assuming Bose statistics, we would have obtained the plus sign instead. However, except for very low temperatures, $f(k,t_0)\ll 1$ for all k, which corresponds to Boltzmann statistics. Then the $f(k,t_0)$ term in the square brackets in Eq. (33) can be neglected. As a further approximation, we will neglect the deviation of the phonon distribution function $N_q(t)\equiv\langle b_q^{\dagger}b_q\rangle_t$ from equilibrium, and will take

$$N_q(t)\approx\frac{1}{\exp\left\{\frac{\hbar\omega_q}{T_0}\right\}-1}\approx\exp\left\{-\frac{\hbar\omega_q}{T_0}\right\}, \tag{34}$$

since $\hbar\omega_q/T_0$ is greater than 1.

The usual approximation for acoustic phonons is $N_q \approx T_0/\hbar\omega_q \gg 1$. However, in our model, we have to consider high-frequency phonons near the ends of the Brillouin zone. For acoustic phonons that are near the center of the Brillouin zone, $\hbar\omega_q \ll \hbar\omega_0$ and the thermodesorption of the type we are interested in is impossible. Therefore to simplify the calculations, we can substitute the high-frequency phonons $\hbar\omega_q$ by $\hbar\omega_D$, where ω_D is the phonon frequency corresponding to Debye temperature. This simplification makes our description suitable for optical phonons too. Therefore in the final result, one should take a sum over all (not just acoustical) modes of phonons.

Now from Eq. (33), we find the collision integral

$$J_d(k)=\frac{2\pi}{\hbar}\sum_{n,q}|\mu_{kn}(q)|^2 f_0(n)N_q\delta(\beta), \tag{35}$$

and the mean thermodesorption rate

$$\begin{aligned}R_d &\equiv \frac{1}{N_{im}}\sum_k J_d(k)\\ &=\frac{1}{N_{im}}\frac{1}{2\pi\hbar^2}\sum_n f_0(n)\int_{-\infty}^{\infty}dq\,\eta[q]\\ &\quad\times\int_{-\infty}^{\infty}dp_k\,\eta[p_k]|\mu_{kn}(q)|^2N_q\delta(\beta).\end{aligned} \tag{36}$$

The step function $\eta[q]$ in Eq. (36) accounts for the fact that thermodesorption only occurs with absorption of a phonon propagating from inside of the crystal *towards its surface*. Similarly, $\eta[p_k]$ accounts for the fact that desorbed particles fly away from the crystal surface.

Substituting the explicit forms of $f_0(n), |\mu_{kn}(q)|^2, \beta$, and N_q (with $\omega_q=\omega_D$) into Eq. (36), we find an explicit form for the thermodesorption rate

$$\begin{aligned}R_d &=\frac{2M_0K^2}{\sqrt{\pi}\alpha^3\rho\hbar\omega_D}\left[1-\exp\left(-\frac{\hbar\omega_0}{T_0}\right)\right]e^{-\hbar\omega_D/T_0}\\ &\quad\times\sum_n\frac{1}{2^{n+1}n!}e^{-n(\hbar\omega_0/T_0)}\int_{-\infty}^{\infty}dq\,\eta[q]\\ &\quad\times\int_{-\infty}^{\infty}dp_k\,\eta[p_k]e^{-z^2}\{2nH_{n-1}(z)-ZH_n(z)\}^2\\ &\quad\times\delta\{p_k^2-2M_0[\varepsilon(n)+\hbar\omega_D-\varepsilon_a]\},\end{aligned} \tag{37}$$

where α and z are defined in Eqs. (27) and (31), respectively.

Taking the integral over momentum p_k and replacing integration over q by integration over z in Eq. (37), we arrive at

$$\begin{aligned}R_d &\approx\frac{\sqrt{2M_0}K^2}{4\alpha^2\rho\hbar\omega_D}\left[1-\exp\left(-\frac{\hbar\omega_0}{T_0}\right)\right]e^{-\hbar\omega_D/T_0}\\ &\quad\times\sum_n\frac{\eta[\Delta\varepsilon]}{\sqrt{\Delta\varepsilon}}\frac{1}{\sqrt{\pi}2^n n!}e^{-n(\hbar\omega_0/T_0)}\\ &\quad\times\int_0^{\infty}dze^{-z^2}\{2nH_{n-1}(z)-zH_n(z)\}^2,\end{aligned} \tag{38}$$

where $\Delta\varepsilon\equiv\varepsilon(n)+\hbar\omega_D-\varepsilon_a=(n+1/2)\hbar\omega_0+\hbar\omega_D-\varepsilon_a$.

The non-negative value of $\Delta\varepsilon$ is assured by $\eta[\Delta\varepsilon]$. The case of negative $\Delta\varepsilon$ would correspond to the phonon energy insufficient to cause the thermodesorption transition. The step function $\eta[\Delta\varepsilon]$ also determines the range of summation over n, i.e., defines the truncated oscillator's upper levels from which thermodesorption transitions are possible, given $\varepsilon_a, \omega_0, \omega_D$, and T_0.

Hermitian polynomials properties allow for the following transformation:

$$\begin{aligned}&\{2nH_{n-1}(z)-zH_n(z)\}^2\\ &\quad=\frac{1}{4}[4n^2H_{n-1}^2(z)+H_{n+1}^2(z)-4nH_{n-1}(z)H_{n+1}(z)].\end{aligned} \tag{39}$$

Note that

$$H_n(z)=[\sqrt{\pi}2^n n!]^{-1/2}e^{(1/2)z^2}\psi_n(z), \tag{40}$$

where $\{\psi_n(z)\}$ is a set of orthogonal normalized wave functions of an oscillator in the space of "momentum" z. It is easy to prove that $\psi_n(z)$ are orthogonal and normalized not only on the interval $(-\infty,\infty)$, but also on the interval $(0,\infty)$,

$$\int_0^{\infty}dz\,\psi_n^*(z)\psi_m(z)=\frac{1}{2}\delta_{mn}. \tag{41}$$

Utilizing the property (41), we can easily evaluate the integral in Eq. (38),

$$\begin{aligned}R_d &\approx\frac{\sqrt{2M_0}K^2}{8\alpha^2\rho\hbar\omega_D}\left[1-\exp\left(-\frac{\hbar\omega_0}{T_0}\right)\right]e^{-\hbar\omega_D/T_0}\\ &\quad\times\sum_n(n+1/2)\frac{\eta[\Delta\varepsilon]}{\sqrt{\Delta\varepsilon}}e^{-n(\hbar\omega_0/T_0)}.\end{aligned} \tag{42}$$

Since we only consider the upper levels, $n\gg1$, then in Eq. (42), $n+1/2$ can be replaced by n. Now our result for the thermodesorption rate can be put in the standard form

$$R_d=\nu_d\exp\left\{-\frac{\varepsilon_a}{T_0}\right\}, \tag{43}$$

where ν_d is the characteristic frequency of thermodesorption (a term introduced analogously to the characteristic frequency of diffusion jumps in Ref. [16]),

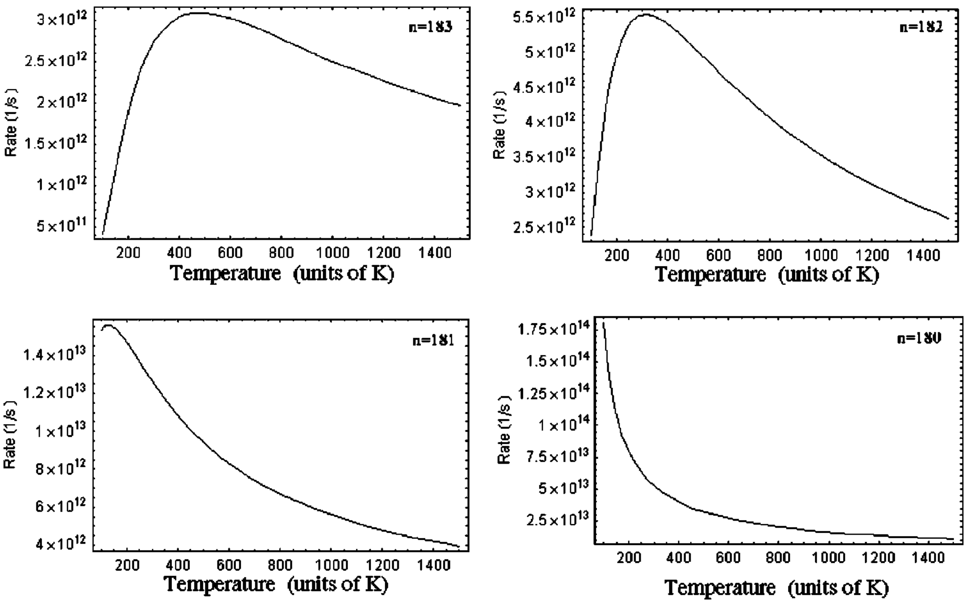

FIG. 1. Characteristic partial thermodesorption frequencies $\nu_d(n)$ for $n=180,181,182,183$ as functions of temperature.

$$\nu_d=\sum_n n\nu_d(n)$$

$$=\frac{\sqrt{2M_0}K^2}{4\alpha^2\rho\hbar\omega_D}\sinh\left(\frac{\hbar\omega_0}{2T_0}\right)\sum_n n\frac{\eta[\Delta\varepsilon]}{\sqrt{\Delta\varepsilon}}e^{-\Delta\varepsilon/T_0}. \qquad (44)$$

To estimate the partial characteristic thermodesorption frequencies $\nu_d(n)$ and the total rate of thermodesorption R_d, we select the following set of parameters: $\varepsilon_a=2.5$ eV,$M_0=8.35\times10^{-23}$ g,$a=3\times10^{-8}$ cm. From these we find the value of $\hbar\omega_0\approx0.0136$ eV. The typical value of $\hbar\omega_D$ is 0.05 eV. Assuming the crystal density ρ_0 equal to 5 g/cm^3, the linear density is $\rho\approx4.5\times10^{-15}$ g/cm.

For the above set of parameters, thermodesorption is only possible from four highest levels of the truncated oscillator, namely, $n=180,181,182,183$. Characteristic frequencies for those levels are given in Fig. 1 as functions of temperature. We see that the peaks in Fig. 1 shift by ≈160 K (0.0138 eV) to higher temperatures for higher levels. This shift is very close to the levels spacing (0.0136 eV in our calculations), which suggests the common nature of the peaks and relates their position to the level number and the oscillation frequency.

The total desorption rate R_d, on the other hand, exhibits a very fast increase for higher temperatures that comes from the exponential factor in Eq. (43) and is to be expected. This rate is plotted as a function of temperature in Fig. 2. Its value at a room temperature (300 K) is as tiny as 5×10^{-26} s^{-1}, while already at 800 K it reaches ≈1.8 s^{-1} which is easily observable.

IV. RESULTS AND DISCUSSION

Thermal desorption of impurities off a transparent dielectric surface has been studied in the framework of the truncated-harmonic-oscillator model. In spite of the formal similarities in the ways the tasks are formulated, the physical concepts, mathematical methods, and qualitative results of the present work are clearly distinct from the concepts, methods, and results of the earlier works [2,3] (although some numerical estimates are close). The obtained results have a very simple and transparent analytical form, which helps in understanding the roles of physical mechanisms underlying the phonon-induced thermodesorption and can be easily used for direct comparison with experimental results.

The mixed quantum-classical approach to desorption [2] is based on the concept of a stochastic force exerted by the phonon system on an impurity atom. This concept requires introducing the Fourier transform of a friction kernel [2], which is hard to define. In contrast to this approach, we carry out a consistent quantum-statistical description of the process and obtain elegant analytical results. We also rely on the concept of a phonon-raised stochastic force causing desorption, but we have treated the phonon interaction with the impurity differently than in Ref. [2] and the analytical results are obtained. The role of desorption from the lower-lying levels of the potential well is emphasized. Figure 1 shows that each level's contribution to the cumulative desorption rate increases as the level number decreases, as long as the energy conservation permits it. Thus, the largest thermodesorption rate is reached for the lowest allowed level. This is a manifestation of modification of the energy threshold conditions [17] that is important, as we have shown, for a variety of inelastic kinetic processes, including photodesorption [1]. The reason for this desorption rate increase is the exponential growth of a level's population with decrease in its number.

The contrast of our thermodesorption model with the one in Ref. [3] is even more drastic. First, in Ref. [3], the adsorbed particle is considered to reside *above* the surface, as opposed to being *on* the surface as in our treatment. For a particle *above* the surface one has to take into account its degrees of freedom corresponding to motion in the plane perpendicular to the surface, as well as to the motion on the cone surface whose axis is perpendicular to the sample surface. Both types of motion are sometimes called "rotator." Taking these degrees of freedom into account may signifi-

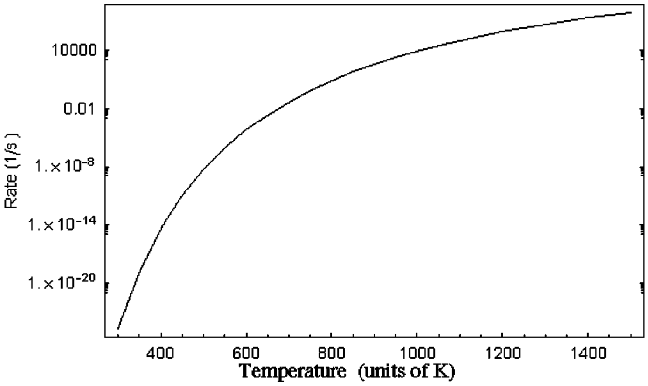

FIG. 2. Total desorption rate R_d as a function of temperature.

cantly change the energy and momentum conservation laws for the adsorbed particle, and hence, the probability and rate of its desorption. The "rotator" is not considered in Ref. [3], despite the presence of the corresponding degrees of freedom. In our treatment these degrees of freedom are not present.

Similarly, drastic changes in the results may come from taking into account the electrons and electronic excitations scattering on the adsorbed particle, in addition to phonon scattering. The electronic mechanisms are expected to be especially significant in metals.

For these two reasons, it is surprising to see the agreement of the results of Ref. [3] (derived based on the Morse model) with experiment for the K-W system but not for Xe-W, whereas it is in the latter case that the Morse and truncated-oscillator models give nearly the same numeric result. Perhaps, the answer lies in the fact that the results obtained by these two approaches can in fact be made to agree for a selected system by a small tweak in parameters (see Fig. 7 in Ref. [3]).

Another distinction of our approach from Ref. [3] is that we define the desorption event when the impurity undergoes a transition into continuum and emerges as a free particle flying away from the surface. In Ref. [3], the first passage time is defined as a transition time into a predissociation state. The latter state can dissociate, but it also can deexcite (via the $\nu \rightarrow \nu - 1$ transition) which will reduce the desorption rate. Therefore our result for thermodesorption rate appears to be more adequate. These arguments suggest that in fact the Morse potential model is not any more rigorous than the truncated-oscillator model.

We have not found experimental data for the systems matching our model. This model is designed to describe desorption (or similar processes) from wide zone transparent crystals such as diamond. These systems have properties very different from those of metal samples.

Let us mention other important features of the results we obtained for our case of thermodesorption. It has been pointed out [see Eq. (44)] that the characteristic desorption frequency ν_d is determined by two factors of completely different physical nature. The first factor is the rate of thermodesorption occurrences $\nu_d(n)$ that is a few times smaller than the frequency of the "phonons' attempts" [16] to induce thermodesorption. This factor is analogous to and has the same physical meaning as the preexponential frequency factor in the equilibrium diffusion coefficient [16]. The frequency $\nu_d(n)$ is close in the order of magnitude but somewhat smaller than the phonon frequency $\nu_D \approx 10^{13}\ \mathrm{s}^{-1}$. The relation $\nu_d(n) < \nu_D$ implies that not every phonon oscillation causes an actual desorption transition.

The second factor determining ν_d appears in the present theoretical treatment of thermodesorption for the first time. This is the number n of the level from which desorption occurs. The presence of this factor can be understood from quasiclassical representation of an oscillator. Indeed, n is the number of nodes of the quasiclassical standing wave that correspond to an oscillator in the nth state. The phonons can be interpreted to cause thermodesorption as they scatter at each maximum of the oscillator wave function. This interpretation is fundamental for understanding thermodesorption, without it, the result for the total thermodesorption rate exceeding the photon frequencies (such as ν_D) appears meaningless.

One of the results related to description of desorption as a transition into continuum is the possibility to determine the distribution function of desorbed particles over the kinetic energy [see Eq. (33)]. In particular, Fig. 1 shows that each level yields a different contribution to the thermodesorption rate. These contributions reach the maximum values at different temperatures. When the temperature is fixed, each level will give its own energy distribution function. As a result, the total flux of desorbed matter should contain series of peaks separated by about the energy difference between the truncated oscillator levels $\hbar\omega_0$. This result is especially important as it provides for comparison of our theoretical predictions with time-of-flight experiment data.

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