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Photodesorption of charged impurities from a transparent crystal surface

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Photodesorption of impurity ions is studied in the framework of a truncated harmonic oscillator model and is considered as a direct photon absorption process without substrate heating. The desorption rate is found by methods of quantum statistics, using the system's evolution operator. The desorption rates estimates appear realistic. Our results predict a series of new physical effects in desorption processes.

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I. INTRODUCTION

Virtually any significant impact on a solid surface causes various nonequilibrium transport processes. Many such processes have been studied for more than a decade, e.g., thermodesorption of impurities, evaporation and sublimation, surface chemical reaction, and others. Other surface processes have been studied only recently, such as nonequilibrium processes caused by hot and cold plasma, by high-energy particles beams, or by strong laser fields. Current interest to the later processes is due to their great significance for many directions in the theoretical and experimental physics, as well as in chemistry and biology, and also for creating foundations for modern high technology.

Experimental study of stimulated transport processes on solid surfaces is an especially active area, e.g., Refs. [1–4], while the theoretical description of experimental results usually has Heuristic or phenomenological character. Many purely theoretical works are also based on phenomenological methods. The reason for this is that it is hard to build a ''calculatable'' physical model for a nonequilibrium process on a solid surface. Therefore constructing of an adequate theoretical model (e.g., building a model of thermal desorption [5]) attracts great interest.

In this paper, we would like to discuss the photodesorption occurring with direct absorption of light quanta. This process does not rely on heating of the sample by laser light, which distinguishes our treatment from the standard concept of photodesorption. We will use a truncated harmonic oscillator model (see, e.g., the publications quoted in Ref. [5]) for a impurity ion bound on a transparent crystal surface. This model will be applied for the nonequilibrium transport process of photostimulated ion desorption in laser fields with the photon energies that are greater (i) or less (ii) than the binding energy of the charged impurity on the surface.

Atomic and molecular desorption, as well as other surface chemical reactions, is often studied by modeling the particle-surface interaction using the Lennard-Jones potential [6,7] in one or another form. In addition to the fact that the parameters determining the potential cannot be found theoretically, the main weakness of this model is the following. It is very mathematically difficult to find the eigenfunctions and energy eigenvalues for any realistic system and to solve the quantum problem completely. In addition, a real ''particle on a surface'' system has various oscillation degrees of freedom [7] not included in the Lennard-Jones potential. Taking these arguments into consideration we choose a truncated harmonic oscillator model which will allow us to completely solve the quantum problem analytically.

An essential difference of our model from the one studied before [5] is that we do not introduce the concept of a random force acting on a particle from the crystal and causing thermodesorption. Instead, we use the standard description of a bound particle interacting with a random phonon field in terms of the phonon creation and annihilation operators.

II. PHYSICAL MODEL

Consider desorption of an impurity ion bound on a solid surface. Let us take into account a laser field and thermal vibration of the lattice acting on the ion. Three subsystems weakly coupled to each other are relevant: the laser field, the ion in the surface potential well, and the phonon ensemble causing random displacements of the well.

The laser field is off-resonance with all of the phonon frequencies, the frequency of the ion oscillation in the potential well, and with any atomic electron transition frequencies. We will use the dipolar approximation for laser field interaction with ions. The crystal will be considered a clear transparent dielectric. This means that the energy band gap is larger than the photon energy and the light does not create excitons and electron-hole pairs, which is a good approximation for a large class of materials.

Consider an impurity ion in the surface potential well. The ion has an effective charge Ze where Z is a positive or negative number which can be noninteger, and e is the electron charge. Let us use the truncated harmonic oscillator approximation to describe the potential well, see Fig. 1. Following the approach in Ref. [5], we consider a one-dimensional well with the coordinate x perpendicular to the sample surface.

The harmonic oscillator is truncated at the energy level equal to the ion-to-surface binding energy. Therefore the

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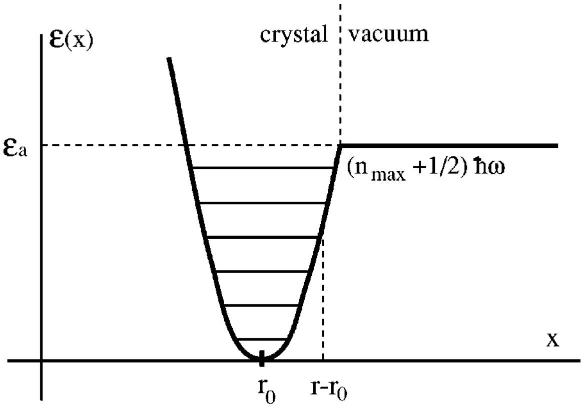

FIG. 1. Truncated harmonic potential for a particle on a surface. r_0 is the particle's equilibrium position.

elastic constant K of the quadratic potential

$$U(x)=\tfrac{1}{2}Kx^2 \tag{1}$$

can be defined by the following condition:

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

where $2l=a$, and a is the width of the surface potential well which is about the lattice period, see Fig. 1.

The energy spectrum of the bound ion is [8]

$$\varepsilon_n=-\varepsilon_a+(n+1/2)\hbar\omega_0, \quad n=0,1,2,\ldots, \tag{3}$$

where, taking Eq. (2) into account,

$$\omega_0=\sqrt{\frac{2\varepsilon_a}{M_0 l^2}}. \tag{4}$$

The potential (1) corresponds to an immovable potential well, when the energy minimum corresponds to the zero coordinate. Thermal fluctuations result in the random displacements $\vec{\zeta}$ of the potential well, so the ion coordinate x is replaced by $\vec{i}x+\vec{\zeta}$, where $\vec{i}$ is the unit vector in the x direction. It is known that the displacement ζ is small compared to the lattice period and to the potential well width up to the melting temperature. Therefore we assume that the displacement $\vec{\zeta}$ does not alter the shape of the potential, only changing the origin:

$$U(x,\vec{\zeta})=\tfrac{1}{2}K(\vec{i}x+\vec{\zeta})^2\approx U(x)+Kx(\vec{i}\cdot\vec{\zeta}). \tag{5}$$

Small displacements in a crystal can be represented as a superposition of normal oscillations [9]. Each mode μ of such oscillations corresponds to phonons with quasi momentum $\hbar\vec{q}$ and with unitary polarization vector $\vec{e}_{\vec{q},\mu}$. Introducing the phonon creation and annihilation operators $b^{\dagger}_{\vec{q},\mu}$ and $b_{\vec{q},\mu}$, the displacement operator $\vec{\zeta}$ can be put in the form [9]

$$\vec{\zeta}=\sum_{\vec{q},\mu}\vec{e}_{\vec{q},\mu}\zeta^{(C)}(b_{\vec{q},\mu}e^{i\vec{q}\cdot\vec{r}}+b^{\dagger}_{\vec{q},\mu}e^{-i\vec{q}\cdot\vec{r}}) \tag{6}$$

or

$$\vec{\zeta}=\vec{i}\sum_{\vec{q}}\zeta^{(C)}(b_{\vec{q},\mu}e^{i\vec{q}\cdot\vec{r}}+b^{\dagger}_{\vec{q},\mu}e^{-i\vec{q}\cdot\vec{r}}) \tag{7}$$

for a longitudinal acoustic mode polarized along the x axis. The normalization constant $\zeta^{(C)}$ is

$$\zeta^{(C)}=\sqrt{\frac{\hbar}{3\rho V_0\omega_{\vec{q},\mu}}}, \tag{8}$$

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

Using the relation (7), we can clearly see the physical meaning of the term neglected in Eq. (5). This term is proportional to ζ^2 and hence takes into account the much less likely processes of two-phonon creation and annihilation (arising from the terms $b^{\dagger}_{\vec{q}_1}b^{\dagger}_{\vec{q}_2}$ and $b_{\vec{q}_1}b_{\vec{q}_2}$) as well as the processes of phonon scattering from the impurity (arising from the terms $b^{\dagger}_{\vec{q}_1}b_{\vec{q}_2}$ and $b_{\vec{q}_1}b^{\dagger}_{\vec{q}_2}$). The longitudinal acoustic phonons are not charged and do not generate distributed dipole momenta in crystal, so there is no direct photon-phonon interaction.

In our model, phonons are considered a thermal bath whose temperature T_0 is the same as the crystal temperature. Possible deviations from the equilibrium distribution of phonons under the influence of a strong laser light will not be discussed in this work. We escape these complications by considering a transparent dielectric.

Summarizing the above discussion we write a complete Hamiltonian for the considered system

$$\hat{H}=\hat{H}_{im}+\hat{H}_{ph}+\hat{H}_1+\hat{H}_2, \tag{9}$$

where the following terms are included. The unperturbed energy operator for an ion in the potential well (1) with the kinetic energy operator $\hat{K}$:

$$\hat{H}_{im}=\hat{K}+U(x). \tag{10}$$

The unperturbed energy operator for phonons:

$$\hat{H}_{ph}=\sum_{\vec{q}}\hbar\omega_q b^{\dagger}_{\vec{q}}b_{\vec{q}}. \tag{11}$$

The operator of dipole interaction of an ion with laser wave:

$$\hat{H}_1=Zex(\vec{i}\cdot\vec{E}_0)\cos\omega t. \tag{12}$$

The interaction operator of the ion bound in the potential well with the random oscillations of the lattice:

$$\hat{H}_2=Kx(\vec{i}\cdot\vec{\zeta})=Kx\sum_{\vec{q}}\zeta^{(C)}(b_{\vec{q}}e^{i\vec{q}\cdot\vec{r}}+b^{\dagger}_{\vec{q}}e^{-i\vec{q}\cdot\vec{r}}). \tag{13}$$

In the following we will only consider the displacements along the x axis, i.e., the phonons with the wave vectors $\vec{q}=\vec{i}q$. This will allow us to use the scalar index q in Eqs. (11)

and (13). The operators (12) and (13) are considered small perturbations added to operators (10) and (11) which allows us to use perturbation theory.

Note that the quantum mechanical problem that has been formulated above uses the coordinate representation for an ion and the second quantization representation for phonons. This is not convenient for applying methods of quantum statistics. Therefore we need to introduce a secondary quantization representation for the ion.

In the energy spectrum of the ion, we select the negative discrete energy levels $\varepsilon_n = -\varepsilon_a + \varepsilon(n) < 0$ [the energy $\varepsilon(n)$ is measured from the bottom of the well whose depth is ε_a] corresponding to the bound states of the ion, and the positive continuous energies $\varepsilon_k > 0$ corresponding to a desorbed ion.

Indices n and k span a full set of exact orthogonal and normalized ion wave functions. For the bound states, these are the harmonic oscillator eigenfunctions $\psi_n(x)$. A desorbed ion will be considered free, neglecting its residual interaction with the surface. Then, its wave functions $\psi_k(x)$ are plane waves. For this choice of $\psi_k(x)$,

$$\varepsilon_k = \frac{p_k^2}{2M_0}, \tag{14}$$

where p_k is the ion momentum along the x axis.

Note that transitions of an ion from the n state to the k state do not conserve momentum (whose excess is taken up by the crystal), which is similar to momentum nonconservation for an electron in the process of atomic photoionization.

Now we can introduce the ion field operator

$$\hat{\Psi}(x) = \sum_n \hat{A}_n \psi_n(x) + \sum_k \hat{B}_k \psi_k(x), \tag{15}$$

where $\hat{A}_n$ and $\hat{B}_k$ are the annihilation operators of the ion in the n and k states, respectively.

We do not know the ion statistics, and hence we do not know the commutation relations of the operators $\hat{A}_n$ and $\hat{B}_k$. But for the discussed problem it has no practical importance, because eventually we will consider the ions to be heavy, quasiclassical particles adequately described by Boltzmann statistics. Mathematically, however, it is more convenient to assume at this stage that the ions are fermions.

Applying operator (15) in a usual second quantization procedure

$$V = \int dx\, \hat{\Psi}^{\dagger}(x) \hat{H} \hat{\Psi}^{\dagger}(x), \tag{16}$$

we find, instead of Eq. (10),

$$V_{im} = \sum_n \varepsilon_n \hat{A}_n^{\dagger} \hat{A}_n + \sum_k \varepsilon_k \hat{B}_k^{\dagger} \hat{B}_k . \tag{17}$$

Operator (11) will not change, while Eqs. (12) and (13) will take on the form

$$V_1 = \sum_{n,k} \{\lambda(k,n) \hat{B}_k^{\dagger} \hat{A}_n + \lambda^*(k,n) \hat{A}_n^{\dagger} \hat{B}_k\}(e^{i\omega t} + e^{-i\omega t}) + \cdots, \tag{18}$$

$$V_2 = \sum_{n,k,q} \hat{B}_k^{\dagger} \hat{A}_n [\mu(q,k,n) b_q + \mu(-q,k,n) b_q^{\dagger}] + \sum_{n,k,q} \hat{A}_n^{\dagger} \hat{B}_k [\mu^*(-q,k,n) b_q + \mu^*(q,k,n) b_q^{\dagger}] + \cdots . \tag{19}$$

In expressions (18) and (19), only the terms describing ion desorption (and the reverse process) are shown explicitly. Other higher order terms, including those describing transitions between different levels $n \to n'$ and resulting into levels broadening, will not be considered in this work.

The transitions matrix elements in Eqs. (18) and (19) are

$$\lambda(k,n) = \frac{1}{2} Ze(\vec{i} \cdot \vec{E}_0) \int dx\, \psi_k^*(x)\, x\, \psi_n(x), \tag{20}$$

$$\mu(q,k,n) = K \zeta^{(c)} \int dx\, \psi_k^*(x)\, x e^{iqx}\, \psi_n(x). \tag{21}$$

Operator V_1 (18) describes photodesorption accompanied by direct absorption of light by a particle, without heating of the sample or exciting of additional degrees of freedom, such as emission of phonons, excitation or re-charging of the desorbed particle, and so on. Operator V_2 in Eq. (19), on the contrary, describes thermal desorption. The latter may include the type of photodesorption which depends on heating of the sample by light, in which case the light intensity indirectly enters V_2 via the temperature. This is a ''traditional'' approach to photoassociation. In this work, however, we would like to study the effects related to V_1, so we will exclude V_2 from consideration in this framework, and return to it elsewhere. Therefore we will discuss a particular desorption mechanism that contributes to desorption together with other mechanisms that may exist.

III. SOLUTION METHOD

The complete Hamiltonian of our system (11), (17) – (19) allows us to write the Schrodinger equation and solve it within some approximation. Then, probabilities of various kinds of desorption can be found. This is a standard quantum mechanical way of handling the problem. This way, however, is not adequate if the external fields are strong enough to alter the distributions of the considered subsystems from equilibrium.

In order to have a universal method for describing various specific features of the nonequilibrium desorption, we will use the density operator method utilizing the evolution operator $\hat{u}(t,t_0)$ (e.g., see Ref. [10]).

We transform the Schrodinger equation with perturbation (18) to the interaction representation, arriving at

$$i\hbar\frac{\partial\psi}{\partial t}=V_{1i}(t)\psi, \tag{22}$$

where

$$V_{1i}(t)=\sum_{n,k}\left[\lambda(k,n)\hat{B}_k^{\dagger}\hat{A}_n e^{(i/\hbar)\beta_1 t}+\lambda^*(k,n)\hat{A}_n^{\dagger}\hat{B}_k e^{-(i/\hbar)\beta_1 t}\right] \tag{23}$$

and

$$\beta_1=\varepsilon_k-\varepsilon_n-\hbar\omega. \tag{24}$$

In the operator (23) all irrelevant terms have been omitted.

Now, let us define the evolution operator $\hat{u}(t,t_0)$ as [10]

$$\psi(t)=\hat{u}(t,t_0)\psi(t_0), \tag{25}$$

where $\psi(t_0)$ is the initial wave function of the system. Substituting Eq. (25) into the Schrodinger equation (22), we obtain an operator equation

$$i\hbar\frac{\partial\hat{u}(t,t_0)}{\partial t}=V_{1i}(t)\hat{u}(t,t_0) \tag{26}$$

with an initial condition $u(t_0,t_0)=1$.

Solving Eq. (26) we will be able to compute the statistical operator [10]

$$\rho(t)=\hat{u}(t,t_0)\rho_0\hat{u}^{\dagger}(t,t_0), \tag{27}$$

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

$$f(k,t)\equiv\langle\hat{B}_k^{\dagger}\hat{B}_k\rangle_t=\mathrm{tr}(\hat{u}^{\dagger}\hat{B}_k^{\dagger}\hat{B}_k\hat{u}\rho_0), \tag{28}$$

and to find the part of the kinetic equation collision integral which corresponds to desorption:

$$J_d(k)\equiv\left.\frac{\partial f(k,t)}{\partial t}\right|_{\mathrm{scatter}}=\frac{\partial}{\partial t}\mathrm{tr}(\hat{u}^{\dagger}\hat{B}_k^{\dagger}\hat{B}_k\hat{u}\rho_0). \tag{29}$$

Averaging the collision integral (29) over the initial states, and summation over the final states of ions will result into the total desorption rate R_d which is what we look for. In all following expressions for R_d we will assume the initial Boltzmann distribution of ions. To conclude this section, let us point out that to find the nonvanishing contributions to the mean desorption rate it is sufficient to evaluate the evolution operator in the first order of perturbation theory

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

$$\hat{u}_1(t,t_0)=-\frac{i}{\hbar}\int_{t_0}^{t}dt\,V_{1i}(t). \tag{30}$$

IV. THE WAVE FUNCTION, TRANSITION MATRIX ELEMENTS, AND THE INITIAL DISTRIBUTION FUNCTION

To derive equations that would be practically useful for analytical study of the desorption processes we need to know the transition matrix elements and the initial distribution function $f_0(n)$ of the impurity ions. The energy spectrum of the bound ions is given by Eq. (3). It can be shown that the number of the potential well levels $n_{\max}\gg1$, the frequency ω_0 lies in the range of acoustic phonons frequencies ω_q, and the ratio $T_0/\hbar\omega_0$ is equal to $2\cdots4$ for the temperatures $T_0=0.025\cdots0.05$ eV $(300\cdots600$ K). Therefore the function $f_0(n)$ cannot be considered as a continuous Boltzmann distribution over energies. The discrete character of ε_n should be taken into account, and instead of integration over the initial distribution one should take a sum. In this sum we can put $n_{\max}\to\infty$ because of a large number of levels in the well, the strong inequality $\varepsilon_a\gg T_0$, and rapid decrease of the $f_0(n)$ for large n. The initial distribution function of ions is

$$f_0(n)=C\exp\left\{-\frac{\varepsilon_n}{T_0}\right\}=C\exp\left\{\frac{1}{T_0}\left(\varepsilon_a-\frac{1}{2}\hbar\omega_0\right)\right\}\times\exp\left\{-\frac{\hbar\omega_0}{T_0}n\right\}, \tag{31}$$

where C is found from the normalization condition

$$\sum_{n=0}^{\infty}f_0(n)=N_{im} \tag{32}$$

and N_{im} is the number of the impurity ions on the sample surface

$$C=N_{im}\exp\left\{-\frac{1}{T_0}\left(\varepsilon_a-\frac{1}{2}\hbar\omega_0\right)\right\}\left\{1-\exp\left(-\frac{\hbar\omega_0}{T_0}\right)\right\}. \tag{33}$$

To calculate the matrix elements of the desorption transitions the wave functions $\psi_n(x)$ and $\psi_k(x)$ should be given explicitly. Taking into account the above notes on the truncated harmonic oscillator properties, we can put

$$\psi_n(x)=N^{(0)}H_n(\alpha x)\exp\left\{-\frac{1}{2}\alpha^2x^2\right\}, \tag{34}$$

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

$$N^{(0)}=\sqrt{\frac{\alpha}{\sqrt{\pi}2^n n!}},\quad \alpha=\sqrt[4]{\frac{M_0K}{\hbar^2}}. \tag{35}$$

The final states of the ion are represented by plane waves

$$\psi_k(x)=\exp\left\{\frac{i}{\hbar}p_kx\right\}, \tag{36}$$

where we put all sizes of the quantization volume equal to unity. Let us now express $\lambda(k,n)$ introduced in Eq. (18) as

$$\lambda(k,n)=\frac{1}{2}Ze(\vec{i}\cdot\vec{E}_0)\frac{N^{(0)}}{\alpha^2}I_{kn}, \tag{37}$$

where

$$I_{kn}=\int_{-\infty}^{\infty}dy\,y e^{iyz(k)}e^{-(1/2)y^2}H_n(y),\quad z(k)=-\frac{p_k}{\alpha\hbar}. \tag{38}$$

Using properties of Hermitian polynomials (e.g. Ref. [11]) we find

$$\lambda(k,n)=\tfrac{1}{2}Ze(\vec{i}\cdot\vec{E}_0)\sqrt{2\pi}N^{(0)}\alpha^{-2}i^{n-1}e^{-(1/2)z^2(k)}\times\{2nH_{n-1}[z(k)]-z(k)H_n[z(k)]\}. \tag{39}$$

V. PHOTODESORPTION RATE

From the perturbation equation (30) we find

$$\hat{u}_1=-2\pi i\sum_{n,k}\{\lambda(k,n)\hat{B}_k^{\dagger}\hat{A}_n+\lambda^*(k,n)\hat{A}_n^{\dagger}\hat{B}_k\}\delta(\beta_1) \tag{40}$$

for the photostimulated desorption process. This is true in the approximation of the long times ($\Omega t\gg 1$), where Ω is any of the frequencies characterizing the studied subsystems.

Now taking into consideration expression (28) we can write the nonequilibrium distribution function of the desorbed ions with respect to the final k states

$$f(k,t)=\langle\hat{u}^{\dagger}\hat{B}_k^{\dagger}\hat{B}_k\hat{u}\rangle_0\approx\langle(1+\hat{u}_1^{\dagger})\hat{B}_k^{\dagger}\hat{B}_k(1+\hat{u}_1)\rangle_0. \tag{41}$$

The index 0 here emphasizes that the averaging is done with respect to the initial statistical operator ρ_0, or more generally, with respect to a statistical operator which is diagonal similar to ρ_0.

Since $\hat{u}_1$ contains two Hermitian conjugate terms, the right-hand part of Eq. (41) consists of nine terms representing various multiparticle distribution functions. We can split a multiparticle distribution function into single-particle ones using Wick's theorem [12]. Skipping the calculational detail, we derive from Eq. (41) to

$$f(k,t)=f(k,t_0)+\frac{2\pi}{\hbar}t[1\pm f(k,t_0)]\times\sum_n|\lambda(k,n)|^2f(n,t_0)\delta(\beta_1), \tag{42}$$

where "+" corresponds to Bose-statistics and "−" corresponds to Fermi-statistics. As it has been pointed out earlier, we will have to switch to the quasiclassical statistics type at some point in our calculations. Let us do it now, assuming that $f(k,t_0)$ is a quasi-Boltzmann distribution and $f(k,t_0)\ll 1$.

Returning to expression (29) and differentiating Eq. (42) with respect to time, we find the collision integral which describes the desorption transitions of bound ions caused by the laser light, that is, the cumulative desorption rate from all initial n states to a final k state:

$$J_d(k)=\frac{2\pi}{\hbar}\sum_n|\lambda(k,n)|^2f(n,t_0)\delta(\beta_1). \tag{43}$$

If we wish to find the statistical average photodesorption rate (which is measured by the total flux of desorbed matter), we need to integrate Eq. (43) over all final states k and normalize the result to the total number N_{im} of the impurity ions capable of desorption.

As a result, we find the mean rate of the photoinduced desorption

$$R_{ph}=\frac{1}{N_{im}}\sum_k J_d(k)=\frac{1}{N_{im}}\frac{1}{\hbar^2}\sum_n f_0(n)\int_{-\infty}^{+\infty}dp_k\,\eta[p_k]|\lambda(k,n)|^2\delta(\beta_1), \tag{44}$$

where the unitary step function $\eta[p_k]$ is introduced to emphasize that only the desorbed ions are accounted for, i.e., the ones that fly *away* from the surface.

Integration over the momentum p_k yields the final expression

$$R_{ph}=\frac{1}{N_{im}}\frac{\sqrt{2M_0}}{2\hbar^2}\sum_n f_0(n)|\lambda(k_0,n)|^2\frac{\eta[\varepsilon_n+\hbar\omega]}{\sqrt{\varepsilon_n+\hbar\omega}}, \tag{45}$$

where k_0 is defined by

$$p_{k_0}=p_0\equiv\sqrt{2M_0(\varepsilon_n+\hbar\omega)}. \tag{46}$$

Each term of the sum (45) represents the photodesorption mean rate from a level n and is equal to

$$R_{ph}(n)=[Ze(\vec{i}\cdot\vec{E}_0)]^2\frac{\sqrt{2\pi M_0}}{2^{n+2}\hbar^2\alpha^3n!}\left[1-\exp\left(-\frac{\hbar\omega_0}{T_0}\right)\right]\times\exp\left(-n\frac{\hbar\omega_0}{T_0}\right)\exp\left(-\frac{p_0^2}{\alpha^2\hbar^2}\right)\frac{\eta[\varepsilon_n+\hbar\omega]}{\sqrt{\varepsilon_n+\hbar\omega}}\times\left[2nH_{n-1}\left(-\frac{p_0}{\alpha\hbar}\right)+\frac{p_0}{\alpha\hbar}H_n\left(-\frac{p_0}{\alpha\hbar}\right)\right]^2. \tag{47}$$

In Eqs. (45) and (47) the step function $\eta[\varepsilon_n+\hbar\omega]$ selects only those levels n for which $\varepsilon_n+\hbar\omega>0$ and momentum (46) is physically meaningful, when photodesorption transitions are allowed by the energy conservation law. In particular, $\eta[\varepsilon_n+\hbar\omega]$ demands that for $\hbar\omega>\varepsilon_a$ photodesorption occurs from all levels of the oscillator, while for $\hbar\omega<\varepsilon_a$ it occurs only from sufficiently high levels, $n\geq n_{\min}$, where

$$n_{\min}=\mathrm{Int}\left[\frac{\varepsilon_a}{\hbar\omega_0}-\frac{1}{2}\right], \tag{48}$$

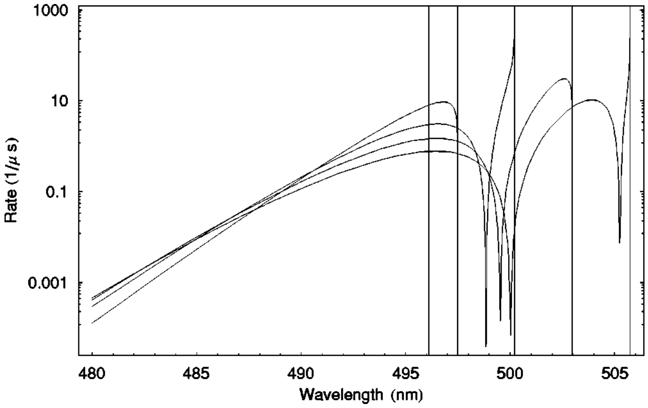

FIG. 2. Photodesorption rates $R_{ph}(n)$ as functions of the laser wavelength for $n=0,1,2,3$ at $T=300$ K. The leftmost vertical line marks the wavelength corresponding to the binding energy ε_a; other lines represent levels n. Each $R_{ph}(n)$ turns to zero for wavelengths ''redder than the nth level.''

$\mathrm{Int}[\gamma]$ denoting the integer part of the γ.

It is interesting to model photodesorption rates for different levels (47), as well as the total rate, for various parameters. Let us choose the impurity charge to be equal to the charge of an electron, $M_0=50\,m_p=8.35\times10^{-23}$ g, $\varepsilon_a=2.5$ eV, $2l=a=3\times10^{-8}$ cm, $E_0=3\times10^5$ V/cm. Temperature dependence of the rates is given by Boltzmann distribution function (31). Their dependence on the laser light wavelength is shown in Fig. 2. We see that desorption rates dramatically increase as we approach the binding energy ε_a from the blue part of the spectra, reaching the first maximum in vicinity of the bottom of the binding potential. Then each rate $R_{ph}(n)$ oscillates between zero and some peak values and turns to zero when we pass the nth level (and the photon energy is no longer sufficient to desorb a particle bound at this level).

This behavior of desorption rates is determined by the transition matrix elements λ. In particular, the nodes in the rates' dependence on wavelength are related to zeros of the Hermitian polynomials in Eq. (47), specific for the harmonic oscillator wavefunctions. So the photodesorption rates in the ''red'' part of spectrum, when the photon energy is less than the binding energy, may be expected to strongly depend on the exact shape of the binding potential. In addition, in a real system the energy levels n will be broadened (e.g., due to multiphonon transitions $n\rightarrow n'$; this will be discussed elsewhere). Therefore the peak values of the rates may in reality be lower.

However, this should not significantly affect the behavior of rates in the ''blue'' part of spectrum, i.e., just below the bottom of the well, so we may consider our estimates in that region more reliable. Adding up all rates given by Eq. (47) we find the total photodesorption rate R_{ph}. It is plotted in Fig. 3 as a function of wavelength for three different temperatures 100, 300, and 700 K. Notice that the temperature dependence of the total rate is not very significant (it is given by equilibrium population of the lowest levels in the well), while the numerical values of the rates are large enough to make the effect observable in experiment.

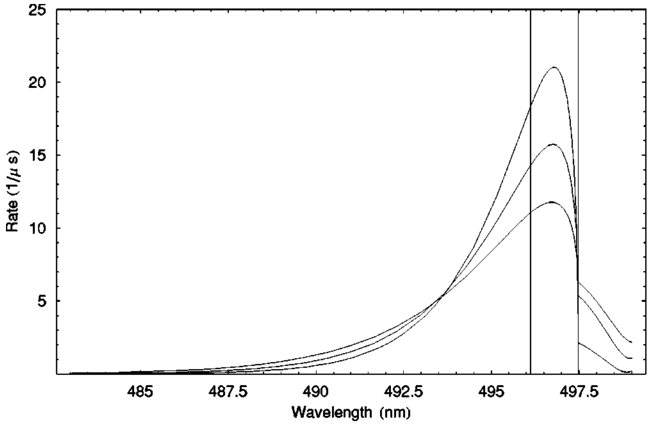

FIG. 3. Total photodesorption rate R_{ph} as a function of the laser wavelength different temperatures: $T=100$ (highest peak value), 300, 700 K (lowest peak value).

VI. DISCUSSION OF RESULTS

The following conclusions can be derived from describing the photoinduced desorption in the framework of the truncated harmonic oscillator model. Expression (47) yields qualitatively similar dependencies of the rate on the light wave frequency and intensity as the expression for probability of photoionization of atoms in the external photoelectric effect [8].

First, the rates (47) decrease rapidly with the increase of the photon energy $\hbar\omega>\varepsilon_a$, just us in the photoelectric effect. It follows from Eq. (47) that if $\hbar\omega\gg\varepsilon_a$, $\exp(-Z^2)\approx0$ (disregarding the umklap processes), that is this type of photoinduced desorption is practically absent. The maximum of photodesorption rate is reached when $\hbar\omega\approx\varepsilon_a$.

This sort of frequency dependency of the effect suggests that it can be useful for selective cleaning of substrates surfaces: tuning the laser frequency to the binding energy of an impurity one will be able to cause photodesorption of that particular impurity. Sweeping the frequency (while $\Delta\hbar\omega\gg\hbar\omega$, $\hbar\omega<\varepsilon_a$) should cause jumps in the desorption rate and emerging of new groups in the desorbed particles energy distribution.

Second, the factor $(\vec{i}\cdot\vec{E}_0)^2$ in Eq. (47) provides an angular dependency, typical for the photoinduced processes. It is well known [9] that the photoelectrons emerge from atoms mostly in the directions perpendicular to the direction of light propagation, which is determined by the same factor. Formally, the photodesorption effect would be impossible for normal incidence of light on the sample surface, when $(\vec{i}\cdot\vec{E}_0)=0$. This is a consequence of using a one-dimensional model. Considering a spherical potential well instead of the one-dimensional one described by Eq. (1), and studying an impurity atom on the surface as a semispherical rotator, should result in the averaging over angles and replacing $(\vec{i}\cdot\vec{E}_0)^2$ by approximately E_0^2. Validity of the rotator model can be verified in experiment if the light incidence angle and its polarization plane are varied. If the rotator model is valid, the variation of desorption rate in such experiments will be insignificant.

Speaking of possible experimental verifications of our results, we would like to point out that experiments have been carried out [13,14] in support of our theoretical treatment. However, even more specialized experiments are desirable. In particular, our results show that each level n in the well contributes a distinct input into the mean rate of photodesorption, producing particles with a certain momenta $p_0(n)$ (46). It is easy to show that the particles' velocities $v(n)$ lie in the range of 320 to 410 m/s (for $n \leqslant 5$) and vary by steps of $\Delta v \approx 18$ m/s. Detection of the discrete structure of $v(n)$ in experiment could confirm correctness of the truncated harmonic oscillator model. Numerical comparison of the experimental data on velocity distribution with the predicted values of $v(n)$ and Δv, and verifying predicted independence of these parameters of the sample temperature T_0, could prove correctness of our approach and calculations. An even more dramatic test of our theory would be a measurement of the flux of desorbed ions from various levels and comparing their ratio to the result (47). This test is feasible as a time-of-flight experiment.

Obtaining laser fields of the order of 3×10^5 V/cm is not difficult. Transparent dielectrics such as considered here can usually withstand even stronger fields. Our results (see Fig. 3) suggest that we may get a desorption rate of the order of 10 $\mu \mathrm{s}^{-1}$. It means that during a 30 ns laser pulse of the right wavelength, some 30% of all impurity ions will be removed from the surface. This is a significant fraction which can be easily measured in a time-of-flight experiment. The nonthermal desorption considered here has a property of accumulation. Therefore a series of a few laser pulses should result in a virtually perfect cleaning of the surface of the impurity ions, which raises hopes for other experimental methods to test our theory, and for its practical use.

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