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Resonant heating in photodesorption via laser-adsorbate coupling

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Based on the master equation for photodesorption of molecules by resonant laser-molecular vibrational coupling and on the equation of heat conduction, we calculate the heating of the solid through transfer of laser energy resonantly absorbed in the internal vibration of the adsorbed molecule. For the system CH_3F on NaCl we find that for large laser intensity resonant heating can raise the surface temperature by some 30% for realistic surface-potential parameters. The desorption time, being mainly laser induced and not thermal, changes only by at most a factor of 2–3 as a result of resonant heating.

I. INTRODUCTION

In photodesorption of molecules by resonant laser-molecular vibrational coupling a laser beam impinging onto an adsorbate-covered surface of a solid is resonantly coupled into some internal vibrational mode of the adsorbed molecule.[1] For most systems the energy $\hbar\Omega$ of the vibrational mode is much larger than the spacing between the energies $(E_{i+1}-E_i)$ of bound states in the surface potential, i.e., in a classical picture, the internal vibrational frequency of the molecule is larger than the oscillation frequency of its surface bond. Treating the internal mode as a harmonic oscillator for the lowest few excited states the energy of the adsorbed molecule is then $E_i^v=E_i+(v+\frac{1}{2})\hbar\Omega$ where i labels the bound states in the surface potential and v counts the quanta excited in the internal vibrational mode of the molecule. The latter can be changed by ± 1 through absorption or emission of a photon from a laser resonantly tuned into this frequency. At low temperatures an adsorbed molecule will be in the ground state of energy

$$E_i^v=E_0^0=E_0+\tfrac{1}{2}\hbar\Omega\ . \tag{1}$$

Upon absorption of a laser photon the molecule will be in a state E_0^1 from which it can either absorb more photons to go up to higher v or emit a phonon of energy $\hbar\omega$ such that $E_i^0=E_0^1+\hbar\omega$. It is then in an excited state of the surface potential from which it can cascade down to $i=0$, emitting more phonons and thus heating up the solid. This process one might call resonant heating.[1] It occurs in addition to direct heating of the solid by coupling the laser into its electronic degrees of freedom.

If a molecule can be excited into a higher internal-vibrational state such that its total energy

$$E_0^v=E_0+(v+\tfrac{1}{2})\hbar\Omega=p^2/2m+(v'+\tfrac{1}{2})\hbar\Omega \tag{2}$$

is degenerate with some continuum state of momentum p (with v' possibly zero) then elastic tunneling into the latter state will desorb the molecule. This process has been examined by Lucas and Ewing.[2] Tunneling can also be inelastic, i.e., aided by the emission and adsorption of phonons, a process investigated by Kreuzer and Lowy.[3] We will refer to both elastic and inelastic tunneling processes as photodesorption by resonant laser-molecule vibrational coupling. Its feasibility has been demonstrated by Heidberg *et al.*[4] for the system CH_3F on NaCl and by Chuang[5] for pyridine on KCl and silver.

In our previous paper[1] we have calculated photodesorption rates as a function of the laser fluence with the temperature of the solid fixed. (Fluence is the time integral of the intensity of a pulsed laser.) The computational basis was a master equation for the occupation functions $n_i^v(t)$ of a molecule in a state (i,v), i.e.,

$$\frac{d}{dt}n_i^v(t)=\sum_{v'=0}^{\infty}\sum_{i'=1}^{i_{\max}}[(\mathscr{L}_{ii'}^{vv'}+P_{ii'}^{vv'})n_{i'}^{v'}(t)-(\mathscr{L}_{i'i}^{v'v}+P_{i'i}^{v'v})n_i^v(t)]-\sum_{v'=0}^{\infty}(P_{ci}^{v'v}+Q_{ci}^{v'v})n_i^v(t)\ . \tag{3}$$

Here $\mathscr{L}_{ii'}^{vv'}$ is the rate at which the coupling of the molecular dipole to the electromagnetic field of the laser causes transitions up or down the vibrational excitations; we note that it is only nonzero for $i=i'$ and $v=v'\pm 1$. $P_{ii'}^{vv'}$ is the transition rate between bound states mediated by one-phonon absorption and emission processes calculated according to Fermi's golden rule from a microscopic Hamiltonian. $P_{ci}^{v'v}$ and $Q_{ci}^{v'v}$ are the transition rates from a bound state (i,v) into all continuum states with the first mediated by phonons and the second being an elastic tunneling process. These two terms lead to desorption. Details can be found in Ref. 1, where the transition probabilities have been calculated for a surface Morse potential. A schematic picture of all processes involved is given in Fig. 1.

The above theory assumed that during the photodesorption process the solid is kept at the initial temperature T_0. If this precaution is not taken then the laser energy, resonantly captured in the vibrational mode of the adsorbed molecule, will in part be used to heat the solid via bound-state—bound-state transitions mediated by one-phonon processes in $P_{i'i}^{v'v}$. Whenever a particle makes a transition from a state with energy E_i^v into one with a lower energy $E_{i'}^{v'}$, a phonon is emitted into the solid; if $E_{i'}^{v'} > E_i^v$, on the other hand, a phonon is absorbed. Thus the phonon occupation functions will deviate from the initial equilibrium at temperature T_0 during the desorption process. Of course, relaxation processes within the phonon system will tend to restore equilibrium within times of the order of phonon collision times. If the latter are much shorter than the desorption time one can assume that the phonon system remains, to a good approximation, in its initial equilibrium state. Once nonequilibrium effects become noticeable, a theory must be devised that takes account of the time-dependent changes in the phonon system. In a fully microscopic approach one would attempt to formulate a kinetic equation for the phonon occupation functions that takes into account the sink and source terms for phonons at the surface, phonon collisions, and spatial variations.[6] Fortunately this is not necessary in the case of photodesorption because the nonequilibrium effects in the phonon system remain small enough to be treated in the local equilibrium approximation. That is to say, phonon relaxation processes are fast enough to establish local equilibrium, implying that a space- and time-dependent temperature field $T(\vec{r},t)$ can be introduced which varies little over distances of the mean free path for phonon collisions and over times of the order of the phonon collision time. In such a situation the temperature field is subjected to Fourier's law of heat conduction

$$\frac{\partial T}{\partial t} - \chi\nabla^2 T = \frac{\dot{E}}{k_B} , \tag{4}$$

where $\dot{E}$ is the rate at which energy is transferred to or from the solid during the desorption process at the surface. χ is the thermal diffusivity.

We will in the next section outline the calculation of $\dot{E}$. Section III then gives details on how the coupled set of equations (3) and (4) was solved followed by a presentation of numerical results.

II. THEORY

To compute the temperature field $T(\vec{r},t)$ in the solid during the desorption process we must know the energy sink or source $\dot{E}$ on the right-hand side of (4). It can be written as

$$\dot{E} = \text{const} \sum_{\vec{p},\sigma} \hbar\omega_{\vec{p}\sigma} \frac{dn_{\vec{p}\sigma}}{dt} , \tag{5}$$

where $n_{\vec{p}\sigma}$ is the occupation function for phonons of wave number $\vec{p}$, polarization σ, and frequency $\hbar\omega_{\vec{p}\sigma}$. In equilibrium we have

$$n_{\vec{p}\sigma}^{(\mathrm{eq})} = (e^{\beta\hbar\omega_{\vec{p}\sigma}} - 1)^{-1} . \tag{6}$$

The $n_{\vec{p}\sigma}$ increase whenever an adsorbed molecule makes a transition from an initial state with energy E_i^v into one with lower energy $E_{i'}^{v'}$ emitting a phonon; they decrease for the inverse process accompanied by absorption of a phonon, i.e.,

$$\begin{aligned} \frac{dn_{\vec{p}\sigma}}{dt} = {} & \sum_{i,v} \sum_{i',v'}^{(\mathrm{em})} \widetilde{R}_{i'i}^{v'v}(\vec{p},\sigma) n_i^v(t) \\ & - \sum_{i,v} \left[\sum_{i',v'}^{(\mathrm{abs})} \widetilde{R}_{i',i}^{v'v}(\vec{p},\sigma) \right. \\ & \left. + \sum_{q,v'}^{(\mathrm{abs})} \widetilde{R}_{qi}^{v'v} \right] n_i^v(t) , \end{aligned} \tag{7}$$

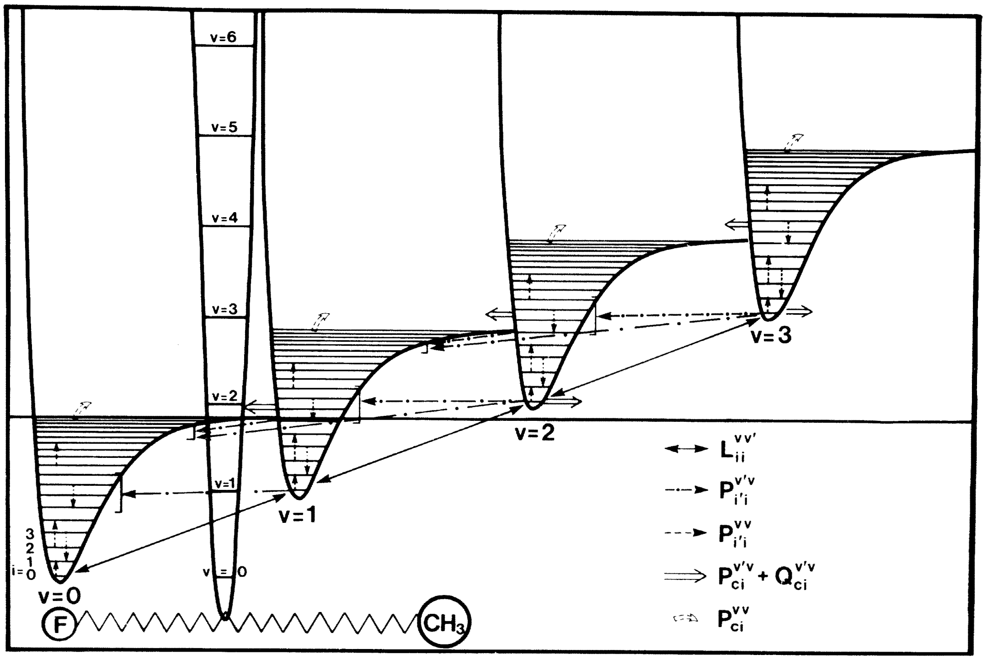

FIG. 1. Schematic energy diagram of a molecule adsorbed on a surface with some of the processes included in the theory indicated by arrows with the following transition probabilities: $P_{i'i}^{v'v}$ is the phonon-mediated bound-state—bound-state; $P_{ci}^{v'v}$ is the phonon-mediated bound-state—continuum; $Q_{ci}^{v'v}$ is the elastic tunneling into continuum; $L_{ii}^{v'v}$ is the laser coupling.

where the sum over q exhausts the continuum states; i and i' label the bound states of the surface potential. $\tilde{R}_{i'i}^{v'v}(\vec{p},\sigma)$ is the transition probability per unit time for a particle to go from state (i,v) to (i',v') accompanied by emission or absorption of a phonon of momentum $\vec{p}$. To ensure energy conservation in this process it must contain a δ function

$$\delta(E_i^v - E_{i'}^{v'} \pm \hbar\omega_{\vec{p}\sigma}) \ . \tag{8}$$

Its use in (5) allows us to express it in terms of the $P_{i'i}^{v'v}$ transition rates in (3) as follows:

$$\dot{E}(t) = N_a S \sum_{i,v} n_i^v(t) \left[\sum_{i',v'} (E_i^v - E_{i'}^{v'}) P_{i'i}^{v'v} + \sum_{q,v'} (E_i^v - E_q^{v'}) P_{qi}^{v'v} \right] \Big/ \sum_{j,v} n_j^v(0) \ . \tag{9}$$

We note that $P_{qi}^{v'v}$ summed over all continuum states q is equal to $P_{ci}^{v'v}$ in (3). To understand the appearance of the factor $(N_a S)$ in (9) we recall that the theory of photodesorption based on the master equation (3) is valid only at such low coverage that the interaction between adsorbed particles is negligible. Equations (3) and (7) then hold for each adsorbed particle separately. Thus the energy source $\dot{E}$ on the surface must be made explicitly proportional to the total number of adsorbed particles $(N_a S)$ where N_a is the number of particles adsorbed per unit surface area and S is the total area of adsorption. To assess the validity of this approximation we first look at the more familiar case of thermal desorption. Most gas-solid systems show a marked dependence of the prefactor ν and the desorption energy E_d, defined in the Frenkel-Arrhenius parametrization of the desorption time

$$t_d = \nu^{-1} e^{E_d/k_B T} \tag{10}$$

on the coverage. This restricts a theory of desorption based on a master equation (3) to very low coverage of perhaps a tenth of a monolayer, with considerable theoretical complications appearing at higher coverage.[7] These effects not withstanding what is more important in the case of photodesorption at nonzero coverage is the fact that the energy absorbed by the adsorbed molecules out of the laser beam can readily be dissipated via v-v coupling into areas of the adsorbate not illuminated by the laser. This will essentially lead to a reduction of the energy stored in the vibrational mode of the molecule by the ratio of the illuminated to the dark area of the total adsorbate. With v-v coupling the intensity of the laser is therefore effectively reduced as far as its function of causing desorption and resonant heating is concerned. We feel that the simple proportionality to $(N_a S)$ in (9) should give a useful estimate of resonant heating up to a coverage of half a monolayer.

III. RESULTS

To calculate the change in surface temperature during the desorption process we have to solve the master equation (3) and the heat conduction equation (4) together with (9) simultaneously. It is advantageous to solve (4) using the appropriate Green's function.[8] Assuming that the solid has infinite depth and that no lateral structure is present along the surface we get

$$\begin{aligned} T(z,t) = {} & \frac{1}{2\sqrt{\pi\chi}} \int_{-\infty}^{\infty} ds \left(e^{-(z-s)^2/4\chi(t-t_0)} + e^{-(z+s)^2/4\chi(t-t_0)} \right) \frac{T(s,t_0)}{(t-t_0)^{1/2}} \\ & + N_a \frac{V_m}{C_V} \frac{1}{\sqrt{\pi\chi}} \int_{t_0}^{t} dt' e^{-z^2/4(t-t')} \frac{\dot{E}(t')}{(t-t')^{1/2}} \ . \end{aligned} \tag{11}$$

Here C_V is the specific heat per mole and V_m is the molar volume of the solid; z is the distance into the solid. Obviously the temperature change will, for a given $\dot{E}$, be larger the smaller the thermal diffusivity χ and the specific heat are. The former controls the rate of energy transport in the solid whereas the latter gives by definition the temperature change accompanying a given energy change.

To solve (3) and (11) simultaneously we have chosen discrete time intervals $t_0 = 0, t_1, t_2, \ldots$ and we have assumed that the temperature $T(z,t) = T_n(z)$ remains constant in each interval $t_n < t < t_{n+1}$. Starting at $t_0 = 0$ with a uniform temperature T_0 throughout the solid we calculate the transition probabilities in (7) and solve (5) by diagonalizing the matrix $(\mathscr{L} + P + Q)$ yielding eigenvalues λ_k, so that we get (for details see Ref. 1)

$$n_i^v(t) = \sum_k A_{ik}^v e^{-\lambda_k t} \ . \tag{12}$$

Inserted in (9) we get the rate of energy uptake for times $t_0 < t < t_1$, which inserted in (11) yields the temperature field $T(z,t_1)$. Its value at the surface $z = 0$ (which can actually be calculated algebraically if we put $\dot{E}$ constant in each time interval) is used to calculate $P_{ij}^{v'v}$ which contains the phonon occupation function (6) for the next time interval for which the above procedure is repeated. The overall solution is found to be stable for time intervals that are smaller than about one tenth of the desorption time at the particular time.

We have calculated resonant heating for the system CH_3F on NaCl for which Heidberg *et al.*[4] have done laser-induced photodesorption experiments and for which an extensive theoretical study of photodesorption rates as a function of temperature and fluence was reported in Ref. 1. We recall that CH_3F is physisorbed on NaCl with a heat of adsorption of about 25 kJ/mol; this is modeled in the theory by a surface potential of Morse-type of adequate depth and width. The ν_3 vibration (F against CH_3) which is active in the photodesorption process is lowered from 1048 cm^{-1} in the free molecule to 970 cm^{-1} in the adsorbed species. Important for the excitation of this vibration by the laser is the derivative of the corresponding dipole moment which we took[9] to be $\partial\mu/\partial x = 4.8$ D/Å. A recent calculation[10] suggests that (in the free molecule) $\partial\mu/\partial x = 1.67$ D/Å. This implies that the laser fluences in Ref. 1 should be increased by a factor $(4.8/1.67)^2 \approx 8.3$ a trend in the right direction as far as comparison with Heidberg's experiments is concerned. For sake of easier comparison with Ref. 1 we keep the first value of $\partial\mu/\partial x$ in the present calculations.

In the temperature region of interest from 50 to 150 K the specific heat of NaCl (Ref. 11) rises from 16 to 47 J/mol whereas its thermal diffusivity drops from 7×10^{-5} m^2/s at 50 K to 5×10^{-6} m^2/s at 150 K so that the factor $C_V\sqrt{\chi}$ in (11) can be parametrized as

$$C_V\sqrt{\chi} = 4.1\times10^{-3}T - 3.4\times10^{-5}T^2 + 8\times10^{-8}T^3 \, . \tag{13}$$

As discussed in Ref. 1 there is some uncertainty in choosing range and depth of the surface Morse potential that physisorbs CH_3F onto NaCl. We present numerical results for two such choices and begin with a potential of depth $V_0 = 2750k_B$ and range $\gamma^{-1} = 0.35$ Å for which Fig. 4 in Ref. 1 gives the photodesorption rates as a function of laser fluence for $T = 50$ and 100 K. We recall that the rates saturate for large fluences, i.e., for $F_e \gtrsim 1$ J/m^2 at values that increase with the maximum number $v_{\max}$ of oscillator states of the ν_3 vibration in resonance with the laser.

In Fig. 2 we have plotted the relative change in surface temperature as a function of time measured in units of the initial laser-induced desorption time at temperature $T_0 = 50$ K. The initial coverage was chosen as half a monolayer. We observe that the proportionality of $\dot{E}$ to $\langle N_a S\rangle$ in (9) implies a like behavior for the maximum temperature rise at the surface. We see that the surface temperature rises quickly to a maximum of about 62 K for $F_e > 1$ J/m^2 after which the surface cools off slowly back to 50 K with the excess heat being conducted into the solid. The photodesorption time at $T_0 = 50$ K is 2.2×10^{-5} s for $v_{\max} = 3$; it drops to 1.5×10^{-5} s at the time the surface temperature has reached a maximum. For $v_{\max} = 4$ the change is from 1.1×10^{-5} to 9×10^{-6} s.

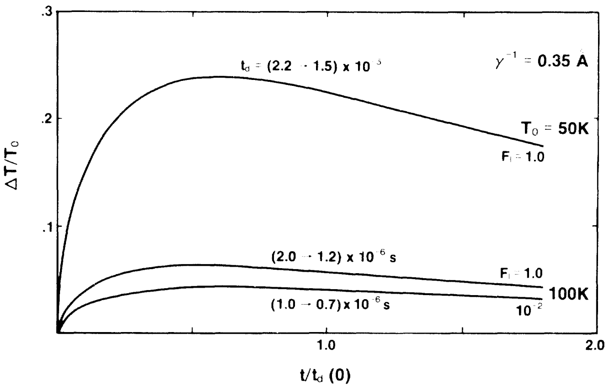

FIG. 2. Relative change in surface temperature for CH_3F-NaCl. $\Delta T/T_0 = [T(z=0,t) - T_0]/T_0$ as a function of time, measured in units of the desorption time at time $t = 0$. Fluence F_e is measured in J/m^2. Also indicated in the change in t_d during desorption. Initial coverage is half a monolayer. Depth of surface potential (heat of adsorption) $V_0/k_B = 2750$ K; its range is 0.35 Å. The maximum number of vibrational states CH_3F is 4.

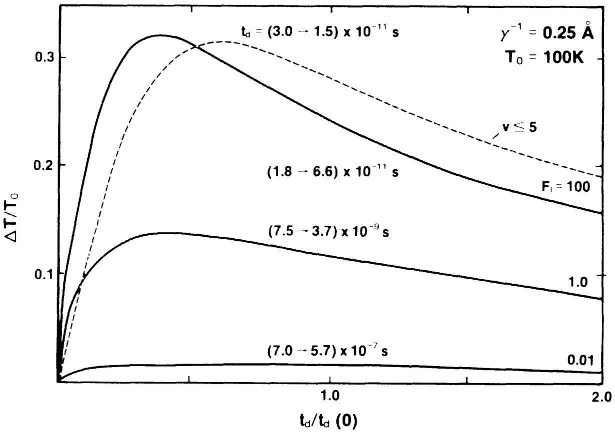

FIG. 3. See Fig. 2 but note the different range.

We note that in a time t thermal conduction has effected the solid to a depth

$$L = \sqrt{\chi t} \tag{14}$$

which for $\chi \approx 10^{-5}$ m^2/s and $t \approx 10^{-5}$ s is 10^5 Å. Because the transition probabilities $P_{i'i}^{v'v}$ in (3) that cause the resonant heating are analytically closely related to the ones causing desorption, namely $P_{ci}^{v'v}$ and $Q_{ci}^{v'v}$, slow desorption also means poor heating and in turn a small temperature rise due to efficient heat transport.

We have already seen in Ref. 1 that increasing the number of oscillator states $v_{\max}$ of the adsorbed molecule into which the laser is still resonantly tuned will increase the photodesorption rate in the saturation regime for large fluences. This, of course, implies that the additional desorption channels dominate over the energy loss, i.e., heating, channels. It is therefore not surprising that we now find

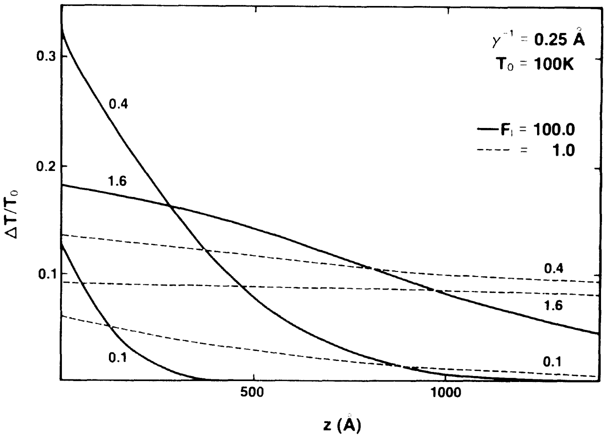

FIG. 4. Temperature profile into the solid for Fig. 3 at various times $t/t_d(0) = 0.1$, 0.4, and 1.6.

that the maximum temperature rise at the surface is fairly insensitive to $v_{\max}$. For the above model we have also calculated the temperature rise beginning initially at $T_0 = 100$ K; it is about 6 K with the photodesorption time decreasing some 20% also. It can therefore be concluded that for this choice of surface potential parameters resonant heating is a rather minor effect.

The situation is drastically different if we reduce the range of the surface Morse potential that physisorbs CH_3F onto NaCl from 0.35 to 0.25 Å. The coupling to the phonons, being proportional to the derivative of the surface potential in the one-phonon approximation, becomes much stronger as evidenced by the fact that the photodesorption rates in the saturation regime become faster by about 5 orders of magnitude; compare Figs. 3 and 4 in Ref. 1. One would think that a reduction in the range of the surface potential from 0.35 to 0.25 Å has less dramatic effects but we must recall from Ref. 1 that it had a qualitative implication in that for the narrower potential the lowest three bound states $i = 0$, 1, and 2 were separated by more than a Debye energy. Thus they cannot be connected by a one-phonon process. Desorption in the saturation region for high fluence therefore effectively takes place from the shallower $i = 2$ state; hence it is so much faster. But so does resonant heating become more efficient.

In Fig. 3 we plot the change in surface temperature as a function of time for the narrower surface potential for various fluences. Qualitatively the picture is similar to Fig. 2 but the maximum temperature rise is now from an initial $T_0 = 100$ K to a maximum of 132 K for which the photodesorption time is about half of what it was initially. The substantial temperature rise is in part also due to the fact that within the much shorter desorption time of some 10^{-10} s at $F_e = 100$ J/m^2 heat conduction effects the solid only to a depth of some 10^3 Å rather than the 10^5 Å as was the case in the previous model. It is fortunately still larger than the phonon mean free path of about 100 Å so that the local equilibrium assumption underlying the use of Fourier's equation of heat conduction is still satisfied. To demonstrate the point we have plotted in Fig. 4 temperature profiles for two fluences at various times as calculated from (11). We have seen that with resonant heating included the desorption time changes during the course of desorption implying that the process is no longer exponential. This is demonstrated explicitly in Fig. 5 where we plot the time dependence of the coverage. The initial curvature is a reflection of transient effects[12] due to the fact that it takes the laser some 10^{-11} s at a fluence of 10^2 J/m^2 to populate the higher oscillator states of the ν_3 vibration in CH_3F. The dashed curve represents photodesorption with resonant heating suppressed. In Fig. 6 we lastly give the surface temperature rise starting initially at $T_0 = 50$ K. Resonant heating is now a dramatic effect with the maximum temperature rise to about 100 K.

In summary, we have calculated the temperature rise at the surface of NaCl due to resonant heating from the laser coupled into the ν_3 vibration of adsorbed CH_3F. In a first model for the surface potential with which CH_3F is bound to NaCl we found (Fig. 2) a small temperature rise of a few degrees. A second model, which we argued in Ref. 1 to be less realistic within the present context of the one-phonon approximation, gave substantial heating of up to 100% of the initial temperature. Yet, even then the photodesorption rate, being mainly laser induced and not thermal (see Figs. 3 and 4 in Ref. 1) only increased by a factor of 2 or 3, i.e., well within greater uncertainties arising from possible choices of surface potential parameters, the dipole moment of adsorbed CH_3F, etc.

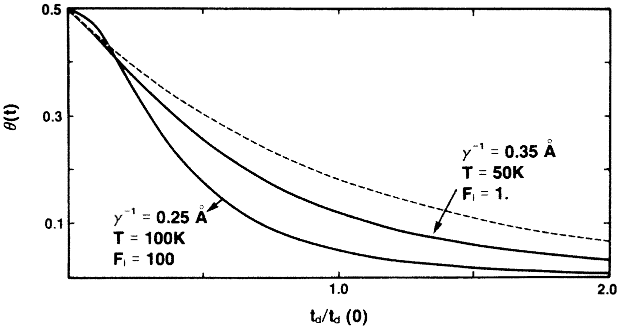

FIG. 5. Time dependence of the coverage for the models of Figs. 1 and 2. Dashed line: pure exponential.

Reality hopefully lies somewhere between these two extreme models. It would therefore be worthwhile in future photodesorption experiments to carefully monitor the surface temperature. Our theory assumed that the NaCl crystal is infinitely thick. For a thin film of a few thousand angstroms on a poor thermal conductor like graphite the temperature rise could be increased. An interesting experiment would be to coadsorb with CH_3F a substance with about the same or a smaller heat of adsorption but without an internal resonance at ν_3. A resonant temperature rise would then cause the coadsorbate to desorb thermally. A candidate might be CD_3F or some other isotopic species.

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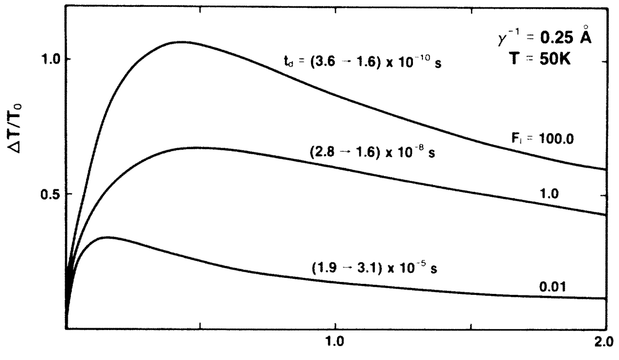

FIG. 6. Model of Fig. 3 but at lower temperature.

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