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Scattering of excited molecules at a surface: The effect of van der Waals forces

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The effect of the van der Waals potential on the processes of quenching and inelastic scattering of an excited quantum particle at a surface is considered. Regimes of high superelasticity at metallic surfaces and of capture at a dielectric surface covered with a layer of molecules of the same kind are apparent. Effective potentials due to multiple absorption-quenching steps are calculated for heavy and slow particles in laser fields. A consistent quasiclassical description of the translational motion of a two-level quantum particle interacting with a continuum is outlined and the dispersion of the trajectories after scattering is analyzed.

I. INTRODUCTION

Many investigations of atomic and molecular-beam scattering at surfaces were carried out during the last decade.¹ Usually an initially well-collimated beam of monoenergetic particles becomes, after reflection, spread in angles due to the surface corrugation and in kinetic energies due to the energy transfer to the bulk phonons. In the latter case the scattering is an inelastic process. A number of experiments in surface scattering were carried out with particles excited to a higher electronic state before the collision.^{2,3} These particles mainly become quenched in the course of the collision.

In our opinion the translational and internal dynamics should be considered in combination, taking into account their mutual interference. The motivation of such an investigation is also given by the fact that the phenomena resulting from the coupling of these quantum and classical dynamics should manifest itself in scattering at a surface under conditions close to current experiments. We will demonstrate here that the combined effect of the scattering and quenching processes may result in superelastic scattering, i.e., part of the internal energy of the scattered particle is transferred to the translational motion. This phenomenon is reciprocal to inelastic scattering and was briefly mentioned in Ref. 4. For a sufficiently narrow kinetic-energy width of the beam and a high detection accuracy it seems possible, at least in principle, to detect the superelastic process among the elastic and nonelastic ones. The technique of laser-beam cooling⁵ looks most promising from the viewpoint of the possibility to observe this phenomenon. In this paper we give an estimate of the size of the effect under the assumption that all the competing processes like surface roughness and energy losses due to the interaction with the phonons are neglected.

It is well known that the internal quantum state of a particle can affect its translational motion in the course of a gas-phase collision. The most evident manifestations of this phenomenon are inelastic and superelastic impacts^{6,7} where

a rather large quantum of the particle's internal energy is transferred to (or from) translational energy. A typically low probability for this process is a natural consequence of the qualitative difference between the quasiclassical translational and the essentially quantum internal motions. The long-ranged dipole-dipole interaction seems, however, to be most efficient in coupling these two different dynamical systems. Even without a significant difference in the energies of the levels involved in the process, it allows the internal quantum structure of the particles to affect the translational motion. For example, the dipole-dipole interaction of identical molecules, is responsible for $V-V$ exchange if one of them is vibrationally excited, but simultaneously also influences their transport properties in a binary collision.⁸ This is completely evident from the quantum treatment of the van der Waals force. If both molecules are unexcited this force arises from the dipole-dipole interaction in the second order of perturbation theory over a small parameter, the ratio of the dipole potential to a typical energy spacing. In contrast, the interaction of an excited with an unexcited molecule is significantly larger and characterized by the presence of a resonance and by an off-diagonal term in the secular equation which is proportional to the perturbation itself.

The aim of the present paper is to consider similar processes for the case of an excited particle approaching a surface. A surface naturally supplies a large number of levels for energy exchange, and thus promotes quenching of the particle's excitation. The interaction leading to quenching is expected to influence simultaneously the translational motion. For rather light particles even a single quantum of excitation can be sufficient to affect drastically a trajectory, while for the heavy ones several transitions are necessary. In the latter case we assume the presence of a laser field to maintain the excitation.

The phenomenon considered here is of a rather general nature. Being responsible for partial transfer of energy from the internal quantum degrees of freedom to the translational, classical ones, it can manifest itself, although with a varying extent, in a number of physical situations where an atom or a molecule approaches metallic, dielectric or even

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semiconductor surfaces. In the following, we consider three of these cases. Certainly, the effect should also have practical applications, if it can be observed under realistic conditions. If excited molecules are quenched and scattered differently from the unexcited ones, then by some pulsed excitation, e.g., a laser, acting on a molecular beam directed towards a surface, a short bunch of molecules may be deflected by some angle from the direction of elastic scattering, or even accelerated considerably. In this way one can realize a laser control of the molecular beam.

In Sec. II we start our analysis with the simple example of a two-level atom or molecule approaching a metallic surface and interacting with this surface by the dipole-dipole mechanism. We will implement a simple quasiclassical theory for the description of these processes. The translational degrees of freedom will be treated classically and the internal ones quantum mechanically. A consistent analysis performed in the spirit of semiclassical theories^{9,10} is given in the Appendix. More-refined models can be developed in order to take into account the effects of molecular orientation and of electromagnetic field retardation,¹¹ atomic forces,¹² temperature, nonlocal response, and surface roughness,¹³ and multipole corrections.¹⁴

The general theory of the van der Waals forces was developed almost 30 years ago.¹⁵ This and subsequent considerations¹⁶⁻¹⁹ were based on the assumption that the system is almost in thermal equilibrium. In this case the van der Waals potential of a particle near a surface is proportional to the product of the linear susceptibilities of the surface and of the particle integrated over all frequencies. But in the presence of a population inversion, e.g., when either the particle is excited or the medium is inverted this law does not hold anymore. The constant c_6 entering the expression for the van der Waals potential $U = c_6 R^{-3}$ may then considerably exceed its equilibrium value. The main reasons for this are the resonant denominators in the perturbation series, where instead of a sum of the excitation energies of the particle and the medium now their difference enters. In the further analysis we will therefore neglect the van der Waals potentials for particles in the ground state.

The example discussed here already shows the typical features of the phenomenon considered. The dipole-dipole interaction provides both an attraction between the particle and its dipole-image and a mechanism for excitation quenching, e.g., via creation of electron-hole pairs.² In Sec. III we describe the interaction of a vibrationally excited molecule with a monolayer of molecules of the same kind that are adsorbed on a dielectric surface. In this case the quenching of excitation takes place by energy exchange between a free molecule and the molecules on the surface and among the molecules on the surface. We consider in some detail the example of CO molecules on a NaCl surface where experimental data together with a theoretical analysis²⁰ are available. The data for the three atomic molecules²¹ are more difficult for the analysis. Finally, in Sec. IV, we include the pumping of a system by an external laser which seems to be particularly important for heavy particles and leads to an effective potential force resembling the one typical for the photon pressure problem.^{22,23}

II. REFLECTION OF AN EXCITED PARTICLE FROM A METALLIC SURFACE

Let us consider a two-level quantum particle approaching a metallic surface. The potential energy due to the interaction of a dipole with its image

$$\hat{U} = \frac{1}{x^3} (\hat{\mu}_y \hat{\mu}'_y - 3 \hat{\mu}_x \hat{\mu}'_x) = \frac{\mu^2}{x^3} (\hat{J}^2 + \hat{M}^2) \quad (1)$$

acts, after averaging over the quantum state, in addition to the potential for the translational motion. In Eq. (1) $\hat{\mu}'_{y,x} = \hat{\mu}_{y,x}$, $\hat{\mu}'_x = -\hat{\mu}_x$, and \hat{J} and \hat{M} are the angular momentum operator and its normal projection. In this way the interaction energy depends on the orientation of the orbital with respect to the surface. The spatial derivative of this potential represents an additional force entering Newton's equation of motion

$$m\ddot{x} = F - \frac{3\mu^2}{x^4} (J^2 + M^2) \rho_{J,M}, \quad (2)$$

where m is the mass of the particle and F is the adsorption force. We assume an atomic particle with a ground and excited state corresponding to $J = 0$ and $J \neq 0$, respectively. Then $J^2 + M^2$ is nonvanishing only for the excited state and $\rho_{J,M}$ corresponds to a population of the magnetic sublevels of this state. The interaction with metal electrons possessing an energy close to the Fermi level leads to a quenching of the excitation, e.g., by means of electron-hole pair creation. For this mechanism the analysis is most simple. According to Ref. 24, this mechanism results in a quenching rate that is inversely proportional to the fourth power of the distance, and we thus take an expression for this process in the form

$$\dot{\rho}_{J,M} = -\gamma_{J,M} (a/x)^4 \rho_{J,M}, \quad (3)$$

where γ is the quenching rate at the distance a from the surface. Here, we consider only the transfer of excitation from the particle to the surface. In the opposite direction the process is unlikely because of the much higher statistical weight of excited surface states compared to the single excited state of the atom. Thus, even though we do not explicitly consider surface excitation quenching at all, the reverse flow of excitation from the surface to the particle is excluded in practice. The system of Eqs. (2) and (3) has an integral of motion

$$m\dot{x} - \int F(t') dt' - \frac{3\mu^2}{a^4} \frac{J^2 + M^2}{\gamma_{J,M}} \rho_{J,M} = \text{const.} \quad (4)$$

This implies that a particle in the excited state that is initially at rest, acquires a velocity after quenching

$$v_x \sim \frac{6\mu^2}{ma^4 \gamma_{J,M}} \quad (5)$$

solely due to the action of the van der Waals force. Another part of the velocity change, i.e., $(1/m) \int F(t) dt$, results from the elastic scattering. Setting values $J = M = 1$, $\mu = 1$ D, $m = 10m_p$, $a = 1.6$ Å, $\gamma = 10^{11} \text{ s}^{-1}$, we obtain the estimate for the velocity of Eq. (5), $v_x \sim 10^6 \text{ cm/s}$. The kinetic energy of this particle, $E_{\text{kin}} \sim 1 - 10 \text{ eV}$, is of the order or may even

exceed typical values of adsorption potentials. In order to obtain such a large value of the kinetic energy at all, the energy of the quantum itself must of course be much larger than the energy of adsorption. Evidently, in a dynamical situation the particle moves towards and backwards from the surface and may have insufficient time for complete quenching, thus acquiring less translational energy. But the estimate in Eq. (5) shows the need to consider this process among others in the analysis of scattering phenomena on surfaces.

It should be mentioned that Eqs. (2) and (3) together form a classical description for the translational motion of the particle interaction with the surface. Of course such an approach is not always valid. From the quantum point of view the condition for its applicability is the smallness of the potential-energy change during the quenching time with respect to the energy width of the translational de Broglie wave packet

$$v_x F \tau_{\text{quenching}} \sim 3v_x \mu^2 / \gamma a^4 \ll v_x \delta p = \delta E_{\text{kin}}. \quad (6)$$

Otherwise, the process should be treated quantum mechanically.

Figures 1–3 show the results of a numerical solution of Eqs. (2) and (3) using parameters typical for electronic and vibrational transitions. It was assumed that the particle initially was in the excited state and had a velocity v_x in the direction towards the surface. The influence of the adsorption potential on the trajectory was taken into account by a potential of the form

$$U = U_{\text{ads}} [3(x_{\text{min}}/x)^8 - 4(x_{\text{min}}/x)^6], \quad (7)$$

depending on two parameters U_{ads} and x_{min} , the energy of adsorption, and the distance of the potential minimum from the surface, respectively. We consider here the case of physical adsorption when both excited and unexcited terms have almost the same potentials that differ only by the dipole–

dipole interaction. If this difference is larger due to chemical adsorption the phenomenon discussed should manifest itself even more pronounced. To avoid a possible misunderstanding we mention that the momentum of the particle changes because of the action of the dipole–dipole force which changes or even vanishes after the quenching. The momentum transfer from the particle to the electron–hole pairs in the course of the quenching process is negligible.

Figure 1 shows a typical trajectory of the particle and the time dependence of the excited-state population. The dipole–dipole interaction accelerates the excited particle in the direction toward the metallic surface as a result of the attraction by the image and simultaneously quenches the excited state. After reflection the particle is thereby no longer exposed to the decelerating action. However, large values of U_{ads} and x_{min} reduce the overall action of the dipole–dipole interaction and hence the quenching. This circumstance sets a limit for the acceleration phenomena to manifest itself to a full extent (Fig. 2).

As an illustration, Fig. 3 shows the dependence of the velocity after reflection on the initial velocity for different values of the adsorption potential parameters. One observes that the relative superelasticity of this process decreases with increasing velocity for two reasons: the increase of the total energy and the decrease of the transferred energy due to the shorter interaction time. But for slow particles the process is extremely superelastic and the velocity after collision can be of the order of 500 m/s for favorable values of the parameters.

If the probability of quenching is small and the main contribution to the phenomenon comes from the turning point of the trajectory, one obtains an explicit formula for Δv —the velocity acquired. Indeed, using (4) for finite increments, i.e., by substituting the difference between the initial and finite values of $m\dot{x}$, one obtains

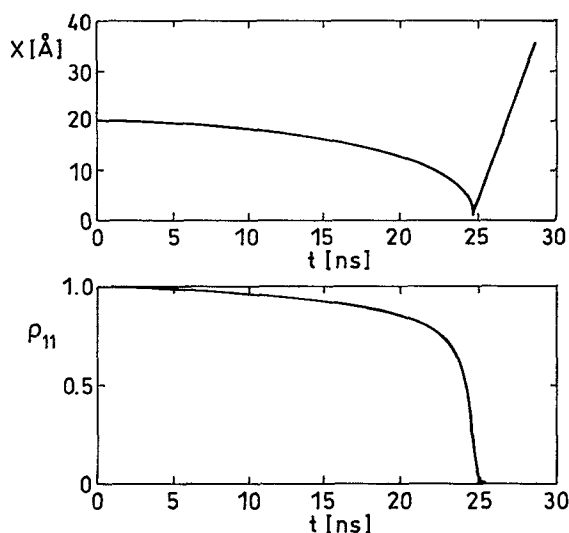


FIG. 1. Trajectory (top) and population (bottom) for the case $\mu = 3$ D, $m = 4m_p$, $a = 1.6$ Å, $\gamma = 10^{14}$ s $^{-1}$.

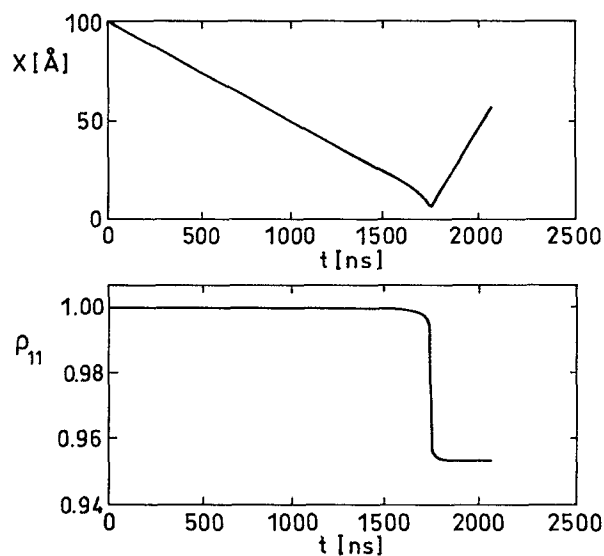


FIG. 2. Trajectory (top) and population (bottom) for the case $\mu = 0.1$ D, $m = 28m_p$, $a = 1.6$ Å, $\gamma = 10^{11}$ s $^{-1}$.

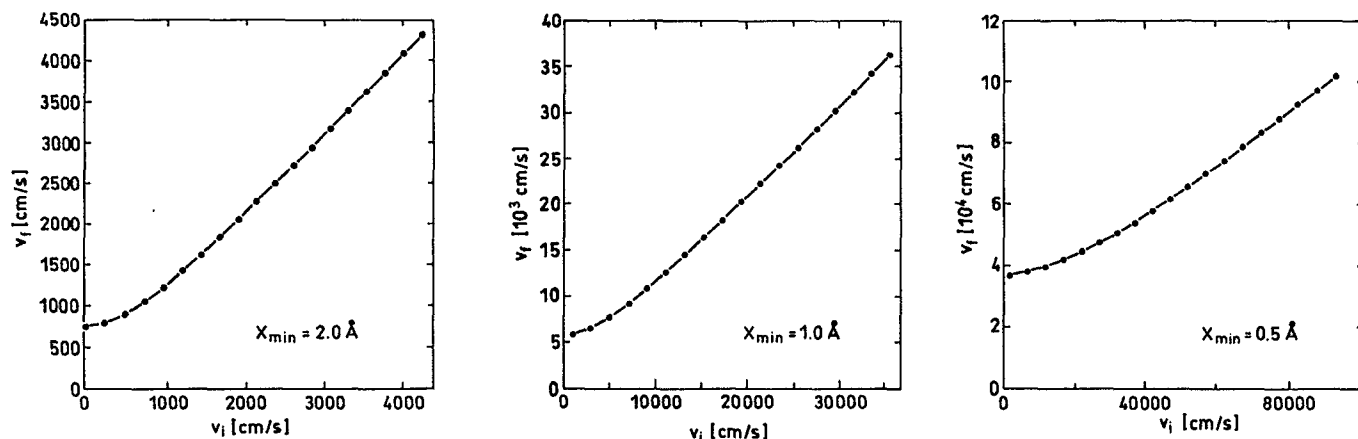


FIG. 3. Dependencies of final on initial velocity for $x_{\min} = 0.5, 1.0, 2.0 \text{ \AA}$; the parameters μ, m, a, γ are as in Fig. 1.

$$\Delta v = \frac{6\mu^2}{ma^4\gamma} \Delta\rho. \quad (8)$$

This velocity change occurs in addition to the change due to the adsorption potential. The force arising from this potential is responsible for the elastic scattering and inverts the normal component of the velocity. We substitute here the expression for $\Delta\rho$ obtained by integrating the quenching probability along a classical trajectory in the vicinity of the turning point $x = x_0 + t^2 F_0/2m$,

$$\Delta\rho = 1 - \left[\exp \int_{-\infty}^{\infty} \frac{\gamma a^4}{(x_0 + F_0 t^2/2m)^4} dt \right] \quad (9)$$

with x_0 and F_0 being the coordinate and force evaluated for the potential, Eq. (7) at the turning point $U(x_0) = E_{\text{kin}} \ll U_{\text{ads}}$. We obtain

$$\Delta v = \frac{15\pi\mu^2}{x_{\min}^3} \left(\frac{m}{3U_{\text{ads}}} \right)^{1/2}. \quad (10)$$

This formula explains the ratio of

$$\frac{\Delta v(x_{\min} = 0.5)}{\Delta v(x_{\min} = 1)} = \frac{\Delta v(x_{\min} = 1)}{\Delta v(x_{\min} = 2)} = 8 \quad (11)$$

at $v_{\text{initial}} \rightarrow 0$ observed in the numerical solutions represented in Fig. 3.

A consistent quantum-mechanical description is given in the Appendix and shows that the classical results can be seen as an average over two qualitatively different types of trajectories—a single elastic one with no change of the velocity and a swarm of “weakly populated” ($\sim \Delta\rho$) superelastic trajectories with a distribution of energy in the x direction

$$w(E_x) = \frac{2\pi\gamma(a/x_0)^4}{(E_x - 2\mu^2/x_0^2)^2 + \gamma^2(a/x_0)^8}. \quad (12)$$

We will further discuss the difference between the classical and quantum-mechanical approaches in the Appendix.

III. RESONANT INTERACTION OF AN EXCITED MOLECULE WITH A COVERED DIELECTRIC SURFACE

Let us consider the role of the van der Waals interaction for the more complex case of a molecule interacting with a

dielectric surface covered by a monolayer of adsorbed molecules of the same kind. This particular case illustrates the general situation when the existence of energy band edges leads to repulsion of the free molecule. The essence of the phenomenon is as follows: First, due to the dipole–dipole interaction the excitation of the free molecule may be transferred to the molecules on the surface. The same interaction among the adjacent molecules leads to a series of subsequent transitions of the excitation among them. This exciton propagation effect thus becomes responsible for the quenching. Second, in the presence of the excitation the dipole–dipole interaction has resonant character and hence the same value of the dipole moment affects the translational degrees of freedom much more effectively than the typical van der Waals forces among unexcited molecules. Both of these circumstances lead to a change of the molecular trajectory as a result of the force accompanying the quenching process. Here we will use a quasiclassical approach to the problem, i.e., describe the translational degrees of freedom classically and the internal ones quantum mechanically. A consistent semiclassical approach is discussed in the Appendix.

The explicit expressions for this force and the quenching probability result from the exciton dynamics on the surface that will be described here by the following Schrödinger equation:

$$\begin{aligned} i\hbar\dot{\psi}_1 &= \mu^2 \sum_{n,m} \frac{\psi_{n,m}}{[x^2 + (y - y_{n,m})^2 + (z - z_{n,m})^2]^{3/2}}, \\ i\hbar\dot{\psi}_{n,m} &= \Delta\psi_{n,m} + \sum_{n',m'} V_{n,m}^{n',m'} \psi_{n',m'} \\ &\quad + \frac{\mu^2\psi_1}{[x^2 + (y - y_{n,m})^2 + (z - z_{n,m})^2]^{3/2}}. \end{aligned} \quad (13)$$

It is thus assumed that the excited molecule at the point x, y, z interacts with molecules adsorbed at the surface $x = 0$ and located at y_{mn}, z_{mn} . The parameter Δ denotes the shift of the transition energy of the adsorbed molecules relative to the free ones. The variables ψ_1 and ψ_{nm} represent the complex probability amplitudes for the excitation of the free molecule and of the surface molecules, respectively. The matrix ele-

ments $V_{nm}^{n'm'}$ are due to the interaction among the surface molecules and are responsible for exciton propagation, μ being the dipole moment. We assume for simplicity that the adsorbed molecules form a square lattice on the surface with a lattice constant b , i.e., $y_{mn} = bn$, $z_{mn} = bm$, and that the interaction $V_{nm}^{n'm'}$ is nonzero only for nearest neighbors $V_{n,m}^{n\pm 1,m} = V_{n,m}^{n,m\pm 1} = \mu^2/b^3$. We also neglect the variation of the interaction with the displacement along the surface, i.e., the velocities in y and z directions— v_y and v_z —are conserved. The interaction of a particle with excitons is assumed to be instantaneous and no retardation of electromagnetic interaction is taken into account. It implies that the Hamiltonian corresponding to Eq. (13) is independent of the kinetic energy of the particle. The motion of the particle will be considered classically in a self-consistent way. Fourier transforming Eq. (13) in n and m leads to

$$i\hbar\dot{\psi}_1 = \int G(p,q,x)\psi_{p,q}dpdq, \quad (14)$$

$$i\hbar\dot{\psi}_{p,q} = \left(\Delta - 2\frac{m^2}{b^3}\cos\frac{pb}{\hbar} + 2\frac{m^2}{b^3}\cos\frac{qb}{\hbar} + v_y p + v_z q \right) \psi_{p,q} + G(p,q,x)\psi_1,$$

where

$$\psi_1(E) = \frac{1}{2\pi i} \left[E - \int_{-\pi}^{\pi} \frac{G^2(p,q)dpdq}{E - \Delta + 2(\mu^2/b^3)\cos(pb/\hbar) + 2(\mu^2/b^3)\cos(qb/\hbar) - v_y p - v_z q} \right]^{-1}. \quad (17)$$

The expression (17) is an analog of the well-known Fano formula²⁵ with the specific dependence of the square interaction matrix element and the level density distribution in the band. Figure 4 illustrates this dependence for the case $v_y = v_z = 0$.

The singularities of Eq. (17) determine the behavior of the system. If $\Delta \gg G$ the real part of the integral in Eq. (17) is responsible for the dependence of the energy shift on x , i.e., for the force acting on the molecule. The imaginary part is responsible for the quenching. The main contribution to the

$$G(p,q,x) = \frac{\mu^2}{b} \sum_{n,m} \frac{\exp(-inpb/\hbar - imqb/\hbar)}{(x^2 + b^2n^2 + b^2m^2)^{3/2}} \sim \frac{\mu^2}{b^2} \frac{\exp[-(p^2 + q^2)^{1/2}x/\hbar]}{x}. \quad (15)$$

The variables p and q have a clear meaning—they are the quasimomenta of the exciton on the surface. The factor before $\psi_{p,q}$ on the right-hand side of the second equation (14) expresses the dispersion law of the excitons.

Equations (14) and (15) are supplemented by Newton's equation of motion

$$m\ddot{x} = -\frac{\partial U}{\partial x} + 2\operatorname{Re}\psi_1^*(t) \int \frac{\partial G(p,q,x)}{\partial x} \psi_{p,q}dpdq, \quad (16)$$

where the last term represents the quantum average force due to the dipole-dipole interaction. We make a preliminary analysis of Eq. (14) by assuming $x = \text{const}$. By Fourier transformation in time and with $\psi_1 = 1$ as an initial condition, the elimination of $\psi_{p,q}$ from Eq. (14) yields

real part (force) is from the interaction of the level with the detuned states at the bottom of the band. Interaction with resonant states leads to quenching as a result of the imaginary part of the pole at

$$E - \Delta = v_y p + v_z q - 2\mu^2 b^{-3} \cos(pb/\hbar) - 2\mu^2 b^{-3} \cos(qb/\hbar).$$

For $\Delta b^3/4\mu^2 - 1 \ll 1$ the cosines can be expanded into power series around the point $p, q = 0$. Assuming $V \ll 4\mu^2 b^{-3} - \Delta$, these values are found to be equal to

$$\begin{aligned} \operatorname{Re} I &= \frac{\pi\mu^2 b}{2x^4} \frac{1}{E + 4\mu^2 b^{-3} - \Delta}, \\ \operatorname{Im} I &= \frac{\pi^2\mu^2}{bx^2} \exp\left\{ \frac{-2xb^2}{\mu^2} \right. \\ &\quad \times [(v\hbar/2b)^2 + E + 4\mu^2 b^{-3} - \Delta]^{1/2} \} \\ &\quad \times \left[I_0\left(\frac{\hbar b v x}{\mu^2}\right) - \frac{v\hbar}{2b(E + 4\mu^2 b^{-3} - \Delta)^{1/2}} \right. \\ &\quad \left. \left. \times I_1\left(\frac{\hbar b v x}{\mu^2}\right) \right] \right], \end{aligned} \quad (18)$$

where $v = (v_y^2 + v_z^2)^{1/2}$ and $I_{0,1}$ are Bessel functions. One can see that as a result of the repulsion between the state corresponding to excitation of the free molecule and the state

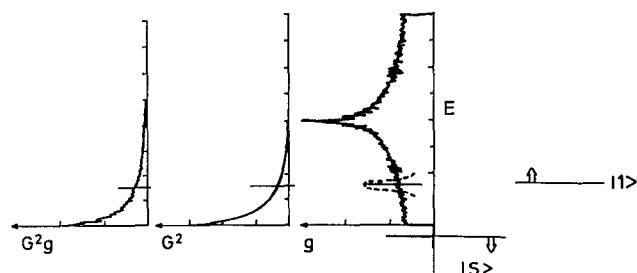


FIG. 4. Density of the levels g , squared interaction G^2 , and transition probability gG^2 as functions of energy for $v_y = v_z = 0$. Splitting of a single level from the bottom of the exciton band.

corresponding to excitation at the bottom of the band, the dipole-dipole interaction leads to an increase of the potential energy of the excited molecule. Hence, contrary to the previous case, the molecule is repelled from the surface. The force and the quenching rate are now qualitatively different not only because of the different dependence on the coordinate but also due to the fact that both of them are influenced by the transverse velocity as well.

One point is important for the further analysis. As a result of the interaction one level detaches to form a single state below the bottom of the exciton band. In other words, Eq. (17) has one additional singularity—a pole at $E < 4\mu^2/b^3$. The energy gap between this level and the band is determined by setting the denominator in Eq. (17) equal to zero, and increases when the particle approaches the surface. It equals

$$\delta E = -\frac{\mu^2}{bx^2} \exp\left[-C - \frac{4 - \Delta b^3 \mu^{-2}}{2\pi} \left(\frac{x}{b}\right)^2\right] \quad (19)$$

if $\delta E \ll 1$, $v_x = v_y = 0$, and C is Euler's constant. When this state is populated it provides an attraction between the surface and the particle and corresponds to exciton capture by the dipole-dipole interaction in the vicinity of the latter. This phenomenon is inoperative when the interaction is switched on adiabatically. However, it can play an important role in the dynamical process characterized by a finite width of the perturbation frequency spectrum.

One interesting phenomenon should also be mentioned. Contrary to the case of scattering at a metallic surface, the interaction with a monolayer of adsorbed molecules on a dielectric surface is repulsive; the approaching molecules now may become captured by the adsorption potential for certain ranges of the parameters. Indeed, the dipole-dipole interaction which decelerates the particle on its way towards the surface vanishes after quenching near the turning point and hence cannot accelerate it on its way back. In other words, the particle loses its kinetic energy.

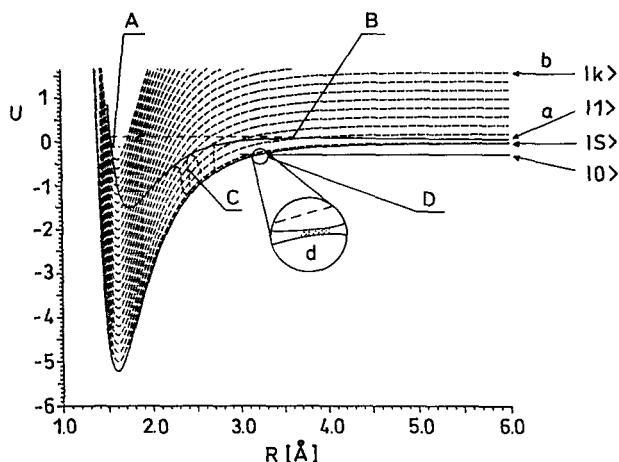


FIG. 5. Translational terms, corresponding to different location of the excitation. (a) Excitation of the free molecule, (b) excitation at the surface, (c) dynamical oscillations, (d) radiative transition. Potential energy in arbitrary units.

The main feature of this process is illustrated by Fig. 5, where the potential curves for the cases of the excitation located either at the molecule or at the surface are plotted as functions of the distance x . The Franck-Condon points near the surface (A) are responsible for the quenching process. There the repulsion induced by dipole-dipole interaction is lifted and a slow particle may become trapped by the surface. Because of the rather large velocity of the molecule in this region the frequency spectrum of the interaction is rather wide and hence nonresonant transitions to the detached level mentioned above may play a notable role. For a large dipole moment of molecular transition or a rather small translational velocity in the direction of the surface, the repulsion force should be taken into account even at long distances. The term crossing far from the surface (point B) can be responsible for the trapping process as well. Figure 6 shows the swarm of trajectories close to the critical one for this case.

We considered the dynamical process by a numerical solution of Eqs. (14)–(16), substituting parameters corresponding to the interaction of CO molecules with a CO layer on the NaCl surface. The vibrational-rotational spectrum of CO molecules in the gas phase is well known²⁶ and spectral data for adsorbed molecules are represented in Ref. 20. The IR-absorption line of CO adsorbed on NaCl at 70 K is shifted by almost 12 cm^{-1} to the short-wavelength side with respect to the frequency of the free CO molecule transition. The linewidth is about 0.4 cm^{-1} , and at least half the estimate μ^2/b^3 for the typical energy of interaction at $\mu = 0.1 \text{ D}$, $b = 3.9 \text{ \AA}$,²⁰ and thus at least 16 times smaller than the exciton bandwidth. This latter circumstance may look strange at first sight, but is, in fact, quite natural if we recall that for an ideal surface at zero temperature only one of the levels at the bottom of the band interacts with radiation. Its quasimomentum vector coincides with the projection of the wave vector of the photon on the surface. At higher temperatures this state adopts a finite linewidth because of transverse relaxation due to the interaction with bulk phonons.

The vibrational absorption spectrum of gaseous CO has a rotational structure. In a diatomic molecule like CO the Q branch of vibrational-rotational transitions is absent and the P and R branches have a rotational constant $B = 1.93 \text{ cm}^{-1}$.²⁶ In a quantum state with angular momentum $J = 3$ the transition frequency in the R branch thus almost coincides with the absorption line of CO on NaCl, being much

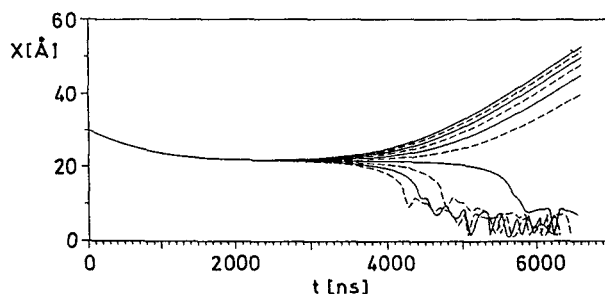


FIG. 6. The swarm of trajectories near the critical trajectory.

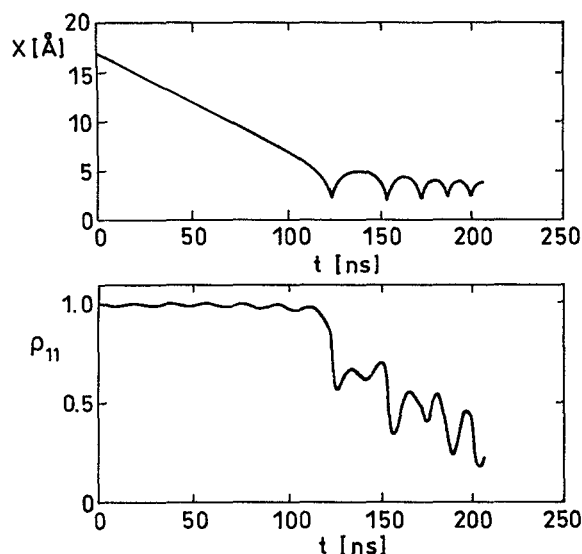


FIG. 7. Trajectory (top) and excited-state population (bottom) of a free molecule for the case $J = 3$.

less than the typical interaction μ^2/b^3 . This case may be treated by classical trajectory methods. Of course in the present consideration we do not take into account any other possibility for rotational energy transfer to the translational degrees of freedom except by the vibrational-rotational radiative transition $R3$. Thus we assume that the direct transformation of rotational energy into a translational one is an independent process which contributes to the nonelastic scattering only for times outside the range considered.

Numerical solutions of the system (14)–(16) were performed in order to obtain the trajectory $x(t)$, the population of the excited state of molecule as a function of time $\rho(t)$, and the distribution of population over exciton energy and over quasi-momenta (p, q) of the excitons as the output of this computation. For this purpose we discretized the quasi-momentum space, using typically 20×20 cells in the (p, q) plane. We used $U_{\text{ads}} = 1137 \text{ cm}^{-1}$, $x_{\text{min}} = b = 3.9 \text{ Å}$ as the parameters of the adsorption potential. Figures 7 and 8 represent the results of the calculation for $J = 3$, transverse velocities of CO molecule $v_y = 60 \text{ m/s}$, $v_z = 30 \text{ m/s}$, and a perpendicular velocity somewhat below the threshold for capture— $v_x = 6 \text{ m/s}$. As a result of the interaction with the surface the molecule may become trapped. Even in the case when the detuning of the molecular level with respect to the bottom of the band is negative at $v_y = v_z = 0$, it comes into resonance with the exciton states at larger transverse velocities because of the energy shift $pv_y + qv_z$. After the collision event these states are populated as a consequence of partial quenching of the incident molecule. Since the interaction of a molecule with a copropagating exciton is larger than that with a contrapropagating one of the same energy the distribution of population over quasimomenta is asymmetric.

CO molecules in other rotational states are also affected by the processes of repulsion and quenching and undergo inelastic and superelastic collisions. Figures 9–12 represent the trajectory, the population, and the distribution of excitations among the energy levels and the quasimomenta of exci-

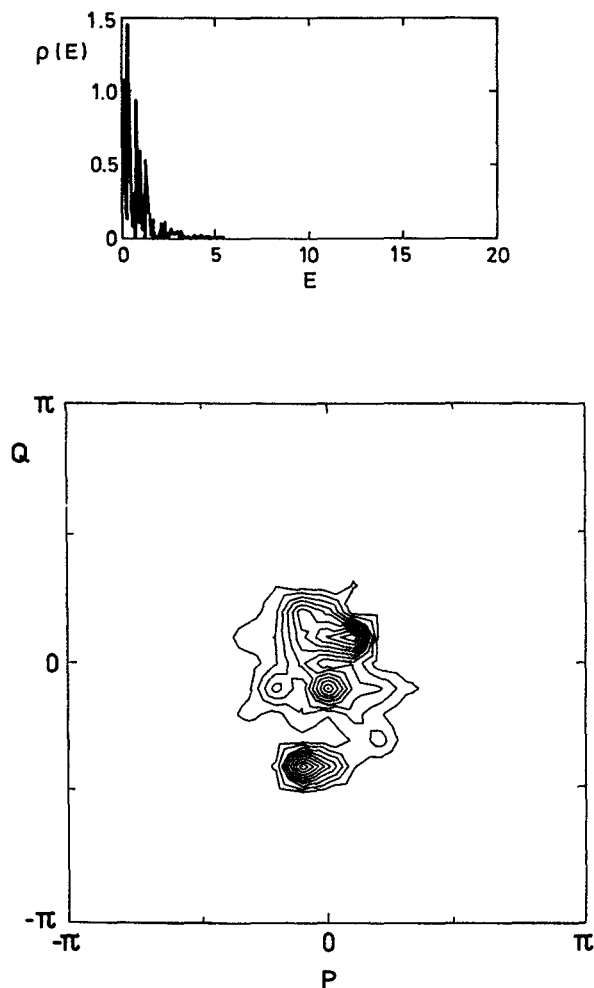


FIG. 8. Population distribution (top curve, in arbitrary units) over the energy (in units of μ^2/a^3) and a map of quasimomenta distribution (bottom), step size 0.1. Quasimomenta scale is \hbar/a , and values of the quasimomenta belong to the interval $(-\pi, \pi)$. The decrease of the envelope of the energy distribution has physical meaning. It shows that only states at the bottom of the band are involved in the process. The structure of this dependence has no physical meaning, but rather is an artifact resulting from discretizing the quasimomenta in the numerical calculations.

tions for the cases $J = 2$ and $J = 4$. The impact character of the process leads to a distribution of population over the band states proportional to the squared matrix element of the interaction. The molecule in the rotational state $J = 2$ loses its translational energy as a result of the quenching while the energy of the quantum system increases. For $J = 4$ the opposite is the case and the translational degree of freedom gains the energy.

These cases are in qualitative agreement with a consistent quantum-mechanical treatment but nevertheless drastically differ from the latter. The main reason is that the transitions take place with a considerable exchange of energy between the classical and the quantum parts of the system. The quantum nature of this phenomenon should manifest itself in a large dispersion of the results obtained. Indeed, energy conservation allows the existence of two types of particle trajectories after collision—the single elastic one corre-

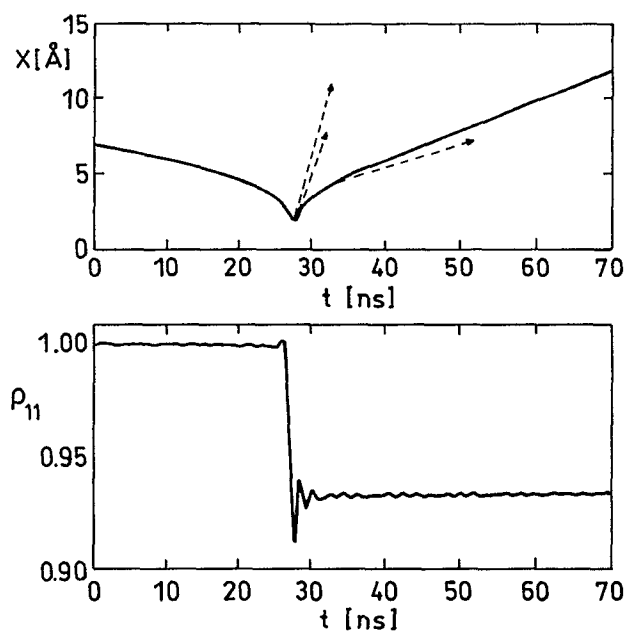


FIG. 9. Trajectory and population for the case $J = 4$. The classical trajectory method gives a superelastic collision. The quantum description should give different trajectories (indicated by dashed lines).

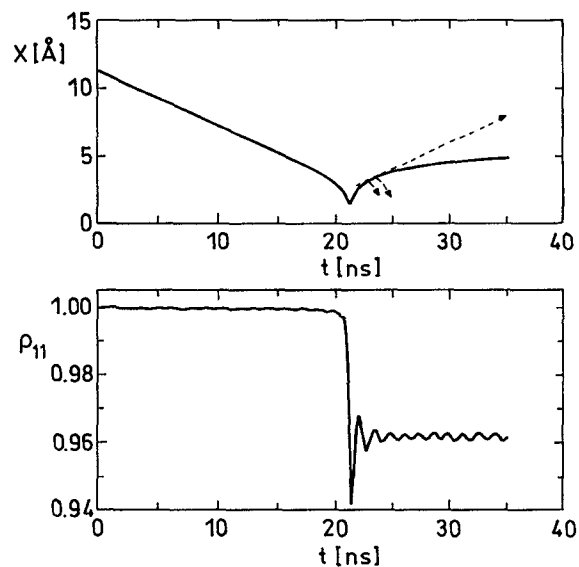


FIG. 11. Trajectory and population as in Fig. 9 for the case $J = 2$. The classical trajectory method gives inelastic collisions.

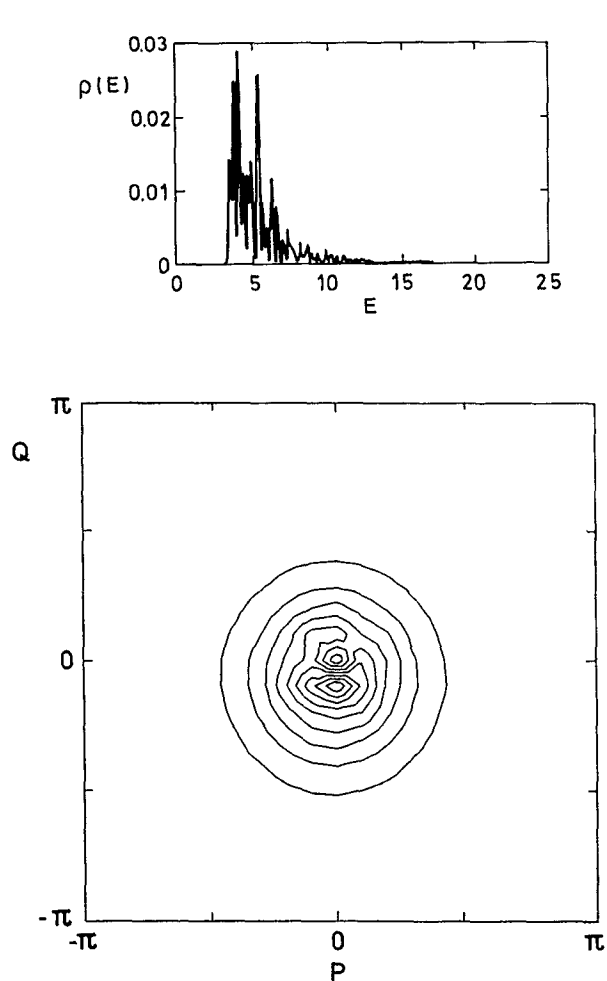


FIG. 10. Population distribution over energy (top) and map of quasimomenta distribution for the case $J = 4$. Scaled variables are used (see capture of Fig. 8).

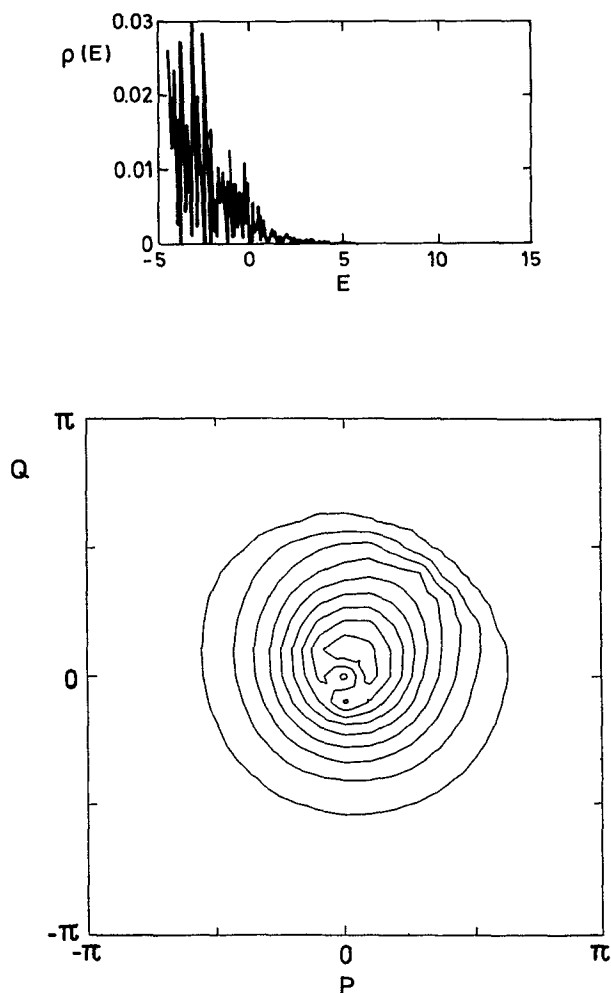


FIG. 12. Population distribution over energy and map of quasimomenta distribution as in Fig. 10 for the case $J = 2$.

sponding to translational energy conservation, and a swarm of nonelastic trajectories with a dispersion determined by the energy distribution of population over the exciton band. At the same time the classical method gives just the quantum-weighted mean trajectory. It ignores the facts that for inelastic scattering and negative detuning there is a set of trapped trajectories besides the single elastic one, while for positive detuning there is a swarm of highly superelastic trajectories with a large angular dispersion. Both these effects manifest themselves just in slight shifts of the classical trajectories because of the small probability of the inelastic processes.

IV. HEAVY-PARTICLE INTERACTION WITH AN ADSORBED MONOLAYER IN THE PRESENCE OF A LASER FIELD

A heavy particle interacting with a surface in the presence of a laser field often moves slow enough that it can absorb many laser quanta on its way towards the surface. Of course the intensity of the laser field determines the rate of photon absorption and thereby the specific values of velocity and mass when a particle has to be considered as heavy and slow.

We now consider this problem with the following approach. We assume the particle to be at a given distance x from the surface and calculate the momentum acquired as a result of a single act of photon absorption and subsequent quenching. Multiplication of this value by the absorption probability yields the net force. In order to investigate this process we have to supplement Eqs. (14) and (15) by an

equation describing the ground-state dynamics and to insert the corresponding term responsible for excitation into Eq. (14). The complete set of equations then takes the form

$$\begin{aligned} i\hbar\dot{\psi}_0 &= V\psi_1, \\ i\hbar\dot{\psi}_1 &= \delta\psi_1 + V\psi_0 - \int G(p,q,x)\psi_{p,q}dp dq, \\ i\hbar\dot{\psi}_{p,q} &= \left(\Delta - 2\frac{\mu^2}{b^3}\cos\frac{pb}{\hbar} + 2\frac{\mu^2}{b^3}\cos\frac{qb}{\hbar} + v_y p + v_z q\right)\psi_{p,q} \\ &\quad + G(p,q,x)\psi_1, \end{aligned} \quad (20)$$

where $V = \mu E$, δ is the detuning of the laser from the frequency of the free-particle transition, and G is given by (15). We do not take into account the direct excitation of adsorbed molecules, since the excitons interacting with the molecule are distinct from those interacting with the radiation. Indeed, at zero surface temperature and because of the phase-matching condition, the exciton interacting with the radiation possesses a quasimomentum of the same order as the photon. On the contrary, excitons responsible for quenching have quasimomenta of the order of the reciprocal distance between the molecule and the surface. The absorption line becomes broadened at nonzero temperatures by the dephasing interaction with phonons.²⁷ This process is, however, negligible since it involves three or more particles.

After Fourier-Laplace transformation in time $t \rightarrow \epsilon$ and assuming $\psi_0(t=0) = 1$, we get

$$\begin{aligned} \psi_0 &= \frac{i(\epsilon\hbar - \delta\hbar - I)}{\epsilon\hbar(\epsilon\hbar - \delta\hbar - I) - V^2}, \\ \psi_1 &= \frac{-iV}{\epsilon\hbar(\epsilon\hbar - \delta\hbar - I) - V^2}, \\ \psi_{p,q} &= -\frac{G(p,q)}{\epsilon\hbar - \Delta + 2\mu^2 b^{-3} \cos(pb/\hbar) + 2\mu^2 b^{-3} \cos(qb/\hbar) - v_y p - v_z q} \psi_1, \end{aligned} \quad (21)$$

where the value of I is determined by Eq. (18). The force acting on the free particle is

$$\langle F(t) \rangle = 2 \operatorname{Re} \psi_1^*(t) \int \frac{\partial G(p,q,x)}{\partial x} \psi_{p,q} dp dq. \quad (22)$$

By an integration in time we obtain the momentum transferred to the surface as a result of the quenching. In the Fourier representation this is given by

$$\delta p = \int dp dq d\epsilon \frac{G(p,q,x) [\partial G(p,q,x)/\partial x] \psi_1(\epsilon) \psi_1^*(\epsilon)}{\epsilon\hbar - \Delta + 2\mu^2 b^{-3} \cos(pb/\hbar) + 2\mu^2 b^{-3} \cos(qb/\hbar) - v_y p - v_z q} + \text{c.c.} \quad (23)$$

When multiplied by the absorption cross section this expression gives the force acting on the particle.

In the case $\delta \ll 1$, instead of the direct solution of Eq. (21), one may use the explicit form of photon absorption cross section given by the Karplus-Schwinger formula.²⁸ We get as a result

$$F = \frac{1}{2} \frac{\partial \operatorname{Re} I}{\partial x} \frac{V^2}{(-\delta + \Delta + \operatorname{Re} I)^2 + (\operatorname{Im} I)^2 + V^2}, \quad (24)$$

which is seen to represent the force acting on the particle in the excited state multiplied by the quantum average population of this level. The force is repulsive since excited particles increase their energy when approaching the surface. The main point is a sharp dependence of the force on coordinates via the resonant denominator. If the detuning is small enough then the resonance condition is fulfilled at large distances where the quenching rate is sufficiently small ($\sim 10^{-5}$ s if $\mu = 0.1$ D, $x = 100$ Å, $b = 10$ Å). Thus radiation of sufficiently low intensity is capable of saturating the

transition. In this case the potential difference corresponding to the repulsive force can be estimated by the value μE .

With the laser tuned to a frequency close to the bottom of the exciton band, the resulting attractive force is even smaller. In this case the main contribution to the expression for ψ_0 in Eq. (21) is from the region where $\epsilon\hbar \sim \delta\hbar \sim 4\mu^2 b^{-1} - \Delta$. After substitution of the explicit expression for I we get

$$F = - \frac{4\pi^2 \mu^2 b}{x^5 (4 - b^3 \mu^{-2} \Delta)} \times \frac{V^2}{[\delta\hbar + \pi\mu^2 b / 2(4 - b^3 \mu^{-2} \Delta)x^4]^2}. \quad (25)$$

In this case the excitation of the states in the bottom of the band takes place via the highly detuned excited level of the free molecule. The level of the locked exciton becomes involved in the process as well. This level is detached from the bottom of the band and now is much closer in energy to the initial state. Thereby its influence dominates the overall interaction, resulting in attraction. Similar to the previous case the band continuum is responsible for the quenching.

In more intense fields the locked exciton state can be excited by a process analogous to a radiative collision²⁹ at point *D* (Fig. 5) on the way of the molecule towards the surface. For a slow molecule the Landau-Zener formula gives a probability for this transition close to unity and thus the dipole-dipole interaction makes an additional contribution to the adsorption potential. We recall that for light particles this state can be populated mainly at the point of the closest approach.

All considerations above correspond to the case when the quenching takes place because of the interaction with surface states, e.g., of electron-hole pairs or adsorbed molecules. But quite the same situation arises for a quantum particle quenched by the absorption in the metal bulk. This is the case of excited atoms possessing a large dipole moment and a high frequency of transition. If the latter is higher than the frequency of a surface plasmon, the bulk absorption will give the main contribution to the process. Now instead of Eqs. (2) and (3) one should use the following system to describe the dynamics of the process:

$$\begin{aligned} m\ddot{x} &= - \frac{3\mu^2}{x^4} \operatorname{Re} \frac{\epsilon - 1}{\epsilon + 1} \rho_{\text{ex}}, \\ \dot{\rho}_{\text{ex}} &= - \frac{\mu^2}{x^3 \hbar} \operatorname{Im} \frac{\epsilon - 1}{\epsilon + 1} \rho_{\text{ex}}, \end{aligned} \quad (26)$$

where ϵ is the complex dielectric constant of the metal, and ρ_{ex} is the population of the excited state. If the quenching process is very fast, then for a particle making the transition at point *x* we have

$$\delta p = m\Delta\dot{x} = 3 \frac{\operatorname{Re}[(\epsilon - 1)/(\epsilon + 1)]\hbar}{\operatorname{Im}[(\epsilon - 1)/(\epsilon + 1)]x}, \quad (27)$$

and for typical atomic parameters δp can be much higher than the value given by Eq. (23).

V. DISCUSSION

Let us start a discussion of the results by giving some numerical estimates. As already mentioned above the influence of the dipole-dipole interaction on the motion of the particle near a metallic surface can be significant in yielding a maximal change of velocity of as much as 10^6 cm/s for the case of complete quenching of excitation. But even if, as a consequence of the translational dynamics induced by the adsorption potential, the interaction time is too small to provide full quenching, the gain in velocity may be still considerable, about 10^4 – 10^5 cm/s, depending on the distance of closest approach. The large superelasticity of the collision can still be observed in this case. The associated gain in translational energy exceeds the thermal energy at $T = 300$ K. We mention here that only if the transition from the excited state to the ground state of the particle takes place at rather large distances from the surface, e.g., for large values of transition dipole moments, this effect could be unambiguously attributed to the action of the van der Waals forces. Otherwise, it must be considered together with other forces causing the transition.

Contrary to the case of the metallic sample the dipole-dipole interaction at large distances between the free excited molecule and a monolayer of molecules adsorbed at a dielectric surface may lead to inelastic collisions and thus to trapping of particles. Since the adsorbed molecules have a rather sharp line in the photon absorption spectrum, the quenching process is less efficient and can provide a significant change in the translational motion only for relatively slow particles. The typical values of the velocities in the normal direction corresponding to trapping for CO molecules at $J = 3$ on a CO-covered NaCl surface are about 6 m/s, and thus the appropriate translational energy is approximately four orders of magnitude smaller than in the previous case.

Heavy molecules with the same translational energy possess a much lower speed, and the value of the photon field strength plays a more significant role. But the influence of this effect on the single act of surface scattering is rather weak. For a spacing of the molecules on the surface of 10 \AA , a distance of the free molecule of 100 \AA and a laser intensity of 1 W/cm^2 , an estimate of the additional adsorption potential in accordance with Eq. (25) yields

$$\delta E \sim \pi \frac{E^2 \mu^2}{\hbar \Delta} \sim 3 \times 10^{-13} \text{ cm}^{-1}. \quad (28)$$

For the same intensity the expression (24) gives an energy difference $\delta E \sim 5 \times 10^{-3} \text{ cm}^{-1}$.

Excitation of the system to the locked exciton state causes an additional potential of about $\mu^2/b^3 \sim 1 \text{ cm}^{-1}$. The radiative transition to this state during the time the particle approaches the surface requires the presence of an intense laser field. For the effect to manifest itself to a full extent the Landau-Zener parameter $(E\mu)^2/\hbar v_x (\delta E)_x'$ has to be of the order of unity or more. Substituting Eq. (19) for δE using $v_x = \sqrt{2mT}$, $T = 300 \text{ K}$ for v_x at $m = 100m_p$, $\mu = 0.1 \text{ D}$, we obtain for the intensity

$$I [\text{W}] \gtrsim 10^{14} \left(\delta - 4 \frac{\mu^2}{b^3} + \Delta \right) (\text{cm}^{-1}). \quad (29)$$

This implies that for detunings of the order of the adsorbate linewidth, the laser field becomes comparable with typical atomic fields.

Typical values of the transferred momentum evaluated by Eq. (27) for particles with $m = 10m_p$ correspond to a change in the velocities of about $\Delta v \sim 10^4$ cm/s.

The phenomenon under consideration seems to be observable experimentally. Atomic and molecular-beam scattering^{30–32} are the most promising methods for this purpose. The largest effect is expected in the case of electronically excited particles which have the maximal dynamical dipole moment. The molecules are accelerated before attaching to the surface by the attraction of the image dipole up to velocities of the order of several 10^3 m/s and conserve this velocity after quenching and reflection. Superelastic scattering at an angle almost perpendicular to the surface is expected.

Another phenomenon—the trapping of a molecule as a result of the repulsion lifted after the quenching due to vibrational exchange with molecules adsorbed at the dielectrical surface—seems more difficult to observe. The interaction of the translational and rotational degrees of freedom^{30,31} may result in superelasticity which can mask this phenomenon. We did not investigate this effect for different molecules because of the lack of experimental data necessary for this purpose. For the only case considered here, i.e., CO on NaCl, the limiting velocities of capture are of the order of several meters per second and depend slightly on transverse velocities. If the energy of the molecular beam is about kT at room temperature, this implies that the typical angles for observation of this process are of the order of several degrees. Of course in the experiments with slow beams this angle can be much larger. Transitions at large distances (point *B* at Fig. 5) do not play any significant role in this case. They become essential for a transition dipole moment of the order of 1 D.

The last process considered in this paper—laser-enhanced dipole-dipole attraction to the surface—is even weaker at reasonable magnitudes of laser intensity. It could hardly be observed in beam-scattering experiments. Nevertheless, in situations when the elementary act of the photon absorption and subsequent quenching of this excitation repeats itself many times during a collision it can become important. Some experimental results obtained in the laser-controlled diffusion through porous IR-transparent materials³³ may be attributed to the action of this mechanism. Even a very small change of the adsorption potential induced by a laser field entering the Boltzmann exponents

can in this case affect the kinetic coefficients responsible for gas diffusion, and when multiplied by the number of free paths at the typical distance of the system may result in a considerable effect.

APPENDIX

In order to determine the translational behavior of the particle in the framework of a consistent quantum description we use the quasiclassical approach. In terms of the Schrödinger equation one has

$$E\psi_1 = \left(\frac{\hat{p}^2}{2m} + U \right) \psi_1 + \sum_k V_k \psi_k, \quad (A1)$$

$$E\psi_k = \left(\frac{\hat{p}^2}{2m} + U + E_k \right) \psi_k + V_k \psi_1.$$

It seems worth mentioning that these equations take into account both the processes of the excitation transfer from the particle to the surface and the reverse one. After the substitution of ψ_k from the second equation into the first one we use for ψ_1 the form

$$\psi_1 = a(E) e^{iS(E,x)/\hbar}. \quad (A2)$$

This system of equations is solved by implementing the well-known quasiclassical approach. It is valid if the high-order derivatives of the action S are small when compared with the corresponding powers of the low-order derivatives, i.e., when the de Broglie wavelength is small compared to the typical range of the potential. In the present case the product of the typical quenching time and the velocity of the particle should also be large compared to the wavelength. It implies that the quasiclassical approach is valid if the quenching process takes place rather far from the surface. Replacing the summation by an integration over the continuous spectrum E_k , we get

$$E - \frac{(S'_x)^2}{2m} - U = \int \frac{V^2(x, E_k) g(E_k)}{E - (S'_x)^2/2m - U - E_k + i0^+} dE_k. \quad (A3)$$

This equation implicitly determines the value of the action S which by Eq. (A2) gives the expression used on the right-hand side of Eqs. (A1). After convoluting the latter with the quasiclassical expression of the Green's function of the corresponding homogeneous equation, we obtain

$$\begin{aligned} \psi_k = \int_{-\infty}^{\infty} \frac{a(E)}{2\pi} [E - U(x) - E_k]^{-1/4} [S'_x(x', E)] \\ \times \exp \left[iEt\hbar^{-1} + i\hbar^{-1} \int_{-\infty}^{x'} S'(\chi', E) d\chi' + i\hbar^{-1} \int_{x'}^x \sqrt{E - U(\chi) - E_k} d\chi \right] dx' dE. \end{aligned} \quad (A4)$$

By using the stationary phase method to evaluate the integral (A4) we get the following equation for the saddle point:

$$S'_x(x_{sp}, E) = [E - U(x_{sp}) - E_k]^{1/2}, \quad (A5)$$

which when substituted into Eq. (A3) yields

$$E_k = \int \frac{V^2(x_{SP}, E)g(E)}{E_k - E + i0} dE = \text{P.V.} \int \frac{V^2(x_{SP}, E)g(E)}{E_k - E} dE + i\pi V^2(x_{SP}, E_k)g(E_k). \quad (\text{A6})$$

This equation determines a position of the saddle point for each E_k . With the standard substitution of the square root of the second derivative into the denominator of the integrand we get

$$\psi_k = \int_{-\infty}^{\infty} a(E) [E - U(x) - E_k]^{-1/4} \left[\frac{\partial}{\partial x} \int \frac{V^2(x_{SP}, E_k)g(E_k)}{E_k - E + i0} dE_k \right]^{-1/2} \\ \times \exp \left\{ i\hbar^{-1}Et + i\hbar^{-1} \int_{-\infty}^{x_{SP}} S'(x', E) dx' + i\hbar^{-1} \int_{x_{SP}}^x [E - U(x) - E_k]^{1/2} dx \right\} dE. \quad (\text{A7})$$

If the transitions points are located sufficiently far from the turning point $S'_x = 0$, we can use instead of Eq. (A7) an equivalent equation for the populations

$$\rho(E_k) = \int_{-\infty}^{\infty} \exp \left[-2\pi \int_{-\infty}^x V^2(x', \delta U(x')) \frac{dx'}{\sqrt{S'(x', E)}} \right] \frac{2\pi V^2(x, \delta U(x))g(\delta U(x))}{[E_k - \delta U(x)]^2 + [\pi V^2(x, \delta U(x))g(\delta U(x))]^2} dx. \quad (\text{A8})$$

Here $\delta U(x)$ denotes the principal value of the integral (A6), i.e., the energy shift of the particle level, and E is the initial energy of the particle. Integration over $(S')^{-1/2}dx$ is, in fact, equivalent to an integration in time. The exponent in the integrand represents the population of the initial state at the point x and the fraction is the probability of transition to the level detuned at the value $E_k - \delta U(x)$. The fourth-order root in Eq. (A7) cancels with the density of the translational levels $dE = p dp$.

Expression (A8) represents the rather obvious idea that the width of the energy distribution of population is in an unambiguous correspondence to that of the momenta of the reflected particles. This distribution is wide for collisions with high detuning showing that the classical trajectory method is not very suitable for the description in practice. In other words, the elastic trajectory in this case differs drastically from the inelastic ones, and the latter possess a large dispersion that makes them very distinct among themselves. Vice versa, for the resonant transitions the spectrum of transferred energy is narrow and the classical trajectory method seems to form an appropriate description.

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