Boson creation by an atom moving near a surface

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We consider the various mechanisms for energy transfer by an atom moving in its van der Waals potential a distance z from a surface. For the excahnge of either surface optical phonons at an ionic surface or surface plasmons at a metal surface we obtain transition rates which exhibit a maximum at an optimum atomic velocity and which decay exponentially with z. It is found that single-phonon events do not always dominate the exchange rate. At small z the single-quantum monopole porcess is most important but at larger z the two-quantum dipole exchange term is greater. Single-quantum transfers arising from higher-order processes in the Born series are completely negligible.

In this Rapid Communication we examine the possibilities for energy transfer by an atom moving in the van der Waals potential near a solid surface. The quanta transferred are surface optical phonons in the case of an ionic solid or surface plasmons for a metal. Such considerations are of interest relative to recent experiments on scattering of neutral atoms by metal cylinders[1-4] or to the question of surface-optical-phonon transfer in the very recently developed field of surface phonon spectroscopy using thermal-energy atomic beams.[5-8]

The van der Waals potential between an atom and a surface is logically described as the self-energy of the atom created by the exchange of virtual quanta with the surface[9] in analogy with the corresponding problem of the image potential for a charge near a surface.[10] If the atom is moving sufficiently fast, nonconservative imaginary terms appear in the self-energy corresponding to transfer of real quanta of energy. The van der Waals potential is the result of the mutual polarization of the atom-surface system as the atom is excited to higher states by virtual transfers, but since we consider cases where the atom is not given a real excitation to a higher state, the lowest-order contribution to the energy transfer comes from second-order perturbation theory and is a two-quantum process. The lowest-order single-quantum process comes from third-order perturbation theory and we are able to show that this contribution is negligible in comparison to the two-quantum process.

However, as the atom moves close to the surface a different mechanism for energy transfer appears because the atom interacts with the surface as a collection of charges rather than as a neutral polarizable particle. This "monopole" contribution occurs as the atomic charge distribution overlaps the surface region and gives single-phonon transfers in first-order perturbation theory in a manner similar to that of a bare charge.

In the following we develop expressions for the total inelastic transition rates for all the processes mentioned above. We begin by considering the energy transfers through the mechanism of the multipole expansion of the atom-surface interaction potential. The interaction of a charge Ze with the surface excitation field is given by

$$\phi(\vec{r}) = \sum_{Q} \Gamma_Q \exp(i\vec{Q}\cdot\vec{R} - Q|z|)(a_{\vec{Q}}^{\dagger} + a_{-\vec{Q}}) , \quad (1)$$

where $\vec{Q}$ is the parallel momentum of the surface excitation and $\Gamma_Q^2 = \beta Z e^2 \pi \omega_Q \hbar / L^2 Q$ with $\hbar\omega_Q$ the surface excitation energy, L^2 the surface area, $\beta = 1$ for surface plasmons on metals, and

$$\beta = (\epsilon_0 - 1)/(\epsilon_0 + 1) - (\epsilon_\infty - 1)/(\epsilon_\infty + 1) \quad (2)$$

for surface optical phonons. Regarding the atom as a netural charge distribution, we can make a multipole expansion of the atom-surface interaction $H'(\vec{r})$ as follows:

$$H'(\vec{r}) = \sum_{\vec{Q}} \Gamma_Q [\vec{p}\cdot\vec{\mu}(\vec{Q})] \exp(i\vec{Q}\cdot\vec{R} - Q|z|)(a_{\vec{Q}}^{\dagger} + a_{-\vec{Q}}) + \frac{1}{2}\sum_{\vec{Q}} \Gamma_Q [\vec{p}\cdot\vec{\mu}(\vec{Q})]^2 \exp(i\vec{Q}\cdot\vec{R} - Q|z|)(a_{\vec{Q}}^{\dagger} + a_{-\vec{Q}}) + \cdots ,$$

$$(3)$$

where $\vec{p}$ is the atomic displacement operator and $\vec{\mu}(\vec{Q}) = (iQ_x, iQ_y, -Q)$. The total transition rate from an initial state i to all possible final states is

$$R_i = (2\pi/\hbar) \sum_{f} |T_{fi}|^2 \delta(E_f - E_i) , \quad (4)$$

where to lowest order the transition matrix is given by the second-order term in perturbation theory,

$$T_{fi} = \sum_{l} \langle f|H'|l\rangle \langle l|H'|i\rangle / (E_i - E_l + i\epsilon) , \quad (5)$$

the first-order term not contributing because the atom is never raised to a final excited state. The matrix elements are those of the dipole term of Eq. (3) taken with respect to

the state

$$\phi_l = \exp(i\vec{K}_l \cdot \vec{R} - ik_{lz}z)|l\rangle|n_l\rangle \ , \tag{6}$$

a product of a plane wave for particle motion, an atomic state, and a many-body surface excitation state, respectively.

The transition rate of Eq. (4) can be related to the non-conservative imaginary part of the spatially dependent self-energy in the usual way,[10,11]

$$R_i = \int \langle i|\vec{r}\rangle R_i(\vec{r}) \langle \vec{r}|i\rangle d\vec{r} \ , \tag{7}$$

where $R_i(\vec{r}) = 2\,\mathrm{Im}\Sigma_0(\vec{r})/\hbar$; i.e., $\mathrm{Im}\Sigma_0(\vec{r})$ can be considered as the nonconservative imaginary part of the spatial self-energy.

The dipole matrix elements H_{fi} taken with the eigenstates of Eq. (6) are trivial and we can readily obtain the transition rate as a function of distance z from the surface according to the prescription of Eq. (7). We make the reasonable simplifying assumption that the surface excitation energy ω_Q is independent of $\vec{Q}$ and then use closure relations to perform the sum over the many-body states. This results, for zero temperature, in a direct and exchange term as follows:

$$R_2^p(z) = (16\pi m^2/\hbar^4) \sum_{\vec{Q},\vec{Q}'} \Gamma_{\vec{Q}}^2 \Gamma_{\vec{Q}'}^2 \exp[-2(Q+Q')|z|](\vec{Q}\cdot\vec{Q}'+QQ')^2 \delta(Q^2+Q'^2+2\vec{Q}\cdot\vec{Q}'+2\vec{Q}\cdot\vec{K}_i+2\vec{Q}'\cdot\vec{K}_i+2Q_s^2)$$

$$\times \left\{ \left| \sum_l |z_{l0}|^2 (Q^2 + 2\vec{Q}\cdot\vec{K}_i + Q_s^2 + \vec{q}_l^2)^{-1} \right|^2 \right.$$

$$\left. + \sum_{ll'} |z_{l0}|^2|z_{l'0}|^2 (Q^2 + 2\vec{Q}\cdot\vec{K}_i + Q_s^2 + q_l^2)^{-1} (Q'^2 + 2\vec{Q}'\cdot\vec{K}_i + Q_s^2 + q_{l'}^2)^{-1} \right\} \ , \tag{8}$$

where the atom is moving parallel to the surface with wave vector $\vec{K}_i$ (or velocity $\vec{V}_i = \hbar\vec{K}_i/m$), $Q_s^2 = 2m\omega_s/\hbar$, $q_l^2 = 2m\epsilon_l/\hbar^2$ with ϵ_l the atomic excitation energy measured from the ground state. The factor $(\vec{Q}\cdot\vec{Q}'+QQ')^2$ comes from collapsing the products of the $\vec{p}\cdot\vec{\mu}(\vec{Q})$ assuming that the atomic energies are independent of azimuthal quantum number and z_{l0} is an atomic-state matrix element of the z component of the atomic displacement operator $\vec{p}$.

We now choose to ignore all recoil effects, i.e., all terms

quadratic in Q and Q' in the δ function and in the denominators since their effect can be shown to be completely negligible even for atoms as small as helium. We also neglect the terms involving $\vec{Q}\cdot\vec{K}_i$ in the energy denominators, which has the effect of eliminating high-velocity corrections in the asymptotic region. Then the transition rate can be readily reduced to a single integral over modified Bessel functions of the second kind, and by Fourier transforming the Bessel functions we arrive at the final closed form expression

$$R_2^p(z) = (\beta^2 z^2 e^4 Q_s^{14} m\pi/8\hbar^3 K_i^6) \left| \sum_l |z_{l0}|^2/(Q_s^2+q_l^2) \right|^2 (d^4/db^4)[\exp(-\sqrt{b})(\gamma^4+b^2+4\gamma^2 b)/\sqrt{b}]|_{b=\gamma^2} \ , \tag{9}$$

where $\gamma = 2|z|Q_s^2/K_i$. Upon performing the derivations we obtain for the leading term in the asymptotic region

$$R_2^p(z) \xrightarrow[z\to\infty]{} \beta^2 (3Z^2 e^4\pi m Q_s^{12}/128\hbar^3 K_i^5) \left| \sum_l |z_{l0}|^2/(Q_s^2+q_l^2) \right|^2 \exp(-4|z|\delta)/|z| \ , \tag{10}$$

where $\delta = Q_s^2/2K_i$.

Since this transition rate is a two-quantum process, it is of interest to compare it to the various possibilities for single-quantum exchange. One possibility of single-quantum exchange is from higher-order terms in the perturbation series and this is considered below but found to be relatively unimportant. Another possibility is when the atom is near the solid and the individual charges can interact directly with the surface excitation field. This monopole contribution is so named because it gives a single-quantum contribution from the first-order term in perturbation theory just as does a bare charge.

To obtain this contribution we treat the atom as a point charge Ze surrounded by an electron cloud, $\rho(\vec{r}) = \delta(\vec{r}) - \rho_{el}(\vec{r})$. Each individual element of charge interacts with the surface through the potential of Eq. (1). Thus the total interaction Hamiltonian can be written as

$$H'(\vec{r}) = \int d\vec{r}' \rho(r')\phi(\vec{r}+\vec{r}') \ , \tag{11}$$

which can be Fourier convoluted to appear as

$$H'(\vec{r}) = \sum_{\vec{q}} \exp(-i\vec{q}\cdot\vec{r})\rho_{\vec{q}}\phi_{-\vec{q}} \ . \tag{12}$$

Taking the matrix elements of $H'(\vec{r})$ between states ϕ_f and ϕ_i of Eq. (6) differing by a single created phonon and inserting the result into the transition rate of Eq. (4) gives a total transition rate

$$R_i = \sum_{\vec{q}} (2\pi/\hbar)|\rho_{\vec{q}}\phi_{-\vec{q}}|^2 \delta(\hbar^2(q^2-2\vec{q}\cdot\vec{K}_i)/2m + \hbar\omega_Q) \ . \tag{13}$$

If, as above, we let the atom move parallel to the surface in the x direction and use the prescription of Eq. (7) for determining the spatially dependent transition rate, we arrive at

$$R_0(z) = (m/\hbar^3 K_i) \sum_{Q_y} |(\rho_{\vec{q}}\phi_{-\vec{q}})_z|^2 \ , \tag{14}$$

where $\vec{q} = (Q_s^2/2K_i, Q_y, q_z)$ and the notation $(\rho_{\vec{q}}\vec{V}_{\vec{q}})_z$ means the Fourier component of the product in the direction perpendicular to the surface. To evaluate $R_0(z)$ for a specific case we consider a simple form for the charge distribution $\rho(r)$, that of a hydrogen-like atom in its ground state,[12]

$$\rho(\vec{r}) = \delta(\vec{r}) - \alpha^3 \exp(-\alpha r)/8\pi \ , \tag{15}$$

with $\alpha = 2Z_{eff}/a_0$ and a_0 is the Bohr radius. The necessary Fourier transforms are readily carried out and we have

$$R_0(z) = (\beta Z e^2 Q_s^2/16\hbar K_i) \int_{-\infty}^{\infty} dQ_y Q [2Q^2 + 3\alpha^2 + |z|\alpha^2 (Q^2 + \alpha^2)^{1/2}]^2 \exp[-2|z|(Q^2 + \alpha^2)^{1/2}]/(Q^2 + \alpha^2) \tag{16}$$

with $Q = (Q_y^2 + \delta^2)^{1/2}$. The integral cannot easily be carried out in terms of tabulated functions but the asymptotic expansion is readily evaluated as

$$R_0(z) \underset{z \to \infty}{\longrightarrow} \beta Z e^2 \alpha^4 Q_s^4 \sqrt{\pi}/32\hbar K_i^2 \{\delta^2 + \alpha^2\}^{-7/4} |z|^{3/2} \exp[-2|z|(\delta^2 + 4\alpha^2)^{1/2}] \quad . \tag{17}$$

The decay constant for this single-quantum process $2(\delta^2 + 4\alpha^2)^{1/2}$ includes the decay range α of the charge distribution. This indicates that the monopole process will be most important at small separation where the atomic charge density actually begins to overlap the surface.

The monopole process also contributes to the two-quantum exchange rate just as the dipole contribution obtained above. This can be calculated from second-order perturbation theory to give the transition rate

$$R_2^M \underset{z \to \infty}{\longrightarrow} (Z^2 e^4 m Q_s^4/2^{12}\sqrt{2}\hbar^3 K_i^3 \pi^{7/2}) \frac{[|z|\alpha^2(\delta^2 + \alpha^2)^{1/2} + 2\delta^2 + 3\alpha^2]^4}{(\delta^2 + \alpha^2)^{21/4}|z|^{3/2}} \exp[-4|z|(\delta^2 + \alpha^2)^{1/2}] \quad . \tag{18}$$

There is in addition a two-quantum interference term involving both the monopole and dipole constributions:

$$R_2^{MD} \underset{z \to \infty}{\longrightarrow} Z^2 e^4 \delta^4 m/(4\hbar^3 \pi^{3/2}) \left[\sum_l |z_{l0}|^2/(Q_s^2 + q_l^2) \right] \frac{\{|z|\alpha^2(\delta^2 + \alpha^2)^{1/2} + 2\delta^2 + 3\alpha^2\}^2}{(\delta^2 + \alpha^2)^{9/4}[\delta + (\delta^2 + \alpha^2)^{1/2}]|z|^{3/2}} \exp[-2|z|\delta - 2|z(\delta^2 + \alpha^2)^{1/2}] \quad . \tag{19}$$

For completeness and for comparison we have also considered the lowest-order single-quantum process arising from the multipole expansion. This comes from third-order perturbation theory and involves the quadrupole and dipole terms of Eq. (3). In the asymptotic region the result can be expressed in terms of modified Bessel functions and the decay behavior away from the surface is dominated by an exponential of argument $2|z|\delta = |z|Q_s^2/K_i = 2|z|\omega_s/v_i$ while $R_2^P(z)$ decays with exactly twice that argument. This is the general behavior of a single-quantum versus a double-quantum process.

We have carried out a number of calculations for light atoms moving near ionic as well as metallic surfaces. The summations over atomic states appearing in Eqs. (9) and (19) can be related directly to the atomic polarizability and were evaluated using Padé approximants.[13] An example is shown in Fig. 1 which gives the surface-optical-phonon exchange rates for He moving parallel to a LiF surface at a distance of 1 Å. The single- and double-phonon exchange rates are exhibited separately. It is evident that there is an optimum particle energy for inelastic exchange at somewhat less than 1 eV with the transition rates decreasing rather rapidly for both higher and lower energies. At this separation the two-phonon events [which are dominated by the dipole term of Eq. (9)] are non-negligible but considerably smaller than the single-phonon contribution. The single-phonon rate is that due to the monopole contribution of Eq. (17). The single-quantum process coming from third-order perturbation theory is completely negligible.

Figure 2 gives the ratio of R_0 the single-phonon rate, to the total two-phonon rate T_2 as a function of distance between atom and surface for a particle energy of 1 eV (near the maximum exhibited in Fig. 1). Except for the very smallest separations, the two-quantum rate is dominated always by the dipole contribution of Eq. (9). At distances in the neighborhood of 1 Å the single-phonon exchange dominates the scattering, but at larger separation it is the dipole two-quantum process which is larger. This interesting result is characteristic of all energies except the smallest. Only when the atomic energy is comparable to the surface-optical-phonon energy is the single-quantum ex-

change the largest term for all separation distance. However, under these conditions the exponential decay range parameter $\delta = Q_s^2/2K_i = \omega_s/v_i$ is large and all transfer rates become negligibly small as z becomes appreciable.

Since LiF has a rather large surface-optical-phonon frequency [71 meV (Ref. 14)], it is of interest to consider a crystal such as AgBr which has a surface-optical-phonon fre-
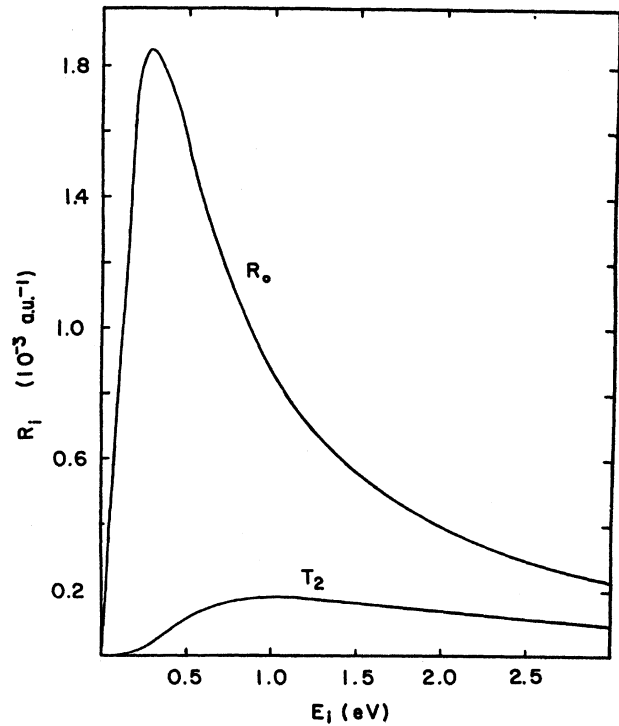

FIG. 1. The one- and two-quantum exchange rates as a function of particle energy for He moving parallel to a LiF surface at a distance of 1 Å. R_0 is the single-surface-phonon transfer rate and T_2 is the total rate for all possible two-phonon processes. The surface optical-plasmon frequency is given by $\omega_s = \omega_{TO}(\epsilon_0 + 1)/(\epsilon_\infty + 1) = 71$ meV (Ref. 14).

quency of 16 meV.[14] The situation is found to be very similar to that for LiF except that the maximum transfer rate occurs at a particle energy of slightly less than 0.1 eV reflecting the smaller phonon frequency. For atomic velocities in the neighborhood of the maximum exchange rates, single-quantum processes dominate for $z < 1.5$ Å and double-quantum processes dominate at larger distances.

We have also considered the exchange of surface plasmons at metal surfaces since the model is virtually identical to that for surface optical phonons. Again there is an optimum particle energy at which the maximum exchange rates occur but this is now in the keV range. It is about 10 keV for the He-Al system which has the relatively large surface plasmon energy of 11.2 eV and it occurs at about 1 eV for He-Cs, where the surface plasmon energy is 2.5 eV. For energies at and above this optimum energy it is the double-plasmon exchange process which dominates and this is due almost entirely to the dipole term of Eq. (9) or (10). Only at lower energies (and where the transition rates are an order of magnitude smaller) do the single-plasmon transfers dominate.

The conclusions that we can draw from this work are similar for the exchange of surface optical phonons at ionic surfaces or surface plasmons at metal surfaces. The major contributors to the inelastic exchange rates are the single-quantum monopole mechanism and the double-quantum dipole process. All other processes examined seem to be relatively unimportant, and in particular single-quantum transfers arising from higher-order terms in the perturbation expansion are totally negligible. The exchange rates decay exponentially with the separation z between surface and atom. As a function of particle energy there is a maximum in the exchange rate at approximately 5 or 10 times the surface-optical-phonon energy, or in the keV range for the exchange of surface plasmons.

An interesting result pertaining to both ionic and metal surfaces is that the single-quantum process is not always dominant. At metal surfaces the single-plasmon process is the most important only in the low-keV range and below, and the single-quantum process is almost negligible at higher energies where the transfer rates are at their maximum. For the exchange of surface optical phonons at ionic surfaces the effect is not so clear cut, but at particle energies which give the maximum inelastic transfer rates the single-quantum process is most important near the surface but for
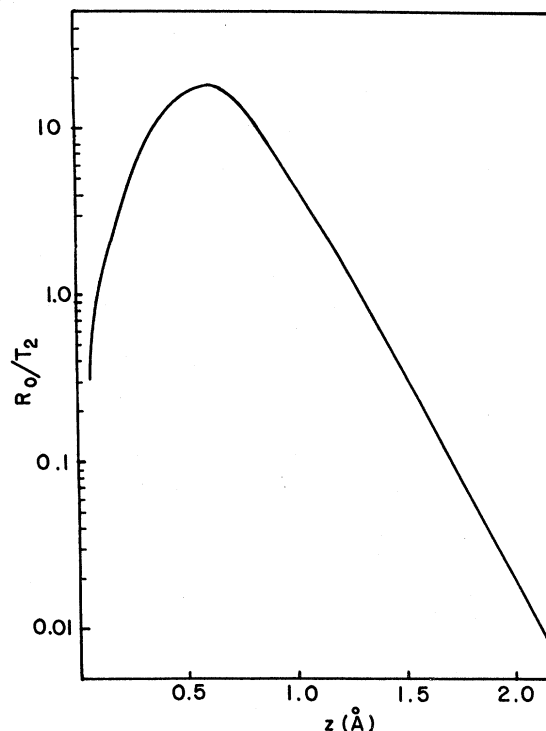

FIG. 2. The ratio of the single-quantum exchange rate R_0 to the double-quantum exchange rate T_2 for He moving parallel to a LiF surface. The He energy is 1 eV corresponding to a speed of 6900 m/s.

$z > 1.2$–1.6 Å it becomes the two-quantum process which dominates.

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