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Theory of molecule-surface scattering

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Abstract

A theory of molecule-surface scattering is developed which includes energy and momentum transfers between the surface and projectile for translational motion, rotational exchange and internal mode excitation for the molecule. The translation and rotation motions are treated with classical mechanics, while a semiclassical quantum treatment for internal vibrational mode excitation is used. Calculations are presented for diatomic molecules and other small molecules scattering from a LiF(001) surface.

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Surface scattering experiments using well-defined molecular beams as projectiles provide an excellent method for obtaining information on surface dynamics as well as information about trapping and sticking, processes that can eventually lead to chemisorption and surface chemical reactions. This work is motivated by a series of new experiments using a novel measuring technique capable of obtaining complete state-to-state scattering information for a large class of small molecules [1–4]. In order to describe these experiments we have developed a scattering theory that includes linear momentum and angular momentum transfer between the molecular projectile and surface as well as excitation of internal molecular modes. The approach used is a combined classical-quantum theoretical method in which translational and rotational degrees of freedom of the molecule are treated classically, while arbitrary numbers of internal vibrational modes are treated with a semiclassical quantum mechanical theory. For molecules appreciably larger than H_2 and with

kinetic energies greater than 0.1 eV the use of classical theory for the translational motion is justified because the number of phonon quanta transferred in a typical collision is large [5], i.e. greater than 10. Similarly, the rotational quantum numbers are of order 10 or larger, justifying a classical treatment of rotational energy transfer. However, the excitation energies of typical internal modes may be significantly larger, leading to small excitation quantum numbers even for the bending modes in the case of smaller molecules such as C_2H_2 , and these processes must be treated quantum mechanically.

The semiclassical transition rate for an initial molecular projectile with well defined translational momentum \mathbf{p}_i , angular momentum \mathbf{l}_i , and excitation quantum number q_{gi} for the g th internal mode, to a final state denoted by \mathbf{p}_f , \mathbf{l}_f , and q_{gf} can be expressed as a convolution of these individual processes:

$$\begin{aligned}
 &w(\mathbf{p}_f, \mathbf{l}_f, q_{gf}; \mathbf{p}_i, \mathbf{l}_i, q_{gi}) \\
 &\sim \mathcal{F}(\mathbf{p}_f, \mathbf{p}_i) \int_{-\infty}^{\infty} e^{-i(E_f^T - E_i^T + E_f^R - E_i^R + E_i^V) t / \hbar} \\
 &\times K_T(t, T_S) K_R(t, T_S) K_V(t, T_B) dt
 \end{aligned} \tag{1}$$

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where \mathcal{F} is the scattering form factor (essentially a squared scattering amplitude), $K_T(t, T_S)$ is the scattering kernel for translational motion with T_S the surface temperature, $K_R(t, T_S)$ is the scattering kernel for rotational transitions, and $K_V(t, T_B)$ is the scattering kernel for internal mode transitions with T_B the vibrational temperature of the incident beam. The energies $E_{i,f}^T$, $E_{i,f}^R$, and $E_{i,f}^V$ refer to the translational, rotational, and internal vibrational energy of the projectile molecule, before and after scattering, respectively.

Classical theories for describing the Gaussian-shaped angular and energy-resolved intensities observed in atom–surface collisions are well developed. Such theories have also been extended to the case of classical scattering of rigid molecules [6]. Using for $K_T(t, T_S)$ the scattering kernel for atomic-like projectiles undergoing classical scattering from a smooth, thermally vibrating surface [7], for $K_R(t, T_S)$ the classical kernel for rotational excitations of a rigid molecule [8], and for $K_V(t, T_B)$ the generalized temperature dependent Poisson distribution for excitation of N_ν independent and orthogonal internal modes [9] results in the following expression for the transition rate [10–12]:

$$\begin{aligned}
 w(\mathbf{p}_f, \mathbf{l}_f, q_{gf}, \mathbf{p}_i, \mathbf{l}_i, q_{gi}) &= \frac{1}{\hbar^2} |\tau_{fi}|^2 \left(\frac{2\pi\hbar^2 v_R^2}{\Delta E_0 k_B T_S} \right) \left(\frac{2\pi\hbar^2 \omega_R^2}{\Delta E_0^R k_B T_S} \right)^{1/2} \\
 &\times \left(\frac{\pi\hbar^2}{(\Delta E_0 + \Delta E_0^R) k_B T_S} \right)^{1/2} \\
 &\times \exp \left[\frac{2\mathbf{p}^2 v_R^2}{4\Delta E_0 k_B T_S} \right] \exp \left[-\frac{2I_z^2 \omega_R^2}{4\Delta E_0^R k_B T_S} \right] \\
 &\times \sum_{\kappa, \kappa'=1}^{N_A} \left\{ \exp \left[i(\mathbf{p}_f \cdot \Delta \mathbf{r}_{\kappa, \kappa'}^f(0) - \mathbf{p}_i \cdot \Delta \mathbf{r}_{\kappa, \kappa'}^i(0)) / \hbar - W_{V, \kappa}^p(\mathbf{p}_f, \mathbf{p}_i) - \right. \right. \\
 &W_{V, \kappa}^p(\mathbf{p}_f, \mathbf{p}_i) \left. \right] \\
 &\times \prod_{j=1}^{N_\nu} \sum_{\alpha_j=-\infty}^{\infty} \left[\frac{n(\omega_j) + 1}{n(\omega_j)} \right]^{\alpha_j/2} I_{|\alpha_j|}(b_{\kappa, \kappa'}) \\
 &\times \exp \left[-\frac{\left(E_f^T - E_i^T + E_f^R - E_i^R + \Delta E_0 + \Delta E_0^R + \hbar \sum_{s=1}^{N_\nu} \alpha_s \omega_s \right)^2}{4(\Delta E_0 + \Delta E_0^R) k_B T_S} \right] \Bigg\}, \quad (2)
 \end{aligned}$$

where $\Delta E_0 = \mathbf{p}^2 / 2M_C$ is the translational recoil energy with M_C the surface molecule mass and $\mathbf{p} = \mathbf{p}_f - \mathbf{p}_i$, and $\Delta E_0^R = (\mathbf{l}_f - \mathbf{l}_i)^2 / 2I$ is the angular

recoil energy with I the surface molecule moment of inertia. The parameter v_R is a weighted average of phonon velocities parallel to the surface [7] and ω_R is a similar average of target molecular angular velocities perpendicular to the surface. $\exp[-W_{V, \kappa}^p]$ is the Debye–Waller factor associated with internal vibrational modes of the κ th atom of the projectile molecule. $|\tau_{fi}|^2$ is the scattering form factor and is chosen to be the squared Jackson–Mott matrix element in the semiclassical limit for a repulsive wall, a choice justified by its ubiquitous use in atom–surface scattering [13]. The argument of the modified Bessel functions $I_{|\alpha_j|}$ of Eq. (2) is given by:

$$\begin{aligned}
 b_{\kappa, \kappa'}(\omega_j) &= \sum_{\beta, \beta'=1}^3 p_\beta p_{\beta'} \frac{1}{N_A \sqrt{m_\kappa m_{\kappa'}} \hbar \omega_j} \\
 &\times e \left(\frac{\kappa}{\nu_j} | \beta \right) e^* \left(\frac{\beta'}{\nu_j} | \beta' \right) \sqrt{n(\omega_j) [n(\omega_j) + 1]} \quad (3)
 \end{aligned}$$

in which ω_j are the mode frequencies, $n(\omega_j)$ is the Bose–Einstein function, m_κ is the mass of the κ th molecular atom, and $e \left(\frac{\kappa}{\nu_j} | \beta \right)$ is a polarization vector for the ν_j th mode which is determined through normal modes analysis. p_β is a cartesian component of \mathbf{p} . Inclusion of an attractive adsorption well in the potential is accomplished by adding a one-dimensional square well of depth D in front of the surface. The effect of the square well on the classical translational motion is to refract the incoming projectile, increasing its energy and reducing the angle of incidence inside the well.

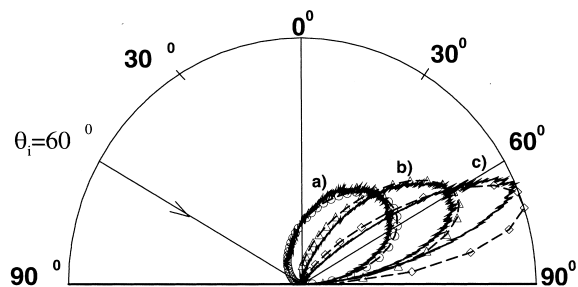


Fig. 1. Polar plots of the measured angular distributions for the scattering of C_2H_2 by $LiF(001)$; (a) $E_i^T = 110$ meV, (b) $E_i^T = 275$ meV, and (c) $E_i^T = 618$ meV, the incident angle is in each case $\theta_i = 60^\circ$ as shown by the solid straight line.

Three angular distributions for the scattering of C_2H_2 by Li(001) measured at different incident energies [2] are shown in Fig. 1 and compared with calculations carried out using Eq. (2), after multiplying by the appropriate density of states to convert the transition rate into a differential reflection coefficient. The calculations, shown as long dashed curves with symbols, agree well with the measured data. The effective surface phonon velocity v_R was chosen to be 130 m s^{-1} for the lowest energy $E_i^T = 100 \text{ meV}$, 520 m s^{-1} for $E_i^T = 275 \text{ meV}$, and 1050 m s^{-1} for $E_i^T = 618 \text{ meV}$. The value of v_R is expected to be smaller than the Rayleigh wave velocity [7], which is about 4000 m s^{-1} for LiF, and previous treatments of atomic scattering have indicated that v_R is energy dependent with values increasing with higher incident energy [5]. The value of ω_R is chosen to be $2 \times 10^{10} \text{ s}^{-1}$ and the mass M_C of the surface is taken to be 51.9 a.m.u. which is two times the mass of LiF. The need for a larger effective mass is indicative that the incoming C_2H_2 collides with more than one LiF molecule. The attractive well is relatively unimportant at the highest energy, but at low incident energy larger well depths tend to broaden the angular distributions. The value chosen to fit the data was $D = 90 \text{ meV}$ which is slightly smaller than the

estimated value of about 100 meV [1]. Further investigations of average energy losses in the collision process indicates that the major contributing process in forming the shape of the angular distributions is vibrational energy transfer, i.e. multiphonon excitation of the surface. Further comparisons between experiment and calculations were made for the scattered intensity as a function of final molecular rotational energy, and for the final rotational temperatures as functions of the incident translational energy of the beam. Good agreement was obtained indicating that the theory gives a reasonable description of energy and momentum transfers in the collision process [12].

An example of the excitation probability for the internal molecular mode is shown in Fig. 2 for the case of CO/LiF(001). The incident energy is $E_i^T = 3 \text{ eV}$, the incident angle is $\theta_i = 45^\circ$, and the final angle is the position of the maximum in the angular distribution which is $\theta_f = 72^\circ$. The surface temperature is 300 K . Plotted as a function of the final translational energy of the scattered beam E_f^T is the fractional excitation probability for creation of the $\alpha_j = 1, 2, 3$, and 4 quanta of the CO stretch mode. It is seen that the CO stretch mode excitation probabilities are strongly varying functions of the final translational energy E_f^T . They are small, but nonzero at small E_f^T , and very small at large E_f^T , forming a smooth curve with a single maximum. The position of this maximum decreases slightly with higher excitation quantum number α_j .

Additional calculations have been carried out that make interesting predictions for further possible experiments. There is a strong effect of the quantum mechanical phase interference in the excitation of internal modes exhibited explicitly (in Eq. (2)) by the momentum-dependent phase factors. Our calculations indicate that the scattered intensity measured as a function of well-defined final angular momentum state should exhibit readily observable structure as a result of this phase interference, and this structure persists even when the angular momentum is large enough to be considered classical. The predicted structure disappears when averaging over all final orientations as is done in most current experimental measurements.

Another effect revealed by our calculations is the importance of molecular symmetry. In the current

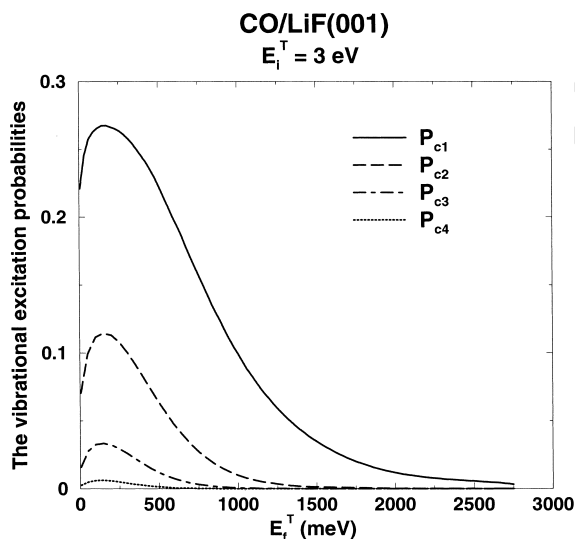


Fig. 2. Excitation probability of the CO internal vibrational mode versus final translational energy for CO scattering from LiF(001), $\theta_i = 45^\circ$ and $\theta_f = 72^\circ$, with an incident energy $E_i^T = 3 \text{ eV}$. The probabilities of the first four quantum excitations are shown.

calculations for C_2H_2 scattering the excitation probability for the asymmetric ν_5 bending mode is negligible, while the excitation probability for the symmetric ν_4 bending mode can be as high as 3%. However, if the symmetry of these modes is broken by replacing one H atom by a D (deuterium) atom, the excitation probability of the ν_5 mode increases substantially, and for some scattering configurations approaches that of the ν_4 mode which is only slightly affected.

It is of interest to discuss the temperature effects predicted by this theory, although at present relatively few experimental studies of molecule-surface scattering have made extensive temperature-dependent measurements. The Gaussian-like terms in Eq. (2) show that the scattering intensity as a function of final translational energy will be of the form of broad peaks whose half-widths increase as the square root of surface temperature T_s . Calculations of the angular distributions, as in Fig. 1, show that with increasing T_s , the angular distribution broadens and the position of its maximum intensity shifts subspecularly towards the surface normal [12].

At the present stage of development this theory does not include mechanisms for the excitation of elementary electron excitations such as electron–hole pairs. In the case of scattering of atoms from surfaces such excitations are usually unimportant, except in situations involving effects such as Peierls transitions or charge density waves [14]. However, in the case of molecule scattering, electronic excitations will need to be investigated in the future, because the generally higher translational energies and the additional internal degrees of freedom will allow new mechanisms for such elementary excitations.

This work clearly demonstrates the essential theoretical features needed to describe the experimental results for molecules larger than hydrogen and hyperthermal energies. These are (1) exchange of large numbers of phonons with the surface (i.e. classical vibrational energy exchange), (2) classical exchange of rotational energy, (3) correct conservation of both linear and angular momentum in the

collision, (4) inclusion of an attractive well in the interaction potential, and (5) quantum mechanical excitation of the low energy internal modes of the molecular projectile. Direct comparisons of calculations with the experimental measurements show that all five of these essential qualities are important, and if any one of them is ignored then agreement with experiment cannot be obtained on all measured quantities.

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