

Theory of Molecule-Surface Scattering at Thermal and Hyperthermal Energies

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A theoretical model of molecule-surface scattering is developed which includes energy and momentum transfers between the surface and projectile for both translational and rotational motions and internal mode excitation for the projectile molecule. The translation and rotation motions are treated in the classical limit, while a quantum treatment for internal vibrational mode excitation is used. The results of calculations are compared with recent high-precision measurements of the scattering of a beam of C_2H_2 molecules from a clean, ordered LiF(001) surface at energies of up to nearly 1 eV. The calculated results for angular distributions and rotational excitations are in good agreement with experiment.

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Measurements of the intensities of molecules scattered from surfaces reveal features of the interaction potential such as mechanisms for energy transfer which include exchange of phonons, rotational excitations, and excitation of internal molecular modes [1]. Such measurements also provide information about trapping and sticking, processes that eventually can lead to chemisorption and surface chemical reactions. Molecular beam scattering is not so highly developed as atom-surface scattering where, in particular, helium atom scattering has emerged as a major tool for microscopic surface diagnostics [2]. However, extensive work has been carried out, primarily involving NO [3] or other diatomic molecules such as CO, HF, HCl, H_2 , and N_2 [4,5]. Relatively few larger molecular projectiles have been investigated, but several important examples are CO_2 , SF_6 , NH_3 , and CH_4 [4]. To obtain the maximum information from a molecular scattering experiment requires measurements using an incident molecular beam with a well-defined initial state for which the translational, rotational, and internal states are known, and then after collision measuring the probability of transition to an equally well-defined final state.

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 [1,6,7]. These experiments consist of multiple-pass laser illumination of both the incident and scattered projectile beams, and when combined with time-of-flight analysis, allow for determination of the complete translational, rotational, and internal vibrational state of the molecular projectile. Initial experiments have been carried out on the small polyatomic molecules C_2H_2 [1,7] and CH_4 [6]. The purpose of this Letter is to develop 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.

This theory is used to interpret the recent experiments for the scattering of C_2H_2 from clean, ordered LiF(001) [1].

The approach used is a combined classical-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, i.e., greater than 10 [8]. Similarly, the rotational quantum numbers are of the order of 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, and such processes must be treated quantum mechanically.

An appropriate starting point for describing molecular scattering from a many-body target is the state-to-state 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} . 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 [9]. Extensions of these approaches show that a treatment of scattering with several mechanisms for energy transfer can be written as a Fourier convolution over each of the individual processes, i.e., the separability limit in which there is no direct coupling between independent processes, but each process occurs taking into account the energy exchange due to the others. Thus the transition rate can be written in the form:

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

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.

Using for $K_T(t, T_S)$ the scattering kernel for atomic-like projectiles scattering from a smooth, thermally vibrating surface [10], for $K_R(t, T_S)$ the kernel for rotational excitations of a rigid molecule [11], and for $K_V(t, T_B)$ the generalized temperature dependent Poisson distribution for excitation of N_ν independent and orthogonal internal modes [12] results in the following expression for the transition rate, expressed as a summation over all internal modes:

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

where N_A is the number of atoms of the projectile molecule, $\Delta E_0 = \mathbf{p}^2/2M_C$ 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 [10] 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 [2]. The argument of the modified Bessel functions $I_{|\alpha_j|}$ of Eq. (2) is given by

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

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, $e^{(\kappa}_{\nu_j} | \beta)$ is a polarization vector for the ν_j th mode which is determined through normal modes analysis, and p_β is a Cartesian component of \mathbf{p} .

In the case of the C_2H_2 molecular projectile the internal bending modes are the ν_4 and ν_5 at energies of 76 and 90 meV, respectively. The other internal vibrations are bond stretching modes at higher energies that are not significantly excited at low collision energies. The present

calculations also show that at incident energies of less than 1 eV single-quantum excitation of these bending modes is sufficient, i.e., first order expansion of the modified Bessel functions is an adequate approximation.

The final element of the theoretical model is to include an attractive adsorption well in the potential. This is accomplished by including 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, thus the well width is unimportant as long as it is larger than the selva region of the repulsive barrier.

Three angular distributions measured at different incident energies 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 for the lowest energy $E_i^T = 110$ meV, 520 m/s for $E_i^T = 275$ meV, and 1050 m/s for $E_i^T = 618$ meV. The value of v_R is expected to be significantly smaller than the Rayleigh wave velocity [10], which is about 4000 m/s for LiF [2,9], and previous treatments of atomic scattering have indicated that v_R is energy dependent with values increasing with higher incident energy [8,13]. 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 amu which is 2 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

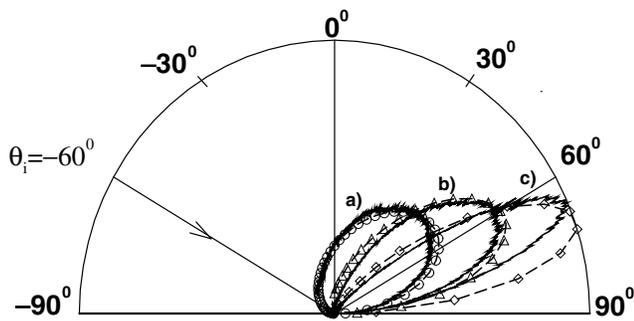


FIG. 1. Polar plots of the measured angular distributions for the scattering of C_2H_2 by $LiF(001)$; (a) $E_i^T = 110$ meV, (b) $E_i^T = 275$ meV, and (c) $E_i^T = 618$ meV; the incident angle is in each case $\theta_i = 60^\circ$ as shown by the solid straight line. The long dashed curves with symbols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

low incident energy larger well depths tend to broaden the angular distributions. The value chosen to fit the data was $|D| = 90$ meV which is somewhat smaller than the estimated value of above 100 meV [6]. Further investigations of average energy losses in the collision process indicate that the major contributing process in forming the shape of the angular distributions is vibrational energy transfer, i.e., multiphonon excitation of the surface.

Figure 2 shows the scattered intensity as a function of final rotational energy. The final angle is, for each incident energy, the position of the maximum in the angular distribution (see Fig. 1). The differential reflection coefficient was averaged over an initial Maxwell-Boltzmann distribution of rotational states with a temperature $T_{iR} = 30$ K (corresponding to the experimental estimate of $20 < T_{iR} < 40$ K), summed over final translational energies, and averaged over all angular orientations of incident and scattered molecule. The values of v_R for the intermediate energies were obtained by interpolation of those used in Fig. 1 and all other parameters are the same as in Fig. 1.

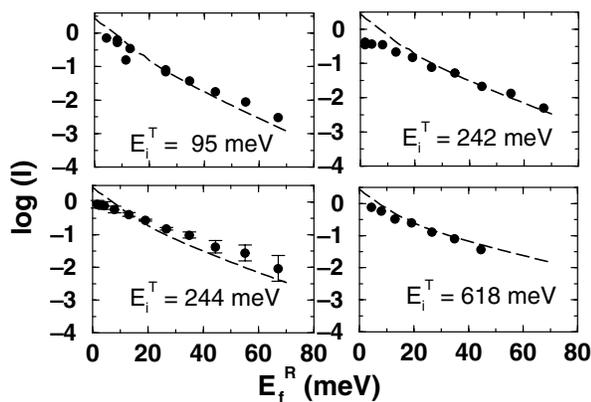


FIG. 2. Logarithmic plots of the scattered intensity as a function of final rotational energy. The incident angle is $\theta_i = 60^\circ$ and the final angle is, for each incident energy, at the maximum in the angular distribution. The experimental measurements are shown as data points and the calculations are shown as dashed lines.

In Fig. 3 the experimental data points shown with error bars are the measured final rotational temperatures as functions of incident translational energy E_i^T [1]. These rotational temperatures are extracted from a series of plots such as Fig. 2 by fitting the logarithm of the measured intensity to a straight line, and the slope of the line gives the temperature of the corresponding Maxwell-Boltzmann distribution. The theoretical curves presented in Fig. 2 are not exactly straight lines, indicating that the calculated rotational distributions do not correspond to equilibrium distributions. However, effective final rotational temperatures were calculated by making a least-square fit over the range $8 < E_f^R < 70$ meV, the same range over which the experimental data were taken. The solid curve shown in Fig. 3 gives the calculations, using the same parameters as in Figs. 1 and 2. There are two other curves exhibited in Fig. 3 and these show calculated results for simpler models of the scattering process. The dash-dotted curve is the result of calculations assuming a rigid projectile molecule and a surface of discrete isolated LiF molecules [9]. Although the shape of this curve is qualitatively correct, the calculated rotational temperatures are far too large. The results shown in the dashed curve of Fig. 3 are also calculated for rigid C_2H_2 molecules, but with the surface represented as a smooth, vibrating, repulsive barrier with no attractive well [11]. Again, the general trend of the calculations is qualitatively correct, but the values are too large. However, the current calculations for a scattering model that includes correct conservation of both linear and angular momentum at a two-dimensional surface barrier, and also includes an attractive potential well and the possibility of internal bending mode excitations give good quantitative agreement with the experimental measurements.

Additional calculations have been carried out that make interesting predictions for further possible experiments.

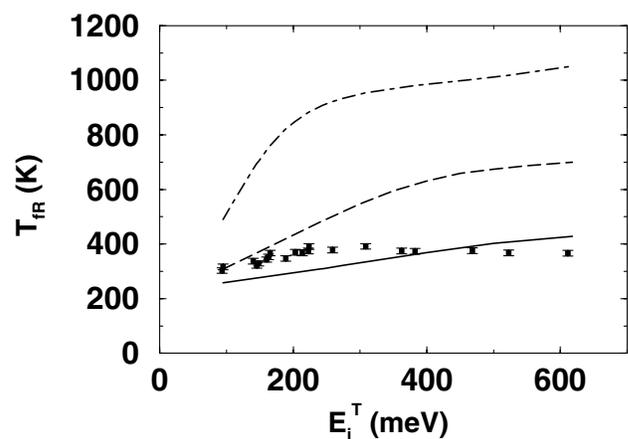


FIG. 3. Incident energy dependence of the final rotational temperature for $\theta_i = 60^\circ$ and θ_f at the maximum in the respective angular distribution. The experimental measurements are shown as data points and the present calculations are shown as a solid curve. The other curves are two different and simpler theoretical calculations as explained in the text.

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 if it were possible to observe molecules scattered in a particular orientation relative to the surface plane, then these phase factors would cause structure to appear in the scattered intensity. This structure is not apparent in the data or calculations shown in Fig. 2 because the measurements are made as a function of final rotational energy, implying a summation over all possible angular momentum orientations. Averaging over all orientations, as is done by the detector, removes this underlying structure; however, the effect of this quantum interference from the vibrational modes is to give an overall reduction to the effective final rotational temperatures (see Fig. 3).

Another effect revealed by our calculations is the importance of the symmetry of the C_2H_2 molecule. Typical excitation probabilities for the ν_4 and ν_5 modes rapidly rose from the creation thresholds and at the higher energies fully 3%–5% of the scattered molecules become vibrationally excited. The ν_4 mode is a symmetric vibration, with the two H atoms vibrating in opposition to the two C atoms. The ν_5 mode, on the other hand, is antisymmetric and its excitation probability was found to be smaller than that of the ν_4 mode over the incident range of roughly $100 < E_i^T < 500$ meV. If the symmetry of these modes is broken by replacing one H atom by a D (deuterium) atom, the excitation probability of the ν_4 mode increases more than 2.5 times, while that of the ν_5 mode is only slightly affected. Calculations indicate that the effects of this broken symmetry should be detectable in the experiments shown in Figs. 2 and 3 as a decrease in final rotational temperature.

This work clearly demonstrates the essential theoretical features needed to describe the experimental results [1]. 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 con-

servation 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 cannot be obtained on all measured quantities.

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