PHYSICAL REVIEW B VOLUME 36, NUMBER 9 15 SEPTEMBER 1987-II

Effects of gas-phase collisions on particles rapidly desorbed from surfaces

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(Received 7 April 1987)

The influence of postdesorption collisions on the experimentally measured angular and energy distributions of the rapidly desorbed molecules is investigated using direct Monte Carlo simulation procedures. By simulating the desorption of NO from LiF(100), we find that the postdesorption collisions have a significant effect on the final angular, rotational energy, and translational energy distributions of the desorbed molecules.

I. INTRODUCTION

The rapid desorption of atoms and molecules from surfaces occurs in a number of important processes including laser-induced desorption (LID), flash desorption of rare-gas adsorbates, and particle-induced desorption. The dynamics of these processes can be understood in detail by obtaining the distributions of the atoms or molecules leaving the surface. When the density of particles leaving the surface is high enough, there can be a significant number of collisions in the gas phase which occur between desorption and detection. Thus, to study such desorption processes, one must first be able to quantitatively understand the effects of the gas-phase collisions. There have been several experiments where the collisions between the rapidly desorbed molecules have been found to distort the observed distribution of the desorbed molecules.[1-6] Postdesorption collisions are also believed to be important in sputtering of organic ions from solids and liquids,[7] and in the laser desorption-ionization experiments.[8] In spite of these observations, the gas-phase collisions are either ignored or not taken into account in a number of laser-induced desorption experiments[9-12] where the experimental conditions are such that a significant number of collisions between desorbed molecules would occur.

In view of this frequent neglect of the effects of gas-phase collisions in rapid-desorption experiments it is important to study the existence and influence of these effects in the experimentally measured distribution of the desorbed particles. A qualitative discussion of the effects of postdesorption collisions on the final translational energies as well as a first-order estimate of the number of gas-phase collisions as a function of surface coverage was given by Cowin *et al.*[1] Kelly and Dreyfus[13] have interpreted the postdesorption collisions in terms of the formation of a Knudsen layer for which the steady-state distributions of the particles leaving the surface have been worked out.[14] However, their calculations are restricted to the translational energy distribution along the surface normal and do not include rotational degrees of freedom. Hence, such a model is not suitable for studying the angular dependence of the translational and rotational energy distributions. Recently we have implemented[15] direct Monte Carlo simulation procedures[16] to investigate the effects of gas-phase collisions on the measured distributions[1] of the D_2 molecules rapidly desorbed from polycrystalline tungsten and obtained good agreement with the measured final flux and translational energy distributions. In this article we report the results of the first quantitative theoretical investigations of the effects of postdesorption collisions in a system with significant probability for energy transfer involving internal degrees of freedom (e.g., rotational motion). As a model system, we have studied the angular dependence of the flux and the translational and rotational energy distributions of NO molecules rapidly desorbed from LiF(100). The dynamics of the LID of NO from LiF (100) have been previously investigated using stochastic trajectory methods.[17] Additionally, NO molecules have a large intrinsic probability for rotational energy transfer and the gas-phase collisions can be expected to play a critical role in the precise description of the measured rotational energy of the desorbed molecules.

II. METHOD

The details of the direct Monte Carlo method have been described elsewhere.[15,16] Briefly, the molecules are assumed to be hard spheres and rigid rotors and are introduced into the system as a function of time determined by the mean residence time of the NO molecule on the surface. The flux of the desorbing molecules is determined on the basis of the number of exposed molecules. If the surface coverage Θ is greater than unity, then the flux is determined by the number of molecules in one monolayer till Θ decreases below unity, after which the value of Θ at the time of desorption is used to calculate flux. The initial distributions of the desorbed molecules are obtained by fitting the stochastic trajectory data[17] to appropriate distribution functions. The initial distributions used in the present calculations correspond to the simulation *D* of Ref. 17 for which the mean residence time was 3.43×10^{-12} s. The angular distribution obtained in the trajectory calculations is found to follow a $\cos^{1.94}\theta$ distribution, where θ is the desorption angle measured from surface normal. The distribution of the translational temperature is fitted to a function of the form: $T(\theta)=A-B\theta^2$, where the parameters A and B are found to be 562.1 K and 114.25 K/rad^2, respectively. The mean rotational temperature (562 K) of the desorbing NO molecules was found to be lower than surface temperature at the time of desorption and independent of the desorption angle.[17] Hence, in the present simulations, the initial rotational temperature is taken to be 562 K at all values of θ.

In the Monte Carlo calculations, the position of the molecule is characterized only by the distance normal to the surface, the z coordinate, but the velocity components are retained for all three dimensions. The assumption of a one-dimensional distribution in space has been discussed in Ref. 15 and because of this simplification the Monte Carlo calculations presented here overestimate the number of postdesorption collisions to an extent which depends on the laser spot size. During each Monte Carlo time step the molecules move in the z direction according to v_z, and collisions occur in each cell. The possibility of a collision between a pair of molecules in a cell is determined on the basis of the collision cross section and the relative velocity of the collision pair, using the acceptance-rejection method. The collision cross section for NO is assumed to be[18,19] 38 Å^2. The occurrence of elastic and inelastic collisions is determined on the basis of the collision number for rotational energy transfer. For NO this collision number is assumed to be unity.[18,19] The collision number for vibrational relaxation[20] of NO is 2700. Thus we neglect vibrations in these simulations.

The motions of the molecules were followed for 5×10^{-6} s. By the end of the simulation, the density has decreased by velocity segregation to such an extent that collisions at later times are not significant. During the simulation the density and rate of change of the distributions vary over several orders of magnitude. To increase the efficiency of sampling with such a wide variation in density and collision frequency, the propagation incremental time Δt_m and the cell size are changed several times during the simulation as has been discussed in detail elsewhere.[15] We have used 66 600 molecules in this simulation and the appropriate Θ is obtained by varying the surface area.

III. RESULTS AND DISCUSSION

The results of the Monte Carlo simulation for the mean translational energy $\langle E_t\rangle$, mean rotational energy $\langle E_r\rangle$, $\langle\cos\theta\rangle$, and the average number of collisions per desorbed molecule, $\bar{n}$, of NO LID from LiF(100) at the coverages $\Theta=0.1$, 1.0, and 3.0 (in monolayers) are given in Table I. Even at the lowest coverage which we have studied, the desorbed NO molecules make 1.9 collisions per molecule. The postdesorption collisions are found to increase dramatically as the surface coverage increases and there is a corresponding increase in $\langle\cos\theta\rangle$ and $\langle E_t\rangle$, and a progressive decrease in $\langle E_r\rangle$. The increase in $\langle\cos\theta\rangle$ suggests that the angular distribution becomes more forward peaked due to gas-phase collisions between desorbed molecules. The mean rotational energies as a function of angle for the three coverages are given in Fig. 1. At all angles of desorption, the postdesorption collisions significantly decrease the mean rotational energy compared to that of the nascent distribution and there is a systematic decrease in $\langle E_r\rangle$ with an increase in the desorption angle. The calculated final translational energy distribution of the desorbed molecules is found to deviate from the Boltzmann distribution and these deviations are very significant at higher coverages. Hence, in our discussions we have used mean translational energy values expressed as temperatures using $\langle E_t\rangle/2k_B$. A detailed characterization of the translational energy distribution of the desorbed molecules will be presented elsewhere. The angular distributions of the mean translational energies of the desorbed molecules are shown in Fig. 2. It is significant to note that the mean translational energy of the molecules desorbing close to surface normal are very much higher than the initial translational energy, suggesting that the experimental measurements made along the surface normal should be interpreted with caution. By comparing Fig. 1 with Fig. 2 we can also see that there is a positive correlation between the translational and rotational energies as a function of angle.

TABLE I. Average number of collisions per particle $\bar{n}$, average $\cos\theta$, and average energies of the desorbing molecules at different coverages. Uncertainties correspond to the 95% confidence level.

Θ	$\bar{n}$	$\langle\cos\theta\rangle$	$\langle E_t\rangle$ (K)	$\langle E_r\rangle$ (K)
0.1	1.90	0.75±0.01	573±2	415±3
1.0	12.91	0.87±0.01	710±6	140±1
3.0	32.62	0.92±0.01	751±7	59±1
1.0[a]	11.01	0.90±0.01	499±4	562±4
initial distribution		0.7462	500	562

[a] Results obtained using 10^{-4} as the collision number for rotational energy transfer.

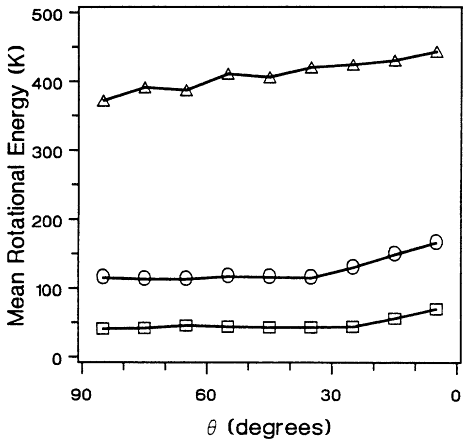

FIG. 1. Mean rotational energy vs the desorption angle θ, at different coverages. Open triangles, circles, and squares represent the results for surface coverages 0.1, 1.0, and 3.0, respectively. The 95% confidence error bars are smaller than the size of the symbols. The points are connected by straight lines.

The results of the Monte Carlo simulations presented here can be qualitatively understood by an extension of the arguments of Cowin *et al.*[1] to include effects of internal degrees of freedom of NO. The number density of molecules in the vicinity of a given molecule depends strongly on the v_z of the molecule. If the v_z is much smaller or much larger than the most probable normal velocity, $\bar{v}_z$, then the density will be low. This fact combined with the variation of relative velocities leads to an enhanced collision rate for slow molecules at small θ and fast molecules at large θ.[1] This "kinetic altering" of the velocity leads to an increase in the fraction of the hot molecules with velocities near the normal direction and cold molecules with velocities far from the surface normal.

The energy transferred during the collisions also affects the final distributions. Due to velocity segregation, most collisions will occur between particles with similar normal velocity components. Thus in the center-of-mass frame of an average collision the relative kinetic energy in the z direction is much smaller than either the relative kinetic energy in the directions parallel to the surface or the internal energy. Then on average the kinetic energy in the direction normal to the surface will be increased in a collision at the expense of both the kinetic energy parallel to the surface and the energy in the internal degrees of freedom. This leads to both a focusing of velocities towards the surface normal and a cooling of the internal degrees of freedom.

A final consideration is the effect of the conservation of momentum and energy in a collision on the final distributions. In a collision the particle with the larger final velocity is directed closer to the center-of-mass motion of the collision pair than the particle which has the smaller final velocity. This effect averaged over all collisions tends to focus the higher-velocity molecules towards the surface normal and the lower-velocity molecules away from the surface normal. Then as discussed above, in an inelastic collision, energy in the center-of-mass frame is on average transferred from rotations to translations. An increase in the relative translational energy leads to a broader final angular distribution in the laboratory frame. Thus the increase in the relative translational energy in inelastic collisions tends to scatter molecules to angles further from the surface normal compared to molecules scattered in elastic collisions. This would lead to rotationally colder molecules being detected at larger θ. Thus, in a comparison of the desorption processes with and without inelastic collisions, we expect to find a broader angular distribution in the final translational energies when inelastic collisions are included. This qualitative argument is seen to agree with the smaller value of $\langle \cos\theta \rangle$ shown in Table I when inelastic collisions are included.

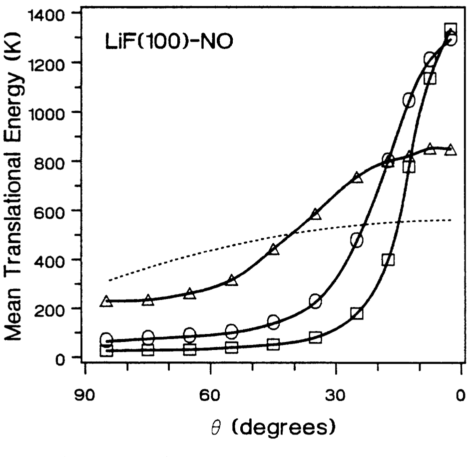

FIG. 2. Mean translational energy vs the desorption angle θ, at different coverages. · · · · represents the initial distribution. The symbols have same meaning as in Fig. 1. The points are connected by smooth curves. The 95% confidence error bars are smaller than the size of the symbols.

IV. CONCLUSIONS

From our calculations, we then conclude that the gas-phase collisions between rapidly desorbed molecules can distort the nascent distribution due to desorption in several ways: (a) the average translational energy of the desorbed molecules increases at the expense of the rotational energy of the molecules; (b) the molecules desorbing at small θ have relatively larger rotational energy; (c) the molecules are focused towards surface normal; and (d) the translational energy of the molecules desorbing at small θ is increased and the translational energy of the molecules desorbing at large θ is decreased.

Clearly, the effects of gas-phase collisions depend on the mean residence time of the adsorbates on the surface. In this paper we have assumed a mean residence time of 3.43×10^{-12} s for NO molecules. For longer residence times the gas density above the surface will be smaller and consequently the desorbing molecules will make fewer collisions. Currently we are studying the effects of postdesorption collisions in the rapid desorption of mixtures of gases in model systems.[21] In this study[21] we have assumed a mean residence time of 10^{-9} s. These calculations show[21] that, compared to the present results, there is $\sim 10\%$ reduction in the average number of collisions experienced by a molecule and similar reduction in the net changes of the final distribution due to these collisions. Thus we expect to see a significant reduction in the importance of postdesorption collisions only when the surface residence life time becomes greater than $\sim 10^{-8}$ s.

The results of our Monte Carlo calculations can be used to interpret a number of published experiments. Several LID experiments have recorded changes in the final distributions as a function of increasing desorption flux and found both increased focusing of the desorbed molecules at high coverages,[1,4,9,10] and an increase in the translational energy of the molecules desorbing in the normal directions.[10-12] Higher rotational energies for molecules with higher velocities have also been observed.[5] Although these effects may be due to both the dynamics of the desorption process and the gas-phase collisions between the desorbed molecules, the results presented here suggest that the experimentally observed dependence of the final distribution of the rapidly desorbed molecules on surface coverage or laser power is in large part due to the postdesorption collisions.

ACKNOWLEDGMENTS

Acknowledgment is made to the Dow Chemical Company Foundation, to the Monsanto Company, and to the Celanese Chemical Company for partial support of this research. This research is based upon work in part supported by the National Science Foundation under Grant No. CHE-8351414. In addition this work has been supported by a grant from the Office of International Coordination of Texas A&M University.

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