

Internal state dependence of HCl/Ar(111) desorption rates

John E. Adams

Citation: *The Journal of Chemical Physics* **85**, 4073 (1986); doi: 10.1063/1.450878

View online: <http://dx.doi.org/10.1063/1.450878>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/85/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

A quasiharmonic model calculation for two nonMarkovian farinfrared spectra of diatomic polar molecules in a raregas liquid. II. Correlation functions of the interaction and spectral application to a HCl–Ar solution
J. Chem. Phys. **86**, 4607 (1987); 10.1063/1.452735

Classical and quantum centrifugal decoupling approximations for HCl–Ar
J. Chem. Phys. **66**, 2854 (1977); 10.1063/1.434343

Pressurebroadened infrared linewidths of HF:Ar and HCl:Ar at moderate densities
J. Chem. Phys. **66**, 3121 (1977); 10.1063/1.434331

Calculations on the HCl–Ar van der Waals complex
J. Chem. Phys. **64**, 354 (1976); 10.1063/1.431930

Proton Spin–Lattice Relaxation in HCl–Ar Mixtures
J. Chem. Phys. **54**, 769 (1971); 10.1063/1.1674910



Internal state dependence of HCl/Ar(111) desorption rates

John E. Adams

Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211

(Received 7 May 1986; accepted 20 June 1986)

The rate of desorption of HCl from an Ar(111) surface as a function of the internal state of the physisorbed molecule is studied via a quasiclassical trajectory simulation of the system dynamics. Results from these calculations indicate that the desorption rate passes through a maximum at an initial rotational quantum number of 6, with the maximum rate being enhanced but the rate behavior not being altered qualitatively when a quantum of vibrational energy is added to the molecule. This observed rate dependence may be understood in terms of a transition of the system between distinct dynamical regimes that occurs as the rotational energy of the molecule is increased. Surface of section plots analogous to those used in the study of intramolecular energy transfer are found to provide a convenient means for identifying a transition of this sort.

I. INTRODUCTION

Only in the last few years has technology advanced to the point that detailed state-to-state measurements can be made on processes occurring at a gas-solid interface.¹ Consequently, the sort of dynamical information that previously has been derived from the detailed study of gas-phase collisions, dissociations, and energy transfer is just now becoming available for the analogous surface processes. We note, as an important example, the several studies that have been directed towards the illumination of the nature of the molecule-surface potential from the distribution of rotational states of diatomic molecules either scattered or desorbed from a crystal surface.² (One must worry here, of course, whether the observed distributions are truly reflective of the adsorbed state or whether instead exit channel effects obscure the actual dynamics of the adsorbed molecule.) Additional closely related work has focused on the internal state dependence of molecular sticking probabilities,³ with microscopic reversibility being invoked in order to permit the deduction of relative rotational state desorption probabilities.

In a previous work⁴ we suggested a means for calculating the absorption spectrum of a simple physisorbed molecule that is based on the semiclassical spectral intensity formalism proposed by Marcus and co-workers as a method for investigating energy flow in simple model systems and molecules.⁵ The prototypical system considered in that earlier study was HCl adsorbed on an Ar(111) surface, this system being chosen in part because the spectroscopy of the isolated molecule is very well characterized (sufficiently so that highly accurate potential energy and dipole moment functions have been determined^{6,7}) and in part because the analogous matrix isolation problem (HCl trapped in an Ar matrix) has also stimulated considerable interest.⁸ (One of the anticipated future directions of this work includes the application of the semiclassical spectral synthesis method to a study of the spectra of dopant molecules.) While in the process of carrying out that investigation, we observed that at particular values of the initial molecular angular momentum, a large fraction of the trajectories led to desorption over the time period considered (roughly 25 ps). In addition,

from the nondesorptive fraction of these trajectories, we calculated a spectral line shape function that was much broader than the ones obtained for either lower or higher rotational energy. Our results suggested that in this physisorption system a dynamical transition occurs as the molecules' angular momentum is increased; while at low J values rotational dephasing collisions that do not produce desorption are the rule, raising J leads to increasingly violent collisions and to a tumbling of the molecule. Even higher J 's, though, yield a very different sort of dynamics, characterized by nearly free rotation and fewer desorption events. In the present work we describe a quantification of the unexpected desorption behavior seen in this system, with our goal being a better understanding of the transition that was first implied by the calculated vibration-rotation spectral features.

II. DESORPTION RATE CALCULATIONS

Since molecular desorption may be viewed as a special case of a unimolecular decomposition reaction, the rupture of a molecule-surface bond will be described by a first-order rate law. Woodruff and Thompson,⁹ as well as a number of others,¹⁰ have demonstrated that classical trajectory simulations can provide a convenient means for investigating such decomposition reactions as long as a significant fraction of the trajectories lead to dissociation during the time interval over which a trajectory can be followed accurately (say, 25–50 ps). Our previous investigations have indicated that in the HCl/Ar(111) system one can expect almost 90% of the adsorbed HCl molecules initially having a rotational energy intermediate between the energies of the states $J = 5$ and $J = 6$ to desorb over a 25 ps time span.⁴ These particular internal state-dependent desorption events thus occur sufficiently rapidly that they are well suited to investigation via a classical approach.

The specific system model adopted here is identical with the one selected for our recent study of the infrared line shape of a physisorbed diatomic.⁴ Since the strength of an HCl bond should not be expected to change substantially as a consequence of adsorption on an argon surface (the physisorption well depth is only a few percent of the free molecule

$\nu = 0 \rightarrow 1$ excitation energy), the total potential energy function may be taken to be a sum of an isolated molecule potential and pairwise additive hydrogen–argon and chlorine–argon potentials. In particular, we choose the Dunham oscillator potential of Tipping and Ogilvie⁶ as our model of the hydrogen–chlorine interaction and the truncated Lennard-Jones potentials suggested by Weber and Stillinger¹¹ (using the parameters reported by Diestler¹²) for the forces between the adsorbed atoms and the surface atoms. The surface itself is modeled by replicating in two dimensions a rectangular array of 24 argon atoms (periodic boundary conditions), with the atoms being held fixed in their equilibrium positions in the present study.

In order to set the initial conditions for trajectories constructed using this model, we must specify both the molecular orientation with respect to the surface and also the variables that characterize the desired internal energy state. First, a thermally biased Monte Carlo random walk (Metropolis sampling¹³) provides a convenient means for generating a set of orientation vectors consistent with the system temperature (50 K in this work) and the assumed forces. As in our earlier study, we have fixed the magnitude of the θ orientation angle¹⁴ and the length of the hydrogen–chlorine bond at their equilibrium values. Momentum vectors conjugate to the center of mass position vectors obtained via this walk then may be selected by a random sampling from the appropriate Boltzmann velocity distribution. Since we wish to simulate the dynamics of molecules initially prepared in well-defined quantum states, we follow the usual quasiclassical prescription and choose the initial classical action variables describing the internal degrees of freedom to be equal to the corresponding quantum numbers. Given these variables and a random choice of the plane of rotation, the vibrational and rotational contributions to the H–Cl relative momentum vector are then obtained by means of a standard transformation.¹⁵

Having set the initial conditions in the above manner, we construct the classical trajectories describing the motion of the system via a numerical integration of Hamilton's equations of motion. These calculations yield the position of the molecule (defined by the center of mass coordinates) as a function of time, with a desorption event being tallied when the following conditions are satisfied: (1) the molecule is sufficiently far from the surface that either the hydrogen–surface or chlorine–surface potential is zero and (2) the molecular center of mass momentum vector is directed away from the surface. From a set of these trajectories (typically 200–300) one then constructs a plot of the logarithm of the fraction of the trajectories that at time t are as yet not desorptive vs time, the slope of this plot being the negative of the (first-order) desorption rate constant. An example of such a plot is given in Fig. 1 for the case $\nu = 0, J = 6$. In fitting the points to a straight line via a least squares procedure, we have ignored the nonlinear short time data, since these points reflect differences in the velocities of the desorbing molecules. The neglect of this sort of data in the analysis of unimolecular decomposition lifetimes has been shown to yield results that differ only negligibly from those obtained when one instead defines the trajectory lifetime to be the

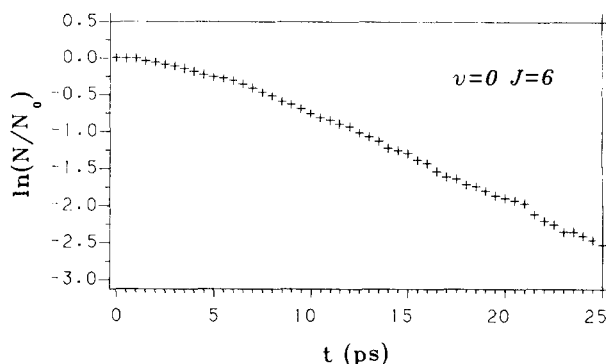


FIG. 1. Plot of the logarithm of the fraction of trajectories that are non-desorptive vs trajectory time. The negative of the slope of the line fit to this data is the (first-order) rate constant for desorption. 200 trajectories having initial classical action variables of $\nu = 0$ and $J = 6$ are included here.

time up until the molecule reaches its final inner turning point prior to dissociation.⁹

We summarize the results of our calculations of state-dependent desorption rate constants in Fig. 2 and Table I. Only a limited range of initial rotational quantum states have been considered here due to the practical limitation of the classical method—other initial states yield desorption rates that are too slow to be tractable via the present approach. Most notable of the trends in evidence in Fig. 2 is, of course, the local maximum in the rate constant appearing at $J = 6$. For the $\nu = 0$ case, the desorption rate nearly doubles upon passing from a J value of 5 to one of 6, with the higher result roughly three times the magnitude observed when the rotational energy is more than doubled (i.e. in going to $J = 9$). Clearly there is no simple correlation between rotational energy and desorption rate; an alteration of the under-

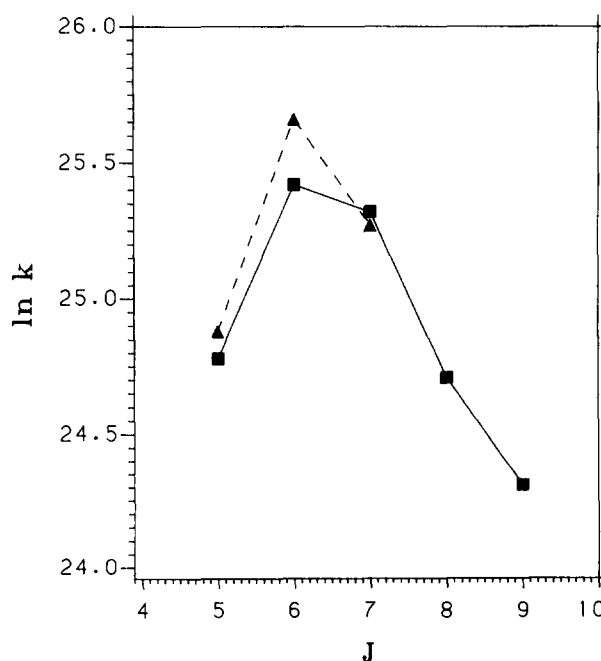


FIG. 2. Logarithm of the desorption rate constant (s^{-1}) vs the initial rotational action variable. The squares correspond to results obtained for the ground ($\nu = 0$) vibrational state, while the triangles correspond to the analogous $\nu = 1$ results. (The lines are meant to guide the eye only.)

TABLE I. Desorption rate constant and average molecule-surface separation.

ν	J	No. of trajectories	$k(\text{s}^{-1})$	Average distance of HCl from surface (\AA)
0	5	300 (136) ^a	5.8×10^{10}	3.64
0	6	200 (55)	1.1×10^{11}	3.65
0	7	240 (70)	9.9×10^{10}	3.48
0	8	250 (131)	5.4×10^{10}	3.37
0	9	200 (134)	3.6×10^{10}	3.34
1	5	200 (92)	6.4×10^{10}	3.62
1	6	200 (35)	1.4×10^{11}	3.65
1	7	200 (54)	9.4×10^{10}	3.56

^aThe number in parentheses is the number of molecules which have not desorbed within 15 ps, the time at which the trajectories were ended.

lying molecular dynamics must be occurring concurrently with the increase in rotational energy. On the other hand, increasing the vibrational energy, even though such an addition represents the addition to the molecule of a far larger amount of internal energy than can be supplied through an excitation of a few quanta of rotational energy, does not appear to produce a qualitative change in the desorption behavior. Rather such an excitation merely enhances, by about 25%, the rate maximum observed for $\nu = 0$.

An insight into the rate behavior noted above is suggested by the results of the spectral intensity calculations reported previously.⁴ At low values of the initial rotational angular momentum, we found that rotational dephasing collisions dominated the dynamics, with the time average of the molecular angular momentum vector vanishing. These collisions then become increasingly violent as quanta of rotational energy are added to the system, and the molecule begins to tumble. It is just here that the desorption rate increases to its maximum value. Even higher initial rotational energies, however, are associated with a quite different dynamical regime, one characterized by the nearly free rotation of the molecule in a plane lying (on the average) parallel to the crystal surface. Now that molecular tumbling has ceased, the desorption rate falls, returning to a value comparable with that observed at much lower J . These results imply that an important mechanism for desorption involves an impulsive kick to the molecule which is contributed when the vibration of the diatomic becomes oriented in the direction normal to the surface plane. Thus, in the absence of molecular tumbling, i.e., at high and low initial J , the desorption proceeds slowly, whereas at an intermediate J the three-dimensional rotation that periodically directs the vibration along an axis perpendicular to the surface produces an enhancement of the desorption probability. Note that this interpretation is corroborated by our calculations that begin with HCl in its first excited vibrational state, the only significant difference between these results and those obtained with $\nu = 0$ appearing at the J value for which the desorption rate is a maximum. Only with an alignment of the molecular axis normal to the surface plane is the additional vibrational energy available for transfer into translational motion, and thus it is here that one observes a significant enhancement of the rate constant. However, when the motion chiefly involves rotation parallel to the surface, this extra energy is not

available for transfer except via the slow exchange of energy due to a weak coupling of the vibrational and rotational degrees of freedom.

III. TRAJECTORY CHARACTERIZATION

Inasmuch as the desorption rate apparently varies markedly depending on the dynamical regime in which the molecule is found, we wish to determine a convenient means for classifying trajectories on the basis of their type of motion. Such a method, of which much use has been made in the last few years in the study of intramolecular energy transfer, involves the construction of Poincaré surfaces of section.¹⁶ These plots, representing the projection of a trajectory onto a surface of lower dimension than the full phase space, permit one to distinguish easily between quasiperiodic motion (the trajectory fills only a fraction of the energetically accessible lower dimensional space) and chaotic motion (the trajectory uniformly covers the entire phase space available to the system at a given fixed energy).

In the present study the molecules' motion can be separated into the motion of the center of mass and the relative motion of the hydrogen and chlorine atoms, described by an interatomic distance and two orientation angles.¹⁴ We shall assume that to a first approximation that vibration and rotation in this system are only very weakly coupled, and so since our previous investigations have indicated that the molecular dynamics is best characterized via an examination of the time behavior of the orientation angles, we can ignore the vibrational degree of freedom and focus our attention on the angular part of the problem. There still may be, however, a correlation between the molecular center of mass motion, particularly the component which lies normal to the surface, and the angular motion that arises due to the corrugation of the surface (the potential interaction with the argon atoms becomes progressively smoother as the molecule moves away from the surface). We will return to a consideration of this point below.

Surfaces of section have been constructed here by plotting the magnitude of the ϕ angle vs the relative momentum in the ϕ direction whenever $\theta = \pi/2$ (i.e., the molecular axis lies parallel to the surface) and $p_\theta > 0$. Note that in the absence of the molecule-surface potential and of energy transfer between vibrational and rotational degrees of freedom, a single trajectory yields a plot of this sort that consists of a single point. By changing the initial plane of rotation, one obtains a different point, such that an ensemble of these trajectories may be represented by a uniform distribution of phase points in the energetically accessible ϕ, p_ϕ space. An example of a plot deriving from a single typical adsorbed molecule trajectory in the low J regime is shown in Fig. 3. We find here an essentially random filling of the available phase space, a result that confirms our previous analysis of the dynamics in this system in terms of rotational dephasing collisions. The basic pattern is not retained, however, when the initial molecular angular momentum is increased. In Fig. 4 we give the surface of section deriving from a $\nu = 0, J = 6$ trajectory that begins from the same set of initial conditions (save for the magnitude of the initial angular momentum) that gave rise to the results appearing in the previous figure.

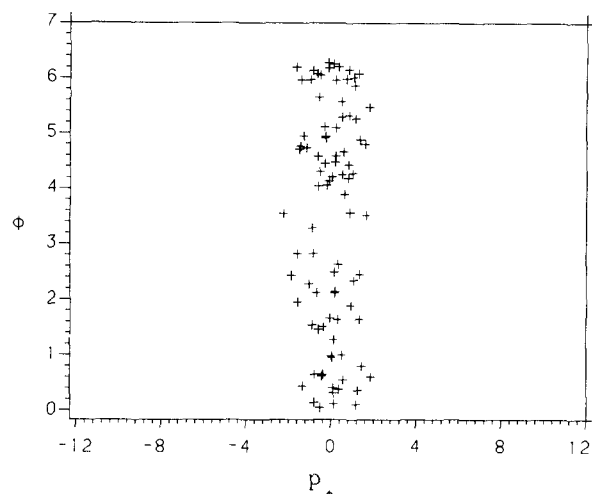


FIG. 3. Poincaré surface of section for a single trajectory begun with $v = 0$, $J = 1$. The total trajectory time is 75 ps. Here the angle ϕ is in radians and its conjugate momentum (p_ϕ) is in atomic units.

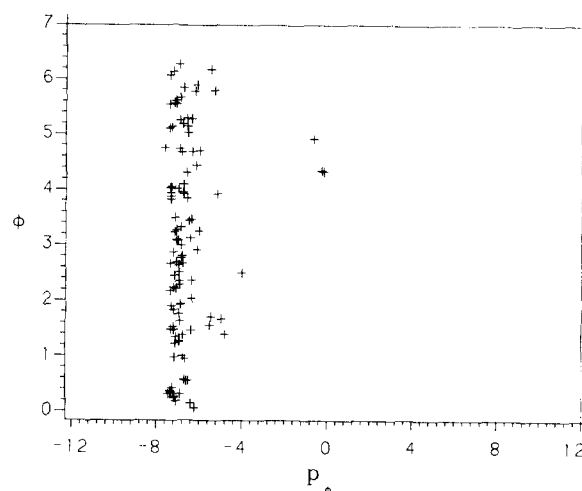


FIG. 5. Surface of section for the same trajectory shown in Figs. 3 and 4 except that $J = 7$. The trajectory is desorptive in 21.4 ps.

This plot involves a wider range of p_ϕ values since we have here a higher initial rotational energy, and it does not display the random coverage of the energetically accessible phase space that was seen in Fig. 3. From a detailed examination of the trajectory one in fact finds that during the first 4 ps, all of the points fall with the range $p_\phi = -6.6$ to -4.9 a.u., with the remaining points being generated after that time but before desorption of the molecule at 11.6 ps (the small cluster of points at $\phi \approx 0.5$ rad, $p_\phi \approx 0.5$ a.u. reflects essentially free-molecule dynamics immediately prior to desorption). These observations suggest that while initially the motion of the adsorbed molecule is fairly regular, repeated collisions with the surface atoms rapidly perturb the motion to the extent that tumbling dominates the dynamics and desorption ensues. We should point out that the particular trajectory considered here may be considered quite typical; the lifetime of the adsorbed molecule is such that (roughly) half of our calculated trajectories at this rotational energy are desorptive within this period (11.6 ps).

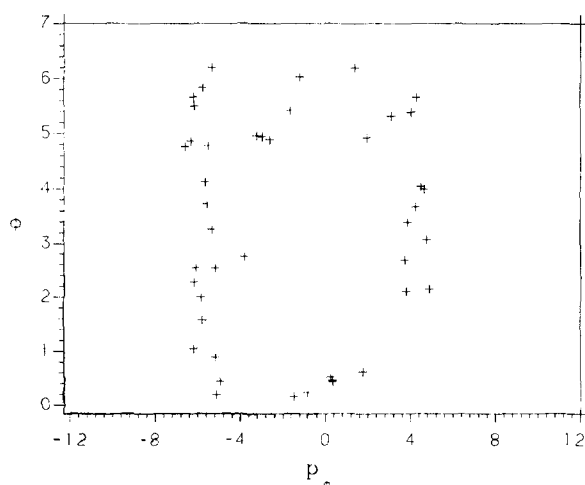


FIG. 4. Surface of section for a trajectory with the same initial conditions as trajectory represented in Fig. 3 except that now $J = 6$. The trajectory is desorptive in 11.6 ps.

Addition of one more unit of rotational angular momentum to this system yields a surface of section that reflects a reduced influence of molecule-surface collisions on the overall molecular dynamics. While the trajectory is still desorptive (the lifetime here is roughly 21.4 ps), we see in Fig. 5 that it accesses a far smaller fraction of the available phase space than does the lower energy trajectory. This result should be compared to the higher energy $v = 0$, $J = 10$ surface given in Fig. 6. There we find only a narrow band of phase points generated by what is now a nondesorptive trajectory, and we infer from such a plot the absence of significant collision-induced energy transfer between θ and ϕ motions, where the frequencies of these two types of oscillations (the θ motion is librational while the ϕ motion is nearly a free rotation) are incommensurate. In this dynamical regime the molecule rotates more nearly parallel to the plane of the surface and does not suffer the frequent rotational dephasing collisions characteristic of the motion at small J . We thus suggest that the appearance of "banded" surfaces of section of this type provides a useful marker for detecting the onset of the transition to (essentially) free rotor dynamics of an adsorbed molecule.

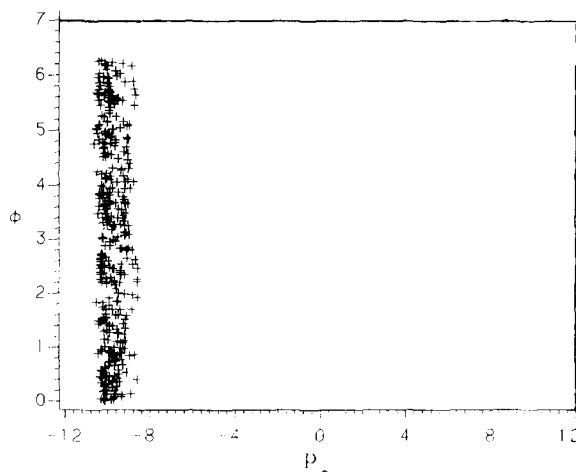


FIG. 6. Surface of section for the same trajectory shown in Figs. 3-5 except that $J = 10$. The total trajectory time is 50 ps.

If one is to investigate more fully the dynamics in the low angular momentum regime, it might seem preferable to construct surfaces of section in a different way that takes into account the fact that since the effective surface corrugation changes with the distance from the surface, there may be a reduced hindrance of planar rotation when the molecule is located relatively far from the crystal face. One thus might consider, e.g., plotting pairs of ϕ , p_ϕ values obtained when the distance between the molecular center of mass and the surface exceeds some appropriately chosen value and the center of mass velocity is directed away from the surface. In practice, however, such an analysis does not appear to be as useful as one might hope. At low values of the initial angular momentum where we find that rotational dephasing collisions dominate the dynamics, the frequency with which the diatomic moves sufficiently far from the surface that one finds an effective decrease in the surface corrugation is not high enough for there to be many points on the surface of section plot generated over the time of a trajectory (< 50 ps). A higher angular momentum, on the other hand, leads to the tumbling of the molecule, but the significance of this type of surface of section in such a case is unclear. And then still higher J values are associated with a return to essentially planar rotation for which the characterization carried out above is clearly of more value. We thus conclude that the plots that seek to show a correlation between the distance to the surface and the ϕ -angle rotation of the molecule do not provide any practical insight into the dynamics.

There is, however, an interesting trend that should be noted here concerning the variation with angular momentum quantum number of the average distance between the surface and the molecular center of mass. For the set of trajectories at fixed v and J that did not lead to desorption within the total allotted time, we calculated such a mean distance, with the averaging extending both over the entire length of each individual trajectory and over all trajectories of the set. A summary of the results obtained via this process appears in the rightmost column of Table I. Note that as the system passes through the transition to (nearly) free planar rotation, the average distance between the adsorbed molecule and the surface *decreases* by roughly 0.3 \AA . Thus, the free rotation behavior clearly does not derive from a lessening of the effective surface corrugation due to an increase in the average distance from the crystal, but rather it likely stems from a smearing out of the potential energy anisotropy felt by the molecule as a consequence of the higher rotational velocities. This averaging out of the interaction tends to make the (average) plane of the hydrogen motion parallel to the surface (i.e., $\theta = \pi/2$), thereby reducing the probability of a close collision occurring between hydrogen and argon atoms even though the molecular center of mass actually lies closer to the surface in this dynamical regime. This analysis was also suggested by results given in our previous study, in which we noted that the oscillations about $\theta = \pi/2$ were in fact more symmetric at high J values than they were at low J values.

IV. SUMMARY

In summary, we find that a change in the dynamics of an HCl molecule physisorbed on an Ar(111) surface can be

correlated with a variation in the molecular desorption rate as a function of initial angular momentum. A maximum in the rate constant appears at an intermediate value of J , with the same qualitative behavior being displayed when a quantum of vibrational energy is added to the molecule. Such results suggest that an absorption spectrum of physisorbed HCl should show weaker lines corresponding to transitions between intermediate J states than might otherwise be expected due to a depletion of population in these levels. We hope that the present work will stimulate experimentalists to undertake a study of a simple physisorbed system such as HCl/Ar(111) so as to check the validity of the dynamical picture described here.

We have also shown that a convenient means for characterizing the dynamics of the physisorbed molecule is afforded by surface of section plots analogous to those that have been used in the study of intramolecular energy transfer and unimolecular decomposition dynamics. In particular, the transition from tumbling at an intermediate J value to nearly free planar rotation at a higher angular momentum may be associated with a reduction in the phase space accessible to the system. This dynamical change is not, however, abrupt in that a particular value of the angular momentum, one can find some trajectories that yield surfaces of section showing characteristics both of planar molecular rotation and also of tumbling motion.

ACKNOWLEDGMENT

The author wishes to thank R. M. Stratt for several useful discussions concerning this work.

¹For an overview of recent work in gas-surface dynamics, see, for example, *Dynamics of Gas-Surface Interaction*, edited by G. Benedek and U. Valbusa (Springer, Berlin, 1982); *Dynamics on Surfaces*, edited by B. Pullman, J. Jortner, A. Nitzan, and B. Gerber (Reidel, Dordrecht, 1984).

²See, for example, A. W. Kleyn, A. C. Luntz, and D. J. Auerbach, *Phys. Rev. Lett.* **47**, 1169 (1981); *Surf. Sci.* **117**, 33 (1982); A. C. Luntz, A. W. Kleyn, and D. J. Auerbach, *J. Chem. Phys.* **76**, 737 (1982); *Phys. Rev. B* **25**, 4273 (1982); F. Frenkel, J. Hager, E. Krieger, H. Walther, G. Ertl, J. Segner, and W. Vielhaber, *Chem. Phys. Lett.* **90**, 225 (1982); G. D. Kuibak, J. E. Hurst, H. G. Rennagel, and R. N. Zare, *J. Chem. Phys.* **79**, 5163 (1983); M. Asscher, W. L. Guthrie, T. -H. Lin, and G. A. Somorjai, *ibid.* **78**, 6992 (1983); J. W. Hepburn, J. F. Northrup, G. L. Ogram, J. C. Polanyi, and J. M. Williamson, *Chem. Phys. Lett.* **85**, 127 (1982); D. S. King and R. R. Cavanagh, *J. Chem. Phys.* **76**, 5634 (1982); D. A. Mantell, R. R. Cavanagh, and D. S. King, *ibid.* **84**, 5131 (1986); R. P. Thorman and S. Bernasek, *ibid.* **74**, 6498 (1981); as well as other references by these authors cited therein.

³J. C. Tully, *Surf. Sci.* **111**, 461 (1982); E. K. Grimmelmann, J. C. Tully, and E. Helfand, *J. Chem. Phys.* **74**, 5300 (1981); J. E. Adams, *Chem. Phys. Lett.* **110**, 155 (1984); R. J. Wolf and R. C. Davis, *J. Phys. Chem.* **89**, 2757 (1985).

⁴J. E. Adams, *J. Chem. Phys.* **84**, 3589 (1986).

⁵D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *J. Chem. Phys.* **67**, 404 (1977); M. L. Koszykowski, D. W. Noid, and R. A. Marcus, *J. Phys. Chem.* **86**, 2113 (1982); D. M. Wardlaw, D. W. Noid, and R. A. Marcus, *ibid.* **88**, 536 (1984). An application to the vibrational spectra of some simple diatomics is described by J. R. Stine and D. W. Noid, *J. Chem. Phys.* **78**, 1876 (1983).

⁶R. H. Tipping and J. F. Ogilvie, *J. Mol. Struct.* **35**, 1 (1976).

⁷J. F. Ogilvie, W. R. Rodwell, and R. H. Tipping, *J. Chem. Phys.* **73**, 5221 (1980).

⁸See, for example, M. Allavena, H. Chakroun, and D. White, *J. Chem. Phys.* **77**, 1757 (1982); H. Kono and S. H. Lin, *ibid.* **78**, 2607 (1983); **79**, 2748 (1983); W. H. Flygare, *ibid.* **39**, 2263 (1963).

⁹S. B. Woodruff and D. L. Thompson, *J. Chem. Phys.* **71**, 376 (1979).

¹⁰See, for example, D. L. Bunker, *J. Chem. Phys.* **37**, 393 (1962); E. R. Grant and D. L. Bunker, *ibid.* **68**, 628 (1978); W. L. Hase, R. J. Wolf, and C. S. Sloan, *ibid.* **71**, 2911 (1979); **76**, 2771 (1982).

¹¹T. A. Weber and F. H. Stillinger, *J. Chem. Phys.* **80**, 2742 (1984).

¹²D. J. Diestler, *J. Chem. Phys.* **78**, 2240 (1983).

¹³J. P. Valleau and S. G. Whittington, in *Statistical Mechanics, Part A*, edited by B. J. Berne (Plenum, New York, 1977).

¹⁴The orientation angles used in the present work are as follows: θ is defined

to be the angle between the surface normal and a vector that extends from the HCl center of mass to the H atom. The angle between a vector extending from the HCl center of mass in the $[\bar{1}10]$ surface direction and the projection of the vector described above onto a plane parallel to the surface is then defined to be ϕ . Thus a change in θ reflects rotational motion perpendicular to the plane of the surface, while ϕ motion represents a rotation in a plane that lies parallel to the crystal surface.

¹⁵See, for example, R. N. Porter and L. M. Raff, in *Dynamics of Molecular Collisions, Part B*, edited by W. H. Miller (Plenum, New York, 1976).

¹⁶M. Henon and C. Heiles, *Astron. J.* **69**, 73 (1964); B. Barbanis, *ibid.* **71**, 415 (1966). A review of many recent approaches to the study of intramolecular energy transfer, including the use of surfaces of section, is given by D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *Annu. Rev. Phys. Chem.* **32**, 267 (1981).