Photodissociation of HCl adsorbed on the surface of an Ar_{12} cluster: Nonadiabatic molecular dynamics simulations

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The photodissociation of HCl adsorbed on the surface of an Ar_{12} cluster is studied by semiclassical molecular dynamics simulations, using a surface-hopping approach for the nonadiabatic transitions. The DIM method is used to construct the 12 potential energy surfaces that are involved, and the nonadiabatic couplings. The results are compared with previous studies on HCl embedded inside Ar clusters and on the triatomic Ar–HCl cluster. The main findings are the following: (1) There is a yield of about 1% for recombination onto the ground electronic state of HCl, roughly the same as for HCl embedded inside Ar_{12}. (2) Photodissociation lifetimes much longer than for Ar–HCl are found. (3) The kinetic energy distribution of the H atom shows large energy transfer to the cluster, greater than in the case of HCl in the embedded geometry in $(Ar)_{12}HCl$. (4) An interesting mechanism leads to the formation of some fraction of very ''hot'' Cl atoms. (5) About 10% of the Cl is left trapped in $(Ar)_m Cl$ clusters. (6) The branching ratio $P_{1/2}:P_{3/2}$ for the Cl atoms that leave the cluster shows electronic cooling compared to the isolated HCl molecule case. The results throw light on the role of local geometry in photodissociation/recombination processes, and in particular on the mechanisms pertinent in the case of surface-adsorbed species. The nature of the results, showing strong cage effects at the surface geometries is to a large extent a consequence of the encapsulation of the H atom, obtained for the structure of the $(Ar)_{12}HCl$ cluster. © *1999 American Institute of Physics.* [S0021-9606(99)70222-9]

I. INTRODUCTION

Photodissociation and recombination of molecules in chemically inert media is a fundamental topic in chemical dynamics. Studies of such processes have been vigorously pursued in recent years in solids, liquids, and clusters. The specific attraction of clusters as media for exploring the processes is that the finite number of degrees of freedom may simplify the analysis, compared with condensed matter in bulk, while at least some aspects of the processes in clusters (e.g., the interaction potentials) should be closely related to those in solids and liquids. There have been extensive experimental and theoretical studies of photodissociation and recombination of diatomic and polyatomic molecules in clusters.[1–12] The present paper is motivated mainly by the following question: How does the photodissociation/recombination dynamics of a molecule adsorbed at the surface of a chemically inert cluster differ from the corresponding processes in the case that the molecule is embedded inside the cluster? To explore this question, we carry out simulations on the photodissociation (and subsequent recombination, when it occurs) of HCl adsorbed at the surface of an $(Ar)_{12}$ cluster. There are several reasons for choosing this system: (1) Studies on the corresponding process for HCl embedded inside an $(Ar)_{12}$ cluster were carried out by three of the present authors.[13] Calculations for other $(Rg)_n HX$ systems, with X a halogen and Rg a rare gas, all for the ''inside'' position of the HX, were also reported in the literature.[8,14,15,44] Also photolysis and recombination of HCl in solid Ar were investigated in detail.[16–18] (2) Photodissociation of HCl in the triatomic cluster Ar–HCl was studied most extensively[9–11,19–21] in recent years, and the same process was investigated also for several other Rg–HX clusters of similar structure.[6,8] For Ar–HBr, both experimental and theoretical results are available.[6,42] These triatomic clusters have an element of structural similarity to the ''surface isomer'' of $(Ar)_{12}HCl$, since in both cases the hydrogen points towards the ''solvent.'' (3) Both the ''embedded'' and the ''surface adsorbed'' isomers of $(Ar)_{12}HCl$ are predicted to be (locally) stable minima on the potential energy surface of the system.[13] With the available state of the art potentials[13] it appears that the ''surface adsorbed'' structure corresponds to the global minimum of the potential energy.[13,22] However, the barrier between the ''embedded'' and the ''surface adsorbed'' isomers is very high, so in principle, with suitable experimental approaches it may be possible to prepare and study both isomers.

Calculations for photodissociation of HCl in Ar matrices,[17] and in the ''embedded'' isomer of $(Ar)_n HCl$ ($n = 12, 54$) (Ref. 13) showed that nonadiabatic transitions be-

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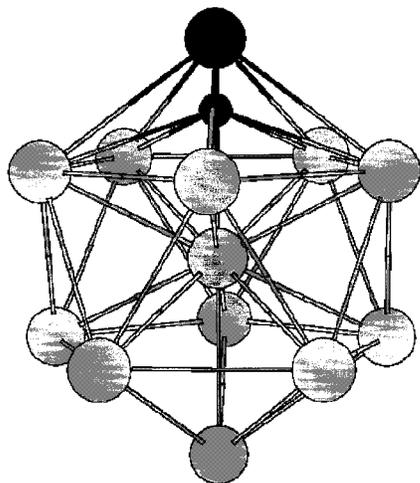
FIG. 1. Minimum energy structure of $Ar_{12}(HCl)$.

tween 12 different potential energy surfaces play a major role in the process, and they are in fact the key for even qualitative understanding of some of its important features. We therefore carried out the calculations of the present study in the framework of nonadiabatic (semiclassical) molecular dynamics simulations.

The structure of the article is as follows: Section II describes very briefly the system, the interaction potentials used for the system in the ground and in the excited electronic states, and the semiclassical "surface hopping" simulation method for dynamics. The description is brief since the interaction potentials and simulation method are the same as used for the "embedded" isomer $(Ar)_{12}HCl$ in a previous study.[13] In Sec. III the main findings are discussed in relation to the properties found for other systems. Concluding remarks are brought in Sec. IV.

II. SYSTEM, INTERACTIONS, AND SIMULATION METHOD

A. Ground-state potentials

The interaction potentials used in the present study were the same as employed for the "embedded" isomer of $(Ar)_{12}HCl$ in Ref. 13. The potential function for the electronic ground state was written as a sum of Ar–HCl interactions and of Ar–Ar pair potentials. We used Hutson's potential for Ar–HCl,[23] an Ar–Ar pair potential from Aziz and Slaman[24] and the H–Cl vibrational potential from Bettendorf *et al.*[25] The minimum energy structure of $Ar_{12}(HCl)$ found by simulated annealing is shown in Fig. 1.

Based on our studies so far, this seems to be the lowest energy isomer, lower in energy than the isomer with HCl embedded inside the cluster.

As mentioned earlier, also the "embedded HCl" structure of $(Ar)_{12}HCl$ is, however, locally quite stable. The energy barrier between the two isomers is very high, so if formed, each of them should be stable in experimental conditions. Since cluster formation is often controlled by kinetic factors, it should be possible to obtain experimentally both structures, each by a different mechanism. Note that in the structure of Fig. 1 the H atom is quite strongly "encapsu-

lated" between the Cl and the neighboring argon atoms. This obviously will have a major effect on the photodissociation dynamics.

B. DIM potentials for the excited states

There are 12 electronic states, in terms of electronic angular momentum and spin, relevant to the photodissociation $HCl \rightarrow H(^2S) + Cl(^2P)$ in a medium of closed shell chemically inert atoms. Krylov and Gerber[17] used the diatomic-in-molecules (DIM) method[26,27] to construct the potential energy surfaces and the nonadiabatic couplings for photodissociation of HCl in solid Ar, and this was followed by Niv *et al.*,[13] for the "embedded" isomer of $(Ar)_{12}HCl$. We use the same method here. We note that the DIM method has been used quite extensively in recent years for a variety of systems including the halogen–molecule/rare gas complexes, and hydrogen–halide/rare gas complexes.[16,28–31] Some support for the DIM potentials validity for the HCl/Ar systems comes from agreement between the simulations of Krylov and Gerber[17] and experiments by Godderz, Schwentner, and Chergui[32] on several properties of the photodissociation of HCl in solid Ar. However, not enough data are available yet for a full quantitative comparison and evaluation of the DIM potentials. The DIM modeling of the system uses valence bond formulation for the H–Cl interaction. Potential energy curves of the HCl molecule taken from Bettendorf *et al.*[25] are used as input data for the construction of the DIM surfaces. The interaction between the Cl atom and an Ar atom, modeled in terms of an effective p orbital on the Cl atom was taken from Aquilanti *et al.*[33] The interaction depends on the orientation of the p orbital with respect to the Ar–Cl axis. For H–Ar interactions we used pair potentials from Ref. 34. Spin–orbit coupling, with a strength equal to that for isolated $Cl(^2P)$ atom was incorporated in the Hamiltonian. The diagonalization of the electronic DIM Hamiltonian was performed "on the fly," at each point of the trajectory of the atomic motions. The calculation of the adiabatic potential energy surfaces, of the electronic eigenfunctions and of the nonadiabatic couplings between any two electronic states, all done "on the fly," along the trajectories of the nonadiabatic molecular dynamics simulations, followed the procedure of Refs. 17, 13, where detailed descriptions are given.

C. Semiclassical "surface hopping" simulations of the dynamics

The algorithm used for the dynamics is discussed in Refs. 13 and 17. It is a variant of the "surface hopping" method for nonadiabatic processes, developed by Tully[35] and by others. In this approach, nuclear motions are treated as classical and described by classical trajectories. The electronic state is described by a time-dependent wave function that incorporates the effect of nonadiabatic coupling. The electronic state is evaluated along each trajectory. At each instant in time, the nuclei are taken to move on one of the adiabatic potential energy surfaces. Changes in the computed electronic wave function are used as the criterion for the probability of "hopping" to another adiabatic potential en-

ergy surface. When the criterion for a ''hopping'' event is satisfied at some point, the nuclei are taken to experience an instantaneous switch to the other potential surface, and their propagation is pursued classically on the latter until the criterion for the next ''hopping'' event is met. The criteria for ''hopping'' events, and the initial conditions for propagation of the nuclei (after hopping has occurred) on the new potential surface, are discussed in Refs. 17 and 13. These criteria and conditions can be different in different variants of the ''surface hopping'' method, though for HCl in solid Ar some testing suggests that the results of the variant used by Tully[35] and that employed by Krylov and Gerber[17] seem to give similar results. Also, suitable adaptations of the ''surface hopping'' method are necessary for treating case of exact degeneracy of electronic states (such as Kramers degeneracy),[36] and for cases where spin–orbit interactions are present in the Hamiltonian (the system studied here, with spin–orbit coupling included, is of that type).[36,37] We note that several other groups have used the ''surface hopping'' method in recent applications to photodissociation/recombination processes in solids, liquids, or clusters,[12,31,37,38] and that comparisons with experiment suggest the method is successful also for these systems.

D. The initial state

We took the cluster to be in its vibrational ground state before electronic excitation. A normal-mode calculation was carried out for the structure shown in Fig. 1. An all-mode separable wave function was obtained in the harmonic approximation. Using the Wigner function a distribution of positions and momenta from the above wave function were computed as initial values for the classical simulation.[13] The normal mode harmonic treatment is probably mostly in error for the libration motion of the HCl. Though this is likely to be a significant error, e.g., for vibrational spectroscopy in the electronic ground state, some exploration of the possible role of libration anharmonicity on the photodissociation dynamics has indicated that our results should not be strongly affected.

Using the computed Wigner positions-momenta distribution, initial conditions were sampled from this set. Excitation was modeled in the spirit of the classical Franck–Condon vertical promotion onto the excited potential energy surface with a given excitation energy. We chose excitation energy of 6.42 ± 0.07 eV, which corresponds (approximately) to 193 nm laser. The HCl molecule was excited into the $^1\Pi_1$ state. 120 excited-state ''surface-hopping'' trajectories were propagated for the $(Ar)_{12}HCl$ system, providing reasonable statistics for our purposes here.

III. RESULTS AND DISCUSSION

In the presentation of the results, we focus on several main findings.

(1) *Electronic transitions and recombination:* Most trajectories describe very fast photodissociation, on a time scale of 100 fs or less. In many of these cases, the energetic hydrogen produced upon photolysis just strikes one or two of the argon atoms of the cluster, then recoils and
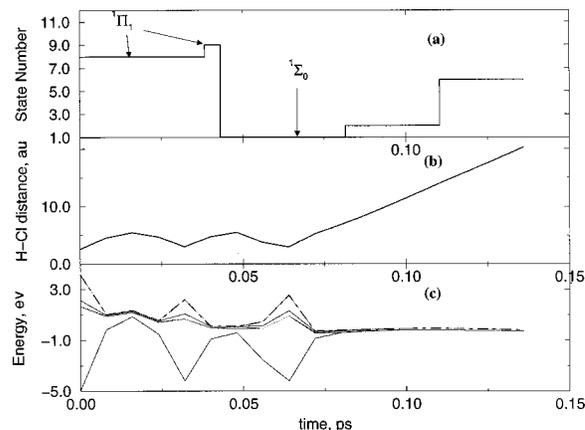

FIG. 2. (a) The electronic state of $Ar_{12}(HCl)$ vs time along a particular trajectory. (b) The H···Cl distance along the trajectory. (c) The adiabatic potential energy surfaces of the system along the trajectory.

leaves the cluster. However, in all of the computed trajectories at least one nonadiabatic transition between different electronic states took place in the course of the dynamics. Indeed, the average number of nonadiabatic transitions per trajectory is between 5 and 6. Figure 2 shows the electronic state of the system vs time along a particular trajectory. The electronic states were enumerated from 1 to 12, with increasing number corresponding to increasing electronic energy. For simplicity of interpretation, we also assigned the potential energy surfaces by projecting the wave functions onto the states of the isolated HCl molecule. Obviously such an assignment is always approximate and can be meaningless at some configurations, for which the symmetry breaking effects of the environment on the states if HCl is extremely severe. As Fig. 2 shows, the system makes a ''hopping'' transition some 40 fs after photoexcitation, from the initially excited state, that has mostly a $^1\Pi_1$ character, to another excited state, also of (mostly) $^1\Pi_1$ character. Then, at about 45 fs after excitation, the system makes a transition to the ground electronic state. No recombination, however, takes place; the kinetic energy of the H atom is way above the attractive well of the $^1\Sigma_0$ curve of HCl, and the H atom is at this stage already on its way out of the ''cage'' seen in Fig. 1. Other nonadiabatic transitions take place at later times; these occur for configurations where the H atom is relatively far from the remaining $(Ar)_mCl(^2P)$ cluster, and the relevant potential energy surfaces are degenerate for these asymptotic H···Cl distances. Indeed, these transitions have no significant physical consequences for the process. The lowest part of Fig. 2 shows the adiabatic potential energies of the system computed along the trajectories. Thus the transition between $^1\Pi_1$ and $^1\Sigma_0$ at about 45 fs occurred indeed at a point of near crossing between the relevant potential surfaces. The nonadiabatic transition at about 110 fs took place essentially in the asymptotic region of the potential surfaces, for large H···$(Ar)_mCl$ distances. Another aspect of the dynamics is shown in the middle part of Fig. 2. It shows the H···Cl distance vs time.
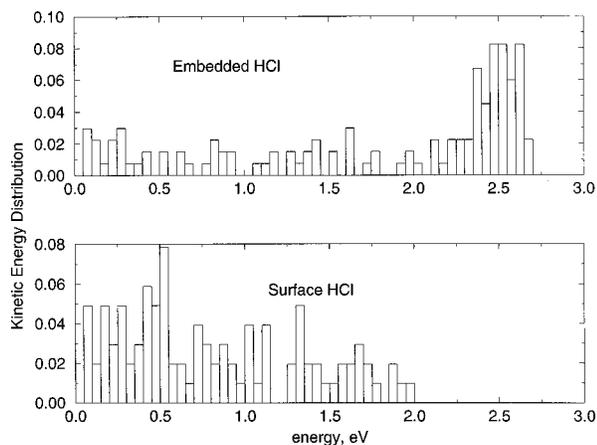
FIG. 3. Kinetic energy distribution of H atoms from photolysis of $Ar_{12}(HCl)$. Results for ''embedded HCl'' and for ''surface HCl'' cluster isomers are compared.

Clearly, there was a cage effect in the course of part of the trajectory, since two oscillations of the $H \cdots Cl$ distance are visible, before the departure of the H atom from the cluster (which begins after $t \approx 60$ fs). The $^1\Pi_1 \rightarrow {}^1\Sigma_0$ nonadiabatic transition took place, however, during the second oscillation of the $H \cdots Cl$ distance, when the H atom was still inside the cage. In summary, in this trajectory, a nonadiabatic transition to the ground state took place, but without recombination since the H atom has not imparted sufficient energy to the Ar atoms. A cage effect is present in this trajectory as reflected in the oscillations of the $H \cdots Cl$ distance. There is a fraction of trajectories showing qualitative behavior of this type. We conclude therefore that nonadiabatic transitions as well as cage effects play a significant role in the process. *Indeed, we found that recombination of HCl onto the ground state takes place in two of the trajectories computed.* Despite the poor statistics, we think this result is physically significant. In studies of photodissociation of HCl in ArHCl no recombination event was found in many thousands of trajectories. The crude recombination yield we estimate here, of the order of 1%, roughly the same as computed previously for the case of the ''embedded'' HCl in $(Ar)_{12}HCl$.[13] Interestingly, about 10% of the trajectories sample the ground state in the ''surface'' geometry, and 2% dissociate from this state, vs only 1% of the trajectories that sample the ground state in the ''embedded'' geometry. In general, the number of nonadiabatic transitions is higher for the present ''surface'' geometry; the average number of nonadiabatic transitions is 5.5 ± 0.5 per trajectory for the ''surface'' geometry, 3.6 ± 0.4 transitions per trajectory on average for the ''embedded'' geometry. The same tendency is found for cage effects, as we shall see later. We conclude that the ''encapsulated'' geometry of surfaces-adsorbed HCl gives rise to significant nonadiabatic and caging effects, perhaps more so than ''embedded'' structures.

(2) *Kinetic energy distribution of H atoms:* The kinetic energy distribution of the hydrogen atoms from photolysis of $Ar_{12}(HCl)$ is shown in Fig. 3. The results for the

present ''surface adsorbed HCl'' (that was excited by 6.42 eV) geometry are compared with those for the ''embedded HCl'' isomer (that was excited by 7 eV).[13]

The comparison is quite striking. The energy distribution in the ''embedded HCl'' case is dominated by hot H atoms; trajectories with H atoms having kinetic energies above 2.0 eV constitute $55 \pm 5\%$ of the ensemble. In the ''surface'' geometry, trajectories with H atoms having kinetic energies above 1.42 eV constitute only $14 \pm 2\%$ of the ensemble. In both cases, the number of nonadiabatic transitions in the ''hot'' trajectories is lower by factor of 2 than in the ''cold'' trajectories.

Interestingly, in the small ArHCl cluster, essentially only hot hydrogens are produced, with a relatively small amount of energy transfer to the Ar atom.[6,9] Clearly the ''encapsulated'' geometry implied by the structure of Fig. 1 is very conducive to energy transfer, as the H atom impacts on the Ar_{12} subsystem (and subsequently recoils, striking also the Cl atom). From the ''embedded HCl'' isomer, most H atoms emerge through ''holes'' in the surrounding argon shell, imparting only modest amounts of energy. This prediction merits experimental attention.

(3) *Comparison with preliminary results on photolysis of $Ar_n(HBr)$ cluster:* Experiments corresponding to our calculations for $Ar_{12}(HCl)$ were not reported yet. However, very recently Baumfalk and Buck[39] carried out experiments on the photolysis of HBr in $Ar_n(HBr)$ clusters. Some preliminary results are at hand, and we shall briefly comment on the relation to the present calculations. The experiments of Baumfalk and Buck involve passing a beam of $(Ar)_n$ clusters through a cell which contains HBr molecules at low pressures (pick up arrangement). The conditions are such that capture of no more than a single HBr molecule at the surface of the cluster is expected. This arrangement suggests formation of the ''surface adsorbed'' $Ar_n(HBr)$ geometry (calculations by the present authors indicate this is also energetically more stable than the ''embedded'' one). The ''captured'' HBr molecule is then photolysed using a laser of wavelength 243 nm, and the kinetic energy distribution of the H atoms is measured by a $(2+1)$ REMPI technique at the same wavelength in a time-of-flight mass spectrometer. The very preliminary results give a distribution peaked at zero velocities.[39] In contrast with results previously obtained for neat $(HBr)_n$ clusters[7] and in agreement with the present calculations for the ''surface-adsorbed'' isomer of $Ar_{12}(HCl)$, Baumfalk and Buck did not observe a component of fast H atoms.[39] The results of this experiment, including dependence of the behavior upon cluster size will be published soon, when more details are available. The experimental arrangement is, of course, very suitable also for studies of ''surface adsorbed HCl'' in $Ar_n(HCl)$, and such experiments will be attempted in the near future.

(4) *Lifetime distribution of the photodissociated cluster:* Figure 4 shows the probability $P(t)$ of finding the hydrogen inside the cluster at time t after photoexcitation. The mean lifetime of the excited cluster is of the order of
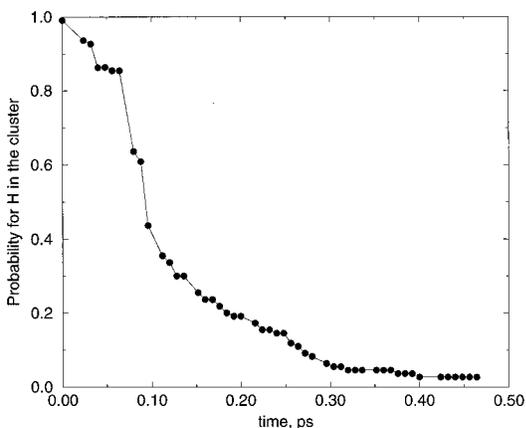
FIG. 4. Probability $P(t)$ of finding the H atom in the cluster at time t after photoexcitation.

140 fs, and there is an appreciable probability of the order of 20% for finding the hydrogen in the cluster at $t \approx 200$ fs. In the case of ArHCl, for instance, the lifetimes are much shorter. The issue of whether resonances exist in the photolysis of Ar–HCl was discussed extensively in the literature.[9–11,19–21] However, any resonances predicted in that case are far shorter in lifetime than found here. The present system thus represents a qualitative jump from ArHCl to $Ar_{12}(HCl)$ in the strength of the cage effect, when measured in terms of the lifetimes induced.

(5) *Kinetic energy distribution of the Cl atom:* Figure 5 shows the kinetic energy distribution of Cl atoms dissociated from $Ar_{12}(HCl)$ after excitation. The surprising feature is the long tail of very hot Cl atoms produced. Possibly measurable numbers of Cl atoms with energies of the order of 0.8–1.0 eV are produced, though as expected, the distribution peaks at much colder Cl atoms. The following mechanism seems at work in producing the very hot Cl atoms: in the initial impact on the Ar_{12} part of the system, in some of the trajectories the hydrogen compresses very strongly the soft cluster. When the compressed cluster expands, it pushes the H atom, which
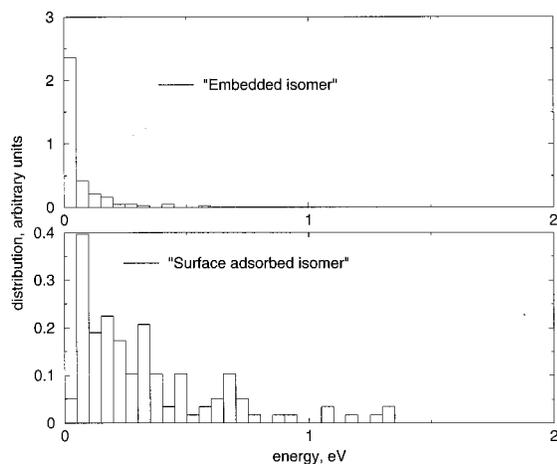

FIG. 5. Kinetic energy distribution of the Cl atom from photolysis of $Ar_{12}(HCl)$—"embedded" and "surface-adsorbed" isomers are compared.

in turn pushes the Cl atom. The hard core of the H atom interaction with the Cl is thus the potential which transfers almost directly the impulse of an Ar atom in its expansion. This gives rise to large energy transfer, more so than in a single isolated "collision" of an H atom and a Cl.

(6) *Effect of clustering on the $Cl(P_{1/2})/Cl(P_{3/2})$ branching ratio:* The model used in this work cannot address the issue of the branching ratio in photodissociation of isolated HCl. In order to quantitatively calculate the branching ratio in pure HCl a very accurate description of the transition moments and of the adiabatic potentials and nonadiabatic couplings (especially at long ranges) is needed. This topic has been treated by rigorous calculations treating both electronic structure and nuclear dynamics at a quantum level.[40] Unfortunately, such approaches are presently restricted to small, few atom systems. The potentials used in the present study are not accurate enough for this purpose. We can, however, use the present model to approximately calculate the effect of the solvation in argon cluster on the $P_{1/2}/P_{3/2}$ branching ratio. Nonadiabatic dynamics following photoexcitation to the highest electronic state of the system correlating with the $Cl(P_{3/2})$ limit yielded 20% $\pm$2% of the Cl atoms on the $Cl(P_{1/2})$ state, while excitation to the lowest state correlating with the $Cl(P_{1/2})$ limit yielded 35% $\pm$2% of the Cl atoms on the $Cl(P_{1/2})$ state. Using the experimental branching ratio for photoexcitation at the wavelength 193.3 nm, 0.69$\pm$0.02, for the free HCl molecule,[43] which is in good agreement with the theoretical value,[40] we can provide a rough estimate for the branching ratio in the case of $Ar_{12}(HCl)$. We evaluate this branching ratio to be approximately 0.4. Our prediction is, therefore, that the interaction with the Ar_{12} cage causes electronic cooling of the Cl atoms emerging from the cluster, resulting in branching ratio measurably lower than the branching ratio of the isolated molecule.

(7) *The anisotropy factor for the photodissociation of $Ar_{12}(HCl)$:* The anisotropy factor is one of the most important quantities used to characterize photodissociation processes.[41] It can be conveniently computed as follows. Let $\boldsymbol{\epsilon}$ be the electric field vector of the polarized light, and $\boldsymbol{\mu}$ be the transition moment vector associated with the excitation. Then, each photodissociation trajectory is weighted by a factor

$W = |\boldsymbol{\epsilon} \cdot \boldsymbol{\mu}|^2$.

The direction of $\boldsymbol{\mu}$ in the laboratory frame is sampled for the initial state (it is determined by the orientation of the H–Cl axis in the initial conditions). γ is defined as the angle between the final velocity vector of the H atom, and the direction of $\boldsymbol{\epsilon}$. The final γ-angle distribution will be of the following form:

$I(\gamma) \propto 1 + \beta P_2(\cos(\gamma))$,

where P_2 is second-order Legendre polynomial. The anisotropy parameter β ($-1 \leq \beta \leq 2$) can readily be extracted from the calculated angular distribution. The angular distributions for the "surface adsorbed HCl" isomer of $Ar_{12}(HCl)$ and for the "embedded HCl" iso-
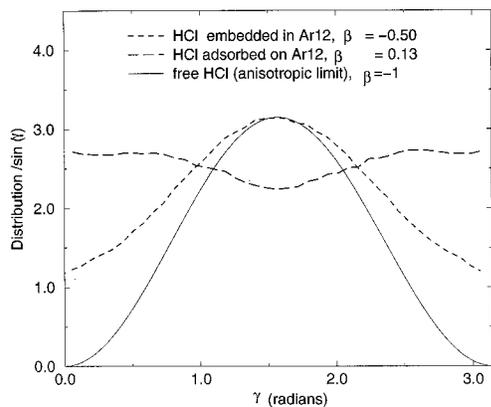
FIG. 6. Angular distribution of H atoms from photodissociation of $Ar_{12}(HCl)$. The distribution is with respect to the direction of the polarized light electric field.

FIG. 7. Cluster-size distribution of pure argon clusters after photodissociation of $Ar_{12}(HCl)$.

mer are both shown in Fig. 6, and compared with the distribution for the free HCl. The case of free isolated HCl represents, of course, the extreme case of an anisotropic distribution with $\beta=-1$. The value of β for the ''adsorbed HCl'' isomer of $Ar_{12}(HCl)$ is 0.13 ± 0.05, close to the isotropic limit ($\beta=0$) and to the calculated value for the ArHCl system ($\beta=0.11$).[9] The error estimate is not small, but the result is significantly different from zero. The reason for the positive sign is the following: In the ''surface adsorbed'' case the H atom always undergoes collisions with one or more of the argon atoms, which greatly change the direction of the initial velocity. The consequence is that the distribution is almost isotropic, but there is a slight preference for H atoms to recoil at directions almost perpendicular to the original HCl axis (these directions are close to parallel to the electric vector of the polarized light). The situation therefore somewhat resembles the dissociation of a free molecule with parallel excitation (where β is $+2$) and results in positive sign in β.

In the ''embedded HCl,'' the hydrogen can break out in some cases with only soft collisions with the argon atoms of the solvation envelope, and the distribution obtained from the ''embedded HCl'' isomer is somewhat closer to the free HCl limit, with $\beta=-0.50\pm0.05$.

(8) *Fragmentation of the cluster in the photodissociation process:* There is extensive ''evaporation'' of heavy atoms from the cluster, due to the energy imparted by the initially hot hydrogen in collisions with argon atoms and with Cl. Getting the accurate, final size distributions is difficult, since the evaporation follows energy redistribution between the atoms of the cluster which takes place on a much slower time scale than the primary photolysis. From the molecular dynamics simulations, we find that about 90% of the Cl atoms leave the cluster as free atoms, and about 10% are trapped also after a long time in $(Ar)_m Cl$ clusters. As for the ''evaporation'' of Ar atoms from the cluster, consider Fig. 7. It shows the size-distribution of the cluster (only pure Ar clusters are considered) at several time points after photoexcitation. It is evident that appreciable loss of Ar atoms from the clus-
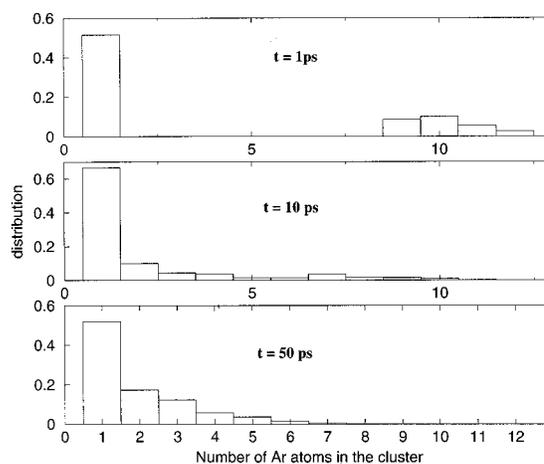
ter occurs already within 1 ps of the excitation. The most probable number of Ar atoms in the cluster at this stage is 10, and the evaporated Ar atoms leave the cluster as single atoms. However, evaporation on much slower time scales continues. After 10 ps, a very broad cluster size distribution is obtained, with an average size of about 6 Ar atoms. The shift towards smaller cluster sizes goes on, and after 50 ps the abundancy of a cluster goes down monotonously with its size. It should be of great interest to attempt time-domain experiments of the ''evaporation'' process.

IV. CONCLUDING REMARKS

In this study we investigated by simulations photodissociation, electronic transitions and recombination in a realistic model of HCl adsorbed at the surface of a rare-gas cluster. The results and comparison with previous studies of the same process in other clusters throw light on the role of local geometry in the basic photochemical processes studied. One conclusion is that the surface-adsorbed geometry in this realistic model leads to very important caging effects, and also to appreciable nonadiabatic transitions in the process, these two aspects being related at least to an extent.

The qualitatively important occurrence of some recombination onto the ground state following photolysis; the dramatic effect of the clustering in this case on the velocity distribution of the hydrogen atoms; the substantial effect of the clustering on the $Cl(P_{1/2}):Cl(P_{3/2})$ ratio; the almost isotropic angular distribution obtained in this system—all these offer potentially useful future experimental handles on the dynamics in this case, and provide possible tests for the simulation results. It is gratifying that very preliminary experimental results for $Ar_n(HBr)$ seem to be in accord with the prediction regarding the velocity distribution of the H atoms. However, a more detailed and definite experimental test is still underway, and should be very important for this topic. An important point that must be kept in mind is the following. The initial state geometry of the $(Ar)_{12}HCl$ cluster in our calculations implies encapsulation of the H atom by the neighboring Ar and Cl atoms. This undoubtedly is a key

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factor for the relatively strong cage effects found for this case of ''surface adsorbed'' system. We do not expect such strong effects for surface structures for which the H is not encapsulated. Interpretation of experimental data must be carried out with attention to the nature of surface geometries.

We stress that the results should be relevant also to photochemistry at surfaces. Studies of related surface systems, e.g., photolysis of molecules adsorbed on rare-gas films should be very desirable in the light of the results obtained here.

ACKNOWLEDGMENTS

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