Solvation Effects on Chemical Reaction Dynamics in Clusters: Photodissociation of HI in Xe_NHI

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The photodissociation of HI in clusters of the type Xe_NHI is studied theoretically to explore the possible occurrence and dynamics of the cage effect in small clusters (from N = 1 to 12). The method used describes the H atom quantum mechanically, the heavy atoms classically. It is found that a cage effect, corresponding to transient vibrations of the H between heavy atoms, exists for all clusters, including XeHI. For N < 5 these resonances are short lived and contribute little. For N > 5 the resonances are long lived and dominate the process. Steric and structural factors cause this behavior.

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Chemical reactions in van der Waals and in hydrogen-bonded clusters offer a unique framework for exploring solvent effects on molecular processes in microscopic systems. This makes it possible, in principle, to also study the evolution of solvent effects with the size of the system. Pioneering experimental studies of photoinduced molecular reactions in well-characterized cluster systems have been reported very recently by several groups.¹⁻⁷ Also classical trajectory simulations of several such processes were carried out.^{8,9} A very fundamental source of differences between reactions in condensed-matter and isolated molecular processes in the gas phase is the celebrated cage effect: When a reaction occurs, the surrounding solvent molecules may, with some probability, prevent the mutual separation of the reaction products, or delay such a separation in time, confining the two species formed to the same cage for some duration. It is of considerable interest to establish whether such effects can occur also in a "microsolution" of a cluster, and how does such behavior depend upon cluster size. This Letter deals with several basic questions regarding "microsolvent" effects on photodissociation in clusters. Is there a cage effect for molecular photolysis in small clusters?⁷ What is the dynamical nature of the effect, and what are its measurable consequences? How does the effect depend upon cluster size? We chose to explore these questions for a system in which quantum-mechanical behavior is expected, since such a case has not received treatment in previous theoretical studies. As the model system for our studies, we adopted the photodissociation of HI in clusters of the type Xe_NHI , with N in the range from 1 to 12 (the latter represents the first full solvation layer). The quantum effects that we treat are those associated with the light H photofragment. A major advantage of this system is that due to the H/Xe and H/I mass ratios the cage effect gives rise to an interesting, new type of resonance behavior, as will be seen later. Cluster systems studied theoretically so far involved different mass ratios, and did not show such resonances.8,9

The model.— The photodissociation processes studied here result from electronically exciting the HI molecule within the cluster from its ground state ${}^{1}\Sigma_{+}$ to the purely repulsive excited state ${}^{1}\Pi$. The potential function of the cluster system in the excited state was constructed from pairwise interactions between the atoms of the system. The necessary Xe-Xe, Xe-H, Xe-I, and H-I ($^{1}\Pi$) pair potentials were all taken from fits to experimental (spectroscopic and scattering) gas-phase data.¹⁰⁻¹³ The same potentials were used in recent molecular-dynamics simulations on HI photodissociation in a Xe crystal.¹⁴ The ground-state potential function of the cluster was constructed from the pairwise Xe-Xe potential, from the H-I (Σ_{+}) potential, and from additive interactions between each Xe and the HI molecule. The Xe/HI potential surface used was of a form previously employed for other rare-gas-hydrogen halide systems.¹⁵ The details of the potential functions will be published elsewhere.

The method. - It is expected that the main quantum effects in this system will be associated with the H-atom motion. This suggests using a mixed quantum-classical approach in which the H atom is treated by timedependent wave packets, while the heavy atoms are described by classical trajectories. This approach was used by several authors in treating somewhat related problems.¹⁶⁻¹⁹ The method as used employs the classical and quantal time-dependent self-consistent field (TDSCF) approximation to couple mutually the quantal and the classical parts of the system.^{16,17} The strongest justification for this approach here is that in a recent study we tested the validity of the mixed classical and quantal TDSCF against numerically exact quantum calculations for photodissociation of HI in a collinear model of the XeHI cluster, and found that the approximation works extremely well over the relevant time range (< 0.1 ps).²⁰ The scheme is as follows. Let $V(\mathbf{r}, \mathbf{R})$ be the potential function of the system, r the H-atom position vector, and **R** a collective label for the heavy-particle coordinates. If $\mathbf{R}(t)$ is the trajectory function of the heavy particles, then $V_O(\mathbf{r},t) \equiv V(\mathbf{r},\mathbf{R}(t))$ is used as the time-dependent

potential for the H-atom motion. The time evolution of the H-atom wave function is obtained by solving

$$i\hbar \frac{\partial \psi(\mathbf{r},t)}{\partial t} = [T_r + V_Q(\mathbf{r},t)]\psi(\mathbf{r},t), \qquad (1)$$

where T_r is the H-atom kinetic-energy operator. The motions of the classical particles are computed from the mean potential:

$$V_{C}(\mathbf{R},t) \equiv \langle \psi(\mathbf{r},t) | V(\mathbf{r},\mathbf{R}) | \psi(\mathbf{r},t) \rangle_{\mathbf{r}}, \qquad (2)$$

by solving the Newtonian equations of motion for the trajectory $\mathbf{R}(t)$. The equations for $\mathbf{R}(t)$ and $\psi(\mathbf{r},t)$ must be solved self-consistently. Only limited knowledge is available on the validity and accuracy of the quantal and classical TDSCF, ^{16,17} hence the importance of the successful test calculations for the collinear model of XeHI.²⁰ The algorithm used in solving the time-dependent Schrödinger equation will be described elsewhere.²¹

Initial conditions.- In simulating the photodissociation process, we assumed for simplicity that the cluster was initially in the ground state, i.e., the heavy atoms at the classical equilibrium configurations, and the H atom carrying out zero-point vibrations on the ground-state potential-energy surface. The classical equilibrium structures of the three clusters XeHI, Xe₅HI, and $Xe_{12}HI$ are shown in Fig. 1. We assume excitation by an extremely fast pulse. The wave function of the H atom is then just thrown upstairs, to the excited-state potential-energy surface, and is the initial state for the subsequent dissociation dynamics. Likewise the classical atoms are thrown upstairs vertically, at their groundstate positions, by the Franck-Condon principle. The quantum and the classical particles are then propagated by solving the TDSCF equations. The calculations reported here are for photodissociation (photon) energy of 3.5 eV (corresponding to translational energy of 1.5 eV for H produced from HI).

Results.- The two most important findings pertain to the existence and nature of the cage effect in the cluster, and its dependence upon cluster size. The first result is that resonances induced by the presence of the solvent atoms contribute to the photodissociation process for all the cluster studied, including the single solvent-atom case of XeHI. These resonances correspond to the rattling vibrations of the H between the heavy atoms. This cage effect causes some delay of the fragmentation process compared with the case of isolated HI. The possibility of resonances of this type was qualitatively suggested by Wittig, Sharp, and Beaudet for other clusters.² These resonances should definitely be observable; their experimental signature is discussed below. Although resonance, transient-vibration contributions were identified in the wave packets of all the systems studied, their lifetimes and relative weight in the wave function differ greatly across the range of the clusters. In the cluster



FIG. 1. Classical equilibrium structures of the clusters.

XeHI, the resonance corresponds to no more than two complete vibrations of the H between the heavy atoms before leaving the cluster, the time scale being of the order of 40 fs. Also the contribution of the resonance event in the wave packet is small. In Xe₁₂HI, the resonances dominate the dissociation behavior completely. The H atom typically undergoes ≈ 50 collisions with heavy atoms before leaving the cluster, and the delay time in the H-atom departure is about 0.5 ps. Indeed, the delay time for the H exit from the "cage" in the $Xe_{12}HI$ cluster is very similar to the delay time of the H exit from the cage following photolysis of HI impurities in a Xe crystal (order of 1 ps). This leads to the second important result that the photodissociation dynamics, and in particular the delay time for the H exit, is dramatically different for N > 5 clusters than for N < 5clusters, the transition in behavior at N=5 being very pronounced. This can be seen from Figs. 2 and 3. Figure 2 gives the probability that at time t the H atom has still not left the cluster ("survival probability"). The re-



FIG. 2. The "survival probability" of the cluster as a function of time.



FIG. 3. Final energy distribution of the H atom vs E.

sult for Xe₅HI is fairly similar to that for Xe₁₂HI, and different from that for XeHI. This behavior is due to the structure of the clusters, and the orientation of the HI within the clusters (see Fig. 1). For Xe_5HI and the larger clusters, the H atom is locked fairly tightly between the heavy atoms, and can only leave after it has transferred much energy to these atoms, thus "opening up" the structure. This takes roughly fifty hard collisions between the energetic light atom and the Xe atoms. We do not show here results for N < 5 clusters, but there the heavy atoms do not lock the H photofragment tightly, and the behavior is very similar to that of XeHI. Figure 3 gives the final kinetic-energy distribution of the H-atom product for the N = 1, 5, and 12 clusters. The H atom from XeHI is very hot, since it leaves the cluster directly. One or two collisions with the Xe atom do not provide sufficient energy transfer to substantially reduce the kinetic energy of the H atom. (Only part of the wave packet corresponds to "collisions," or resonances-mostly the wave packet describes direct exit of the H atom from this cluster.) In the case of $Xe_{12}HI$, the kinetic-energy distribution indicates that the system underwent extensive internal energy redistribution before the H atom had exited. It seems indeed likely that an almost statistical distribution is obtained after ≈ 50 hard collisions between the H and the Xe atom. The result for the Xe₅HI is very similar to the N = 12 case. Thus photolysis in the larger clusters (N > 5) results not only in a time delay for the photofragment departure, but also in extensive energy redistribution within the cluster. Additional useful insight is obtained by considering the auto correlation function $a(t) = |\langle \psi(\mathbf{r}, t) | \psi(\mathbf{r}, 0) \rangle|^2$, which is shown in Fig. 4. For XeHI this temporal correlation decays rapidly as the cluster disintegrates (there is some numerical noise, and also a weak local maximum due to contribution from the short-lived resonance). The behavior for N = 5 and 12 shows several pronounced sharp peaks which indicate the occurrence of phase coherent vibrations of the H atom within the cluster before the departure of the atom. Thus collisions of the H with the heavy atoms do not cause complete dephasing of the



FIG. 4. The temporal correlation $a(t) = |\langle \psi(t) | \psi(0) \rangle|^2$ vs time.

wave packet over a time scale of ≤ 0.1 ps. A final observation deals with the formation of new clusters as products in this photodissociation process. These simulations showed that photodissociation of XeHi yields XeI with $\approx 57\%$ probability (the rest corresponds to complete H+I+Xe fragmentation). Photolysis of Xe₂HI yields Xe₂I products (76%), XeI products (6%), and complete fragmentation (18%). A full analysis of the branching ratios for the various clusters will be published elsewhere. The reason for the formation of these new clusters, is that when the H atom leaves the cluster, the Xe and the I atoms are still trapped in the mutual attractive potential between them, energy transfer from the H having been insufficient in most events for complete fragmentation. These new clusters should definitely be experimentally observable.

In conclusion, photodissociation in clusters of the type Xe_NHI shows a pronounced transition from small-cluster to large-cluster behavior at N = 5. The large-cluster behavior involves a ps time-scale delay for the exit of the photofragment, and this corresponds to a solvent cage behavior very similar quantitatively to the corresponding condensed-matter reaction. However, some cage effect occurs even for the smallest clusters, corresponding to transient vibrations of the light atom before leaving the cluster. These aspects have pronounced experimental signatures. The effects predicted here are directly observable, and an experimental study should be of great interest.

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FIG. 1. Classical equilibrium structures of the clusters.