Librational Control of Photochemical Reactions in Small Clusters

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A novel approach to the enhancement of photochemical reaction yield in hydrogen-containing clusters is outlined and applied to the process of the Cl_2 molecule formation from a UV-photolyzed Cl···HCl species. The control mechanism consists of a far-IR preexcitation of the large-amplitude hydrogenic bending (librational) mode prior to the HCl photodissociation. Molecular dynamics simulations that properly sample the initial quantum state of the system show that this leads to more than a factor of 2 enhancement of the Cl_2 yield both in the parent and deuterated clusters.

I. Introduction

Hydrogen-containing weakly bound clusters possess unusual properties connected with the quantum mechanical motion of the light atom in a shallow intermolecular potential. Namely, the large-amplitude hydrogenic bending motions in clusters such as $HCl(Ar)_n$, $n = 1, 2, ...,$ strongly influence the electronic ground-state properties as well as the (photo)excited-state dynamics.[1−15] For the hydrogenic bend in these clusters a significant delocalization from the equilibrium geometry is typical already for the ground $v_b = 0$ state, this effect being even much stronger for $v_b = 1$ and higher states.[2] In the case of a completely solvated HCl molecule in large argon clusters or matrices, this bending motion changes into an almost free rotation.[11,12] Therefore, terms such as hindered rotation[1] or libration,[16] rather than vibration, are often used in this context.

In a recent study, we have proposed replacement in the above clusters of one of the argon atoms by a chlorine radical and exploitation of the large difference between the $v_b = 0$ and $v_b = 1$ wave functions for a photochemical reaction yield control.[17] The idea of vibrational control has been pursued by several groups for more than a decade. It has been demonstrated that, for example, for a partially deuterated water molecule different photofragmentation channels can be opened by UV photolysis depending on a particular IR vibrational preexcitation of the OH or OD bond.[18−22] The scheme outlined in this paper differs in two major points. First, a weak intermolecular mode in a cluster is preexcited instead of a strongly bound intramolecular vibrational degree of freedom. More importantly, we propose to control by IR-preexcitation the yield of an association chemical reaction initiated by UV photolysis instead of controlling the relative yields of photofragments. Namely, using molecular dynamics simulations, we have demonstrated that in a cluster consisting of an HCl molecule trapped on a $Cl(Ar)_{12}$ cluster, the Cl_2 yield is enhanced from 2 to 70% by the hydrogenic librational $1 \leftarrow 0$ far-IR preexcitation prior to HCl molecule UV photolysis.[17] From an experimental point of view this should be a strong, directly observable effect.

However, technical difficulties connected with the isolation of the $Cl(Ar)_{12}$ HCl species are nontrivial. In this paper, we focus on a much smaller and simpler Cl···HCl cluster and show that the idea of librational control works here too.

The ClHCl species has been intensively studied both theoretically and experimentally in connection with the symmetric hydrogen exchange reaction $Cl + HCl \rightarrow HCl + Cl$ and the strongly exothermic $Cl_2 + H \rightarrow HCl + Cl$ exchange reaction.[23−30] The van der Waals region of the system, corresponding to the Cl···HCl cluster, has been mapped in terms of potentials and vibrational/librational eigenstates.[31] It follows from this analysis that the Cl···HCl cluster should be more stable than its thoroughly investigated closed-shell Ar···HCl analogue, and the possibility of the isolation of the Cl···HCl species under supersonic jet conditions has been considered.[32]

The paper is organized as follows. In section II we briefly describe the system and computational methods. In section III we present and discuss the results, and a brief summary is given in section IV.

II. System and Computational Methods

The equilibrium ground-state geometry of the Cl···HCl cluster is collinear with the hydrogen atom lying asymmetrically between the two chlorines.[31] The collinear arrangement is primarily due to the quadrupole−quadrupole and dipole−quadrupole interactions between the HCl molecule and the Cl radical, which significantly contribute to the attractive intermolecular potential, resulting in a 383 cm^{-1} deep minimum at a Cl−Cl separation of 3.9 Å.[31] These interactions align in a collinear geometry the singly occupied p orbital of the Cl radical perpendicular to the HCl molecular axis. Although the optimal geometry is collinear, the bending potential is very shallow and the hydrogenic librational wave functions also sample extensively bent structures. A general nonlinear geometry with a bending H−Cl (of the HCl molecule)−Cl (radical) angle θ is schematically depicted in Figure 1. It follows from a simple analysis of the intermolecular forces[31] as well as from test ab initio HF/6-31G* calculations performed by the authors that in order to optimize the electrostatic interaction, the p orbital of the Cl radical rotates upon bending approximately by the same angle θ from its equilibrium orientation (perpendicular to the

* To whom correspondence should be addressed. E-mail: jungwirt@jh-inst.cas.cz. Fax: ++420-2-8582307.
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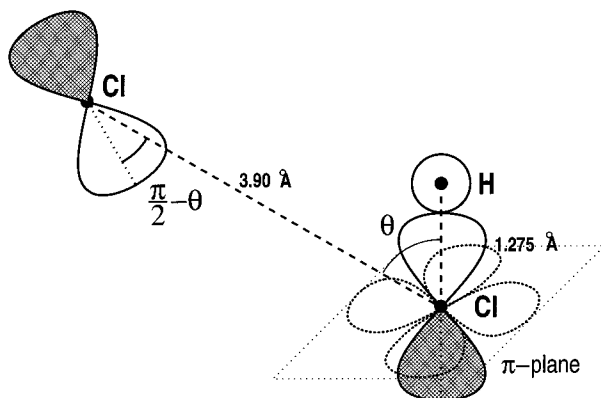**Figure 1.** Structure of the Cl···HCl complex for a general value of the bending angle θ with a schematic plot of the singly occupied p orbital of the Cl radical and the bonding situation in the HCl molecule. Upon HCl UV photoexcitation the unpaired p orbital of the HCl chlorine is twisted into the π plane (dotted orbital contours).

Figure 2. Squares of the delocalized ground and first excited librational (bending) wave functions for the Cl···HCl and Cl···DCl cluster.

Cl–Cl axis) but in the direction opposite the HCl axis. This leads to the fact that for $\theta = 90°$ this p orbital lies along the Cl–Cl axis,[31] which is, as is also shown below, the most favorable orientation for Cl_2 molecule formation by HCl photolysis. The ground electronic potential energy surface is further shaped by the spin–orbit coupling, especially for large bending angles.[31] Here, we take the spin–orbit interaction into account only implicitly (by employing the lowest adiabatic surface from ref 31 for the construction of librational states), neglecting its influence on the p orbital dynamics in the ground and (photo)excited electronic states. This makes a simple orbital analysis possible; however, quantitative errors may be introduced for higher librational states that extensively sample regions with large values of the bending angle θ where strong spin–orbit mixing occurs.

The initial librational wave functions are generated using the ground adiabatic θ-dependent potential at a fixed optimal Cl–Cl distance of 3.9 Å, using a spherical harmonics basis (up to $J = 10$) similarly as in ref 31. This gives for the Cl···HCl system the ground and first excited librational state energies of -304 and -236 cm^{-1}, in good agreement with the published values of -299 and -237 cm^{-1} from the fully coupled calculation.[31] This agreement indicates that the simple calculations presented here should provide reliable librational wave functions for the low-lying states. The calculations in ref 31 also show that the $1 \leftarrow 0$ librational transition has sufficient oscillator strength to be realized experimentally.

An empirical rule stating that a satisfactory description of photochemical processes is usually achieved using classical trajectories, provided the initial quantum state of the system is properly sampled,[32] is applied to the dynamical process under study. Namely, during photodissociation the hydrogen atom acquires a large portion of kinetic energy that brings it close to the classical limit. The chlorine atoms are much colder, but they are also significantly heavier, which again makes the classical approach plausible. However, we have to account for the fact that prior to photolysis the cold and light hydrogen atom, which moves with a large amplitude in a very shallow potential well, is a strongly quantal object. In this work, we adopt a semiclassical approach in which a swarm of classical trajectories, the initial coordinates of which sample properly the initial quantum delocalized hydrogenic librational wave function, are propagated and analyzed. At typical experimental temperatures of only a few kelvins, the initial classical momenta of all particles can be approximately set to zero and the trajectories of the heavy atoms are initiated from their equilibrium positions.
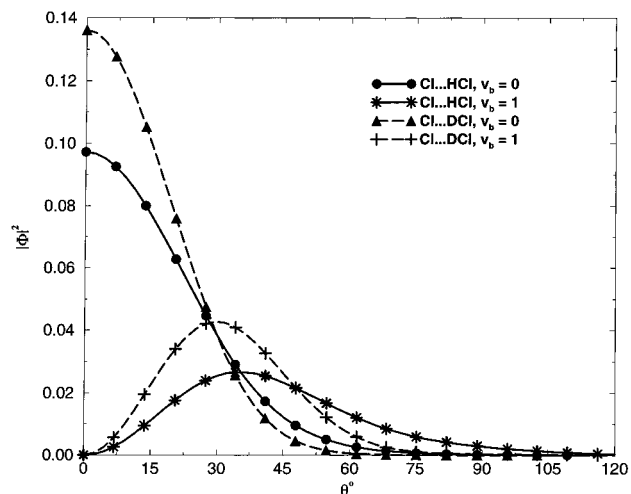
Classical trajectories, starting at the moment of HCl photo-excitation and sampling different values of the bending angle θ, are propagated for 1 ps with a 0.25 fs time step using a standard Gear algorithm.[33] The attractive ground-state Cl–Cl potential is taken from ref 34, while the ground $^1\Sigma$ and first excited $^1\Pi$ HCl potentials are the same as in ref 35.

In the end of this section we stress the fact that the computational approach adopted here is a compromise between accuracy and feasibility. Ideally, one would like to have a fully ab initio description of the ground and excited electronic states involved together with a numerically exact quantum treatment of the nuclear motions. This would require elaborate post-Hartree–Fock methods including spin–orbit treatment for massive numerical evaluation of potential energy surfaces and possibly also nonadiabatic couplings between them on one side, and at least a three-dimensional wave packet propagation on an extended space grid on the other side. While this is probably beyond the present computational means, the simple semiclassical dynamical method using empirical potentials employed in this study is very economic. At the same time, the observed effect of librational control is qualitative and strong enough to be revealed by the present approximate approach.

III. Results and Discussion

The shapes of the ground and first excited librational wave functions in the Cl···HCl cluster and its deuterated analogue are depicted in Figure 2. The ground wave functions are located around the equilibrium collinear geometry, however, with a significant spread of about 26° for Cl···HCl and 22° for Cl···DCl. The first excited wave functions peak at strongly bent geometries ($\theta = 35°$ for the hydrogenated and $\theta = 29°$ for the deuterated cluster) and are significantly broader than the ground-state functions. As will be seen later, this difference has a crucial effect on the Cl_2 photochemical yield.

Upon UV photoexcitation, the unpaired p orbital of the Cl species in the HCl molecule is twisted into the π plane, perpendicular to the HCl molecular axis (see dotted p-orbital contours in Figure 1). Because of the strongly repulsive character of the excited potential and the light mass, the hydrogen atom flies within few femtoseconds out of the scene (except for practically collinear configurations the weight of which is, however, negligible). In the simple orbital treatment presented here, we assume that after the rapid exit of the hydrogen atom the two unpaired chlorine p orbitals are aligned
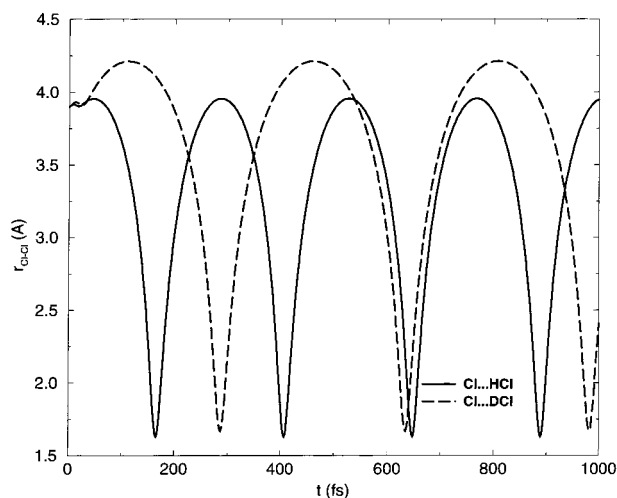
Librational Control in Clusters

J. Phys. Chem. A, Vol. 102, No. 37, 1998 **7243**

Figure 3. Time evolution of the Cl—Cl distance for a reactive trajectory with the initial bending angle $\theta = 40°$ in the Cl···HCl and Cl···DCl clusters. The final Cl_2 vibrational state is $\nu = 76$ in the former and $\nu = 81$ in the latter complex.

in the same way as directly after the photoexcitation, i.e., one is in the π plane while the other lies in the H—Cl—Cl plane with the angle to the Cl—Cl axis being $90° - \theta$. Here, θ represents the initial bending angle, as sampled by the classical trajectory. At this point we project the two p orbitals on the Cl—Cl axis, which gives the contribution to the attractive ground electronic Cl—Cl interaction, the rest having a nonbonding character. It follows from Figure 1 that the weight of the bonding part $\omega_B(\theta)$ equals $(2 \sin^2 \theta)/\pi$. Namely, the factor $2/\pi$ comes from the projection of the p orbital of the photolyzed chlorine into the H—Cl—Cl plane, integrated over all possible orbital orientations in the π plane (see Figure 1). In the H—Cl—Cl plane, the bonding contribution (projection onto the Cl—Cl axis) is $\sin \theta$ for each of the two chlorine atoms. Since the nonbonding part of the interaction with weight $1 - \omega_B(\theta)$ is repulsive with only a very shallow van der Waals minimum, it cannot stabilize the Cl_2 species. As a result, in the nonbonding situation the recoil from the photolyzed H atom leads to direct separation of the two chlorine atoms for all angles θ sampled by the studied librational wave functions. Therefore, from the point of view of the formation of the Cl_2 molecule we only have to consider, with the proper weight $\omega_B(\theta)$, the bonding Cl—Cl interaction in the molecular dynamics simulations.

The following picture is obtained from a set of classical trajectories described in the previous section. Except for very small angles $\theta < \lambda$, which result in a strong H—Cl collision and a consequent complete disintegration of the cluster, a highly vibrationally excited but stable Cl_2 molecule is always formed in simulations employing the ground-state Cl—Cl potential. The limiting angle λ equals $4°$ for the Cl···HCl cluster and grows to $11°$ for Cl···DCl because of a larger recoil and a more efficient light particle—heavy particle collision in the deuterated complex. Figure 3shows the time evolution of the Cl—Cl distance for a typical reactive trajectory started with $\theta = 40°$ for which the librational first excited state population is already significantly larger than that of the ground librational state for both hydrogenated and deuterated clusters. After an initial period of less than 20 fs, which is influenced by the presence of the hydrogen atom, a regular Cl_2 vibrational pattern is observed. The ground-state Cl—Cl Morse potential[34] supports 104 bound vibrational states. For the Cl···HCl case, the Cl_2 molecule is stabilized at $\nu = 76$ (0.264 eV below the dissociation limit) while for the deuterated species at $\nu = 81$ (0.174 eV below

the dissociation limit). The higher final Cl_2 vibrational state in the deuterated complex is due to the doubled recoil energy. Within our model, the Cl_2 photochemical quantum yield Y can be expresses as

$$Y = \int_\lambda^\pi |\Phi(\theta)|^2 \omega_B(\theta) \sin \theta \, d\theta \qquad (1)$$

where $\Phi(\theta)$ is the (ground or first excited) librational wave function, λ is the limiting bending angle for reactive trajectories, and $\omega_B(\theta)$ is the relative weight of the two p-orbital projections on the Cl—Cl axis corresponding to the ground Cl_2 potential, as defined above. For the Cl···HCl cluster initially in the ground librational state a quantum yield of 16% is observed, this number rising to 35% upon the $1 \leftarrow 0$ librational preexcitation. In the deuterated species these numbers are only 11 and 25%, respectively, due to the less delocalized character of the librational wave functions and the fact that geometries with small initial bending angles θ are unfavorable for the photochemical formation of the Cl_2 molecule due to kinematic and even more importantly p-orbital orientation factors. We see that switching on the librational control mechanism results in the hydrogenated (deuterated) cluster in a factor of 2.2 (2.3) increase of the Cl_2 photochemical quantum yield, which is a strong enough effect to be observable in an experiment.

IV. Conclusions

In summary, we present in this paper a new scheme for the photochemical reaction yield control in small hydrogen-containing clusters and demonstrate its efficiency for the Cl_2 molecule formation from UV-photolyzed Cl···HCl and Cl···DCl clusters. The control mechanism consists of the far-IR preexcitation of the large-amplitude librational (bending) motion prior to the photodissociation of the HCl or DCl molecule. Molecular dynamics simulations that account for the quantum nature of the initial librational state show that the librational control mechanism enhances the quantum yield of the formation of the Cl_2 molecule by more than a factor of 2 from 16 to 35% in the Cl···HCl and from 11 to 25% in the Cl···DCl complex.

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