Delayed and Direct Cage Exit in Photodissociation of Cl_2 in Solid Ar

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The yield for photodissociation of Cl_2 in solid Ar was measured experimentally as a function of photon energy and studied by molecular dynamics simulations. The results show that separation of the Cl fragments at low energies occurs by delayed exit ($t \gtrsim 3$ ps) from the surrounding cage of Ar atoms. Above a photon threshold energy of $\gtrsim 9.0$ eV, there is a switchover to direct cage exit, in which the Cl impulsively knocks a cage atom out of its way. The results are a first demonstration of delayed cage exit and of changeover from delayed to direct exit in solid-state photolysis.

The dynamics of molecular reactions in rare-gas crystalline solids has been the topic of intensive experimental [1–4] and theoretical [5] studies in recent years. The structural simplicity of crystalline solids and the availability of reliable potentials for rare-gas systems, at least at the level of pairwise atom-atom forces, offer unique advantages for an understanding of chemical dynamics in condensed matter at the level of first principles. The present paper uses this framework to explore the cage effect on photodissociation in an inert solvent. While the cage effect is a central concept for molecular reactions in condensed phases, little is known as yet of the dynamical mechanisms whereby it operates. Consider, for instance, a molecule known to undergo direct photodissociation in the gas phase upon absorption of a UV photon. When the molecule is immersed in a chemically inert solvent, the process may be drastically altered. A very interesting question is whether the surrounding solvent molecules can significantly delay the mutual separation of the photoproducts, a behavior diametrically opposed to the direct photodissociation in the gas phase. This obviously depends on the probability and rate for fragment exit from the surrounding solvent cage. The present study deals with the dynamics of direct and delayed cage exit, with the physical parameters that govern their relative importance, and with a transition between these two mechanisms. The available (experimental and theoretical) evidence concerning these questions is mostly inconclusive. Molecular dynamics (MD) simulations have suggested, for instance, that cage exit of the H atom in photolysis of HI in Xe at very low temperatures is strongly delayed [5(a),6], while for photodissociation of Cl_2 in Xe, cage exit by the Cl is predominantly direct at the relatively high temperatures of the investigation [5(b)].

Charge transfer states and different dissociation geometries contribute to photodissociation of Cl_2 in Xe according to the experiment [7]; however, the interaction potentials seem to be of an insufficient accuracy for a definitive description to be asserted. Furthermore, it has been proposed, on the basis of threshold measurement, that cage exit of the H atom in the photodissociation of

H_2O in Ar is direct [4], but there are no theoretical calculations as yet to support this interpretation. Perhaps the most rigorous evidence available on this question to date is for photolysis of F_2 in Kr. For this system there are accurate pairwise potentials available, tested against experimental data on the photodissociation yield. Molecular dynamics simulations employing these potentials point to very efficient direct cage exit in this system [8]. The direct mechanism was found to be due to the very short range of the repulsive one of the F/Kr pair potentials resulting in large "windows" for the exiting F atoms.

Of all the investigated systems, Cl_2 in Ar shows the most pronounced cage effect with a strongly reduced dissociation efficiency up to photoenergies of 9 eV, i.e., more than 6 eV above the gas-phase dissociation energy [9]. Therefore it is well suited to analyze variations in this exit mechanism over a large range of excess energies.

In this study we combine MD simulations and experimental studies to investigate the photolysis of Cl_2 in Ar. From an experimental point of view a continuum of photon energies in the VUV up to 12 eV and a selective detection of Cl_2 molecules and fragments is required. The experimental approach is described in Ref. [9]. In the theoretical treatment, the system prior to dissociation was modeled by a Cl_2 molecule immersed in a slab of 400 Ar atoms, with periodic boundary conditions imposed at the ends of the slab. Tests have confirmed that a slab of this size suffices to describe the system both prior to and following photolysis. The potential function of the system was assumed to be a sum of pairwise atom-atom interactions. This includes the assumption that the interaction between an Ar atom and the Cl_2 molecule can be written as a sum of Ar/Cl(atom) potentials which is supported by the studies of Janda and co-workers on the $Cl_2 \cdots Ar$ cluster in the gas phase [10]. For the Ar/Cl interaction we used the electronic (ground) X state potential determined by Aquilanti et al. [11], by their crossed molecular beam studies of Ar scattering from $Cl(^2P)$. The use of this very accurate and elaborate Ar/Cl pair potential was found to be not important for the description of the Cl_2 in Ar systems prior to photolysis, but the results appear very

sensitive to this interaction for the dynamics following excitation. The Ar/Ar pair potential was taken from Aziz and Chen [12], and the Cl-Cl ground-state interaction is given by Herzberg [13]. In the MD simulations, the complete system was brought to equilibrium in the electronic ground state at the temperature of interest, by running sufficiently long trajectories ($t > 20$ ps). In modeling the photodissociation process we assumed, in the spirit of the Franck-Condon principle, a vertical transition, with preservation of configuration of all atoms, to the relevant excited state upon photoabsorption. The excited-state potential was thus switched on suddenly, and a trajectory describing the evolution of the photodissociation process was thus propagated on this potential, starting from each initial "photoabsorption" configuration. The initial configurations on the ground state were sampled at random time points of a trajectory after equilibration. A set of 200 trajectories was used for each excitation energy, and this number is estimated to be statistically sufficient for describing at least the main aspects of the photodissociation process. The most critical aspect of the initial configuration in determining the subsequent photodissociation dynamics turned out to be the orientation of the Cl_2 molecule within the surrounding cage. Each photodissociation trajectory was integrated on the excited state until steady-state behavior had apparently been reached. This required no more than 7 ps in all cases.

Consistent with the experimental assignment [9], and with the electronic state structure of the isolated Cl_2 molecule [14], we assumed that excitation at photon energies 5.5 eV $\leq E \leq 8$ eV involves promotion of the chlorine to the repulsive $^3\Sigma_u$ state. For higher energies we assumed, again based on a proposed experimental assignment [9], that absorption takes place initially to the $1\,^1\Sigma_u^+$ state of Cl_2. The molecule then reaches an $Ar^+Cl_2^-$ charge transfer state which is strongly bound [9,14]. However, the density of electronic states of Cl_2 for $E \gtrsim 9$ eV is high, and, in accordance with the experimental results, we assume an essentially instantaneous crossing into the repulsive states. For a representative choice of repulsive states we fitted experimental functions to the repulsive $^3\Sigma_u^+$ and $2\,^3\Sigma_u^+$ curves from the *ab initio* calculations of Peyerimhoff and Buenker [14]. The results do not seem to be sensitive to which repulsive state is used at the high energies of excitation. As for the excited-state potentials, we used the same Ar/Ar and Ar/Cl potentials as for the electronic ground state, only changing the Cl-Cl potential into the appropriate repulsive potential. Our calculations thus used entirely gas-phase pair potentials without any polarization calculations. Also, we have not attempted treatment of nonadiabatic (curve crossing) effects in the dynamics. These require procedures beyond straightforward classical molecular dynamics. It should also be stressed that the (gas phase) potentials used were not fitted to the solid-state experiments, and comparison between theory and experiment is thus a meaningful test.

The main results obtained can be summarized as follows.

(i) Impurity site: The calculations for the electronic ground state give a disubstitutional site as the energetically favored site for an isolated Cl_2 molecule in Ar at low temperatures. This site can be viewed as resulting from replacement of two neighboring Ar atoms by a Cl_2 molecule, with substantial relaxation of the surrounding atoms due to this change. This conclusion is supported by the observed site distribution of the Cl fragment. In particular, this site gives dissociation yields very different from those calculated for a Cl_2 molecule in a *substitutional* site (in which the center of mass of the Cl_2 replaces an atom from the Ar lattice, again with relaxation). While we do not show the results here, the photodissociation yield versus photoexcitation energy is quite sensitive to the site of the reagent molecule, which should be of considerable interest for solid-state photochemistry.

(ii) Comparison of theory with experiment: Figure 1 shows the experimental and theoretical results for the photodissociation yield of Cl_2 in solid Ar versus photon energy, at temperature $T = 18$ K. The experimental absolute quantum efficiencies [9(a)] have been derived from the dose of dissociation photons and the integrated fluorescence intensity of the Ar_2Cl excimer after calibrating the sensitivity of the fluorescence detection as described in the experimental part of Ref. [9(a)]. Given that the calculations did not involve any fitting of parameters to the experimental data, the agreement must be judged as very good. In particular, theory reproduces the "two threshold" behavior of the experiment. The differences between theory and experiment for the low threshold are reasonable, given the low absolute yields [(2–4)%], which imply that one depends on poor trajectory statistics. The differences for energies, 8.5 eV $\leq E \leq 9.5$ eV, probably stem from the fact that experimental excitation in that region involves several electronic
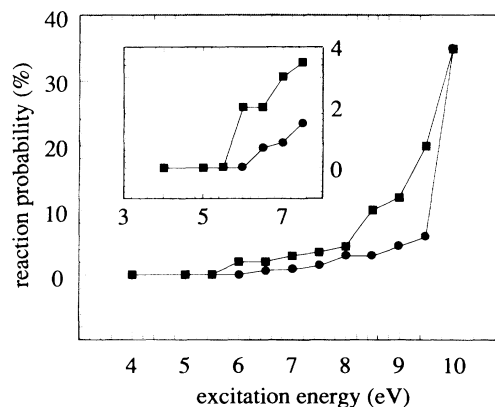
FIG. 1. Photodissociation yield of Cl_2 in solid argon vs excitation energy. ●, experiment; ■, molecular dynamics simulations.

states, and the crossing to either $^3\Sigma_u^+$ or $2\,^3\Sigma_u^+$ is incomplete in the low-energy part of these states [9]. There are certainly other factors for the discrepancy that remains: For example, the potential used did not include many-body (polarization) terms; nonadiabatic effects in the dynamics were not included. However, the generally good agreement in Fig. 1 is strengthened by additional data not shown here: The photodissociation yield is insensitive, both experimentally and theoretically, to the temperature. (The yields calculated and measured for $E = 7.0$ and 10.0 eV at $T = 30$ K are essentially the same as in Fig. 1.) Also, the calculations show that the Cl photofragments end up in substitutional sites of the Ar lattice. Typically one of the two Cl atoms remains in the reagent cage and occupies a substitutional site there, after relaxation. The second Cl atom which exited the cage in the calculations finally replaces an Ar atom in a nearby cage, thus becoming substitutional, while the Ar atom goes temporarily to an interstitial site. (That is essentially the site that was taken by the Cl atom in the disubstitutional initial position in the Cl_2 molecule before dissociation.)

Identical sites for all Cl atoms showed up in crystalline matrices. This observation has been attributed to a decay into two Cl atoms in substitutional sites separated by a matrix atom [9]. This result is in full agreement with the MD calculation. The conclusion from all this is important: *Theoretical MD simulations, using pair potentials from gas-phase data, describe this photochemical reaction with adequate agreement with experiment.* A similar conclusion was previously reached for photolysis of F_2 in Kr [8]. *The existence of "ideal" reactions in the solid state, which can be correctly described by gas-phase potentials without polarization corrections, is of considerable conceptual and practical interest.* However, it is essential to stress *that good agreement with experiment was obtained only when accurate pair potentials were used.* The most critical potential in this respect proved the "reagent/solvent" interaction, Cl/Ar. When several crude Cl/Ar interactions were used in a test, poor agreement with experiment resulted [9]. The use of a quantitative gas-phase potential in treating even the most ideal condensed matter reactions is thus essential.

(iii) Direct and delayed cage exit: The good agreement found between the experimental and theoretical results supports the validity of using the simulations to get detailed insight into the dynamics of the process. We focus now on the physical interpretation of the two thresholds behavior seen in Fig. 1, both for the theoretical and for the experimental results. Detailed examination of the calculated trajectories in the region of the first threshold ($E \approx 6$ eV) reveals a strongly delayed cage exit of the Cl fragments produced. The behavior for one of the (few) trajectories leading to cage exit at these energies is shown in Fig. 2: Upon photoabsorption, the two Cl atoms are strongly repelled from each other. Each Cl atom un-
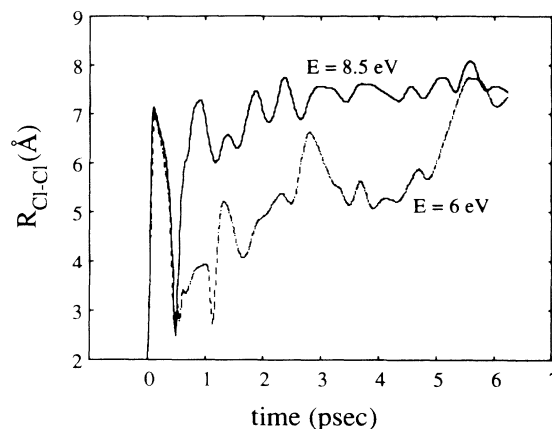

FIG. 2. $R_{Cl\text{-}Cl}$, distance between Cl atoms, vs time. Time shown is from the instant of photoabsorption.

dergoes a "hard" collision with an Ar atom from the surrounding cage, loses a substantial fraction of its energy, and recoils back to a relatively short Cl-Cl distance where mutual repulsion is experienced. The Cl atoms then perform large amplitude motions in the cage, gradually losing more (but not all) of the energy, while the cage becomes hotter and much less tight. Then, in the few events for which exit occurs, a Cl atom reaches a configuration in which the barrier for leaving the cage is sufficiently low. The Cl atom keeps migrating and gradually loses energy. Finally, it replaces one of the Ar atoms in the second shell of neighbors (measured from the center of the initial Cl_2 molecule), as this is energetically more favorable. The Cl atom relaxes to a substitutional positon, while the dislodged Ar atom relaxes from the temporary interstitial site it has occupied for a very short time to a permanent stable substitutional site. The low cage exit probability in this mechanism is due to the efficient energy loss in the hard Cl/Ar collision—few Cl atoms can then survive with enough energy to ultimately leave the cage, although the latter heats up in the process. Above ~ 8.5 eV there is, however, a drastic changeover to direct cage exit: The Cl atoms undergo not one, but two hard collisions in succession with the surrounding cage, because they are left with sufficient energy after the first collision. In the second collision (in which the impact direction is different), the Cl atom dislodges an Ar atom from the second shell of neighbors (measured from the initial Cl_2 c.m.). This Ar atom relaxes and blocks the return of the Cl to the original cage. This direct mechanism, when sufficient energy is available, is far more efficient than the first. Figure 2 shows also such a "direct" cage exit trajectory. In this trajectory cage exit is completed in about 0.75 ps, almost an order of magnitude shorter than the delayed process.

In conclusion, this study demonstrated the transition for a "delayed" to a "direct" mode of cage exit, which occurs when the photoproducts are given sufficient energy

to knock out one of the cage atoms by a direct collision. This direct mechanism is quite different from the delayed regime, in which the photofragments rattle at least several times in the cage before exiting. It obviously should be of considerable interest in the future to carry out the experimental study of the two mechanisms also into the time domain, using ultrafast spectroscopic techniques.

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