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Molecular dynamics simulations of reactions in solids: Photodissociation of Cl_2 in crystalline Xe

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The photodissociation of isolated Cl_2 impurities in a Xe crystal was investigated by molecular dynamics simulations. The calculations were carried out for a photodissociation energy of 3.775 eV, and for several temperatures in the range from 10 to 150 K (the melting point is 162 K). The focus was on the physical mechanisms whereby the product atoms exit from the cage, on the properties of the final sites occupied by the Cl atom, and on the temperature dependence of the processs. The main findings were: (1) exit of a Cl atom from the original reagent cage, when it occurs, is always direct upon photodissociation, and does not involve multiple collisions with the surrounding cage walls. This is in qualitative contrast with the dynamics of cage exit in the case of HI photodissociation in Xe at very low temperatures, found in a previous study. (2) The occurrence of product exit from the cage depends entirely on whether the reagent molecule has been oriented at the direction of a transition state for the exit at the instant of photodissociation. (3) The temperature threshold of Cl exit from the cage is 95 K, and essentially coincides with onset of free rotation for the reagent molecules in the host crystal. (4) The temperature dependence of the probability for cage exit is strongly nonmonotonic: The probability increases as T increases from 95 to 110 K, falls off to 0 around 125 K, then increases again as T approaches melting. (5) At the photodissociation energy used, the only site that the Cl atoms occupy in the new cage is the octahedral interstitial site. Various aspects of reaction dynamics in crystalline solids are discussed in the light of the above results and by their comparison with findings of a previous study on photodissociation of HI in Xe.

I. INTRODUCTION

Photochemical processes in rare-gas solids provide very attractive model systems for exploring basic questions in the dynamics of reactions in condensed matter. The relative structural simplicity of the medium, the chemical inertness of the rare-gas solvents, and the availability of interaction potentials between the particles involved are important advantages in theoretical studies of such systems. Photodissociation and related processes were studied extensively in rare-gas matrices.[1-10] As examples we mention the studies by Bondybey, Brus, and their co-workers on the photodissociation of ICl, Cl_2, CH_3I, and Br_2 in low-temperature matrices of Ne, Ar, and Kr,[2-4] the work by Flynn and co-workers on photodissociation of Br_2 and I_2 in rare-gas matrices[5-7]; and the investigations by Apkarian and co-workers on photoinduced charge transfer processes involving dissociation, e.g., of Cl_2 in Xe.[8-10] Matrices are, however, relatively complicated for theoretical modeling since their structures are not well characterized. Hence the importance of very recent studies by Apkarian et al. on photodissociation of HI in single crystals of Xe,[11] and by Schwentner and co-workers on the photodissociation of H_2O in polycrystalline rare-gas solids.[12]

Very few theoretical studies were reported so far on molecular reactions in rare-gas solvents. Detailed molecular dynamics simulations were carried out by Alimi et al.[13] on the photodissociation of HI in low-temperature Xe crystals. Classical trajectory simulations were also reported for the photodissociation of Cl_2 in large, finite clusters of Ar and Ne at 0 K,[14] and for photoinduced charge-transfer processes of Cl_2 impurities in solid Xe,[15] the latter having, however, a very different dynamical mechanism from photodissociation into neutral fragments.

The molecular dynamics study on the photodissociation of HI in Xe at low T showed several important features in the mechanism of cage exit, and it should be interesting to establish whether these are specific for that system, or hold more generally. In the photodissociation of HI in Xe for $T \leqslant 35$ K, exit of the hydrogen atom from the cage follows many collisions with the surrounding Xe atoms that constitute the cage walls.[13] By the time the H atom reaches the transition state for the exit, it has undergone extensive, although not complete, energy relaxation.[13] It is important to know whether such a highly indirect exit is typical for all systems of reactions in solids. Another finding for HI in Xe was that the probability for exit from the cage following photodissocia-

tion is a nonmonotonic function of the temperature of the crystal.[13] Again, it remains to be established whether such a behavior can be expected also for very different systems.

The present article presents simulations of photodissociation of Cl_2 in single-crystal Xe, over a wide range of temperatures. It appears reasonable to expect a different dynamical behavior than in the case of HI because of the mass symmetry of the reagent, and because the mass ratio between the migrating atom and the solvent atoms is much higher than the hydride. Section II of the article discusses the interacting potentials and several other details of the model system used in the calculations. Section III describes the main results obtained in the molecular dynamics simulations. Section IV presents concluding remarks.

II. THE MODEL SYSTEM

We assume that the Cl_2 impurities in the host solid are so dilute, that one may consider a single guest molecule in the rare-gas solvent. Upon absorption of a UV photon, the molecule is excited to the repulsive $^1\Pi_u$ excited state.[3] In the real system, nonadiabatic transitions between this and other electronic states are definitely expected to play a role, and such transitions are essential in describing recombination of the Cl atoms. We nevertheless assume that such transitions can be neglected over the timescale studied here ($t \leqslant 20$ ps) and for the excitation energy used in the calculations (3.775 eV from the ground state). Although this assumption is supported by crude estimates of the recombination rate in the system, it should be regarded as tentative, and will be explored in future studies that include nonadiabatic transitions between different electronic states. The molecular dynamics simulations were carried out for a system consisting of a Cl_2 molecule and of one hundred and seven surrounding Xe atoms. Tests were carried out to check that the above mentioned "slab" is indeed sufficient to represent the solid with the impurity in it, and that the results for the processes studied are unaffected by the finite size of the cluster used. To represent approximately the effect of the bulk crystal on the cluster treated explicitly in the calculations, periodic boundary conditions were imposed at the ends of the slab. Using a finite-size cluster with periodic boundary conditions may lead to difficulties in some systems because the above boundaries lack the dissipative effect of the true bulk crystal. As we stress, however, we tested this and found that no such difficulties occur for the system studied here. The simulation of the photodissociation process was pursued as follows: First, using interaction potentials correponding to the case when the Cl_2 molecule is in its electronic ground state, classical trajectories were calculated for the system of Cl_2 in Xe, with initial conditions pertinent to the system being at equilibrium at temperature T. Instantaneous transitions to the excited electronic state of Cl_2 were assumed to occur at random points in time, representing events of photoabsorption. The atomic positions and momenta were taken to be conserved at these transitions, but the potential corresponding to the excited state of Cl_2 was now switched on instead of the ground state one. The photodissociation energy corresponds to the vertical distance between the ground and excited Cl_2

potential curves at the configuration when the transition occurred.

The trajectory of the system governed by the Cl–Cl repulsive potential and by the other interactions between the various atoms was computed for a duration of some 20 ps, a timescale sufficient for studying exit from the cage due to photodissociation, and other related processes. After $t \leqslant 20$ psec the chlorine atoms are already essentially thermalized, whether they exited the original reagent cage or not. The initial conditions for each photodissociation trajectory are thus taken from trajectories representing Cl_2 in Xe at thermal equilibrium, sampled at different, random time points. To describe photodissociation at each temperature, and photodissociation energy, 80 trajectories were computed, using corresponding sample sets of initial conditions. We believe this number of trajectories suffices to provide at least a semi-quantitative desorption of photodissociation dynamics.

We used pairwise interaction potentials between the atoms involved, both when the Cl_2 is in the electronic ground state, and for the excited state. For the Xe/Xe interaction we used a Lennard-Jones potential calibrated from gas-phase data.[16] For the ground state Cl–Cl interaction we employed a Morse potential:

$$V^{(0)}_{Cl-Cl}(r) = D\left[1 - e^{-\beta(r - r_e)}\right]^2 \qquad (1)$$

with the values $D = 2.475$ eV, $\beta = 2.036$ Å^{-1}, $r_e = 1.988$ Å for the parameters.[17] The excited $^1\Pi_u$ state of Cl_2 is highly repulsive. We fitted the data given by Bondybey and Fletcher[3] by the approximate function

$$V^{(1)}_{Cl-Cl}(r) = Ae^{-\alpha r^2} \qquad (2)$$

with $A = 247.82$ eV, $\alpha = 1.33$ Å^{-2}. The calculations reported here were carried out for photodissociation energy of 3.77 eV, corresponding to an excess energy of 1.3 eV on the excited $^1\Pi_u$ potential energy curve. This range of energies (and for corresponding internuclear distances) was primarily used in obtaining the fit (2). For the Xe–Cl pair interaction, we used the potential obtained by Becker et al.[18] by fitting their molecular beam scattering data. In the real system of photodissociated chlorine in Xe, several electronic states of Cl (and several corresponding Xe–Cl interactions) probably play a role. Thus, the ground state fourfold degenerate $^2P_{3/2} + {}^1S_0$ atomic asymptote of Xe + Cl gives rise of an $I\,3/2$ as well as an $X\,1/2$ one, and the spin-orbited excited $^2P_{1/2} + {}^1S_0$ atomic asymptote of that system gives rise to an $\Pi 1/2$ state (using Hund's c-case coupling).[18] In the real crystal, these states may well be coupled to some extent by the many-body environment.[19] This will give rise to transitions between the "bare" pairwise Xe–Cl states, as well as to some shifting of the curves. To gain simplicity, we assume a single pairwise Xe–Cl potential, which is tantamount to ignoring the differences between the various curves for the different relevant states mentioned above. Improved treatments, which incorporate in detail the manifold of different Xe–Cl electronic states, and the nonadiabatic transitions between them, are clearly desirable and will be pursued in future studies. The Xe–Cl interaction we used corresponds to the ground state $X\,1/2$Cl–Xe potential cure. Becker et al. give this potential in a Morse–Morse–Hermite–spline van der Waals form.[18] We found that in the energy range rel-
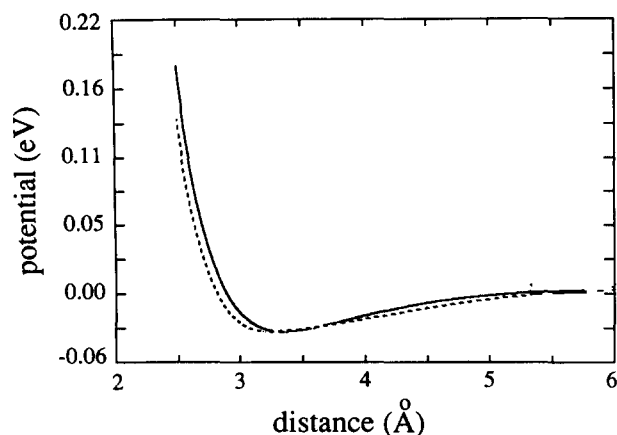
FIG. 1. The Xe–Cl interaction potential. ---The Morse-Morse-Hermite spline van der Waals potential for the $X\,1/2$ ground state from Ref. 18. — The Exp-6 fit, given in the text.
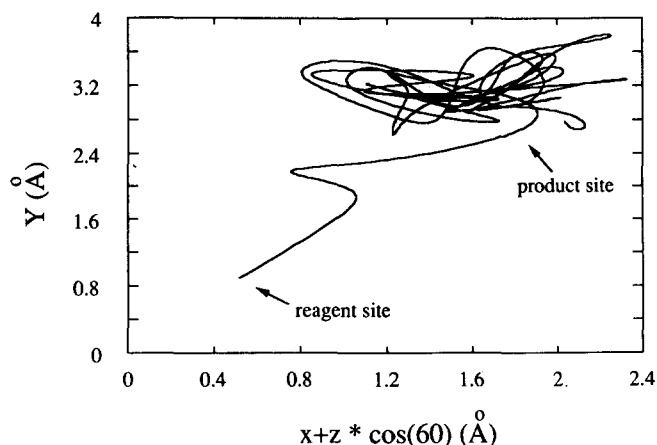

FIG. 2. Path of a Cl atom in a cage-exit event. The result is for a trajectory at $T = 110$ K, computed for a time duration of 8 ps. The behavior is very typical of other trajectories describing cage-exit events. The figure shown is a projection of the actual trajectory in a plane defined by two axes, Y and $X + 1/2\ Z$, from a Cartesian frame.

evant here, this interaction could be fitted with accuracy adequate for our purpose by an Exp-6 form:

$$V_{\text{Xe-Cl}}(r) = Ae^{-br} - \frac{C_6}{r^6} \qquad (3)$$

with the parameters $A = -0.544$ hartree, $C_6 - 270.096$ hartree bohr^6, $b = 0.7266$ au^{-1}. Note that in this fit, the r^{-6} term is the repulsive one, the exponential term the attractive part, but the agreement this gives to the sophisticated spline fit of Becker et al.[18] is excellent, as seen in Fig. 1.

III. RESULTS AND DISCUSSION

It will be convenient to organize the presentation of the results of the simulation around several points, that are the main physical conclusions emanating from this study.

A. The mechanism of cage exit

The mechanism of exit from the enclosing solvent cage of the nascent chemical reaction products is a central issue in condensed-matter dynamics. In a previous molecular dynamics study on photodissociation of HI in Xe at very low temperatures ($T < 35$ K),[13] the exit of the nascent H atoms from the original reagent cage was found to be highly non-direct, following many collisions with the surrounding Xe walls. Indeed, an event of exit from the cage typically followed $\sim 10^2$ vibrations of the H atom between the walls of the cage, by which time its motion has undergone almost complete dephasing and extensive (although incomplete) energy relaxation. We consider now the photodissociation of Cl_2 in solid Xe. Before the reaction, the simulations show that the average position of the Cl_2 center-of-mass is located at a substitutional site of a (somewhat distorted) fcc unit cell of the host Xe lattice. Nonzero probability of exit from the cage is found only for temperatures $T \geqslant 95$ K. Figure 2 shows the path, projected in a plane, traversed by a Cl atom in a typical trajectory in which it exited the original cage after photodissocition. The particular trajectory shown is from a calculation $T = 110$ K. We stress that other trajectories describing cage exit at this or at other temperatures show a very similar behavior. *The trajectory shown indicates direct exit*

from the cage: The Cl atom, initially at a position on the bottom left-hand side of Fig. 2, reached its final site at a neighboring cage without undergoing multiple rattling collisions with the reagent cage walls. There is indeed evidence in Fig. 2 for two "collisions" between the Cl fragment and Xe atoms on its way, but the main behavior is ballistic motion from the reagent to the product site. This picture is extremely different from that obtained for the low T photolysis of HI, in which the H atom carries out many large-amplitude vibrations in the reagent cage before leaving it. In fact, in the present case the Cl atom carries out large amplitude oscillations in the final site, since it reaches that site in the new cage while still having a relatively large amount of kinetic energy (0.1 eV). The large-amplitude motions of the Cl atom in its final site, before it underwent complete relaxtion (which takes several picoseconds) is seen on the top right-hand side of Fig. 2. The very direct, "ballistic," mechanism of exit of the cage is seen clearly also from Fig. 3, describing the variation in time of the distance of the Cl atom from its initial position. The result is for the same trajectory used in obtain-
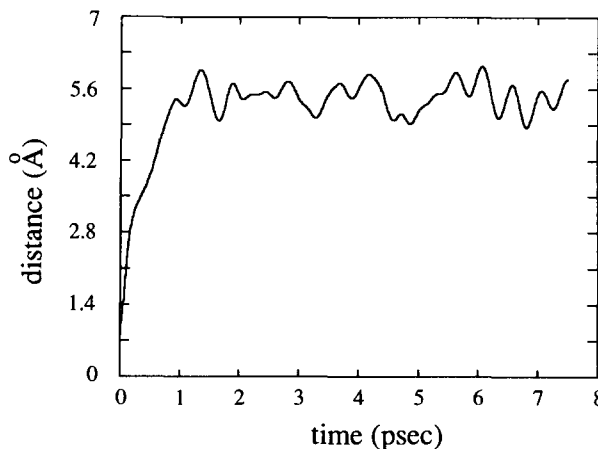

FIG. 3. Distance of the Cl atom from its initial position (upon photoabsorption) as a function of time. The figure is for the same trajectory at $T = 110$ K as in Fig. 2.

ing Fig. 2, but the behavior seems typical also of other trajectories that were analyzed. After the photodissociation, the distance of the H atom from its initial position grows very rapidly, and is approximately linear in time. This is the ballistic stage, in which the exit from the reagent cage occurs. After $t < 0.5$ ps, this stage is over and the Cl begins to carry out oscillations in its new cage, the amplitudes decreasing in time as this atom loses energy to the neighboring Xe atoms. The timescale of the relaxation is clearly several picoseconds.

B. The rotational state of the reagent molecule, and its relation to ballistic cage exit

It is important to understand the causes for the difference between the low-temperature photodissociation of HI, and the direct, ballistic cage exit in the present system. The interpretation emerging from analysis of the classical trajectories is the following. The mass ratio between Cl and Xe suffices for reasonably efficient energy transfer from a hard collision between such two atoms. As a result, indirect cage exit following several large amplitude vibrations of the photofragment between the cage walls cannot occur for Cl, since collisions with the Xe atoms cause the Cl to lose nearly all its kinetic energy. The remaining kinetic energy does not suffice for surmounting the potential barrier for cage exit. Thus, in order to leave the cage the Cl atom must initially be directed towards the "transition state" for this process. That transition state, or minimum energy "bottleneck" for leaving the original reagent cage is located for this system (as for H in the case of HI in Xe) at the center of a "window" consisting of four Xe atoms forming part of the fcc cell in which the Cl_2 was located. This then leads to direct exit before the Cl fragment has lost most of its energy. However, at low temperatures the orientation of the Cl_2 impurity in the host lattice does not point towards all the above windows for exit, even when the vibrational motion of the molecule is taken into consideration. Figure 4 shows the variation of the Cl_2 orientation with time, for a trajectory calculated at $T = 2$ K. The initial direction of the Cl_2 axis for this trajectory was 2.5° off the equilibrium orientation [$\theta(t)$, plotted in Fig. 4 is defined
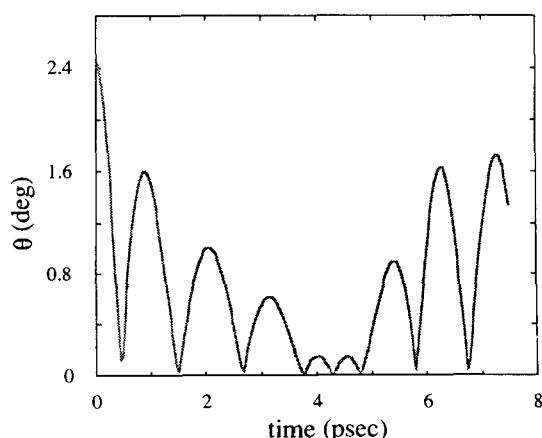

FIG. 4. Variation in time of Cl_2 orientation in a Xe crystal host at 2 K. θ, the orientation angle, is defined here as the positive angle between the Cl_2 axis at equilibrium orientation and the molecular axis at time t. The result shown is for a typical trajectory at $T = 2$ K.
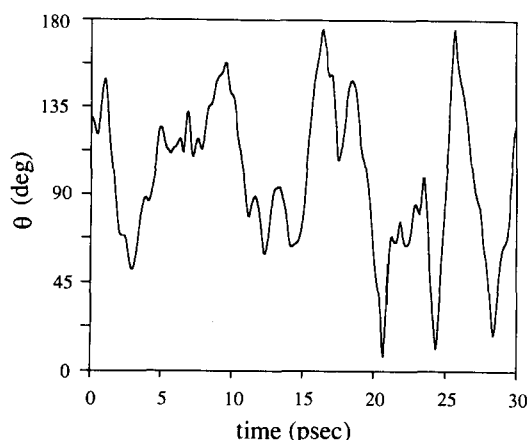

FIG. 5. Variation in time of Cl_2 orientation in a Xe crystal host at 110 K. θ is defined as in Fig. 4.

as the positive angle between the equilibrium position of the Cl_2 axis, and the direction of the latter at time t]. The low temperature libration seen in Fig. 3, having an amplitude of only $\sim 1.6°$, is not sufficient for bringing the molecule into an orientation required for direct exit. The librational amplitudes are expected to increase when zero-point quantum effects (not included here) are taken into account: We estimate then amplitudes of $\sim 3°$, but these are far from sufficient for aiming at the "exit direction." The situation is dramatically different at $T = 110$ K, where, as Fig. 5 shows, free rotation (or rather rotational diffusion) takes place: The angular cones aiming at the exit windows, and leading to direct exit, are accessible to the molecule (with substantial probability of the Cl_2 pointing in these directions): The angles from $\sim 20°$ to $\sim 30°$ result in direct exit. *This explains an interesting finding in our simulations, namely that the temperature threshold for Cl exit from the cage coincides with the T threshold for free rotation of the reagent molecule in the host lattice* (both are around 95 K in our simulations). The difference with the case of HI is also obvious from the above considerations: At very low T, HI does not rotate freely in the Xe crystal.[13] Since the molecule, despite the large librational amplitudes, does not point in the directiion of the "exit window," direct exit is excluded.[13] However, unlike the Cl fragment, H cannot efficiently transfer energy to Xe upon a collision between the two atoms. This leads to indirect exit, in which the H carries out many large amplitude vibrations between the cage walls, gradually losing its energy, and the initial phase of its motion. It reaches the transition state therefore after complete phase and partial energy relaxation.[13] We note that the direct mechanism observed here for cage exit of the Cl, suggests a simple statistical model for this process: The cone of orientation angles necessary for aiming at the transition state region can be estimated, and the probability of the molecule being orineted within this cone of directions can be obtained from statistical considerations. From this, the cage-exit probability can be calculated. Work on such a model is in progress.

C. Properties of the product site

A basic question in solid-state reactions is whether there is a unique site occupied by the product, or can several types
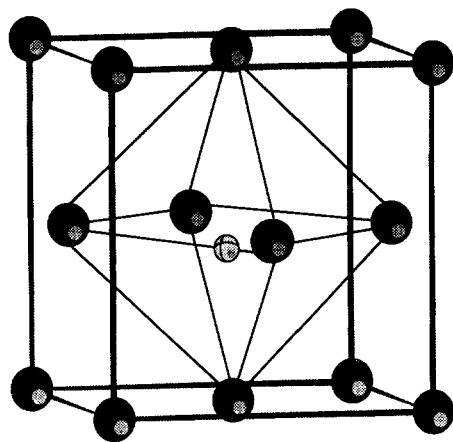
FIG. 6. Geometry of the Cl photofragment site. The Cl atom occupies an octahedral interstitial site in the fcc Xe lattice.

of sites be reached by product particles. In the previous study on photodissociation of HI in Xe it was found that those H atoms which left the reagent cage invariable reached and occupied an octahedral interstitial site in the neighboring cell.[13] This result may, of course, depend on system, temperature, and photodissociation energy. The present simulation of photodissociation of Cl_2 in Xe led, however, to a similar result: *In all trajectories that resulted in exit from the original cage, the atom that left the cage was found to occupy an octahedral interstitial position* (in the neighboring cell) as shown in Fig. 6. As will be discussed later, in some of the cage-exit events both the Cl photofragments leave the cage, in which case both product atoms occupy octahedral interstitial positions. There are also cage-exit events in which one Cl atom leaves the original reagent cage, while the other product atom stays there. For these cases the simulations show that the atom which left the cage reached an octahedral interstitial position, while the atom remaining in the initial cage finally relaxed to the substitutional position previously occupied by the center-of-mass of the reagent Cl_2. On the basis of the previous results for HI and the present ones for Cl_2, we conjecture that *the lowest energy pathway for a photofragment to leave the reagent cage in an fcc host lattice*

leads to an octahedral interstitial site for the product. This, of course, is not in contradiction with the possibility that other sites may also become accessible at higher temperatures or photodissociation energies. Indeed, evidence for such an effect was recently found in simulations of photodissociation of HI at very high energies.[20] The fact that a single site is found at the conditions of the present study suggests that it should be quite feasible to identify the product spectroscopically. Figure 7 shows a Fourier transform of a trajectory of the Cl product at the octahedral interstitial site, obtained at $T = 110$ K. The peak position at $v = 67$ cm^{-1} corresponds to the frequency of the Cl atom oscillation at the octahedral interstitial position, and could be used to spectroscopically identify the product at this site. The peak at 40 cm^{-1} corresponds to a lattice phonon mode, while the peaks at $v = 27$ ($= 67 - 40$) cm^{-1} and $v \approx 94$ ($\approx 67 + 27$) cm^{-1} are combination bands. Spectroscopic studies of product-site frequencies could become a powerful probe of reaction pathways in crystalline solids, especially since few, and perhaps only one type, of sites are occupied by products in simple reactions of this kind.

D. Temperature dependence of the cage exit probability

The temperature dependence of the probability for a cage exit event is shown in Fig. 8. Even when error bounds due to the limited statistics of the simulation are kept in mind, a striking and very interesting nonmonotonic behavior is seen. Part of the behavior seems obvious: following the cage-exit threshold at $T \approx 95$ K (see the discussion in Sec. III A above), the probability for cage exit (or product separation) increases with T. As was mentioned previously, to leave the cage the Cl atom must go through a window determined by neighboring Xe atoms. As T increases so do the amplitudes of lattice vibrations and the exit window becomes larger. The surprising behavior is that for $T > 110$ K the probability of cage exit falls off sharply, being effectively zero for $T = 125$ K within the limited accuracy of our trajectory statistics. As T is further increased and the melting point is approached, the probability of product separation
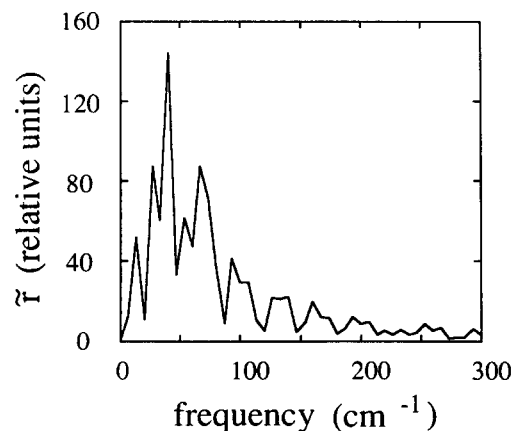

FIG. 7. Fourier transform of a Cl photofragment trajectory at an octahedral-interstitial site. The trajectory is for $T = 110$ K. The peaks show the Cl atom vibrational frequency (67 cm^{-1}), as well as phonon and combination bands.
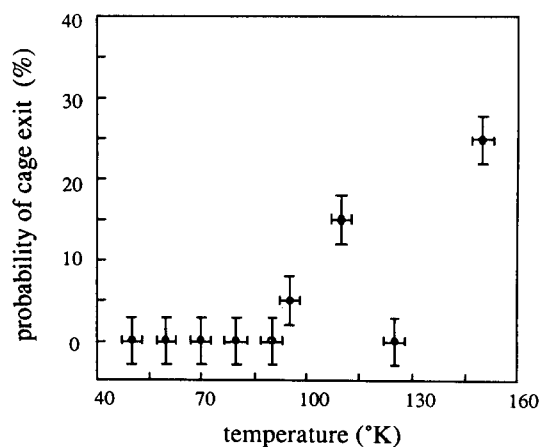

FIG. 8. Temperature dependence of the probability for cage exit. Error bars for both the probability and the temperature as estimated for the simulation results are indicated.

increases again. A nonmonotonic behavior of the cage-exit probability with T was previously found for HI photodissociation in Xe, at a much lower temperature range. Such an effect is clearly not unique to that system, and may be quite typical for cage-exit processes in crystalline solids. The interpretation given in Ref. 13 for HI seems, by analysis of the trajectories, to hold also for the present case: As T is increased beyond some value, the effect of increasing the exit window is no longer the dominant one. The more energetic the neighboring Xe atoms become, the more they seem able to transfer energy to the Cl atom moving on its path towards the transition state. This can be viewed as an inelastic collision with one of the Xe atoms, as they become more energetic, causing a throw off of the Cl atom from the path leading to cage exit. The atoms appear to be "thrown off" their course not far from the transition state, and the Xe atoms involved in transferring energy to the Cl may not be the window atoms but atoms from a second, additional layer. When T is further increased beyond the fall off point of the cage-exit probability, the solid is not far from melting. The amplitudes of the cage atoms become very large, creating many possibilities for cage exit. The transition state region for exit becomes so large, that it more than compensates for the knocking off of some of the Cl atoms from the reaction path. Hence the probability for cage exit again increases. The nonmonotonic behavior of the cage-exit probability appears to be a highly interesting one, and may well be by the above interpretation typical for processes in crystalline solids. We believe it merits an experimenal study.

E. Cage exit by both products versus exit by a single product

So far we considered all cage exit events, leading to separation of the products, regardless of whether one Cl photofragment only leaves the critical reagent cage, or both of the photofragments do. The simulation results show that in the threshold regime, e.g., $T = 90$ K, only a single atom leaves the cage at any cage-exit event. At $T = 110$ K the ratio of two atom exits to single product exits is 3:5. At 150 K, near melting, the ratio of two atom to single atom exits falls again to 1:9. At low T, the exit window is so small and marginal that a slight asymmetry between the two Cl atoms separating impulsively upon photoabsorption makes it very likely that even if one atom hits the transition state, the second one will not, and thus will be deactivated. At very high T, the large amplitude vibrations of the reagent molecule imply low probability for finding the Cl_2 molecule at the center of the cage. The reagent is likely to be found at a position in the cage which is very asymmetric with regard to the two fragments when formed and it is unlikely that both fragments can then reach the respective exit windows. Therefore the most likely range for the exit of both product atoms is that of intermediate temperatures, as was indeed found.

IV. CONCLUDING REMARKS

In this article we presented results of classical molecular dynamics simulations on photodissociation of Cl_2 molecules in a single-crystal Xe host. The results provide considerable insight into the dynamics of elementary reactions in crystalline solvents, especially when compared and contrasted with the findings of a previous study on photolysis of HI in Xe. Mechanistically, one of the most interesting findings is that cage exit for Cl photofragments in Xe, unlike for H products in the same solid at low T, occurs ballistically. It was argued that direct exit is likely to be the dominant or sole mechanism for photofragments that can efficiently transfer energy to the solvent molecules. The indirect mechanism, involving long-lived vibrational states of the products in the initial cage before separation, seemed more likely for light photofragments that do not transfer energy efficiently to the surrounding solvent particles. Clearly, both the "direct" and the "indirect" systems occur for realistic systems, with Cl_2/Xe and HI/Se as prototypical examples corresponding, respectively, to the two limits. A single site was found for the product, in the present case of Cl in Xe as in the previous one of H in the same medium. This may well indicate a specific, selective energy pathway for many reactions in at least cubic crystalline solids. Moreover, the fact that well-defined product sites exist, and may be of one type only, suggests that spectroscopy of the product site should be extremely helpful in understanding reactions in solids. Finally, the nonmonotonic dependence of cage-exit probability on temperature is even more dramatic for photodissociation of Cl_2 than for HI, leading in the present system to zero probability of cage exit at a fairly high temperature. The nonmonotonic temperature dependence of the probability for cage exit may well turn out to be a widely occurring effect in photodissociation reactions in solids. The implications of this effect on the detailed dynamics of the process are very important. It should be highly desirable to search experimentally for its existence.

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