

ION MIGRATION FOLLOWING CHARGE TRANSFER REACTIONS IN RARE-GAS SOLIDS: THE ROLE OF HOLE HOPPING

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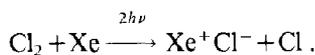
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Recent experiments have shown that photoinduced charge transfer processes in rare-gas solids, such as $\text{Xe} + \text{Cl}_2 + 2h\nu \rightarrow \text{Xe}^+ \text{Cl}^- + \text{Cl}$ result in highly efficient separation of the halogen atoms, even at very low temperatures ($T \leq 20$ K). In this study a mechanism for this is proposed in which hopping of the hole charge among the Xe atoms induces migration of the Cl^- by a Coulomb pulling effect. Simulations combining a stochastic description of hole hopping with classical trajectory (molecular dynamics) calculations of atomic motions yield results in good qualitative accord with the experimental findings. Simulations ignoring hole migration but otherwise employing realistic potentials fail to reproduce the separation of halogen atoms.

1. Introduction

The study of photochemical processes in rare-gas solids is motivated in part by the fact that these systems act as solvents that are in many cases either inert or at least relatively easy to model and understand theoretically. The topics of photodissociation and of isomerization in rare-gas matrices were extensively pursued in recent years [1] and very lately results were also reported on photodissociation of molecules in single crystals or rare-gas solids [2]. In most studied processes, the rare-gas solid seems indeed to act as a chemically inert solvent. One interesting exception is the very recently detected "harpooling", or charge transfer, dissociation processes [3-6]. These involve a two-photon absorption process that leads to charge transfer between the rare-gas host and a molecular dopant, e.g. a guest halogen molecule,



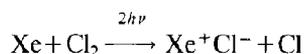
Such reactions, and subsequent processes affecting the ions formed, were studied extensively by Apkarian and co-workers [3-6]. A very interesting finding, central to our purpose here, is that *permanent, complete or extensive dissociation is obtained even at low temperatures, $T \leq 20$ K*. Meaning that separation of the halogen (or other product) atoms is not prevented by the cage down to very low temperatures. This seems to stand in marked contrast to the situation for the usual neutral-channel single UV photon dissociation. Bondybey, Brus and coworkers studied the photodissociation of ICl , Cl_2 and Br_2 in low-temperature Ne, Ar and Kr matrices and found practically complete recombination for the experimental wavelengths used [7-9]. Likewise, Flynn and coworkers found an essentially perfect cage effect preventing photofragment separation for Br_2 and I_2 in low-temperature matrices [10-12]. This is further supported by theoretical molecular dynamics simulations of photodissociation in crystalline rare gases by Alimi et al. [13,14]: Photodissociation at low to moderate energies and at low temperatures

seems to result in perfect recombination for systems such as Cl_2 in Xe. The temperature threshold above which permanent separation of the photoproducts is obtained in that system is about 90 K by the simulations [14]. It is interesting to note that simulations for HI in Xe show that even for the very special case of the small H photofragment, the cage exit probability after photon absorption does not exceed 20% for temperatures under 30 K [15].

This raises the question as to why is cage exit, or photoproduct separation, so efficient for the charge transfer photodissociation processes even at low temperatures. In the present article we propose a mechanism for this effect, and apply it in the framework of model simulations. The basic point of the model is that the positive charges created in the system can hop from one rare-gas atom to a neighboring one, and that the halogen anion, e.g. Cl^- , attracted by the hole in its new position, may be induced to migrate. The model used in the simulations, the assumptions on which it rests and the interaction potentials employed, are described in section 2. The results of the simulations and their analysis are given in section 3. Concluding remarks are made in section 4.

2. The model

In this study we consider the charge transfer process



in solid Xe. Here we assume a crystalline Xe host, although experimental investigations of this process were hitherto pursued mostly in matrices. The modelling of the ordered, crystalline system is far simpler, and we assume that the mechanism leading to the separation of the halogen atom products in this process is the same for the matrix as well as for the crystal. The position of the Cl_2 center-of-mass before the two-photon absorption process will be taken as that of a substitutional site in the host lattice, an assumption supported by molecular dynamics simulations for this system showing it to be the energetically favored location [16]. Spectroscopic studies show that the optically accessed charge transfer states

of solid xenon doped with atomic halogens gives rise to a Rydberg-type series of electron-hole pair excitations [17]. The experimental peaks observed in this case resemble qualitatively the progressions found previously for the excited states of heavier rare-gas atoms doped in lighter rare-gas matrices [18]. From the Rydberg-type energy terms, fitted to the experimental peaks, one can estimate the effective initial excitation radius, being essentially the charge transfer distance that corresponds to each peak. The peak-intensity ratios give the relative probabilities for initially creating the $\text{Xe}^+ \text{Cl}^-$ electron-hole pair at different relative distances. An estimate from the data of Schwentner et al. [17] suggests nearly equal probabilities for forming separated charge pairs at the *second-* and at the *third-order* next-nearest-neighbor mutual positions at the lattice. Probabilities for initial formation of ion pairs of larger mutual separation seem small by these data. For the initial state in our simulation we thus assume a distribution of equal weights between ion pairs at the second- and the third-order next-nearest-neighbor relative positions in the fcc host crystal.

We assume that the holes can migrate in the lattice. In a perfect lattice, migration of free holes is very fast, with a timescale of the order of 10^{-16} s. In the case of solid Xe, hole trapping and localization, associated with the formation of dimer (or higher-order cluster) ions, ultimately occur [19–21]. It is essential to stress that in the process considered here the situation differs drastically from that of the perfect Xe lattice: The hole state formed is partly trapped already in its nascent state because of the strong Coulomb attraction between the hole and the neighboring Cl^- ion. From the widths of the experimental peaks in ref. [17], a lower band can be set for the hole migration timescale: $\tau_h \gg 10^{-13}$ s. As an order-of-magnitude estimate, we suggest a value $\tau_h \approx 10^{-12}$ s, although solid evidence for this is not available, and efforts at theoretical calculations of this quantity, a very difficult challenge, should be most desirable.

In the model adopted here, hole migration will be treated as a stochastic process, involving classical-like hopping of a localized positive charge from one Xe atom to another. The probability per unit time, $P_{i \rightarrow j}$, for hole hopping from site i to site j is assumed to be

$$P_{i \rightarrow j} \propto \exp\left(-\frac{\Delta V_{e-h}(i, j)}{k_B T}\right), \quad (1)$$

$$\Delta V_{e-h}(i, j) = V_{e-h}(R_i) - V_{e-h}(R_j), \quad (2)$$

where R_i is the distance from the site i to the negative ions, and $V_{e-h}(R)$ is the hole-electron interaction potential. $V_{e-h}(R)$ was taken as the Coulomb attraction in the dielectric medium involved, $-C/R$ with $C=1$ au for this system. The postulated probability function (1) has, of course, a built-in propensity for hole hops that shorten the electron-hole pair separation, a preference more pronounced for lower temperatures T . The scale factor for obtaining the absolute $P_{i \rightarrow j}$ from (1) was determined by setting the total hopping rate from the second-order next-nearest-neighbor site equal to $\tau_h^{-1} = 10^{11} \text{ s}^{-1}$ in semi-quantitative accord with the discussion earlier on hole migration timescales in this system.

The simulation of hole migration was thus pursued from the initial state discussed above (of hole-negative-ion separation corresponding to second- or third-order next-nearest-neighbor positions), using a Monte Carlo random-walk procedure governed by the probability function (1). This calculation was made in conjunction, and self-consistently, with a classical trajectory simulation of the atomic motions involved, including the ions, the remaining halogen atom, and a sufficiently large number of rare-gas atoms of the host crystal. The number of atoms used in the molecular dynamics simulation was 366. Probing this result, it was found that with this number of atoms the process studied by the calculations has clearly become independent of the size of the cluster used. Pairwise, realistic potentials were employed between all the atoms and ions involved. All the potentials were of the parametrized form

$$V_{AB}(R) = A \exp(-bR) - \frac{C_1}{R} - \frac{C_4}{R^4} - \frac{C_6}{R^6}, \quad (1)$$

where R is the distance between the atoms (or ions) A and B . The values of the parameters A , b , C_1 , C_4 , C_6 for all the atom or ion pairs are given in table 1.

We note that the main qualitative results of the simulations, which will be presented in section 3, were found to be rather insensitive to the hole hopping rate (the value of which is of considerable uncertainty, as was stressed previously), and also to small changes in the potential used, changes that hopefully cover most of the range of uncertainty within which the interactions are known.

3. Results and analysis

3.1. Ion migration induced by hole hopping

The main result shows that hole hopping induces separation of the Cl^- from the Cl , thus achieving permanent dissociation of the Cl_2^- formed in the primary photoinduced charge transfer process. The mechanism of this effect involves Coulombic "pulling" of the negative ion by the hole; as the latter hops to a new location, Cl^- migration may occur. For a more detailed description, consider the results of a typical trajectory shown in fig. 1. Initially, prior to photon absorption the Cl_2 impurity was located in a substitutional site of the fcc Xe host lattice. Upon photodissociation, the ion pair is formed and one of the possible initial configurations (as described in section 2) is shown in fig. 1a. Following the "switch-on" of ionic interactions, the dynamics of motion leads, in the picosecond timescale, to the formation of a triatomic complex Xe^+Cl_2^- (see fig. 1b), but there is no increased separation of the Cl^- from the

Table 1

Potential parameters for all pairs of atoms. The interaction parameters are defined as in eq. (1). All units are atomic units

	Xe-Xe	Xe-Xe ⁺	Xe-Cl	Xe ⁺ -Cl	Xe-Cl ⁻	Xe ⁺ -Cl ⁻	Cl-Cl ⁻
A	889.456	1097.066	-0.544	-0.544	1165.546	74.814	137.632
b	1.677	1.587	0.726	0.726	2.037	1.329	1.923
C_1	0.0	0.0	0.0	0.0	0.0	1.0	0.0
C_4	0.0	0.0	0.0	13.676	13.676	30.975	0.0
C_6	536.341	5243.004	-270.096	-270.096	100.564	0.0	214.536

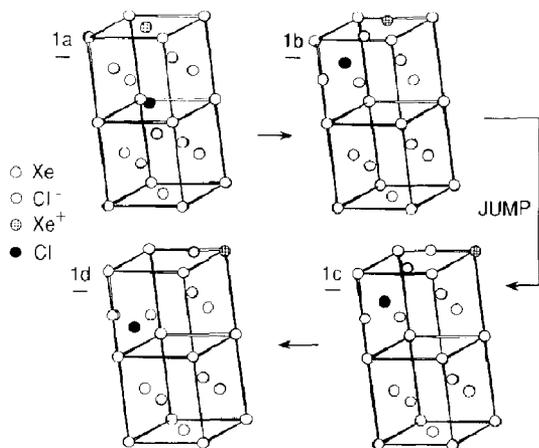


Fig. 1. Hole hopping and atomic motions following the process $\text{Xe} + \text{Cl}_2 + 2h\nu \rightarrow \text{Xe}^+ \text{Cl}^- + \text{Cl}$ in crystalline Xe. The results are from the simulations combining stochastic treatment of hole hopping with molecular dynamics calculations for atomic motions. The result shown is from a single, typical trajectory at $T=20$ K. (a) is the situation at $t=0$; (b) at $t=7.5$; (c) at $t=7.5$; (d) at $t=15$ ps.

Cl at this state. In the Monte Carlo simulation, an event of hole hopping took place at this point, leading to fig. 1c. The Cl^- now experiences a strong Coulombic attraction to the right-hand side of the cage, while the much weaker dispersion forces acting on the neutral Cl have a resultant pulling the latter to the wall on the left. The result, in fig. 1d, is that complete dissociation, or product separation, has been obtained. Such a mechanism of Coulombic pulling of the anion by the hole was found, with some variation in the intermediate steps, to be characteristic of most trajectories. We believe therefore that it provides a plausible explanation for the experimental finding of "complete photodissociation" in the photoinduced charge transfer processes discussed here [3-6]. The migration caused by the Coulombic pulling of the anion by the hole is related to the Dember effect, found e.g. in semiconductors: In this effect hole carriers are pulled along by the more mobile electrons [22]. At this point it is important to say that we performed several simulations in which the hole hopping effect was removed: In all such molecular dynamics simulations, attempted with a variety of potential parameters, separation of the halogen nuclei was not obtained, and basically a triatomic complex $\text{Xe}^+ \text{Cl}_2^-$ was stabilized in the cage after ≈ 1 ps or so.

3.2. Timescale for hole-hopping-induced ion migration

Fig. 2 shows the separation between various pairs of atoms in the system, the $\text{Xe}^+ - \text{Cl}$, the $\text{Cl} - \text{Cl}^-$ and the $\text{Xe}^+ - \text{Cl}^-$ distances, as a function of time. The results are for a typical trajectory at $T=20$ K, and $t=0$ is defined here as the instant of photo-absorption, i.e. creation of the ion pair. As the results show, the separation of the Cl^- from the Cl does not follow immediately the formation of the ion pair: A delay of the order of 2.3 ps is observed. The crowded geometry of the cage requires correlated motions of several atoms before the Cl^- can migrate away from the Cl to reach the energetically preferred configuration in which the halogen atoms are separated. Future experiments, using sub-picosecond probe techniques, may be able to measure and establish this interesting "time delay", in which several successive "soft collisions" between atoms in the cage, ultimately lead to an open path for sufficient ion motion and separation of the halogen photofragments.

3.3. Temporary trapping sites for Cl^- and Cl following separation

Fig. 3 shows the stabilized geometry after a long time interval ($t=20$ ps) following the initial charge transfer event. In reality, additional migrating holes may "pass by" and induce further migration. Nevertheless, for cases where the original Cl_2 (hence hole)

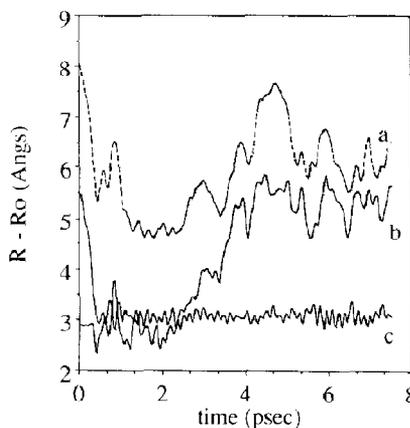


Fig. 2. The $\text{Xe}^+ - \text{Cl}$, $\text{Cl} - \text{Cl}^-$ and $\text{Xe}^+ - \text{Cl}^-$ distances as function of time (a, b, c, respectively). Results are from a single typical trajectory at $T=20$ K.

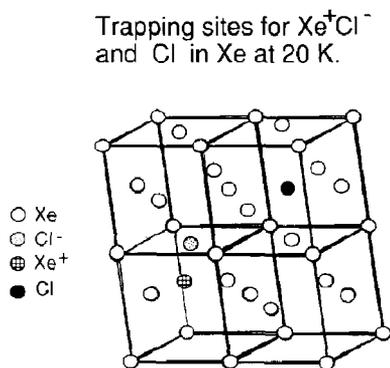


Fig. 3. Stabilized site geometry 20 ps after the formation of Xe^+Cl^- in solid Xe. The result is typical of all trajectories after long times.

concentration is very low, the configuration of fig. 3 is expected to persist over long timescales. It shows clearly that the neutral Cl atom is trapped in an interstitial site of octahedral symmetry. The site appears to be unique, at least for the limited number of trajectories pursued in the simulation. (If other sites can be populated at all, we expect these populations to be very low, of the order of 2%, based on the number of the trajectories used.) There is already partial experimental evidence for the fact that the Cl occupies an essentially unique interstitial site [6]. Direct confirmation through vibrational spectroscopy of the site uniqueness and of site symmetry should be most desirable. Fig. 4 shows a particular trajectory of a Cl atom from the onset of the process, until its stabilization at the trapping site. A vibrational frequency of $\approx 60 \text{ cm}^{-1}$ is estimated from the trajectory, and this could possibly be studied in future experiments.

4. Concluding remarks

In this article it was shown that hole hopping in a rare-gas crystal may induce migration of negatively charged ions due to an effect of pulling by the Coulombic attraction. In the present context of photo-initiated charge transfer processes, this leads to the effect of complete dissociation of the molecule involved, i.e. of separation of the product atoms. We expect the mechanism of ion migration induced by

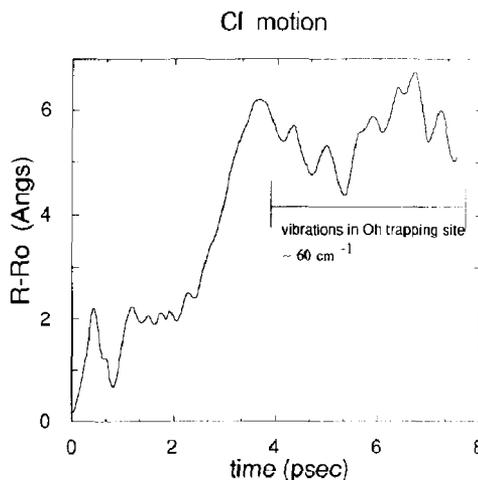


Fig. 4. Distance of neutral Cl product of charge transfer reaction from its initial configuration, as a function of time. $t=0$ pertains to the formation instant of the ion pair.

the hopping of positive charges to be of potential relevance to a wide range of processes, possibly involving also crystals and molecules of types very different from those considered here. A necessary condition for such migration to obtain is obviously that photoinduced charge transfer from the solute molecule to the solvent atoms should be possible. The effect was already established experimentally for several homoatomic and heteroatomic halogen molecules in the heavier rare-gas solvents. More rigorous theoretical studies of the process (especially with regard to the timescale of hole migration), are very desirable, but there is already a strong case for trying to directly test the proposed mechanism. This can be done, for instance, by time-resolved ultrafast spectroscopic measurements of the predicted time behavior and by vibrational spectroscopy of the species after the charge transfer reaction, for both of which we have provided here predictions based on the induced hole-trapping mechanism.

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