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Citation: *The Journal of Chemical Physics* **112**, 4983 (2000); doi: 10.1063/1.481053

View online: <http://dx.doi.org/10.1063/1.481053>

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An energy-resolved study of the partial fragmentation dynamics of Ar–HCl into H+Ar–Cl after ultraviolet photodissociation

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(Received 29 November 1999; accepted 13 December 1999)

The UV photolysis of Ar–HCl is simulated by an exact wave packet calculation. Partial fragmentation of the cluster into H and Ar–Cl fragments is studied by projecting out the asymptotic wave packet onto the product states, at several excitation energies in the range of the Ar–HCl absorption spectrum. The partial fragmentation pathway is found to dominate the photolysis process at very low excitation energies, and to be intense also at high energies. At medium excitation energies the other competing fragmentation pathway, namely total fragmentation into H, Ar, and Cl, dominates almost completely the photodissociation dynamics. The relative intensity of the two fragmentation pathways depends on the extent to which the hydrogen is initially blocked by Ar and Cl. The Ar–Cl radicals are produced with high rotational and low vibrational excitation at most of the Ar–HCl energies studied. The internal energy distributions of Ar–Cl show remarkable differences in shape depending on the regions of the absorption spectrum which are excited. This effect can be exploited to control both the efficiency of Ar–Cl generation and the internal excitation of the radical prepared, by changing the excitation energy of the parent cluster. © 2000 American Institute of Physics. [S0021-9606(00)00210-5]

I. INTRODUCTION

The study of weak interactions between atomic and/or molecular species has attracted a great deal of interest in the last years, due to their fundamental role in condensed matter physics. Much of the research effort was addressed to the interactions between closed-shell systems,^{1,2} while interactions involving open- and closed-shell species were less investigated. Rare gas halides (Rg–X) are the simplest prototypical systems involving the latter type of interactions, and they have been extensively studied. The main interest in the Rg–X open-shell complexes arises from their use in excimer lasers in the UV region. A detailed knowledge of the Rg–X interaction is also central to understand the solvation effects in the photophysics and photochemistry of some impurities (like HX and X₂) embedded in rare gas matrices^{3–5} and liquids.^{6,7}

Different types of experimental techniques have been applied to study Rg–X radicals. Among them are the spectroscopic studies carried out by several groups.^{8–15} A large variety of Rg–X complexes was also explored by means of scattering experiments performed by Lee and co-workers,¹⁶ and Aquilanti and co-workers.¹⁷ A third type of technique consisted of electron photodetachment of the Rg–X[–] anions followed by zero electron kinetic energy (ZEKE) spectroscopy. This technique was applied by Neumark and co-workers to investigate a number of Rg–X complexes and the corresponding anions.¹⁸ Interaction potential curves were obtained from the data generated by all the above experiments.

A new type of experiment has been recently suggested to prepare and probe Rg–X radicals. Wittig and co-workers carried out energy-resolved experiments on the UV photolysis of the Ar–HI cluster, and measured the time-of-flight (TOF) spectrum of the H fragment by means of high-*n* Rydberg TOF (HRTOF) spectroscopy.¹⁹ A blueshift was ob-

served in the hydrogen kinetic-energy release distribution obtained from the TOF spectrum, which was attributed to H fragments hotter than those produced by total fragmentation of the cluster, Ar–HI + *hν* → H + Ar + I. The authors interpreted such a blueshift as an indirect evidence that Ar–I radical complexes were formed as products of the photolysis process. Wittig and co-workers suggested that UV photodissociation of hydrogen-bonded clusters could be a viable method to prepare high concentrations of Rg–X complexes, or even other types of radicals.¹⁹

The HRTOF spectroscopic technique was applied by Wittig and co-workers to explore the UV photolysis of other hydrogen-bonded clusters like (HI)₂ (Ref. 20) and (HCl)₂,²¹ and evidence was found of formation of I–HI and Cl–HCl radicals, respectively. Due to energy conservation, the H fragment TOF spectrum measured, reflected the state distribution of the radicals prepared. The light fragment thus becomes a probe of the radical complexes produced by the photolysis of the parent cluster. In turn, Nesbitt and co-workers have carried out experiments on the UV photodissociation of Ar–H₂O (Ref. 22) and Ar_{*n*}–H₂ (*n* ≤ 2) (Ref. 23) clusters. In the case of Ar–H₂O the authors observed a slight heating in the rotational distribution of the OH photofragment, as compared with that of the OH product resulting from photolysis of unclustered H₂O at the same wavelength. A classical trajectory simulation²⁴ of the Ar–H₂O photodissociation showed that the OH rotational heating could be due to formation of Ar–OH radicals. Photolysis of Ar_{*n*}–H₂S precursors provided the first direct observation of Ar–SH and Ar₂–SH open-shell complexes from laser induced fluorescence (LIF) spectra. A high efficiency of radical formation was obtained for excitation at 248 nm, while it decreased to tenfold lower when photolysis was carried out at 193 nm.

In this paper the UV photodissociation of Ar–HCl is

studied, focussing on the partial fragmentation mechanism of the cluster, $\text{Ar-HCl} + h\nu \rightarrow \text{H} + \text{Ar-Cl}$. The probability of Ar-Cl formation was estimated in an earlier wave packet simulation, and found to be rather high.²⁵ Such an estimated probability was not resolved in energy. More rigorous, energy-resolved calculations were further carried out by projecting the wave packet onto the asymptotic states associated with the H and Ar-Cl fragments, for several excitation energies of the parent cluster. Preliminary results were reported²⁶ showing a high yield of Ar-Cl radical products resulting from photolysis at very low and very high excitation energies of Ar-HCl. In the present work we extend the previous study, with the emphasis on the analysis of the final state distributions of the Ar-Cl complexes formed. To the best of our knowledge, the theoretical study reported here (along with that of Ref. 26) is the first one on the generation of Rg-X radicals from UV photolysis of a Rg-HX precursor, based on a 3D quantum calculation.

The organization of the paper is the following. In Sec. II the method used is described. The results are presented and discussed in Sec. III. Finally, conclusions are given in Sec. IV.

II. THEORETICAL TREATMENT

The UV photodissociation of Ar-HCl is simulated upon optical excitation of the HCl molecule from its ground-electronic state $X^1\Sigma^+$ to the repulsive excited state $A^1\Pi$ [both of which correlating adiabatically with the $\text{H}(^2S) + \text{Cl}(^2P_{3/2})$ asymptote]. As in previous calculations, we shall assume here that the system is excited through an ultrafast Franck-Condon transition, and the photodissociation dynamics takes place only on the $A^1\Pi$ electronic surface. The potential-energy surfaces of the two electronic states have been described elsewhere.^{25,27} We note that by neglecting the nonadiabatic (spin-orbit and rotational) couplings between the $A^1\Pi$ state and other electronic states correlating with the $\text{H}(^2S) + \text{Cl}(^2P_{1/2})$ asymptote,²⁸ we are ruling out the possibility of obtaining $\text{H} + \text{Ar} + \text{Cl}(^2P_{1/2})$ and $\text{H} + \text{Ar-Cl}(^2P_{1/2})$ as products of the photolysis. Only $\text{Cl}(^2P_{3/2})$ and $\text{Ar-Cl}(^2P_{3/2})$ fragments are possible in our calculation. Unfortunately, an exact description of the Ar-HCl photodissociation dynamics including several coupled electronic states becomes prohibitively expensive. The initial state of Ar-HCl used in the simulation corresponds with the vibroelectronic ground state of the cluster, and it is described in earlier works.^{25,27}

It has been found in previous studies^{25,27,29,30} that photodissociation of Ar-HCl takes place through two different and competing fragmentation pathways:

which we shall refer to by total fragmentation [Eq. (1)] and partial fragmentation [Eq. (2)] pathways hereafter. Total fragmentation (TF) of the cluster is produced by an indirect photodissociation mechanism, following which the hydrogen photofragment is temporarily trapped in resonances in between the Ar and Cl atoms. During this trapping the H frag-

ment collides once or more with the heavier atoms, transferring to them part of its initial excess energy, and giving rise to three final fragments. This indirect dissociation mechanism has been recently investigated,³⁰ finding that it accounts for $\approx 13\%$ of the total probability of photodissociation in the energy range of the absorption spectrum. Actually, most of the total fragmentation of Ar-HCl is likely to occur via a nearly direct photodissociation mechanism, in which the recoiling H fragment interacts rather weakly with the Ar atom. In this case the hydrogen would transfer only a small fraction of energy to the Ar atom, which would be enough to break the weak Ar-Cl bond. Such a nearly direct dissociation mechanism seems to dominate at most of the cluster excitation energies. The partial fragmentation (PF) pathway of Eq. (2) is produced by a mechanism of (completely) direct photodissociation, in which the recoiling hydrogen does not interact appreciably with Ar. Through this mechanism the Ar-Cl bond gets a smaller share of energy than in the two above mechanisms, allowing the Ar-Cl radical to survive. The analysis of the partial fragmentation of Ar-HCl leading to Ar-Cl radical complexes is the purpose of the present work.

In the calculation, the Ar-HCl cluster is represented in Jacobian coordinates (r, R, θ) , where r is the HCl distance, R is the separation between the Ar atom and the HCl center of mass, and θ is the angle between the vectors $\vec{r}$ and $\vec{R}$. Zero-total angular momentum is assumed. The total wave function of the system is defined for convenience as

$$\Psi(r, R, \theta) = \Phi(r, R, \theta) / rR, \quad (3)$$

and the Hamiltonian for the reduced wave function $\Phi(r, R, \theta)$ for $J=0$ is

$$\hat{H}(r, R, \theta) = -\frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} + \left(\frac{1}{2\mu_r r^2} + \frac{1}{2\mu_R R^2} \right) \hat{j}^2 + V(r, R, \theta), \quad (4)$$

being μ_r and μ_R the reduced masses associated with the r and R modes, respectively. The excited-state photodissociation dynamics is simulated by solving the time-dependent Schrödinger equation for the $\Phi(r, R, \theta)$ wave packet

$$i\hbar \frac{\partial \Phi(r, R, \theta, t)}{\partial t} = \hat{H} \Phi(r, R, \theta, t), \quad (5)$$

up to $t=80$ fs. The numerical details of the wave packet propagation have been given elsewhere.²⁵

After propagating the wave packet, the second stage of our calculation is to project that wave packet onto the states associated with the products $\text{H} + \text{Ar-Cl}$, for different total energies initially excited in Ar-HCl. As it has been discussed previously,³⁰ the asymptotic states of the fragments $\text{H} + \text{Ar-Cl}$ cannot be precisely defined in the Jacobian coordinate representation (r, R, θ) used for the wave packet propagation. The reason is that the R coordinate does not represent exactly the Ar-Cl stretch mode (although it is quite close, due to the H/Cl mass ratio). Actually, a precise definition of the $\text{H} + \text{Ar-Cl}$ product states is possible in the Jacobian representation (R', r', θ') , where R' is the distance be-

tween H and the Ar-Cl center of mass, r' is the Ar-Cl separation, and θ' is the angle between the vectors $\vec{R}'$ and $\vec{r}'$.

The use of the (R', r', θ') representation in the wave packet propagation demands a larger grid than the (r, R, θ) one, making the problem prohibitively costly. An alternative is to perform a Jacobian transformation of the asymptotic wave packet $\Phi(r, R, \theta, t = \infty)$ to a new grid in the (R', r', θ') coordinates, and then to carry out the projection in this latter representation. This procedure becomes very expensive too, since it requires interpolating a dense, complex, 3D fully coupled wave packet like the present one. Instead, we chose to transform the asymptotic states of the products from the (R', r', θ') to the (r, R, θ) representation, where now the wave packet $\Phi(r, R, \theta, t = \infty)$ is projected out. Since the asymptotic states of H+Ar-Cl can be defined as a product of three one-dimensional functions, as will be seen below, the evaluation of the required interpolations becomes more efficient.

The asymptotic states of the H and Ar-Cl fragments for a given total energy E of Ar-HCl can be represented as the direct product

$$\xi_{\epsilon_k, v, j}^{(E)}(R', r', \theta') = \left(\frac{\mu_{R'}}{2\pi k_{R'} \hbar^2} \right)^{1/2} \times e^{ik_{R'} R'} \chi_v^{(j)}(r') P_j(\cos \theta'), \quad (6)$$

where ϵ_k is the kinetic energy associated with the relative translational motion between the two fragments [$k_{R'} = (2\mu_{R'} \epsilon_k)^{1/2}/\hbar$], $P_j(\cos \theta')$ is a normalized Legendre polynomial, and $\chi_v^{(j)}(r')$ is a vibrational eigenstate of the Ar-Cl stretch mode for a given j state, obtained as a solution of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu_{r'}} \frac{\partial^2}{\partial r'^2} + \frac{j(j+1)\hbar^2}{2\mu_{r'}(r')^2} + V_{\text{Ar-Cl}}(r') \right] \chi_v^{(j)}(r') = E_{v,j} \chi_v^{(j)}(r'), \quad (7)$$

with an associated energy level $E_{v,j}$. A time-dependent phase factor $e^{-iEt/\hbar}$ has been omitted in Eq. (6) for simplicity. In the asymptotic limit the total energy of the fragments can be expressed in terms of ϵ_k and $E_{v,j}$ as

$$E = \epsilon_k + E_{v,j}. \quad (8)$$

In Eq. (6), $\xi_{\epsilon_k, v, j}^{(E)}(R', r', \theta')$ is the reduced form of the asymptotic state wave function in the (R', r', θ') coordinate representation. The total wave function must have a unique value at any point in space, regardless of the coordinate representation used. This can be expressed as³¹

$$\frac{1}{R'(r, R, \theta) r'(r, R, \theta)} \xi_{\epsilon_k, v, j}^{(E)}[R'(r, R, \theta), r'(r, R, \theta), \theta'(r, R, \theta)] = \frac{1}{rR} \eta_{\epsilon_k, v, j}^{(E)}(r, R, \theta), \quad (9)$$

where $\eta_{\epsilon_k, v, j}^{(E)}(r, R, \theta)$ is the reduced wave function of the asymptotic state in the (r, R, θ) representation, and

$R'(r, R, \theta)$, $r'(r, R, \theta)$, and $\theta'(r, R, \theta)$ are the functions which transform any point in space from the (r, R, θ) coordinate representation to the (R', r', θ') one. From Eq. (9) it immediately follows that

$$\eta_{\epsilon_k, v, j}^{(E)}(r, R, \theta) = \frac{rR}{R'(r, R, \theta) r'(r, R, \theta)} \xi_{\epsilon_k, v, j}^{(E)} \times [R'(r, R, \theta), r'(r, R, \theta), \theta'(r, R, \theta)]. \quad (10)$$

Now $\eta_{\epsilon_k, v, j}^{(E)}(r, R, \theta)$ can be used to project out the wave packet $\Phi(r, R, \theta, t = \infty)$ in the (r, R, θ) coordinates,

$$c_{v,j}(E) = \langle \eta_{\epsilon_k, v, j}^{(E)}(r, R, \theta) | \Phi(r, R, \theta, t = \infty) \rangle, \quad (11)$$

and then to obtain the probability $P_{v,j}(E) = |c_{v,j}(E)|^2$ of Ar-HCl photodissociation into an atomic H fragment with kinetic energy $\epsilon_k^{\text{H}} = (m_{\text{Ar}} + m_{\text{Cl}}/m_{\text{H}} + m_{\text{Ar}} + m_{\text{Cl}}) \epsilon_k$, and an Ar-Cl radical fragment in a ro-vibrational state (v, j) and with a translational energy $\epsilon_k^{\text{Ar-Cl}} = E - \epsilon_k^{\text{H}} - E_{v,j}$. In order to ensure that the wave packet $\Phi(r, R, \theta, t = \infty)$ which is projected out is actually asymptotic, only the wave packet components corresponding to distances $r > 19.9$ a.u. have been included in Eq. (11). About 7% of the wave packet is still located at distances $r < 19.9$ a.u. for $t = 80$ fs. As it was shown previously,³⁰ these latter wave packet components correspond to the TF pathway, so removing them from Eq. (11) does not affect the value of the calculated coefficients $c_{v,j}(E)$.

It should be noted that total energy conservation [Eq. (8)] implies that the two quantities ϵ_k and $E_{v,j}$ are not independent ones. For a given energy E , since the spectrum of energy levels $E_{v,j}$ is discrete, only discrete values of ϵ_k (or equivalently, ϵ_k^{H}) are allowed. Therefore, although we retained the four indexes E , ϵ_k , v , and j in the above equations [except in $c_{v,j}(E)$ and $P_{v,j}(E)$], only either E and ϵ_k or E , v , and j are needed to specify a given state of the product photofragments. As a consequence, for a given total energy, the ro-vibrational state distribution of Ar-Cl, $P_{v,j}(E)$, coincides with the kinetic-energy distribution of the H fragment, $P(\epsilon_k^{\text{H}}, E)$, in the energy range of the Ar-Cl spectrum of bound states. The experimental implication is that the H fragment TOF spectrum can be used as a probe of the state distribution in which the radical complexes are prepared.

The vibrational states $\chi_v^{(j)}(r')$ were obtained by solving numerically Eq. (7). A number of 196 bound states $\chi_v^{(j)}(r')$ (with energy levels below the dissociation limit of the Ar-Cl potential) was found with $j \leq 41$. In addition, 76 quasibound states (above the dissociation limit of the potential) supported by the centrifugal barrier $j(j+1)\hbar^2/2\mu_{r'}(r')^2$, were also obtained with $j \leq 60$. Neither bound nor quasibound states were found for $j > 60$. The metastable states are zero-order ones which are expected to decay by tunneling through the barrier. The time scale of decay of these states was analyzed by means of line-shape calculations.³² The results showed that most of the zero-order states were an excellent approximation in the region where the wave packet is to be projected out. Four states very close to the top of the corresponding rotational barrier were found to be spurious and

FIG. 1. Probability of Ar-Cl formation (solid line) and total probability of photodissociation (dashed line) vs the initial excitation energy of Ar-HCl. The limit $E=0$ corresponds to three separated atoms.

were discarded. For the remaining 72 states, the decay lifetimes obtained ranged from a few picoseconds to several tens of picoseconds. Since in all cases the tunneling time scale was much longer than that of direct dissociation of the H fragment (about 15–20 fs), the 72 quasibound states can be considered as bound ones in practice. Therefore the wave packet was projected out onto 268 degenerate states of the H+Ar-Cl products for each total energy studied.

III. RESULTS AND DISCUSSION

A. Probability of Ar-Cl formation for different excitation energies of Ar-HCl

The wave packet projection was carried out for 20 different initial excitation energies E of Ar-HCl, in the range covered by the absorption spectrum (0.8 eV–5.8 eV). Summation of the probabilities $P_{v,j}(E)$ corresponding to the 268 H+Ar-Cl(v,j) product states associated with a given energy E gives the probability of the PF pathway at that energy. Such a probability distribution [denoted in the following as $P_{\text{Ar-Cl}}(E)$] is displayed in Fig. 1 (solid line). The total probability of photodissociation, calculated as

$$P_{\text{total}}(E) = \frac{1}{2\pi\hbar} \times \text{Re} \left[\int_0^\infty dt \langle \Phi(r, R, \theta, t=0) | \Phi(r, R, \theta, t) \rangle e^{iEt/\hbar} \right],$$

is also shown in Fig. 1 (dashed line). Note that by multiplying $P_{\text{total}}(E)$ by the energy $\varepsilon(\lambda)$ of the photon used to excite the system, the absorption spectrum is obtained (within a constant factor).

Integration of $P_{\text{Ar-Cl}}(E)$ over the whole energy range yields the total probability of Ar-HCl photolysis into H+Ar-Cl fragments,

$$P_{\text{Ar-Cl}}^{\text{total}} = \int dE P_{\text{Ar-Cl}}(E).$$

FIG. 2. (a) Total probability of Ar-Cl formation, $P_{\text{Ar-Cl}}$ (solid line), and partial probabilities of Ar-Cl formation in bound states, $P_{\text{Ar-Cl}}^b$ (dashed line), and in quasibound states, $P_{\text{Ar-Cl}}^q$ (dotted line) vs the excitation energy of the parent cluster. (b) Ratios between the above three probabilities of Ar-Cl and the total probability of photodissociation, $P_{\text{Ar-Cl}}/P_{\text{total}}$ (solid line), $P_{\text{Ar-Cl}}^b/P_{\text{total}}$ (dashed line), and $P_{\text{Ar-Cl}}^q/P_{\text{total}}$ (dotted line) vs E .

It is found that 1.1% of the photodissociation process occurs via the PF pathway of Eq. (2). Consequently, in the remaining 99% of the process the Ar-HCl cluster dissociates into three fragments [Eq. (1)]. As said above, the probability of total fragmentation due to an indirect photodissociation mechanism induced by collisions of the hydrogen with the heavy atoms was estimated³⁰ as $\approx 13\%$. Therefore, $\approx 86\%$ of the cluster photolysis would take place through the TF pathway following a nearly direct dissociation mechanism, where the recoiling H fragment interacts to some extent with the Ar atom.

It is interesting to analyze in more detail the behavior of the $P_{\text{Ar-Cl}}(E)$ distribution when different total energies of the parent cluster are excited. To this purpose, the probability $P_{\text{Ar-Cl}}(E)$ is shown in Fig. 2(a) at a different scale as in Fig. 1, along with the partial probability distributions $P_{\text{Ar-Cl}}^b(E)$, and $P_{\text{Ar-Cl}}^q(E)$, associated with formation of Ar-Cl radicals in bound and quasibound ro-vibrational states, respectively. In addition, the ratios $P_{\text{Ar-Cl}}/P_{\text{total}}$, $P_{\text{Ar-Cl}}^b/P_{\text{total}}$, and $P_{\text{Ar-Cl}}^q/P_{\text{total}}$ are plotted in Fig. 2(b) vs the cluster excitation energy.

The most interesting finding is the behavior of the ratio

$P_{\text{Ar-Cl}}/P_{\text{total}}$ with the total energy. At low energies the Ar-Cl radicals are the dominant products of the photolysis process, although the percentage of Ar-Cl formation decreases sharply as the excitation energy increases. The decreasing of the Ar-Cl production with increasing excitation energy is in agreement with the experimental findings on photodissociation of Ar-H₂S and Ar₂-H₂S clusters.²³ Nesbitt and co-workers have proposed a gentle recoil mechanism²³ to explain the high production of radical complexes in the case of Ar_n-H₂S ($n \leq 2$). Such a mechanism is based on the fact that the recoiling H fragment carries most of the excitation energy initially deposited in the cluster, leaving only a small fraction of this energy to be accommodated in the radical formed. By increasing the excitation energy, the fraction of available energy for the radical increases correspondingly, leading to a decrease of the percentage of surviving radicals.

The energy difference between the lowest bound state and the highest quasibound state of Ar-Cl is $\approx 200 \text{ cm}^{-1}$. This is thus the maximum amount of energy which can be accommodated as internal (ro-vibrational) excitation energy of the radical without breaking it (within the time scale of hydrogen dissociation). For $E < 1.9 \text{ eV}$ the amount of energy available for the Ar-Cl fragment (to be distributed among center-of-mass energy and internal energy) is $< 200 \text{ cm}^{-1}$. This fact combined with the gentle recoil mechanism would explain the high survival probability of Ar-Cl products in that energy range.

The gentle recoil mechanism is a ballistic-type model which implies direct dissociation of the hydrogen fragment. Consequently, the energy available for the two fragments H and Ar-Cl is governed by the ratio between their masses. In the behavior of the ratio $P_{\text{Ar-Cl}}/P_{\text{total}}$ three different energy regions can be distinguished. In the first region, $E < 1.9 \text{ eV}$, the ratio decreases sharply from nearly 1, then it stabilizes around 0.01 for $1.9 \text{ eV} < E < 4.7 \text{ eV}$, and finally $P_{\text{Ar-Cl}}/P_{\text{total}}$ raises for $E > 4.7 \text{ eV}$, reaching again a high efficiency of radical obtention. This behavior cannot be explained if the gentle recoil (or direct dissociation) mechanism is the only one governing the probability of formation of Ar-Cl radicals. If this was the case, the ratio $P_{\text{Ar-Cl}}/P_{\text{total}}$ would be essentially determined by the amount of energy available for the Ar-Cl fragment. In this situation one would expect $P_{\text{Ar-Cl}}/P_{\text{total}}$ to be 1 for $E < 1.9\text{--}2.0 \text{ eV}$, and then a more or less gradual decay of the ratio to zero for $E > 1.9\text{--}2.0 \text{ eV}$.

The behavior of $P_{\text{Ar-Cl}}/P_{\text{total}}$ can be understood in terms of a competition between the PF and the TF pathways. This competition occurs along the whole energy range of the absorption spectrum. At very low energies the PF pathway dominates the photolysis process, but the rapidly increasing probability of the TF pathway leads to the opposite situation at $E \approx 2.0 \text{ eV}$. In the energy range $1.9 \text{ eV} < E < 4.7 \text{ eV}$ the low ratio $P_{\text{Ar-Cl}}/P_{\text{total}}$ is likely due to a combination of two factors. The main factor is probably the highly dominant TF pathway, and a secondary factor is the increasing amount of energy available for Ar-Cl after direct dissociation of the hydrogen. At high energies, $E > 4.7 \text{ eV}$, the probability of the TF pathway would decrease, making possible an increase of $P_{\text{Ar-Cl}}/P_{\text{total}}$.

The relative intensity of the two fragmentation pathways depends on the extent to which the hydrogen dissociation is direct or not. This is determined essentially by the Ar-HCl configurations (or the regions of the upper potential-energy surface) which are initially populated at different excitation energies. At very low excitation energies the Ar-HCl configurations mainly populated are probably those where the hydrogen is not blocked by the heavier atoms, which favors direct dissociation of the H fragment. At higher energies, initial cluster configurations in which the light atom is blocked to a larger extent would dominate. Starting from these configurations the hydrogen would collide, either weakly or strongly, with the heavier atoms, transferring enough energy to break the Ar-Cl bond, and thus leading to total fragmentation. Therefore, following this interpretation, the probability of each fragmentation pathway would be determined by the initial Ar-HCl geometries populated at each excitation energy, and more specifically, by the relative position of the hydrogen with respect to Ar and Cl.

It is observed that the ratio $P_{\text{Ar-Cl}}/P_{\text{total}}$ does not decay to zero at energies $E > 1.9 \text{ eV}$, and even grows significantly at very high energies, despite the increasing amount of energy available for the radical. This result is explained if only a fraction $< 200 \text{ cm}^{-1}$ of the available energy is converted into internal energy, and the remaining energy becomes translational (center-of-mass) energy of the Ar-Cl fragment. Since the PF pathway occurs upon a direct dissociation mechanism, the partitioning of the available energy into translational and internal energy is likely to be determined, to a large extent, also by the initial geometry of the parent cluster.

In a previous work²⁵ the quantities $P_{\text{Ar-Cl}}(E_{k_r})$ and $P_{\text{Ar-Cl}}(E_{k_r})/P_{\text{total}}(E_{k_r})$ were calculated (Fig. 10 of Ref. 25), where E_{k_r} is the kinetic energy associated with the Jacobian r mode (the H-Cl stretch vibration). Despite the fact that only bound states of Ar-Cl were included in the calculation, the $P_{\text{Ar-Cl}}(E_{k_r})$ distribution was found to be very intense at most of the kinetic energies E_{k_r} studied. The ratio $P_{\text{Ar-Cl}}(E_{k_r})/P_{\text{total}}(E_{k_r})$ turned out to be very small at low kinetic energies, but rapidly increasing and approaching unity at higher energies. The behavior of $P_{\text{Ar-Cl}}(E_{k_r})$ and $P_{\text{Ar-Cl}}(E_{k_r})/P_{\text{total}}(E_{k_r})$ is apparently in sharp contrast with that of the magnitudes $P_{\text{Ar-Cl}}(E)$ and $P_{\text{Ar-Cl}}(E)/P_{\text{total}}(E)$ shown in Figs. 1 and 2(b).

Two factors contribute to this discrepancy. First, in order to simplify the wave packet projection it was assumed in Ref. 25 that $\chi_v^{(j)}(r')P_j(\cos \theta') \approx \chi_v^{(j)}(R)P_j(\cos \theta)$, and then the wave packet was projected onto the states $e^{ik_r r} \chi_v^{(j)}(R)P_j(\cos \theta) [k_r = (2\mu_r E_{k_r})^{1/2}/\hbar]$. Such an assumption seems reasonable, in principle, since due to the H/Cl mass ratio the r' and R coordinates are quite similar. By making this assumption the Jacobian transformation of the H+Ar-Cl asymptotic states is avoided, but the calculated $P_{\text{Ar-Cl}}(E_{k_r})$ distribution becomes approximate. Second, $P_{\text{Ar-Cl}}(E_{k_r})$ and $P_{\text{Ar-Cl}}(E)$ are actually different magnitudes [and so $P_{\text{Ar-Cl}}(E_{k_r})/P_{\text{total}}(E_{k_r})$ and $P_{\text{Ar-Cl}}(E)/P_{\text{total}}(E)$], not directly comparable. Indeed, the $P_{\text{Ar-Cl}}(E_{k_r})$ distribution is

not resolved in energy, since all the states $e^{ik_r r} \chi_v^{(j)}(R) P_j(\cos \theta)$ with a given energy E_{k_r} are associated with different total energies E . Therefore, the $e^{ik_r r} \chi_v^{(j)}(R) P_j(\cos \theta)$ states should be viewed just as a basis on which the $\Phi(r, R, \theta, t = \infty)$ wave packet can be expanded. The more complete is the basis set, the larger is the amount of wave packet which is possible to expand on it, which would explain the high intensity of $P_{\text{Ar-Cl}}(E_{k_r})$. We believe, however, that the $e^{ik_r r} \chi_v^{(j)}(R) P_j(\cos \theta)$ states do not properly approximate the true asymptotic states of the products $\text{H} + \text{Ar-Cl}$ [Eq. (10)], and this is the main reason of the discrepancy between $P_{\text{Ar-Cl}}(E_{k_r})$ and $P_{\text{Ar-Cl}}(E)$ (and the corresponding ratios $P_{\text{Ar-Cl}}/P_{\text{total}}$). The calculation of sensitive quantities like $P_{v,j}(E)$ seems to require a precise definition of the asymptotic states used in the wave packet projection. This would explain the dramatic failure of the assumption that $\eta_{E_{k_r}, v, j}^{(E)}(r, R, \theta) \approx (\mu_r/2\pi k_r \hbar^2)^{1/2} e^{ik_r r} \chi_v^{(j)}(R) P_j(\cos \theta)$, made in the previous study.

In the work of Ref. 25, the analysis of the asymptotic wave packet showed that most of the wave packet intensity in the R coordinate remained in the interaction region. This was interpreted as an indication that Ar-Cl radicals were formed as products of the photodissociation with very high probability. This interpretation was apparently confirmed by the calculated quantities $P_{\text{Ar-Cl}}(E_{k_r})$ and $P_{\text{Ar-Cl}}(E_{k_r})/P_{\text{total}}(E_{k_r})$, discussed above. In the light of the present, more accurate results, such an interpretation has to be revised. Most of the wave packet intensity remaining in the interaction region of the R coordinate actually corresponds to dissociated Ar-Cl bonds, upon transfer of a relatively small amount of energy from the hydrogen. The resulting cold, slow-moving Ar and Cl fragments take a longer time to leave the interaction region than the 80 fs of the time propagation.

Analysis of the partial distributions $P_{\text{Ar-Cl}}^b(E)$ and $P_{\text{Ar-Cl}}^q(E)$, and the corresponding ratios $P_{\text{Ar-Cl}}^b/P_{\text{total}}$ and $P_{\text{Ar-Cl}}^q/P_{\text{total}}$ provides additional information on the mechanism of the PF pathway. Since the quasibound states of Ar-Cl are supported by centrifugal barriers $j(j+1)\hbar^2/2\mu_{r'}(r')^2$, population of these states is associated with rotational excitation of the Ar-Cl radical formed. In addition, while the bound states provide information on the potential well of the Ar-Cl complex, the quasibound states allow one to probe the shorter- and longer-range Ar-Cl interaction. It thus becomes interesting, from an experimental viewpoint, to know whether there are excitation energies for which the Ar-Cl radicals are produced dominantly either in bound or in quasibound states, and if so, which are those energies. The relative intensities of the distributions $P_{\text{Ar-Cl}}^b(E)$ and $P_{\text{Ar-Cl}}^q(E)$ of Fig. 2(a) show a nonuniform behavior with E , which is also reflected in the ratios $P_{\text{Ar-Cl}}^b/P_{\text{total}}$ and $P_{\text{Ar-Cl}}^q/P_{\text{total}}$. At very low excitation energies ($E < 1.0$ eV) the population of bound states dominates, although this situation is reversed in the energy region 1.0 eV $< E < 2.2$ eV. At medium energies (2.2 eV $< E < 4.7$ eV) the Ar-Cl radicals are again formed mainly in bound states, while for higher energies $P_{\text{Ar-Cl}}^b(E)$ becomes very small and $P_{\text{Ar-Cl}}^q(E)$ and $P_{\text{Ar-Cl}}(E)$ practically coincide. The results

show a clear selectivity in the population of bound or quasibound states of Ar-Cl with the cluster excitation energy, more pronounced at low and high energies. This effect could be exploited experimentally.

B. State distributions of the Ar-Cl radical

In the following we shall analyze the distribution of states in which the Ar-Cl radical fragments are formed for different excitation energies of the parent cluster. Such distributions can be experimentally obtained by probing directly the Ar-Cl complex (e.g., by spectroscopic methods), or indirectly from the hydrogen fragment TOF spectrum converted to the kinetic-energy domain. As discussed in Sec. II, by energy conservation the H fragment kinetic-energy distribution (KED) coincides with the Ar-Cl state distribution in the kinetic-energy region of bound ro-vibrational states, $\epsilon_k^{\text{H}} = (m_{\text{Ar}} + m_{\text{Cl}}/m_{\text{H}} + m_{\text{Ar}} + m_{\text{Cl}})(E - E_{v,j})$. In the region of kinetic energy corresponding to the Ar-Cl quasibound states there may be an additional contribution to the intensity of the hydrogen KED, coming from double-continuum states associated with the TF pathway into $\text{H} + \text{Ar} + \text{Cl}$. These TF states are degenerate with the PF ones $\eta_{E_{k_r}, v, j}^{(E)}$ associated with Ar-Cl quasibound states, both in the total energy E and in the kinetic energy of the H fragment, which implies that $\epsilon_k^{\text{Ar}} + \epsilon_k^{\text{Cl}} = \epsilon_k^{\text{Ar-Cl}} + E_{v,j}$. At those excitation energies for which both the intensity of the PF pathway and the population of the quasibound states are high enough, such states could be resolved in the experimental hydrogen KED.

Indeed, one of the advantages of using the H fragment as a probe of the final state distribution of the radical, is the possibility of detecting the radical quasibound states in the same conditions as the bound ones. Due to the short time scale of hydrogen dissociation as compared with the decay time scale of the metastable states, the recoiling H fragment “sees” these states as truly bound states. Because of energy conservation, the signature of the quasibound states can be detected in the hydrogen KED, same as in the case of the bound states. In contrast, probing the metastable states directly from the radical fragment implies that the time delay between the radical formation and the application of the detection method must be shorter than the lifetime of the states.

It is possible to distinguish three main energy regions in the behavior of the ratio $P_{\text{Ar-Cl}}/P_{\text{total}}$ with E , namely $E < 1.9$ eV, 1.9 eV $< E < 4.7$ eV, and $E > 4.7$ eV. In Fig. 3 the probability distributions of Ar-Cl ro-vibrational states are shown for six different excitation energies of Ar-HCl within the above three regions. These distributions can be plotted either vs the kinetic energy of the H fragment or vs the energy levels of the radical complex. The latter energy scale has been chosen for convenience, since it allows one to identify easily the population associated with bound ($E_{v,j} < 0$) and quasibound ($E_{v,j} > 0$) states. The discrete form of the distributions reflects the discrete spectrum of Ar-Cl ro-vibrational levels, and some (v, j) states have been explicitly labeled in the figure. The energy levels associated with quasibound states are zero-order ones. It should be noted that the intensity associated with Ar-Cl bound states corresponds with H atoms leaving with more energy than the recoil energy. This

FIG. 3. Internal energy distributions of the Ar-Cl radical for six different excitation energies of Ar-HCl. Some (v,j) states have been explicitly labeled in the distributions. See the text for details.

blueshifted intensity of the hydrogen KED is the analogous effect in Ar-HCl to that found experimentally for photolysis of Ar-HI.¹⁹

At very low excitation energies ($E < 1.0$ eV) most of the population is concentrated in bound (v,j) states, since little energy is available for internal excitation of the radical. As E increases the available energy for the Ar-Cl fragment also increases, and the population shifts gradually to the quasibound states, which dominate the ro-vibrational distributions

in the range $1.0 \text{ eV} < E < 1.9\text{--}2.0$ eV. In addition, by increasing E in the above range the maximum of the distributions shifts towards the energetically highest quasibound states (as in the case of the $E = 1.55$ eV distribution), indicating an extensive rotational excitation of Ar-Cl.

The situation changes in the region $1.9\text{--}2.0 \text{ eV} < E < 4.7$ eV, where the bound states become again populated with an intensity comparable to that of the quasibound states. The medium panels of Fig. 3 show two typical distributions of

this energy region. As shown by the distributions $P_{\text{Ar-Cl}}^b(E)$, and $P_{\text{Ar-Cl}}^q(E)$ of Fig. 2(a), for these excitation energies the total population in bound states is higher than that in quasi-bound states. It is interesting to note that the intensity of population spreads over the whole spectrum of energy levels rather uniformly. For $E > 1.9$ eV the energy available for the Ar-Cl radical exceeds the dissociation energy of the highest quasibound state. This means that in the photodissociation events populating the bound states (particularly the lower ones), most of the available energy becomes translational energy of the Ar-Cl fragment. This behavior contrasts with that found at energies $E < 1.9$ –2.0 eV, where the available energy is mostly channeled into internal excitation of the radical complex. The different partitioning of the available energy in the ranges $E < 1.9$ eV and $1.9 \text{ eV} < E < 4.7$ eV can be due, again, to population of different initial geometries of the parent cluster from which the H fragment recoils.

At very high energies, $E > 4.7$ eV, the population in bound states turns to decrease again, and the radicals are produced dominantly in the highest excited metastable states. In this energy range the energy available for the Ar-Cl fragment is rather high, which implies that most of it becomes center-of-mass energy of the radical complex. Actually, the ro-vibrational distributions for $E > 4.7$ eV (lower panels of Fig. 3) are qualitatively similar to those found at energies $1.5 \text{ eV} < E < 1.9$ –2.0 eV. The basic difference is that in the high-energy distributions the population is more concentrated in the highest quasibound states. The similarity of both the distributions and the ratio $P_{\text{Ar-Cl}}(E)/P_{\text{total}}(E)$ in the energy ranges $1.5 \text{ eV} < E < 1.9$ –2.0 eV and $E > 4.7$ eV could indicate that similar initial geometries of Ar-HCl are populated in these two regions of E .

The common feature of all the ro-vibrational distributions is the high rotational excitation of the Ar-Cl radicals produced after photodissociation. However, despite this common trend, the shape of the distributions changes substantially for excitation energies in different regions of the Ar-HCl absorption spectrum. This change is more pronounced when going from very low to very high excitation energies, which in turn are the regions where the ratio $P_{\text{Ar-Cl}}/P_{\text{total}}$ reaches the maximum values. This excitation-energy effect can be used to probe different regions of the spectrum of energy levels of Ar-Cl.

The distributions of Fig. 3, with some (v, j) states identified, provide an approximate idea of the vibrational and rotational excitation of Ar-Cl at different total energies. It is interesting to analyze in more detail the distribution of the internal excitation among the vibrational and rotational modes of the radical. In Figs. 4 and 5 v -state and j -state distributions are displayed, respectively, for different excitation energies of Ar-HCl. The v -state (j -state) distribution is calculated by summing the probabilities $P_{v,j}(E)$ over the j states (v states).

The v -state distributions of Fig. 4 are qualitatively similar in all the range of E , and characterized by a low vibrational excitation. For all the energies the $v=0$ state is the most populated one, and only small differences in the relative population of the higher v states are found for different excitation energies. Essentially two factors contribute to this

FIG. 4. Vibrational distributions of Ar-Cl for four different excitation energies of the parent cluster.

result. One factor is that the number of v states supported by the centrifugal barrier $j(j+1)\hbar^2/2\mu_r(r')^2$ decreases as j increases. For the first lowest values of j the maximum number of v states is 9, while for the highest j values only $v=0$, or at most $v=1$, survives. Since the general trend in the Ar-Cl formation is the high rotational excitation (as seen from Fig. 3), it is expected that most of the population will concentrate in the lowest vibrational states, as found in Fig. 4.

The other factor is related to the direct dissociation mechanism by means of which the radicals are formed. As discussed previously, the radicals are produced by direct recoiling of the H fragment from initial Ar-HCl geometries where the hydrogen is not blocked by the Ar atom. Such geometries imply large initial angles of the H-Cl bond with respect to the Ar-Cl internuclear axis, far from the equilibrium collinear configuration $\text{Ar}\cdots\text{H-Cl}$. By recoiling from these geometries, the hydrogen produces a large torque on the Ar-Cl fragment, which excites the rotational mode, but not the vibrational one. In order to produce extensive vibrational excitation, the hydrogen should recoil from geometries with smaller angles. In these geometries, however, the hydrogen feels the blockage of the Ar atom, and photodissociation follows the TF pathway. The hottest v -state distributions are found for $E < 1.0$ eV, where the Ar-Cl radicals are produced mainly in bound states. This vibrational heating manifests in a somewhat higher population of the states $v \geq 1$ than when $E > 1.0$ eV. Even in these cases, however, the population is already negligible for $v > 5$.

The j distributions of Fig. 5 show a much less monotonic behavior with the excitation energy than the v distributions. As discussed above, the general trend is the high rotational excitation due to the torque produced on the Ar-Cl fragment

FIG. 5. Rotational distributions of the Ar–Cl fragment for six excitation energies E . See the text for details.

by the recoiling hydrogen. The shape of the j distributions resembles closely that of the distributions presented in Fig. 3. The discussion of the (v, j) distributions in terms of the energy available for the Ar–Cl fragment, and its partitioning into translational and internal energy of the radical, is also valid for the j distributions. The rotational excitation of Ar–Cl increases gradually with the available energy in the energy region $E < 1.9$ eV. For energies $1.9 \text{ eV} < E < 4.7$ eV the population spreads over the whole j range, although with larger intensity at high j values. At very high energies, $E > 4.7$ eV, the population gradually concentrates in the highest rotational states.

Interestingly, the j distributions display a structure of sharp peaks, which is more pronounced in the region $1.9 \text{ eV} < E < 4.7$ eV. Such a structure is a reflection of the shape, in the j space (and therefore in the angular coordinate θ'), of the Ar–HCl state which is populated in the upper potential surface for a given excitation energy E . Actually, the structure of the j distributions corresponds with the angular structure of the excited Ar–HCl states in the asymptotic region of the products H+Ar–Cl (i.e., large R' distances), where the wave packet has been projected out. The excited states of Ar–HCl might have a different angular shape at shorter R' distances. However, due to the direct dissociation character

of the mechanism of Ar–Cl formation, the hydrogen recoils retaining the same orientation as initially. Therefore, the structure of the distributions of Fig. 5 reflects also the initial structure in j space (and the corresponding angular structure), of the Ar–HCl state prepared upstairs at short R' distances. The same is true for the v distributions of Fig. 4, which would reflect the initial shape of the excited Ar–HCl wave function in the r' mode.

The similarity of the v distributions would indicate that roughly the same initial configurations of Ar–HCl are excited in the r' coordinate for different energies E . The different shape of the j distributions would be associated with different initial angular geometries of the parent cluster, populated at different excitation energies. These angular geometries would be the main responsibility of the different shapes of the (v, j) distributions in which the radicals are produced by changing the excitation energy. The calculated coefficients $c_{v,j}(E)$ allow one to build the state of Ar–HCl excited at a given energy E in the region of the products H+Ar–Cl,

$$\Psi_E(R', r', \theta') = \sum_{v,j} c_{v,j}(E) \xi_{\epsilon_k, v, j}^{(E)}(R', r', \theta'),$$

and then to identify the parent cluster configurations which are excited at different energies in the r' and θ' modes. Work on this line is currently in progress.

Before concluding, it is interesting to compare two types of experiments leading to formation of Rg–X open-shell complexes: The electron photodetachment of Rg–X[−] anions,¹⁸ and the UV photodissociation of Rg–HX clusters.^{19,33} Both experiments present two basic similarities. First, the radical is formed after removal of the light particle of the parent complex (the electron in one case and the H atom in the other case). Second, this light particle can be used as a probe of the internal energy distribution of the radical prepared, by measuring its velocity distribution (by ZEKE spectroscopy in one experiment, and by HRTOF spectroscopy in the other experiment). Two major aspects differentiate the two types of experiments as well. On the one side, the competition of two fragmentation pathways, the TF and the PF one, implies a globally lower yield of radical production in the UV photodissociation experiment than in the electron photodetachment one. On the other side, the hydrogen mass, although small, is larger than the electron mass, and enough to affect the photodissociation dynamics in terms of energy transferred to the Rg–X radical fragment. Related to this mass effect is the critical influence found in this work for Ar–HCl, of the parent cluster geometries populated initially at different excitation energies. Such an influence manifests itself both in the relative intensity of the two competing fragmentation pathways, and in the shape of the final rovibrational distributions of the radical. This effect could be exploited in order to control the efficiency of radical production and the internal excitation of the radical, which would allow to probe different regions of the Rg–X interaction.

IV. SUMMARY AND CONCLUSIONS

The ultraviolet photodissociation of the Ar–HCl cluster is simulated by exact 3D wave packet calculations. The photodissociation process takes place via two competing fragmentation pathways: Total fragmentation into H+Ar+Cl, and partial fragmentation into H and Ar–Cl radicals. The two fragmentation pathways follow different dissociation mechanisms. Total fragmentation follows either an indirect dissociation mechanism where the hydrogen may collide more than once with Ar and Cl, or a nearly direct dissociation mechanism in which the recoiling hydrogen interacts rather weakly with Ar. This latter mechanism is the most likely one. The partial fragmentation pathway occurs via direct recoiling of the H fragment, without interaction with the Ar atom. The asymptotic wave packet has been projected out onto the states of the H+Ar–Cl products, for several excitation energies in the range of the Ar–HCl absorption spectrum. The global probability of the partial fragmentation pathway is found to be about 1% of the photolysis process, the remaining 99% corresponding to total fragmentation of the cluster.

The probability of Ar–Cl formation relative to the total probability of photodissociation does not distribute uniformly along the range of excitation energies, and three main energy regions can be distinguished. At very low energies the Ar–Cl formation dominates the photodissociation process, although its intensity rapidly decreases with the excitation energy. This behavior is in agreement with recent experimental findings on UV photodissociation of Ar_n–H₂S ($n \leq 2$) clusters. In a large region of medium energies the relative intensity of partial fragmentation becomes stable and very small (about 1% of the process). At very high energies the generation of Ar–Cl radicals reaches again high efficiencies, although total fragmentation is still dominant. The relative intensity of the two fragmentation pathways can be understood in terms of the Ar–HCl geometries populated initially at the different excitation energies. Initial geometries of Ar–HCl where the hydrogen is blocked by Ar and Cl would lead to total fragmentation, while partial fragmentation would be determined by those configurations from which the hydrogen is free to recoil.

The internal energy distributions in which the Ar–Cl complex is produced show a high rotational and a low vibrational excitation at most of the total energies of Ar–HCl. The high rotational excitation is a result of the torque produced by the recoiling hydrogen on the Ar–Cl fragment. The shape of these ro-vibrational distributions is found to change substantially for excitation in different regions of the Ar–HCl absorption spectrum. Again the initial geometries of Ar–HCl excited upstairs (and particularly the hydrogen orientation), along with the energy available for the Ar–Cl fragment, play a major role in determining the specific shape of the ro-vibrational distributions. The combined effect of these two factors could be used to control the efficiency of radical production and its internal excitation, by changing the UV excitation wavelength.

It should be very interesting to investigate whether photodissociation mechanisms similar to those of Ar–HCl also operate in other clusters of the Rg–HX family.

Experiments³³ and calculations^{33,34} on UV photodissociation of Ar–HBr point in that direction. The results of the present work indicate that the yield of Rg–X radical formation strongly depends on the floppiness of the hydrogen bond in the ground-electronic state. Increasing this floppiness would imply increasing the efficiency of radical generation. In this sense, UV photodissociation of RgHX clusters with a collinear equilibrium configuration of the type Rg···X–H in the ground state is expected to produce Rg–X complexes more efficiently. The system Ar···I–H seems to be one of such clusters.^{19,35,36} In Rg–HX clusters where the hydrogen is in between the heavier atoms in the equilibrium configuration, infrared excitation of vibrational overtones of the HX chromophore prior to the UV excitation could increase the floppiness of the hydrogen bond.^{21,37} The amount of energy available for the Rg–X fragment is an additional factor to control and increase the yield of radical formation. This energy can be reduced by increasing the mass of the Rg–X fragment.

Finally, the preparation of open-shell complexes is not restricted to UV photodissociation of Rg–HX clusters, as shown by the experiments on (HI)₂,²⁰ (HCl)₂,²¹ and Ar_n–H₂S ($n \leq 2$).²³ We believe that for these and other hydrogen-bonded clusters (e.g., Rg_n–HX, CO₂–HX, C₂H₂–HX) the photodissociation mechanisms could be similar to those described here. We therefore envision a wide applicability of the UV photolysis of hydrogen-bonded clusters as a technique to generate and probe radical complexes.

ACKNOWLEDGMENTS

This work was supported by D.G.I.C.Y.T., Spain, Grant No. PB95-0071, and by the European network TMR, Grant No. FMRX-CT96-0088.

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