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J. C. Juanes-Marcos and A. Garca-Vela

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Photodissociation of Ar–HCl: An energy-resolved study of the dynamics of total fragmentation into H+Ar+Cl

J. C. Juanes-Marcos and A. García-Vela

Instituto de Matemáticas y Física Fundamental, C.S.I.C., Serrano 123, 28006 Madrid, Spain

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UV photolysis of Ar–HCl is simulated by means of an exact wave packet treatment in three dimensions. The focus of the work is on the mechanism of indirect dissociation of the hydrogen atom, which leads to total fragmentation of Ar–HCl into H, Ar, and Cl. The results predict for this photodissociation path a probability of about 13% of the photolysis process. The remaining probability would be associated with direct photodissociation of the H fragment. Kinetic-energy distributions of the hydrogen fragments produced by indirect photodissociation are calculated for different excitation energies of Ar–HCl. The distributions reflect a pronounced structure of peaks associated with broad and overlapping resonances of the system. The resonance structure is present in the whole energy range covered by the absorption spectrum. Hydrogen atoms initially populating the resonances can dissociate from the cluster extensively cooled down, after several collisions with Ar and Cl. A mechanism is suggested for the fragmentation process due to indirect photodissociation, which involves successive jumps of the hydrogen to lower-energy resonances, induced by the collisions. A classical collisional model is proposed to rationalize qualitatively the fragmentation dynamics. © 1999 American Institute of Physics. [S0021-9606(99)01730-4]

I. INTRODUCTION

The ultraviolet photodissociation of diatomic molecules like hydrogen halides embedded in rare gas clusters has been a subject of increasing interest in the last few years. Such an interest is motivated by the possibility of investigating in these systems typical effects of condensed matter environments like the cage effect. This effect causes the fragmentation of the diatomic chromophore to be sterically hindered by the surrounding solvent. The cage effect manifests itself in a delay in the separation of the initially hot photofragments, which cool down via collision-induced energy transfer to the solvent.

Most of the theoretical^{1–18} and experimental^{8,19} research effort on this line has been addressed to the smallest size of this type of clusters, Rg–HX (Rg=rare gas, X=halogen). Some simulations were carried out for larger systems like Xe_n–HI ($n=1–12$),¹ Ar_n–HF ($n=1–14,54$),¹² and Ar_n–HCl ($n=1,2,12,54$).^{9,14,18} Two attractive aspects of the Rg–HX clusters have contributed to focus the attention on them. One aspect is the relative simplicity in the treatment and interpretation of the photodissociation dynamics, due to the small number of degrees of freedom involved. The other aspect is the possibility of observing a caging effect produced by the smallest solvent size possible, the so-called one-atom cage effect. Among the Rg–HX clusters, Ar–HCl has been the system most extensively studied from the theoretical point of view,^{2–7,9–11,13–16} due to the availability of potential surfaces both for the ground and for the excited electronic state.

Photolysis of Ar–HCl was initially investigated with approximate methods like classical trajectories,^{2,3,9} and hybrid quantum/classical⁴ and quantum/semiclassical^{5–7} approaches of reduced dimensionality, in the framework of the time-

dependent self-consistent-field (TDSCF) scheme.^{20,21} The main finding was that the hydrogen photofragment is temporarily trapped in resonances between the Ar and Cl atoms, colliding with them before dissociating. This hydrogen trapping or cage effect manifested itself in a tail at low energies in the final kinetic-energy distribution (KED) of the H fragment calculated classically^{2,3,9} for given total energies of the cluster. Manifestations of the hydrogen resonances also appeared in the approximate wave packet calculations,^{4–7} in the form of a pronounced structure of peaks in the hydrogen KED. Further exact quantum calculations in 3D have shown that the photodissociation of Ar–HCl^{11,13,15} and Ar–HBr¹⁷ is predominantly a direct process. This means that the intensity of the hydrogen trapping in resonances was overestimated in the previous approximate simulations. The use of an approximate initial state (which determines the population of the resonances), along with the decoupling of modes assumed in the TDSCF scheme,²² originated the enhancement of the resonance effect in the earlier calculations.^{2–6}

At present, photodissociation of Rg–HX clusters is better understood, and a general picture begins to emerge. The intensity of the hydrogen trapping mechanism strongly depends on the amplitude of the van der Waals (vdW) motions in the ground-electronic state.^{3,15,16,22} The smaller this amplitude, the more intense the trapping of the hydrogen in between the heavier atoms. The weak hydrogen bond present in Ar–HCl and Ar–HBr (and in general in Rg–HX clusters) is associated with rather large-amplitude vdW motions. As a consequence, direct dissociation of the hydrogen becomes the dominant photodissociation mechanism. A most interesting result is that Ar–Cl^{15,23} and Ar–Br¹⁷ radicals can be formed with high probability as products of the direct photodissociation of the parent cluster. Indirect experimental

evidence¹⁹ of formation of Ar–I complexes has been found in the photodissociation of Ar–HI. More recently, production of Ar–SH and Ar₂–SH radicals has been directly observed with high efficiency after ultraviolet photolysis of Ar_n–H₂S ($n \leq 2$) clusters.²⁴

Nesbitt and co-workers have proposed a “gentle recoil” mechanism²⁴ to explain the high production of open-shell complexes by photodissociation of the Ar_n–H₂S ($n \leq 2$) clusters. Such a mechanism would also be valid in the photodissociation of Ar–HCl and other related Rg–HX clusters. The gentle recoil 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 (the corresponding recoil energy) to be accommodated in the radical formed. Usually, at most of the excitation energies accessible in the absorption spectrum of the parent cluster, the recoil energy of the nascent radical is larger than the energy required to break its weak vdW bond. Even in those cases, however, the radical can survive if most of the recoil energy remains as translational energy of the radical center of mass, and only a relatively small amount (not enough to fragment the radical) is converted into internal excitation. The extensive vibro-rotational excitation observed in the Ar_n–SH ($n \leq 2$) radicals,²⁴ and predicted for the Ar–Cl radicals^{15,23} seems to indicate that the direct photodissociation process follows a similar mechanism in the clusters Ar_n–H₂S ($n \leq 2$) and Ar–HCl (and probably other Rg–HX systems). Thus direct dissociation of the H atom would lead both to total and partial fragmentation of the cluster, which in the case of Ar–HCl would yield H+Ar+Cl, and H+Ar–Cl products, respectively.

In the above picture the mechanism of hydrogen trapping in resonances is present, albeit with a much smaller intensity than the direct dissociation one. In this case photodissociation of a Rg–HX cluster leads only to total fragmentation, due to the large amount of energy transferred by the hydrogen to the heavier atoms. However, total fragmentation of the cluster occurs through different mechanisms depending on whether the cluster photodissociation is direct or indirect. Several questions still remain open about the fragmentation mechanism in the latter case. Among them is the mechanism intense enough in Rg–HX clusters as to be detected experimentally, and if so, can the excited-state resonance structure be observed? Is there any dependence of the mechanism on the initial excitation energy of the cluster? The aim of this article is to throw light on some of these questions, by analyzing the resonance-mediated hydrogen dissociation in the photolysis of Ar–HCl. To this purpose, the photodissociation process is simulated by means of a 3D wave packet calculation. From the asymptotic wave packet, the energy-resolved hydrogen KED is extracted for different initial excitation energies of the cluster. Such a distribution is the equivalent one in the energy domain to the H fragment time-of-flight (TOF) spectrum measured in an energy-resolved experiment.^{8,19}

The paper is organized as follows. In Sec. II the theoretical treatment employed is described. The results are presented and discussed in Sec. III. Some conclusions are drawn in Sec. IV.

II. THEORETICAL TREATMENT

The Ar–HCl cluster photodissociates upon optical excitation of the HCl molecule from its ground-electronic state $^1\Sigma^+$ to the repulsive excited state $^1\Pi$ [which correlates with the $H(^2S) + Cl(^2P_{3/2})$ asymptote]. As in previous calculations, we shall assume here that the system is excited through an ultrafast Franck–Condon transition, and the photodissociation dynamics occurs only on the $^1\Pi$ electronic surface. The potential-energy surfaces of the two electronic states have been described elsewhere.¹³ The initial state of Ar–HCl corresponds with the vibro-electronic ground state of the cluster, and it is described in previous works.^{13,15}

In the Franck–Condon region the HCl electronic excitation is predominantly a perpendicular transition $A\ ^1\Pi \leftarrow X\ ^1\Sigma^+$, although the $a\ ^3\Pi$ state [correlating with the $H(^2S) + Cl(^2P_{1/2})$ asymptote] is also populated to some extent. During photolysis, spin-orbit and rotational couplings redistribute the initial photodissociation flux into other electronic states which asymptotically correlate with the excited-state fragment $Cl(^2P_{1/2})$. Although there is still a controversy, the branching ratio $[Cl(^2P_{1/2})]/[Cl(^2P_{3/2})]$ appears to be rather high, not far from unity for some excitation wavelengths.^{25–29} An exact description of the Ar–HCl photodissociation dynamics including several nonadiabatically coupled electronic states becomes prohibitively expensive. However, some of the effects of including several electronic states on the calculated product distributions can be qualitatively predicted. At a given excitation energy of the cluster, the available kinetic energy for fragment recoil is different for the two spin-orbit states of the Cl atom [smaller in the case of $Cl(^2P_{1/2})$]. Based on the gentle recoil mechanism,²⁴ the probability of formation of Ar–Cl radicals may significantly change if the two possibilities of radical products, Ar– $Cl(^2P_{3/2})$ and Ar– $Cl(^2P_{1/2})$ (with different binding energies) are considered in the calculation, instead of only the Ar– $Cl(^2P_{3/2})$ one. In addition, interference between resonances associated with different excited electronic states may also change the hydrogen fragment distribution with respect to that calculated for a single electronic surface. Our purpose for the time being is to understand the photodissociation dynamics on a single excited surface.

The system 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 associated with r and R . Zero-total angular momentum of the cluster is assumed. The total wave function of the system is conveniently defined as

$$\Psi(r, R, \theta) = \Phi(r, R, \theta)/rR, \quad (1)$$

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

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

μ_r and μ_R being the reduced masses corresponding to the r and R modes, respectively. The excited-state photodissocia-

tion dynamics is simulated by solving the time-dependent Schrödinger equation for the $\Phi(r, R, \theta)$ wave packet

$$i\hbar \frac{\partial \Phi(r, R, \theta, t)}{\partial t} = \hat{H} \Phi(r, R, \theta, t), \quad (3)$$

up to $t = 80$ fs. The numerical details of the wave packet propagation have been given elsewhere.¹⁵

It has been shown in earlier works^{11,13,15,17} on photodissociation of Ar–HCl and Ar–HBr that the corresponding absorption spectrum presents a structureless profile. Both the direct and the indirect mechanisms of hydrogen dissociation contribute to the absorption spectrum profile. However, the much larger intensity of the direct dissociation masks any possible structure due to hydrogen trapping in resonances.¹⁵ It was suggested^{5,6} that the kinetic-energy distributions of the photofragments (and in particular the hydrogen one) could be more sensitive magnitudes than the absorption spectrum in order to manifest such a structure. Thus the hydrogen KED associated with the whole wave packet became a central quantity in the exact quantum calculations on Ar–HCl^{11,15} and Ar–HBr¹⁷ photodissociation. This distribution is not energy-resolved, and spreads over the same energy range as the absorption spectrum. The corresponding experimental distribution would imply an ultrashort, essentially δ -pulse excitation in time. For Ar–HBr no structure at all is found in the light fragment KED. In the two calculations^{11,15} on Ar–HCl, slightly different potential surfaces were used both for the ground and for the excited state. The calculated hydrogen KED showed no structure in one case,¹¹ and a very diffuse, rather weak structure at low energies in the other case.¹⁵

From the above results one could apparently conclude that the resonance structure is so weak that it is devoid of experimental interest. However, one may also question whether the hydrogen KED associated with the whole energy range is a proper magnitude to observe the structure resulting from a mechanism with a relatively small intensity. In fact, the broad H fragment KED presents the same two disadvantages as the absorption spectrum (although to a lesser extent): (a) It is dominated by the direct dissociation mechanism; (b) Since it contains a vast range of energies (about 6 eV), interference between different energy components may diminish or wash out any possible structure. It then appears interesting to investigate the behavior of the hydrogen KED associated with specific total energies of the cluster projected out from the asymptotic wave packet. This hydrogen distribution would correspond with a monochromatic (CW or long-pulse) excitation of the system.^{8,19}

As was said in Sec. I, photolysis, of Ar–HCl may occur either via partial fragmentation (PF) into H+Ar–Cl (due to direct H dissociation), or total fragmentation (TF) into H+Ar+Cl (due both to direct and indirect hydrogen photodissociation). In principle one can find a coordinate representation $\{\mathbf{q}\}$ in which the information of each fragmentation path can be rigorously separated, and the asymptotic wave packet can be expressed as the sum of two pieces,

$$\Phi(\mathbf{q}, t = \infty) = \Phi^{\text{PF}}(\mathbf{q}, t = \infty) + \Phi^{\text{TF}}(\mathbf{q}, t = \infty), \quad (4)$$

such that Φ^{PF} and Φ^{TF} are orthogonal to one another, $\langle \Phi^{\text{PF}}(\mathbf{q}, t = \infty) | \Phi^{\text{TF}}(\mathbf{q}, t = \infty) \rangle = 0$. In the $\{\mathbf{q}\}$ representation it is possible to establish two sets, orthogonal to each other, of well-defined asymptotic states, each set describing the products of each fragmentation path. Then Φ^{PF} and Φ^{TF} can be expanded in the corresponding set of asymptotic states, and the square modulus of the expansion coefficients is an observable quantity. In this case the information relative to one specific fragmentation path can be projected out from the whole wave packet $\Phi(\mathbf{q}, t = \infty)$, since it is ensured that the components of the other path do not interfere with.

Unfortunately, the Jacobian coordinates used in the present calculations do not correspond with the above $\{\mathbf{q}\}$ representation, and the separation of $\Phi(r, R, \theta, t = \infty)$ into two pieces, $\Phi^{\text{PF}}(r, R, \theta, t = \infty)$ and $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$, is only approximate. Indeed, while the asymptotic states describing the products H+Ar+Cl are precisely defined in the (r, R, θ) coordinates, the final vibro-rotational states of the Ar–Cl(v, j) fragment are not. Actually, the $\{\mathbf{q}\}$ representation discussed above would correspond in our case with the Jacobian coordinates (r', R', θ') in which r' represents the Ar–Cl distance. These coordinates require, however, a much larger three-dimensional grid than the (r, R, θ) representation, in order to reach the same final propagation time, which implies prohibitive computer time and memory requirements. An alternative way is to propagate the wave packet in the (r, R, θ) representation, and then transform it to the (r', R', θ') coordinates where the projection would be carried out. We are currently pursuing this line.

It follows from the above discussion that the information about the TF path cannot be projected out by evaluating the overlapping quadrature of the whole wave packet $\Phi(r, R, \theta, t = \infty)$ with the corresponding asymptotic states. By doing so, the calculated coefficients would contain spurious intensity coming from wave packet components of the PF path, which are nonorthogonal to the TF asymptotic states in the (r, R, θ) coordinates. Therefore, in order to minimize this spurious intensity, it is necessary to separate, as precisely as possible (albeit approximately), the part of the wave packet describing the TF path, $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$, from which the information of interest is to be projected out. In the following discussion we shall assume that $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ has been separated, and the procedure we adopted to carry out the separation will be described in next section.

Now, $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ can be expressed as

$$\begin{aligned} \Phi^{\text{TF}}(r, R, \theta, t = \infty) = & \int d\epsilon_{k_r} \int d\epsilon_{k_R} \sum_j c_j(\epsilon_{k_r}, \epsilon_{k_R}) \\ & \times \left(\frac{\mu_r}{2\pi k_r \hbar^2} \right)^{1/2} \left(\frac{\mu_R}{2\pi k_R \hbar^2} \right)^{1/2} \\ & \times e^{ik_r r} e^{ik_R R} P_j(\cos \theta) e^{-iEt/\hbar}, \end{aligned} \quad (5)$$

where $P_j(\cos \theta)$ is a normalized Legendre polynomial, ϵ_{k_r} and ϵ_{k_R} are the relative kinetic energies of the fragments in the modes r and R , respectively, which implies that $k_r = (2\mu_r \epsilon_{k_r})^{1/2}/\hbar$ and $k_R = (2\mu_R \epsilon_{k_R})^{1/2}/\hbar$, and E is the total

energy of the system. The two variables ϵ_{k_r} and ϵ_{k_R} of Eq. (5) are actually related by the total energy conservation in the asymptotic limit,

$$E = \epsilon_{k_r} + \epsilon_{k_R}. \quad (6)$$

Equation (6) makes possible to rewrite the wave packet expansion of Eq. (5) in terms of E and ϵ_{k_r} as

$$\begin{aligned} \Phi^{\text{TF}}(r, R, \theta, t = \infty) = \int dE \int d\epsilon_{k_r} \sum_j c_j(\epsilon_{k_r}, E) \\ \times \chi_{\epsilon_{k_r}, j}^{(E)}(r, R, \theta, t = \infty), \end{aligned} \quad (7)$$

being

$$\begin{aligned} \chi_{\epsilon_{k_r}, j}^{(E)}(r, R, \theta, t) = \left(\frac{\mu_r}{2\pi k_r \hbar^2} \right)^{1/2} \left(\frac{\mu_R}{2\pi k_R \hbar^2} \right)^{1/2} \\ \times e^{ik_r r} e^{ik_R R} P_j(\cos \theta) e^{-iEt/\hbar}, \end{aligned}$$

or equivalently, in terms of E and ϵ_{k_R} by substituting in Eq. (7) $\int d\epsilon_{k_r}$, $\chi_{\epsilon_{k_r}, j}^{(E)}(r, R, \theta, t)$, and $c_j(\epsilon_{k_r}, E)$ by $\int d\epsilon_{k_R}$, $\chi_{\epsilon_{k_R}, j}^{(E)}(r, R, \theta, t)$, and $c_j(\epsilon_{k_R}, E)$, respectively.

It should be noted that Eq. (6) is strictly correct only in the asymptotic limit $r \rightarrow \infty$ and $R \rightarrow \infty$, where the rotational-energy terms $(1/2\mu_r r^2 + 1/2\mu_R R^2)\hbar^2 j(j+1)$ of the Hamiltonian do vanish. Reaching this limit is actually very hard in a 3D wave packet simulation of a double continuum process like that studied here. It would imply propagating the wave packet for a longer time and using a much larger grid, which would make the present problem intractable. Therefore we are conscious that our results contain some error derived from the noncompletely vanishing rotational terms, although we believe this error is reasonably small.

The coefficients $c_j(\epsilon_{k_r}, E)$ of the expansion Eq. (7) are obtained by projecting the wave packet over the asymptotic states describing three separated fragments,

$$c_j(\epsilon_{k_r}, E) = \langle \chi_{\epsilon_{k_r}, j}^{(E)}(r, R, \theta, t = \infty) | \Phi^{\text{TF}}(r, R, \theta, t = \infty) \rangle. \quad (8)$$

The square modulus of the coefficients is the final distribution of states associated with total fragmentation of the cluster. In this work we are not interested in resolving the j states, so summation over all these states leads to the energy-resolved probability distribution

$$P(\epsilon_{k_r}, E) = \sum_j |c_j(\epsilon_{k_r}, E)|^2. \quad (9)$$

The kinetic energy of the hydrogen fragment in the r and R coordinates can be written as

$$\epsilon_k^{\text{H}} = \frac{m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} \epsilon_{k_r} + \left(\frac{m_{\text{H}}}{m_{\text{H}} + m_{\text{Cl}}} \right) \left(\frac{m_{\text{Ar}}}{m_{\text{H}} + m_{\text{Cl}} + m_{\text{Ar}}} \right) \epsilon_{k_R}, \quad (10)$$

and this expression allows one to change from the variables ϵ_{k_r} and E to ϵ_k^{H} and E , and to obtain the H fragment KED, $P(\epsilon_k^{\text{H}}, E)$ for a given total energy E of the system. The $P(\epsilon_k^{\text{H}}, E)$ distribution would correspond with the hydrogen

TOF spectrum measured with a detector scanning all possible final scattering angles of the fragment, after a monochromatic excitation of the Ar–HCl cluster.

Integration of $P(\epsilon_{k_r}, E)$ over ϵ_{k_r} (or equivalently of $P(\epsilon_k^{\text{H}}, E)$ over ϵ_k^{H}) gives the probability distribution as a function of the total energy,

$$P(E) = \int d\epsilon_{k_r} P(\epsilon_{k_r}, E). \quad (11)$$

Further integration of $P(E)$ over E provides the total probability of the cluster fragmentation path $\text{Ar–HCl} + h\nu \rightarrow \text{H} + \text{Ar} + \text{Cl}$, in the whole range of energies accessible by a Franck–Condon transition.

III. RESULTS AND DISCUSSION

A. Asymptotic wave packet

Once the initial wave packet is prepared in the excited state, it is propagated up to a final time $t = 80$ fs, which will be considered the asymptotic regime in this study. It will be helpful and illustrating for the discussion of the results to show a global picture of the shape of the asymptotic wave packet, both in coordinate and in momentum (or kinetic-energy) space. To this purpose, Fig. 1 displays the probability densities of the final wave packet in the r and R coordinates, and Fig. 2 shows the corresponding distributions¹⁵ of ϵ_{k_r} and ϵ_{k_R} . The $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ distributions are calculated as

$$\begin{aligned} P(\epsilon_{k_r}) = \int_0^\pi d\theta \sin \theta \int_{R_{\text{in}}}^{R_{\text{fin}}} dR \\ \times \left| \int_{r_{\text{in}}}^{r_{\text{fin}}} dr (2\pi\hbar)^{-1/2} e^{-ik_r r} \Phi(r, R, \theta, t = \infty) \right|^2, \quad (12) \\ P(\epsilon_{k_R}) = \int_0^\pi d\theta \sin \theta \int_{r_{\text{in}}}^{r_{\text{fin}}} dr \\ \times \left| \int_{R_{\text{in}}}^{R_{\text{fin}}} dR (2\pi\hbar)^{-1/2} e^{-ik_R R} \Phi(r, R, \theta, t = \infty) \right|^2, \end{aligned} \quad (13)$$

where r_{in} , R_{in} , r_{fin} , and R_{fin} define the radial edges of our grid.

We note that the distributions of Eqs. (12) and (13) are normalized in the momentum domain, but not in the kinetic-energy domain, which is the one shown in Fig. 2. The kinetic-energy scale is used because it is more intuitive and convenient than the momentum one. Normalization of $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ in the energy domain is achieved by multiplying them by the factors $\mu_r/\hbar k_r$ and $\mu_R/\hbar k_R$, respectively. The above factors have not been included in $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ to avoid singularities derived from the fact that the distributions have nonzero intensity in the regions around $k_r = 0$ and $k_R = 0$. Actually, at $t = 80$ fs about 5% of the wave packet still remains in the interaction region, which causes the tail at low energies of $P(\epsilon_{k_r})$ not to decay completely to zero.

FIG. 1. Probability density distributions of the asymptotic wave packet in the radial coordinates r (a) and R (b).

B. Partition of the asymptotic wave packet

As discussed in Sec. II, the $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ wave packet must be defined prior to the projection of the $P(\epsilon_k^H, E)$ distributions. An approximate definition of $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ consists of

$$\begin{cases} \Phi^{\text{TF}}(r, R, \theta, t = \infty) = \Phi(r, R, \theta, t = \infty) & \text{if } r \geq r^*, R \geq R^* \\ \Phi^{\text{TF}}(r, R, \theta, t = \infty) = 0 & \text{otherwise} \end{cases}, \quad (14)$$

where r^* and R^* are distances sufficiently large as to consider that the system is dissociated into three fragments. The problem now becomes to reliably establish the limits r^* and R^* . The value r^* can be decided without much difficulty from inspection of the wave packet in the r coordinate [Fig. 1(a)]. The minimum condition to be fulfilled in this case is to exclude the 5% of the wave packet which is still not asymptotic. Establishing the R^* limit by simple inspection of

FIG. 2. Kinetic-energy distributions of the asymptotic wave packet as a function of the kinetic energies ϵ_{k_r} (a) and ϵ_{k_R} (b).

the wave packet is more problematic, since the distribution of Fig. 1(b) does not reveal any clear separation between the two fragmentation paths. However, there exists an additional criterion based on the physics of the photodissociation process, which can help to define R^* more precisely. This criterion consists of analyzing the asymptotic wave packet in the domain of the kinetic energy ϵ_{k_R} [Fig. 2(b)], in addition to the R coordinate. The fragmentation path we are studying implies the breaking of the Ar–Cl bond, which means that at least a certain amount of energy is transferred to this mode (approximately represented by the Jacobian R mode). On the one hand, the dissociation energy of Ar–Cl is about 100 cm^{-1} . On the other hand, Ar–Cl can be produced not only in bound vibro-rotational states (v, j) (below the dissociation limit), but also in quasibound states, the highest of which is about 100 cm^{-1} above the Ar–Cl dissociation limit.^{22,23} Hence, those wave packet components with $\epsilon_{k_R} > 200 \text{ cm}^{-1}$ can be unambiguously assigned to the TF path. Now, for a

FIG. 3. Kinetic-energy distributions of the wave packet $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ defined by Eq. (14) vs ϵ_{k_R} , for different limits r^* and R^* . (a) In all cases $r^* = r_{\text{in}} = 1.3$ a.u., and $R^* = R_{\text{in}} = 6.0$ a.u. (solid line), $R^* = 10.6$ a.u. (large-dashed line), $R^* = 10.4$ a.u. (short-dashed line), and $R^* = 10.1$ a.u. (dotted line); (b) $R^* = R_{\text{in}}$ and $r^* = r_{\text{in}}$ (solid line). For all the remaining cases $R^* = 10.4$ a.u., and $r^* = r_{\text{in}}$ (large-dashed line), $r^* = 11.6$ a.u. (dashed line), and $r^* = 19.9$ a.u. (dotted line). See the text for details.

previously fixed value of r^* , one can change the R^* limit (from larger to shorter distances), and calculate the corresponding $P^*(\epsilon_{k_R})$ distributions. In the following, by $P^*(\epsilon_{k_R})$ we shall denote distributions calculated with $r^* > r_{\text{in}}$ and/or $R^* > R_{\text{in}}$. When the nonzero intensity of $P^*(\epsilon_{k_R})$ with $R > R^*$ approaches the above limit of ϵ_{k_R} , a value of R^* can be established for which $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ of Eq. (14) contains only components of the TF path. We believe that this procedure, although approximate, is more precise than just choosing an arbitrary R^* distance.

The upper panel of Fig. 3 illustrates the above procedure to define R^* . The four $P(\epsilon_{k_R})$ distributions shown have been calculated for $r^* = r_{\text{in}} = 1.3$ a.u., i.e., including the whole wave packet in the r coordinate. We shall see below that inclusion of the nonasymptotic wave packet components does not affect the definition of R^* . The solid curve is the total $P(\epsilon_{k_R})$ distribution [same as that of Fig. 2(b)], corre-

sponding with $R^* = R_{\text{in}} = 6.0$ a.u. The other distributions are calculated for three different distances R^* , $R^* = 10.6$ a.u., $R^* = 10.4$ a.u., and $R^* = 10.1$ a.u. The four distributions are identical for $\epsilon_{k_R} > 1$ eV, meaning that these energy components are contained in the three R^* limits. Differences appear in the range $\epsilon_{k_R} < 1$ eV, where the $P^*(\epsilon_{k_R})$ distributions develop more intensity as R^* decreases. The three distributions with $R^* \geq 10.1$ a.u. are completely contained in the range $\epsilon_{k_R} > 200$ cm $^{-1}$, so the value $R^* = 10.1$ a.u. could be accepted as a lower limit of R^* .

Interestingly enough, it is observed in the figure that, as R^* decreases, the intensity of $P^*(\epsilon_{k_R})$ at some energies is larger than that of the total $P(\epsilon_{k_R})$ distribution. This is a spurious intensity due to partial inclusion of PF components in $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ by decreasing R^* . Indeed, the highly excited (v, j) states of Ar-Cl have a largely extending tail in R . When R^* diminishes part of this tail contributes to the calculated $P^*(\epsilon_{k_R})$ distributions, causing their intensity to be artificially higher at some energies than that of the total distribution. When the entire R range of the asymptotic wave packet is included in the calculation of $P(\epsilon_{k_R})$, interference lowers the intensity up to the actual value of the solid curve distribution. The appearance of the spurious intensity reflects that we enter the R region where the spatial overlap between the PF and the TF components begins to be appreciable, although the overlap in the energy domain is zero. Unfortunately it is difficult to control the amount of spurious intensity introduced when the R^* limit is smaller than 10.4 a.u. We therefore adopted a conservative criterion, and chose the limit $R^* = 10.4$ a.u. to define the wave packet $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ of Eq. (14). With this R^* limit the defined wave packet is essentially free of contributions from components of the PF path (even with the limit $R^* = 10.1$ a.u. these contributions are very small). We note that this choice of R^* implies that the TF components associated with low ϵ_{k_R} energies are not included in $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$. Actually, these TF components correspond with total fragmentation of the cluster due to direct dissociation of the H fragment. Therefore our present (approximate) definition of $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ contains only TF components resulting from the indirect photodissociation mechanism, the one on which we are interested in this work. Correspondingly, only this type of total fragmentation of Ar-HCl will be analyzed in the remaining of the paper.

Once R^* has been fixed, we turn now to define the other limit, r^* . In the lower panel of Fig. 3 a similar analysis to that of the upper panel is presented. Again the solid curve corresponds with the total $P(\epsilon_{k_R})$ distribution (the same as that of the upper panel). The remaining three distributions $P^*(\epsilon_{k_R})$ have been calculated for the previously chosen limit $R^* = 10.4$ a.u. in all cases, and different values of r^* , $r^* = r_{\text{in}}$, $r^* = 11.6$ a.u., and $r^* = 19.9$ a.u. The distribution corresponding with $r^* = r_{\text{in}}$, $R^* = 10.4$ a.u. has been already shown in the upper panel, and is repeated here along with the total distribution for the sake of comparison.

The behavior of the $P^*(\epsilon_{k_R})$ distributions when r^* increases is just the opposite to that found for decreasing R^* .

The three distributions coincide in the region $\epsilon_{k_R} \leq 0.9$ eV, and differ at higher energies. It is interesting to note that including a larger amount of wave packet $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ in the r coordinate (i.e., decreasing r^*) has the effect of increasing the intensity of the $P^*(\epsilon_{k_R})$ distribution at high ϵ_{k_R} energies. In the limit $r^* = r_{\text{in}}$ the intensity of $P^*(\epsilon_{k_R})$ at high energies coincides with that of the total distribution. It means that the wave packet components associated with small r distances, namely, those components which still remain in the interaction region, contribute to the TF path due to indirect photodissociation. This result was expected since the nonasymptotic components are associated with longer-lived resonances in which the hydrogen suffers several collisions with the heavy atoms. The collisions cause the delay of these components in leaving the interaction region, and the energy transferred to the R mode is reflected in the intensity of $P(\epsilon_{k_R})$ at high energies. As stated above, including or not the nonasymptotic components does not affect the definition of R^* in our procedure, since it depends only on the behavior of the $P^*(\epsilon_{k_R})$ distributions at low energies.

The two limits $r^* = 11.6$ a.u. and $r^* = 19.9$ a.u. exclude the nonasymptotic components. The limit $r^* = 19.9$ a.u. leads to a somewhat more asymptotic wave packet $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$, while with the other limit a larger amount of TF components is included in $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$. We therefore decided to carry out calculations using both r^* limits, along with $R^* = 10.4$ a.u.

By establishing the r^* and R^* limits the wave packet $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ is defined by Eq. (14). Integration of the square modulus of this wave packet in coordinate space [or equivalently, of the corresponding distribution $P^*(\epsilon_{k_R})$ in the ϵ_{k_R} domain] gives the total probability of Ar–HCl fragmentation into H+Ar+Cl due to indirect photodissociation. The calculated probabilities are 4.9% and 8.1% for the two limits $r^* = 19.9$ a.u. and $r^* = 11.6$ a.u., respectively (and $R^* = 10.4$ a.u.). This probability increases up to 12.5% when r^* is extended to $r^* = r_{\text{in}}$, and the nonasymptotic components are included (or even 13.4% is obtained with the limits $r^* = r_{\text{in}}$, $R^* = 10.1$ a.u.). Our present results therefore predict a probability of about 13% for the indirect photodissociation mechanism. Such a probability, although smaller than that of the direct photodissociation mechanism ($\approx 87\%$), is far from being negligible. This result encourages to perform a more detailed analysis of how this probability distributes and behaves for different initial excitation energies of the Ar–HCl cluster, which is aimed in the remaining of this section.

C. Nonresolved kinetic-energy distributions

The distribution $P(\epsilon_{k_r})$ of Fig. 2(a) has been the central quantity in earlier exact calculations^{11,15,17} on the photodissociation of Ar–HX clusters. So far, this distribution has been calculated for the entire wave packet $\Phi(r, R, \theta, t = \infty)$, as in Eq. (12). It now appears interesting to investigate the behavior of the $P(\epsilon_{k_r})$ distribution associated with the $\Phi^{\text{TF}}(r, R, \theta, t = \infty)$ wave packet,

FIG. 4. Kinetic-energy distributions of the asymptotic wave packet vs ϵ_{k_r} , for different limits r^* and R^* . In both panels $R^* = R_{\text{in}}$ for the solid line and $R^* = 10.4$ a.u. for the dashed line. In panel (a) $r^* = 19.9$ a.u. and in (b) $r^* = 11.6$ a.u.

$$P(\epsilon_{k_r}) = \int_0^\pi d\theta \sin \theta \int_{R^*}^{R_{\text{fin}}} dR \times \left| \int_{r^*}^{r_{\text{fin}}} dr \left(\frac{\mu_r}{2\pi k_r \hbar^2} \right)^{1/2} e^{-ik_r r} \Phi^{\text{TF}}(r, R, \theta, t = \infty) \right|^2, \quad (15)$$

or equivalently,

$$P(\epsilon_{k_r}) = \int P(\epsilon_{k_r}, E) dE. \quad (16)$$

The dashed curves of Fig. 4(a) and (b) display the $P(\epsilon_{k_r})$ distributions corresponding with $r^* = 19.9$ a.u. and $r^* = 11.6$ a.u., respectively (in both cases $R^* = 10.4$ a.u.). For comparison the $P(\epsilon_{k_r})$ distributions corresponding with the same r^* limits, but with $R^* = R_{\text{in}}$ are shown (solid curves). These latter distributions also include all the intensity associated with the direct photodissociation mechanism, and will be referred to as “total distributions” in the following. Note that the distributions of Fig. 4 are correctly normalized in the

ϵ_{k_r} domain, since the factor $(\mu_r/k_r\hbar)^{1/2}$ which normalize the plane wave in the energy domain, has been included in Eqs. (15) and (16). As a consequence, the scale of $P(\epsilon_{k_r})$ in Figs. 2(a) and 4) is different.

The most striking feature of the TF distributions of Fig. 4 is that their intensity is mainly concentrated at low kinetic energies, while the total distributions extend over the whole energy range. In Fig. 4(b), the tail at low energies ($\epsilon_{k_r} < 1.5$ eV) of the total distribution belongs entirely to the TF distribution. A diffuse (albeit clear enough) structure is found in the TF distributions. This structure appears also in the energy region of the total $P(\epsilon_{k_r})$ where it is dominated by the TF components [$\epsilon_{k_r} < 1.8$ eV in Figs. 4(b) and 2(a)]. As expected, the structure at higher energies is completely masked in the total distribution by the much higher (and structureless) intensity due to the direct photodissociation mechanism.

The fact that the intensity of the TF distribution appears at relatively low energies can be explained as follows. For a given excitation energy E of Ar-HCl, most of the energy is initially deposited in the r mode (the H-Cl bond), in the form of potential energy. As the hydrogen gets away from the chlorine atom, the potential energy becomes kinetic-energy ϵ_{k_r} which, due to the small H/Cl mass ratio, corresponds mainly to the H fragment. Collisions of the hydrogen with the heavy atoms break the cluster into three fragments, and part of the initial ϵ_{k_r} energy is transferred to the R mode, becoming ϵ_{k_r} kinetic energy. It is clear, therefore, that the final ϵ_{k_r} energy must be lower than the initial one. The amount of energy transferred will depend on the number of collisions and on the way the collisions occur (i.e., whether the collisions are frontal, which maximizes the energy transfer, or not). From the absorption spectrum (see Fig. 5), the maximum ϵ_{k_r} energy initially populated is about 5.5 eV (assuming that initially $\epsilon_{k_r} \simeq E$), while the tail of the final ϵ_{k_r} of the TF distributions dies about 4.0 eV. There is a difference of at least 1.5 eV, which in principle can be considered large taking into account the small H/Cl and H/Ar mass ratios. There are two possible scenarios consistent with the TF distributions of Fig. 4: Little energy transfer due to few and/or nonfrontal collisions, or extensive energy transfer caused by several and/or frontal collisions. The first possibility would imply that the resonance spectrum does not extend beyond $\simeq 4.0$ eV, which would explain the absence of intensity in the TF distributions at high energies. As will be seen below, this is not the case, and the spectrum of resonances extends all over the energy range of the absorption spectrum. Therefore, a fragmentation path involving several collisions (probably frontal or nearly frontal ones) appears to explain the shifting of the TF distributions to lower kinetic energies. This explanation is also consistent with the extensive energy transfer to the R mode shown by the $P(\epsilon_{k_r})$ distribution of Fig. 2(b).

It is expected that high-energy resonances will be shorter-lived than the low-energy ones. Thus the low-energy resonances will be associated with the wave packet components which take longer to reach the asymptotic region. This is consistent with the fact that the intensity of the TF distribution

FIG. 5. (a) Probability distributions vs the total energy of the cluster for different r^* and R^* limits. The solid line corresponds with the total probability distribution. For the other curves $R^* = 10.4$ a.u. in all cases, and $r^* = 11.6$ a.u. (dashed line), and $r^* = 19.9$ a.u. (dotted line). The energy $E = 0$ corresponds to three separated atoms. (b) Ratio between the $P(E)$ distributions for the above r^* limits and the total $P(E)$ distribution: $r^* = 11.6$ a.u. (solid line), and $r^* = 19.9$ a.u. (dashed line).

bution increases at low energies when the r^* limit decreases from 19.9 a.u. to 11.6 a.u. [Fig. 4(b)]. It indicates that the additional components which are incorporated in the TF distribution when r^* diminishes are associated with low-energy resonances.

The distributions of Fig. 4(a) show an interesting result. The total $P(\epsilon_{k_r})$ distribution is structureless and does not manifest any tail at low energies. This distribution is similar to that found by Schröder *et al.*¹¹ using slightly different ground- and excited-state potential surfaces for Ar-HCl. A similar distribution was also obtained for Ar-HBr photolysis.¹⁷ From the absence of structure and tail at low energies in $P(\epsilon_{k_r})$, the authors of those works concluded that the photodissociation process was entirely dominated by the

fast direct dissociation of the light atom. Figure 4(a) shows, however, that the total distribution contains an appreciable amount of intensity [4.9% of the total process and 5.3% of the total $P(\epsilon_{k_r})$ distribution of Fig. 4(a)] associated with fragmentation of the cluster via resonances. The implication is that when two photodissociation mechanisms contribute to the total $P(\epsilon_{k_r})$ distribution, and one of them is highly dominant, this distribution becomes little representative of the less intense mechanism. We are actually in the same situation as with the absorption spectrum, whose profile is quite similar to that of the total distribution of Fig. 4(a). Therefore, in order to extract the information relative to the less intense mechanism, or even to discard that it occurs, one should look at magnitudes more resolved and sensitive to that mechanism.

D. Total-energy distributions

In the following we shall analyze the behavior of the probability distribution as a function of the total energy E of the Ar–HCl cluster. From the experimental viewpoint, this distribution is more interesting than those of Fig. 4, since the total energy to which the cluster is initially excited is directly related with the excitation wavelength λ used in the experiment. In Fig. 5(a) three distributions $P(E)$ are displayed. The solid curve is the total probability of cluster fragmentation, due to both direct and indirect photodissociation. It has been calculated as

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

This distribution is normalized in the energy domain. Note that by multiplying this $P(E)$ by the energy $\epsilon(\lambda)$ of the photon used to excite the system, the absorption spectrum is obtained (within a constant factor). The other two distributions of Fig. 5(a) are calculated through

$$P(E) = \int d\epsilon_{k_r} P(\epsilon_{k_r}, E),$$

for the r^* limits $r^*=11.6$ a.u. and $r^*=19.9$ a.u. (and $R^*=10.4$ a.u. in all cases).

The two total fragmentation distributions extend over essentially the same energy range as the total distribution $P(E)$. This result indicates that total fragmentation of the cluster occurs in the whole energy range covered by the absorption spectrum, which implies that the resonance spectrum also distributes along all the energy range, as stated above. The trend found by decreasing the r^* limit is basically an increasing of the intensity of the $P(E)$ distributions at lower total energies. This behavior is similar to that found for the $P^*(\epsilon_{k_r})$ distributions of Fig. 4. While the $P(E)$ distribution for $r^*=19.9$ a.u. contains mainly components associated with medium- and high-energy resonances, when r^* decreases lower-energy resonances are included in $P(E)$.

The quantity $P^{\text{TF}}(E)/P^{\text{total}}(E)$ provides information on how the percentage of fragmentation due to indirect photo-

dissociation in the total process behaves with the excitation energy of the cluster. In addition, the probability distribution of the partial fragmentation path and its percentage can be simply obtained as $P^{\text{PF}}(E) = P^{\text{total}}(E) - P^{\text{TF}}(E)$, and $P^{\text{PF}}(E)/P^{\text{total}}(E) = 1 - P^{\text{TF}}(E)/P^{\text{total}}(E)$, respectively. Figure 5(b) shows the curves $P^{\text{TF}}(E)/P^{\text{total}}(E)$ corresponding to the two TF distributions of Fig. 5(a). A nonconstant behavior with E is found in all cases, indicating that there are energy regions where the indirect photodissociation mechanism is more intense. Not surprisingly, these regions correspond with the resonances which contribute more to the indirect photodissociation mechanism in each case. The faster the wave packet dissociates, the higher the energy position of the resonances contributing to the total fragmentation of the cluster.

E. Energy-resolved kinetic-energy distributions of the hydrogen fragment

All the quantities discussed so far provide valuable information about the cluster fragmentation resulting from indirect photodissociation, but what is actually measured in an energy-resolved experiment is the TOF spectrum of the H fragment.^{8,9} The theoretical distribution corresponding with this observable is $P(\epsilon_k^{\text{H}}, E)$. Figure 6 shows the $P(\epsilon_k^{\text{H}}, E)$ distributions associated with six different total energies, along the range covered by the Ar–HCl absorption spectrum. For each energy E two distributions have been calculated, one with $r^*=19.9$ a.u. (solid curves), the other with $r^*=11.6$ a.u. (dashed curves). Before analyzing the distributions, a technical point should be commented. It is found that all the distributions show very low intensity in the region of high ϵ_k^{H} (or ϵ_{k_r}) energies, which corresponds with the region of low ϵ_{k_R} values. The absence of intensity in this energy region is due to the exclusion of the TF components corresponding to the direct photodissociation mechanism in our definition of $\Phi^{\text{TF}}(r, R, \theta, t=\infty)$. Our present calculation cannot explore that region of the $P(\epsilon_k^{\text{H}}, E)$ distributions.

The basic difference between the distributions calculated with $r^*=11.6$ a.u., and those obtained with $r^*=19.9$ a.u., is that the first ones develop more intensity at lower kinetic energies, as expected. The two distributions nearly coincide in the region of high ϵ_k^{H} energies. It is also found that the additional intensity of the distribution with $r^*=11.6$ a.u. decreases as the total energy increases. This behavior is consistent with the result previously found that as E increases the high-energy resonances dominate the cluster fragmentation due to indirect photodissociation.

The main feature manifested by all the distributions is a pronounced structure of peaks. Such a structure is associated with the resonances in which the hydrogen is temporarily trapped, before it dissociates. The structure of resonances manifests all along the energy range populated in the absorption spectrum, confirming the previous finding of Fig. 5. However, when the $P(\epsilon_k^{\text{H}}, E)$ distributions [or the corresponding $P(\epsilon_{k_r}, E)$ ones] are integrated over the total energy E , most of the resonance structure whases out, and only the diffuse, very weak structure of the $P(\epsilon_{k_r})$ distributions of Fig. 4 (dashed lines) remains. Extensive overlapping be-

FIG. 6. Kinetic-energy distributions of the hydrogen fragment for initial excitation to six different total energies of Ar-HCl. For each energy the solid line corresponds to the limit $r^* = 19.9$ a.u., while for the dashed line $r^* = 11.6$ a.u. (in both cases $R^* = 10.4$ a.u.).

tween the peaks of each $P(\epsilon_k^H, E)$ distribution indicates that the structure of the resonance spectrum is characterized by overlapping between adjacent resonance states. The resonance overlapping manifests all along the range of total energies considered. Such an overlapping nature of the Ar-HCl excited-state resonances was also found in calculations of the resonance states using a time-independent complex coordinate method.¹⁶ The overlapping structure of peaks makes difficult to assign each peak to a single resonance. In fact, some peaks may be associated with single resonances, while other peaks may correspond to more than one resonance, more strongly overlapping. A trend is found that the width of the peaks increases as the peak energy increases. This trend is more clearly appreciated in the width of the more intense

(and better resolved) peaks appearing at higher kinetic energies in each distribution, for increasing total energies. This behavior reveals a spectrum of resonances which get broader and shorter lived as their energy position is higher.

The $P(\epsilon_k^H, E)$ distributions reflect an extensive energy transfer between the hydrogen and the heavy atoms. The light fragment is effectively cooled down, up to reaching very low or even nearly zero kinetic energies, which implies larger amounts of energy transferred as the total energy excited increases. In a regime of overlapping resonances, excitation of a specific energy of the cluster can populate more than one resonance. If the hydrogen dissociates after a single collision with the Ar atom, the corresponding $P(\epsilon_k^H, E)$ distribution would be expected to show the same number of

(overlapping) peaks as resonances initially populated. Such a distribution would be rather localized in a relatively reduced range of high kinetic energies. Therefore, the large spreading of the distributions of Fig. 6 seems to be the consequence of several collisions between H and the heavy atoms.

The above result can be interpreted in terms of the overlapping structure of the resonance spectrum. The resonances are coupled, on the one side, to the total fragmentation continuum and, on the other side, to the nearby resonances with which they overlap. Each coupling causes different fragmentation dynamics. More specifically, the following total fragmentation mechanism would be consistent with the distributions of Fig. 6. Initial excitation to an energy E prepares the system in one or more resonance states. The mechanism of resonance decay will depend on the shape of the resonance wave function, and in particular, on the angular dependence. Those hydrogen atoms described by the resonance wave function components associated with larger angles are likely to dissociate after a single collision with the Ar atom. Such a collision would not be frontal, involving less energy transfer as the collision angle is larger. In this case the resonance decay is governed by the resonance-continuum coupling. This coupling is the largest and most effective one, since it involves overlapping of the whole resonance width with the continuum, and leads to a rather fast fragmentation of the cluster (after a single collision). In addition to the overlapping with the continuum, part of the initial resonance wave function overlaps with the adjacent lower-energy resonance state. This part is probably associated with the components at smaller angles. The light atoms populating these components suffer a frontal or nearly frontal collision with the Ar atom, which involves more extensive energy transfer. As a result of this collision, the hydrogen jumps to the resonance state immediately below the initial one, through the resonance-resonance coupling between the overlapping resonances. The resonance-resonance coupling is expected to be less effective than the resonance-continuum one, as long as the first type of coupling involves only partial overlapping between resonances. Once the hydrogen is in the lower resonance, it undergoes similar collisional events as those described above, now with the Cl atom. Again part of the hydrogen population in this resonance will dissociate after the collision with chlorine, while the remaining population will jump once more to the next lower-energy resonance. Further collisions with Ar and Cl will cause subsequent jumps to lower resonances, until all the system population initially excited is fragmented. The successive jumps in cascade keep the hydrogen fragment trapped in the interaction region, causing a delay in the dissociation (up to 80 fs).

The spreading of the $P(\epsilon_k^H, E)$ distributions toward low kinetic energies will depend in the above picture on the amount of cluster population initially prepared in resonance states. In the case of the $P(\epsilon_k^H, E)$ distributions calculated with $r^* = 19.9$ a.u., about 4.9% of the total system population is excited to resonances. These distributions show that even for this small population, the hydrogen visits several of the resonances below those initially prepared, being extensively cooled down. This effect is more pronounced as E increases, since the initial population of the resonances is

larger at higher total energies [see the dotted line of Fig. 5(a), and the dashed line of Fig. 5(b)]. By increasing the initial resonance population from 4.9% to 8.1% [which is the case of the $P(\epsilon_k^H, E)$ distributions with $r^* = 11.6$ a.u.], the hydrogen is able to reach the lowest-lying resonance states. Hydrogen fragments emerging from the lowest resonances are almost completely cooled down.

F. Classical collisional model

The above description of the resonance decay mechanism is based on two-body elastic collisions (either frontal or side ones), between H and Ar, and H and Cl. Therefore, a classical collisional model involving two particles could reproduce qualitatively the total fragmentation dynamics. Let us consider two particles with masses m_1 and m_2 , which move with initial momenta P_{1I} and P_{2I} , being $P_{1I} \gg P_{2I}$. In our case $m_1 = m_H$ and $m_2 = m_{Ar}, m_{Cl}$, so $m_1 < m_2$. The ratio between the final and the initial momentum of the incident particle m_1 can be derived from energy and momentum conservation, taking the form

$$\frac{P_{1F}}{P_{1I}} = \frac{m_1}{m_1 + m_2} \cos \theta_1 \left(1 + \frac{P_{2I}}{P_{1I}} \right) + \left[\left(\frac{m_1}{m_1 + m_2} \right)^2 \cos^2 \theta_1 \left(1 + \frac{P_{2I}}{P_{1I}} \right)^2 + \frac{m_2 - m_1}{m_1 + m_2} - \frac{2m_1}{m_1 + m_2} \frac{P_{2I}}{P_{1I}} \right]^{1/2}, \quad (17)$$

where θ_1 is the angle of the scattered particle m_1 , referred to the axis joining the two particles (for backward scattering after a frontal collision of m_1 with m_2 , $\theta_1 = \pi$). The particular case of $P_{2I} = 0$ is a typical textbook example,³⁰ and leads to a simpler expression of P_{1F}/P_{1I} . For a frontal collision $\theta_1 = \pi$, and Eq. (17) becomes

$$\frac{P_{1F}}{P_{1I}} = \frac{-m_1}{m_1 + m_2} \left(1 + \frac{P_{2I}}{P_{1I}} \right) + \left[\left(\frac{m_2}{m_1 + m_2} \right)^2 + \left(\frac{m_1}{m_1 + m_2} \right)^2 \frac{P_{2I}^2}{P_{1I}^2} - \frac{2m_1 m_2}{(m_1 + m_2)^2} \frac{P_{2I}}{P_{1I}} \right]^{1/2}. \quad (18)$$

For the first collision of hydrogen with the Ar atom, it can be considered, to a good approximation, that $P_{2I} \approx 0$, and then Eq. (18) reduces to

$$\frac{P_{1F}}{P_{1I}} = \frac{m_2 - m_1}{m_1 + m_2}. \quad (19)$$

After this collision both Ar and Cl have initial momentum $P_{2I} \neq 0$, and the more general Eq. (18) is to be employed. From the ratio between the final and the initial momenta of the incident particle, the corresponding ratio between kinetic energies is easily obtained

$$\frac{\epsilon_{1F}}{\epsilon_{1I}} = \frac{P_{1F}^2}{P_{1I}^2}. \quad (20)$$

Now a model can be designed to reproduce the kinetic energy of the hydrogen atom after a number n of frontal collisions with Ar and Cl. For excitation to an energy E we can

assume that initially $\epsilon_{k_r} \approx E$ and $\epsilon_{k_R} \approx 0$, such that the initial energy of H before the first collision with Ar is the recoil energy

$$\epsilon_0^H = \epsilon_{1I} = \frac{m_{Cl}}{m_H + m_{Cl}} \epsilon_{k_r}, \quad (21a)$$

and

$$\epsilon_0^{Ar} = \epsilon_{2I} = 0, \quad \epsilon_0^{Cl} = \frac{m_H}{m_H + m_{Cl}} \epsilon_{k_r}. \quad (21b)$$

Since in this case $\epsilon_{2I} = 0$ ($P_{2I} = 0$) Eqs. (19) and (20) can be applied, and the kinetic energy of hydrogen after colliding with Ar is given by

$$\epsilon_1^H = \epsilon_{1F} = \epsilon_0^H \left(\frac{m_{Ar} - m_H}{m_H + m_{Ar}} \right)^2, \quad (22a)$$

while the kinetic energy of Ar becomes

$$\epsilon_1^{Ar} = \epsilon_0^{Ar} + \epsilon_0^H - \epsilon_1^H. \quad (22b)$$

The following collision of H is with Cl, but now $\epsilon_0^{Cl} \neq 0 \Rightarrow P_{2I} \neq 0$, so Eqs. (18) and (20) are applied with $m_1 = m_H$, $m_2 = m_{Cl}$, and

$$P_{1I} = P_H = (2m_H \epsilon_1^H)^{1/2}, \quad P_{2I} = P_{Cl} = (2m_{Cl} \epsilon_0^{Cl})^{1/2}.$$

The kinetic energy of H after the collision with Cl is now

$$\epsilon_2^H = \epsilon_1^H A(m_1, m_2, P_{1I}, P_{2I}),$$

where $A(m_1, m_2, P_{1I}, P_{2I})$ is the square of the right-hand side of Eq. (18), and

$$\epsilon_1^{Cl} = \epsilon_0^{Cl} + \epsilon_1^H - \epsilon_2^H.$$

The third collision of hydrogen is with Ar, and again Eqs. (18) and (20) are applied with $m_1 = m_H$, $m_2 = m_{Ar}$, and

$$P_{1I} = P_H = (2m_H \epsilon_2^H)^{1/2}, \quad P_{2I} = P_{Ar} = (2m_{Ar} \epsilon_1^{Ar})^{1/2}.$$

After this collision

$$\epsilon_3^H = \epsilon_2^H A(m_1, m_2, P_{1I}, P_{2I}), \quad \text{and} \quad \epsilon_2^{Ar} = \epsilon_1^{Ar} + \epsilon_2^H - \epsilon_3^H.$$

The model can be generalized for the n th ($n > 1$) hydrogen collision as

$$\epsilon_n^H = \epsilon_{n-1}^H A(m_1, m_2, P_{1I}, P_{2I}), \quad (23a)$$

where if n is odd

$$m_1 = m_H, \quad m_2 = m_{Ar}, \quad P_{1I} = (2m_H \epsilon_{n-1}^H)^{1/2}, \quad (23b)$$

$$P_{2I} = (2m_{Ar} \epsilon_{(n-1)/2}^{Ar})^{1/2}, \quad (23b)$$

$$\epsilon_{(n+1)/2}^{Ar} = \epsilon_{(n-1)/2}^{Ar} + \epsilon_{n-1}^H - \epsilon_n^H, \quad (23c)$$

and if n is even

$$m_1 = m_H, \quad m_2 = m_{Cl}, \quad P_{1I} = (2m_H \epsilon_{n-1}^H)^{1/2}, \quad (23d)$$

$$P_{2I} = (2m_{Cl} \epsilon_{n-2/2}^{Cl})^{1/2}, \quad (23d)$$

$$\epsilon_{n/2}^{Cl} = \epsilon_{(n-2)/2}^{Cl} + \epsilon_{n-1}^H - \epsilon_n^H. \quad (23e)$$

For $n = 1$ Eqs. (21) and (22) are applied. In Eqs. (22) and (23) it was assumed that the collisions are strictly frontal ($\theta_1 = \pi$), but similar equations can be derived for side collisions where $\theta_1 \neq \pi$. From the final kinetic energy of the

hydrogen fragment, the above model allows one to estimate the number of collisions occurred between the light and the heavy atoms.

The TOF spectrum of the hydrogen atom has been experimentally measured⁸ after photodissociation of Ar-HBr, a system qualitatively similar to Ar-HCl. An excitation wavelength $\lambda = 193$ nm was used in the experiment. In the experimental arrangement the detector of hydrogen fragments was fixed at a position such that only strongly scattered fragments with $\theta_1 \approx 90^\circ$ could be detected. Data corresponding to unpolarized, horizontally polarized, and vertically polarized photolysis radiation were reported in Ref. 8. In the following we shall focus on the vertical polarization data (see Fig. 4 of Ref. 8), since with this photolysis beam polarization the cluster signal is enhanced with respect to the unclustered HBr signal. The right entry of Fig. 4 of Ref. 8 shows a hydrogen signal with two narrow peaks corresponding to photodissociation of essentially unclustered HBr. The peak at higher energy corresponds with HBr dissociation into $H(^2S) + Br(^2P_{3/2})$, and the other peak is associated with $H(^2S) + Br(^2P_{1/2})$ fragments. The left entry of Fig. 4 shows two additional peaks superimposed with the narrow ones, which correspond to hydrogen signal originated from photodissociation of cluster species.

Let us focus on the broad peak of Fig. 4 around $\approx 21\,000$ cm^{-1} . For 193 nm HBr photolysis into $H(^2S) + Br(^2P_{3/2})$, the kinetic energy initially available for hydrogen is $\epsilon_0^H \approx 21\,600$ cm^{-1} . Applying our collisional model to a first collision of H with Ar, for a scattering angle $\theta_1 = 90^\circ$, the hydrogen signal would be detected at

$$\epsilon_1^H = \epsilon_0^H \left(\frac{m_{Ar} - m_H}{m_H + m_{Ar}} \right) = 20\,523 \text{ cm}^{-1}.$$

If this first collision is a frontal one instead of a side one, the energy ϵ_1^H would be given by Eq. (22a),

$$\epsilon_1^H = \epsilon_0^H \left(\frac{m_{Ar} - m_H}{m_H + m_{Ar}} \right)^2 = 19\,498 \text{ cm}^{-1}.$$

In this case the hydrogen would jump to a resonance below the initial one, and would not reach the detector. A second collision of hydrogen (now with the Br atom) with a scattering angle $\theta_1 = 90^\circ$ would produce signal at an energy

$$\epsilon_2^H = \epsilon_1^H \left[\frac{m_{Br} - m_H}{m_H + m_{Br}} - \frac{2m_H}{m_H + m_{Br}} \frac{P_{BrI}}{P_{HI}} \right] = 18\,590 \text{ cm}^{-1}.$$

The experimental peak of Fig. 4 shows signal intensity at the two energies, 20 523 cm^{-1} and 18 590 cm^{-1} . For the total energy of Ar-HBr reached by excitation at 193 nm it is unlikely that the hydrogen can transfer an amount of energy of $21\,600 \text{ cm}^{-1} - 18\,590 \text{ cm}^{-1} = 3010 \text{ cm}^{-1}$ in a single side collision with Ar. However, the results of our simple model assuming two hydrogen collisions (a frontal collision with Ar, and a side collision with Br) would be consistent with the experimental data of Ref. 8. A similar result is obtained for the broad peak corresponding to the $Br(^2P_{1/2})$ state. We stress that the occurrence of the hydrogen collision with Br would involve a previous jump of the hydrogen to a resonance energetically lower than that populated initially. As

explained by the authors,⁸ the experiment is not completely size selected, and $\text{Ar}_n\text{-HBr}$ clusters with $n > 1$ may contribute to some extent to the signal of Fig. 4. In this sense, spectroscopic selection^{8,31} of the cluster size would rule out any spurious contribution of clusters larger than Ar-HBr to the hydrogen TOF spectrum. Such an experiment would be very interesting in order to confirm the present findings.

At this point a comment on the intensity of the indirect photodissociation mechanism should be made. Our present calculation predicts a probability of about 13% for such a mechanism. Of course this probability will depend on the potential surfaces used in the simulation, and previous calculations by Schröder *et al.*¹¹ employing slightly different potentials predicted a lower probability for the indirect mechanism. The same type of approximations (e.g., pairwise additivity) is assumed in the surfaces used by Schröder *et al.* and in the present work. In the absence of experimental data for Ar-HCl photodissociation it is hard to establish which potential surfaces are better. For this reason we cannot rule out the possibility that our results could be somewhat overestimated. The ultimate purpose of this work is to get a deeper insight on how the resonance-mediated fragmentation takes place in a heavy-light-heavy (HLH) system involving a hydrogen bond, like Ar-HCl . The present potential surfaces allow one to analyze the indirect photodissociation mechanism for different regimes of initial resonance population, e.g., $\approx 5\%$ and $\approx 8\%$. Analysis of the results for both regimes leads to the same qualitative conclusions on the fragmentation mechanism, regardless the intensity of the resonance population. What is dependent on the resonance population is the possibility of observing experimentally the signature of the indirect TF path. In this sense, we note that the $P(\epsilon_k)$ distribution recently calculated for Ar-HBr photodissociation¹⁷ is very similar to the total distribution $P(\epsilon_k)$ of Fig. 4(a), which contains $\approx 5\%$ of total intensity of the TF path via indirect photodissociation. The experimental data of Ref. 8 seem to indicate that such a small intensity could be enough to observe the signature of this mechanism. In addition, one can possibly find other HLH systems with stronger hydrogen bonds than Rg-HX clusters, in which the effect of the indirect photodissociation would be more intense. The mechanism of fragmentation in those systems is expected to be qualitatively similar to that found in Ar-HCl .

IV. CONCLUSIONS

The UV Ar-HCl photodissociation dynamics was simulated by an exact wave packet calculation in three dimensions, assuming zero-total angular momentum. The mechanism of total fragmentation of the cluster into $\text{H} + \text{Ar} + \text{Cl}$ via indirect photodissociation is analyzed by projecting the corresponding components out of the asymptotic wave packet. The results predict a probability of total fragmentation of $\approx 13\%$. The remaining probability of the photolysis process ($\approx 87\%$) would be associated with a direct photodissociation mechanism, producing total fragmentation as well as partial fragmentation into H and Ar-Cl radical complexes.

Distributions associated with the whole asymptotic wave packet have been calculated versus the kinetic energy of the

H-Cl stretch mode, and versus the total energy of the cluster. The distributions are found to be essentially structureless, dominated by the more intense direct photodissociation mechanism of the cluster. These plain total distributions suggest in principle that indirect photodissociation plays a rather negligible role in the photolysis process. However, when the components of the indirect photodissociation mechanism are projected out, energy distributions corresponding to this mechanism are obtained, which are little intense but far from being negligible. In the case of the kinetic-energy distribution even a diffuse structure appears. The intensity of the indirect photodissociation mechanism is masked by the larger intensity of the direct dissociation one in the total distributions dominated by the latter mechanism. Therefore, projecting out the information about the less intense mechanism is required in order to establish its actual intensity.

Kinetic-energy distributions of the hydrogen fragment have been calculated for several total energies of the excited cluster in the energy range of the absorption spectrum. Such distributions correspond with the hydrogen time-of-flight spectrum measured in an energy-resolved (CW) experiment. The distributions show a pronounced structure of broad peaks, associated with resonances in which the hydrogen collides with Ar and Cl . The hydrogen distributions reflect a structure of broad and overlapping resonances extending all over the energy range of the absorption spectrum. An extensive cooling of the hydrogen fragment is observed in the distributions, caused by several collisions with the heavy atoms. A fragmentation mechanism consistent with the results is suggested, which would involve successive jumps in cascade of the hydrogen from the resonance (or resonances) initially populated to lower resonances. The jumps would be induced by the successive collisions of hydrogen with Ar and Cl . This mechanism would also explain the delay of some hydrogen fragments in dissociating from the cluster, a manifestation of the cage effect. A classical collisional model involving two-body collisions is proposed in order to reproduce qualitatively the light fragment kinetic-energy distribution. The model is applied to the available experimental data on Ar-HBr photolysis. The results of the classical model show that two hydrogen collisions, with Ar and Br , are consistent with the experimental hydrogen kinetic-energy distribution. The second hydrogen collision would imply a previous jump of the light atom to a lower resonance, supporting the suggested fragmentation mechanism.

Finally, from the present results one can draw the following global picture of photodissociation of a heavy-light-heavy system involving a hydrogen bond, like $\text{Ar} \cdots \text{HCl}$. Excitation of the H-Cl chromophore to a repulsive electronic state deposits initially a large amount of energy in the H-Cl bond. Because of the H/Cl mass ratio, most of this energy corresponds to the H atom. The hydrogen thus becomes an energy carrier which efficiently redistributes the energy among its heavy partners Ar and Cl , leading to total fragmentation of the complex. Hydrogen bonds are present in a large variety of systems (small and large ones), and in particular in large biological systems like proteins and enzymes. A specific hydrogen bond in these systems (there can be one or more hydrogen bonds) can be represented as $\text{A} \cdots \text{H-B-D}$

where A and D denote subsystems composed of several atoms chemically bonded, and $B=C,N,P,O,S,X$ ($X=\text{halogen}$). The difference between the above system and $\text{Ar}\cdots\text{H}-\text{Cl}$ is that the subsystems A and B-D could also be chemically bonded to one another. It appears interesting to ask whether selective excitation of the H-B bond to a repulsive electronic state is possible. If so, and enough energy is deposited in the H-B bond, the hydrogen could fragment the $\text{A}\cdots\text{H}-\text{B}-\text{D}$ system. Site-selective fragmentation of the system could be achieved at the locations of the hydrogen bonds. Further selectivity between different hydrogen bonds of the system would be possible if the H-B bonds (i.e., the B atoms) involved are different.

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