**Selective control of the photolysis reaction in the
Ar-HX (X=F,Cl,Br) clusters through the initial
distribution of intracluster orientations**

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Abstract

The bound state spectrum of the Ar-HX (X=F,Cl,Br) van der Waals (vdW) clusters is investigated. The yield and final state distribution of the ultraviolet photolysis reaction in these clusters is largely affected by the shape of the intracluster orientation distribution initially prepared. Thus, the change of this shape with excitation of the different cluster modes is analyzed. Angular distributions associated either with the Ar-H-X or the Ar-X-H isomer geometries, and with shapes in between these two limiting cases, are found. We conclude that a wide range of cluster angular geometry distributions can be initially prepared, allowing a high degree of selective control on the Ar-HX photolysis reaction products.

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1. Introduction

Weakly bound vdW complexes Rg–HX (Rg=rare gas atom, X=halogen atom) have been the subject of a great deal of experimental [1-8] and theoretical [1,2,7-16] research in the last years. Such systems are prototypes to investigate anisotropic intermolecular forces, large amplitude vibrational motions, and intramolecular energy redistribution processes. Among the Rg–HX complexes, the Ar–HX family has been extensively studied. The infrared spectra of Ar–HF [1-3], Ar–HCl [4-6], Ar–HBr [7], and Ar–HI [8] have been measured. Intermolecular potential surfaces have been obtained both from the spectroscopic data and from *ab initio* calculations for the ground electronic state of Ar–HF [1,2,14,15], Ar–HCl [11,12], Ar–HBr [7,13], and Ar–HI [8].

An interesting feature of the intermolecular potentials of the Ar–HX complexes (and in general of the Rg–HX systems), is that they present two potential minima associated with the Ar–H–X and Ar–X–H linear geometries. There are rovibrational vdW states of the Ar–HX complex which are localized mainly in one or the other potential well, and therefore associated to one of the above two isomeric species. States corresponding to different isomers imply different distributions of intracluster orientations, and thus the possibility to prepare different initial conditions of the cluster for photoinduced reactions. Selecting the initial distribution of reagent orientations within the cluster allows one to control the yield and final state distribution of the reaction products [17-19].

Among the photoinitiated reactions in Ar–HX clusters is the photolysis of the system, which occurs upon ultraviolet (UV) excitation of the HX chromophore from the ground electronic state $X^1\Sigma^+$ to the repulsive electronic state $A^1\Pi$. A hot H fragment is ejected in the photolysis, which can follow two fragmentation pathways, into H + Ar–X products or into H + Ar + X products. This photolysis reaction has been recently investigated for Ar–HBr($v = 1$) by means of quasiclassical trajectory simulations [20]. Photolysis was started from two different initial vdW states of the cluster in the ground electronic state, each of them associated either with the

Ar–H–Br or the Ar–Br–H isomer. The probability of Ar–Br radical products was found to be substantially higher for the initial vdW state corresponding to the Ar–Br–H isomer. In this case the initial distribution of intracuster orientations allows the H fragment to recoil freely, avoiding the collision with the Ar obstacle, which enhances the yield of radical products. The fragment state distributions obtained from the two cluster initial states were also different. These results were further confirmed by wave packet simulations of the Ar–HBr($v = 1$) photolysis [21].

The effect of the initial distribution of intracuster orientations found in the Ar–HBr($v = 1$) photolysis is expected to be present as well in the UV photolysis of other complexes of the Ar–HX family. It bears on the importance of having a detailed knowledge of the spectrum of bound states of these clusters, and more specifically of their shape, which determines the distribution of intracuster geometries that can be prepared before UV excitation of the system. Such a knowledge would provide the possibility to exert a higher degree of control on the photolysis products, by selecting an initial cluster state with the desired geometry distribution.

In the present Letter we analyze the bound state spectrum of the Ar–HX (X=F,Cl,Br) clusters. The purpose is to elucidate how the shape of the distribution of cluster geometries associated to different bound states, changes with excitation of both the vdW modes and the HX vibration, in order to achieve a degree of control as selective as possible. The methodology used to obtain the spectra of bound states of the Ar–HX clusters is described in Section 2, and the results are presented and discussed in Section 3. Conclusions are given in Section 4.

2. Methodology

The ground electronic state potential surfaces of the Ar–HX complexes were represented as a sum of an intermolecular potential describing the vdW interaction, plus a potential term describing the HX chemical interaction. The H6(4,3,2) intermolecular potential of Hutson [14] was used for Ar–HF, for the $v = 0, 1$, and 2 vibrational states of HF. The analytically similar H6(4,3,0) intermolecular potential

[12] was employed for Ar–HCl in the HCl($v = 0, 1$) states. In the case of Ar–HBr, the intermolecular potentials of Hutson [13] and Han *et al.* [7] were used for the HBr($v = 0$) and HBr($v = 1$) states, respectively. The HF potential was represented by a Morse functional form with parameters $D = 6.11$ eV, $r_e = 0.919$ Å, and $\alpha = 2.25$ Å⁻¹. These parameters were obtained by fitting to a Morse function the *ab initio* potential for Na–HF [22] when Na and HF are sufficiently separated. Morse potentials were also used for the HCl and HBr interactions, with parameters $D = 4.617$ eV, $r_e = 1.275$ Å, and $\alpha = 1.868$ Å⁻¹ for HCl, and $D = 3.92$ eV, $r_e = 1.414$ Å, and $\alpha = 1.821$ Å⁻¹ for HBr [23].

The Ar–HX clusters are represented in the Jacobian coordinates (r, R, θ) , where r is the H–X distance, R is the separation from the Ar atom to the center-of-mass of HX, and θ is the angle between the vectors $\mathbf{r}$ and $\mathbf{R}$. In the definition adopted here $\theta = 0$ corresponds to the collinear configuration Ar–H–X. Zero total angular momentum is assumed for the Ar–HX complexes. At this stage we are mainly interested in elucidating how excitation of the vdW and HX vibrational modes affects the shape of the cluster wave function, without considering excitation of the cluster overall rotation.

In order to obtain the bound states of Ar–HX(v), the HX stretching vibration is separated within the vibrational diabatic approximation [24], in which the cluster wave function is expressed as the product

$$\Phi_{v,n,b}(r, R, \theta) = \chi_v(r)\psi_{n,b}^{(v)}(R, \theta), \quad (1)$$

where $\chi_v(r)$ is a vibrational eigenstate of the HX diatomic molecule, and n, b are the quantum numbers associated with the vdW stretching and bending vibrations, respectively. The vdW wave function $\psi_{n,b}^{(v)}(R, \theta)$ is calculated variationally by diagonalizing the vibrationally averaged Hamiltonian $\hat{H}_{v,v} = \langle \chi_v(r) | \hat{H} | \chi_v(r) \rangle$ ($\hat{H}$ being the full Hamiltonian of Ar–HX), once it is represented on a suitable basis set of radial and angular functions. The vibrational diabatic approximation is fully justified here due to the large difference between the frequencies of the HX and vdW vibrations, leading to a quite small vibrational mixing of the χ_v states.

3. Results and discussion

The first vdW energy levels calculated for Ar–HF($v = 0, 1, 2$), Ar–HCl($v = 0, 1$), and Ar–HBr($v = 0, 1$) are collected in Table 1. The (n, b) quantum numbers are assigned to each state. Due to intermode coupling, assignment of these numbers becomes ambiguous for some excited states, and these cases are indicated in the table. The angular distributions

$$P(\theta) = \int dR |\psi_{n,b}^{(v)}(R, \theta)|^2 \sin \theta, \quad (2)$$

of two of those vdW states are displayed in Fig. 1 for the different vibrational states v of HX. All the angular distributions consisting of a single peak at low angles correspond to the ground vdW state of the Ar–HX(v) complexes, with quantum numbers $(n, b) = (0, 0)$. These distributions are associated with the Ar–H–X isomer. The angular distributions with a main peak at large angles and a secondary peak at low angles correspond to the first excitation of the Σ bend (or in-plane bend) vdW mode of the three Ar–HX(v) clusters, with quantum numbers $(n, b) = (0, 1)$. These latter distributions are associated with the Ar–X–H isomer.

The UV photolysis of Ar–HBr($v = 1$) was recently investigated by means of quasiclassical trajectory simulations [20] and 3D wave packet calculations [21]. The UV excitation of Ar–HBr was simulated through an ultrafast Franck-Condon transition (assuming constant transition dipole moment) which excites the HBr chromophore from its ground electronic state $X^1\Sigma^+$ to the repulsive excited state $A^1\Pi$. The photodissociation dynamics takes place only on the $A^1\Pi$ electronic surface, which is modeled as a sum of pairwise interactions [20]. The quantum mechanical treatment employed has been described elsewhere [21,25]. In the quasiclassical and quantum mechanical simulations photolysis was started from both the ground vdW state and the first excited vdW state $[(n, b) = (0, 1)]$, corresponding to the Σ bend excitation of the complex. The angular distributions associated with these two initial states are shown in the lower panel of Fig. 1.

The probability of formation of Ar–Br radical products upon cluster photolysis,

P_{Ar-Br} , was calculated for different excitation energies of the parent cluster in the range of its absorption spectrum. In Fig. 2 the quantum mechanical results for the ratio P_{Ar-Br}/P_{total} , where P_{total} is the total probability of cluster photodissociation, are shown for the two initial states of the cluster. The relative probability $1 - P_{Ar-Br}/P_{total}$ is that corresponding to the $H + Ar + Br$ products. It is found that the yield of Ar-Br radical products is remarkably higher when photolysis starts from the excited vdW state of Ar-HBr($v = 1$).

Formation of Ar-Br radicals occurs upon direct dissociation of the H fragment, without colliding with the Ar obstacle. Otherwise, if a H/Ar collision takes place, the Ar-Br radical complex does not survive. The initial intracuster orientations of the hydrogen determined by the angular distribution of the excited vdW state of Ar-HBr($v = 1$) favors these direct dissociation events, as compared with the angular distribution of the ground vdW state. As a result, the probability of Ar-Br products is enhanced. Thus, the probability of formation of Ar-Br, and in general of Ar-X products, is strongly dependent on the shape of the distribution of intracuster orientations prepared prior to the UV photolysis.

The distributions of Fig. 1 show that the three Ar-HX complexes present a similar angular shape associated with the ground vdW state and with the first excited Σ bend state, corresponding to the Ar-H-X and Ar-X-H isomers, respectively. In addition, the angular shape of these two vdW states remains qualitatively similar when the HX vibrational state v is excited, as seen in Fig. 1 (at least for the vibrational excitations studied here). It is also found that excitation of the vdW stretching mode of Ar-HX(v) (*i.e.*, for $n > 0$) leads to similar angular distributions as those shown in Fig. 1 for $(n, b) = (0, 0)$ and $(0, 1)$, at least for $n \leq 3$. Thus there are several vdW states which can be assigned to the Ar-H-X isomer or to the Ar-X-H isomer. The specific shape of the angular distribution associated to each of them varies to some extent depending on the level of excitation of the HX stretching vibration and the vdW stretching mode. In the following we shall analyze such variations both with halogen substitution and mode excitation in more detail.

It is observed in Fig. 1 that for a given v state of HX, when going from Ar–HF(v) to Ar–HBr(v), the angular distribution of the first excited Σ bend state becomes gradually more concentrated at large angles. The distributions of the ground vdW state exhibit a similar effect, developing an increasing intensity in the angular region close to the Ar–X–H configuration. The origin of this behavior is in the gradual increase of the depth of the potential well corresponding to the Ar–X–H isomer, upon halogen substitution from F to Br [7,12-14]. The implication is that, based only on stereodynamical considerations related to the shape of the angular distributions of both the ground and the excited Σ bend states, the probability of Ar–X formation is expected to increase from Ar–F to Ar–Br.

It is interesting to note that the energy position of the $(n, b) = (0, 1)$ Σ bend state also changes gradually from Ar–HF to Ar–HBr. In Ar–HF this state is the third lowest one, while in Ar–HCl and Ar–HBr it is the second lowest one (see Table 1). Again, this change in the energy position is due to the increase of the depth of the potential well corresponding to the Ar–X–H configuration. *Ab initio* calculations have predicted in the case of Ar–HI [8] that the absolute minimum of the ground state potential corresponds to the Ar–I–H configuration, and the secondary minimum corresponds to the Ar–H–I one. The ground vdW state was found to be located in the main potential well, associated with the Ar–I–H isomeric form. Actually, the situation that the main potential well corresponds to the Ar–X–H configuration is also found in Ar–HBr($v = 1$) [7]. However, in this case the difference between the two well depths is small, and the ground vdW state is still located in the secondary Ar–H–Br well, due to the anisotropy of the potential. The increase of the depth of the Ar–I–H potential well (with respect to the other Ar–HX members of the family) is already enough to locate the ground vdW state in that potential well. Thus, Ar–HI follows the same trend found from Ar–HF to Ar–HBr, with the difference that now the angular distribution of the ground vdW state is associated with the Ar–I–H isomer, and therefore with a higher probability of Ar–I radical formation upon UV photolysis.

Exciting the vibrational state v of the HX moiety has the effect of modifying the angular distribution of the Ar–HX(v) complex, although still keeping the same global shape as for $v = 0$ (see Fig. 1). As expected, upon v excitation, the changes in the angular shape of the vdW states are related to the changes in the depth and anisotropy of the corresponding potential wells where the vdW states are mainly located. In the case of Ar–HF the main potential well ($\theta = 0$) increases its depth from $v = 0$ to $v = 2$ [14], which causes a gradually increasing concentration of the ground vdW state angular distribution at low angles. By contrast, with increasing v the depth of the secondary well ($\theta = 180^\circ$) slightly decreases. The effect in the angular distribution of the $(n, b) = (0, 1)$ state is that intensity of the secondary peak at low angles shifts towards middle angles, $60^\circ < \theta < 120^\circ$, in the main peak of the distribution.

Excitation from $v = 0$ to $v = 1$ increases rather slightly the depth of the primary well ($\theta = 0$) of Ar–HCl(v) [12] (from $D = 176.0 \text{ cm}^{-1}$ to $D = 179.0 \text{ cm}^{-1}$), and the effect in the angular shape of the ground vdW state is smaller than in Ar–HF(v). The depths of the secondary wells ($\theta = 180^\circ$) for $v = 0$ and $v = 1$ are practically the same, $D = 148.3 \text{ cm}^{-1}$ and 148.9 cm^{-1} , respectively, giving rise to nearly identical angular distributions of the $(n, b) = (0, 1)$ vdW state. The slightly higher concentration of the $v = 0$ distribution at large angles is probably due to the anisotropy of the potential. It should be noted that the depth of the secondary well of Ar–HCl(v) increases with v , in contrast with the case of Ar–HF(v).

A similar situation as that of Ar–HCl($v = 0, 1$) is found for the main well ($\theta = 0$) of Ar–HBr($v = 0, 1$). The depth of this potential well is almost the same for $v = 0$ and 1, $D = 165.14 \text{ cm}^{-1}$ and 165.3 cm^{-1} , respectively [7,13], which leads to almost indistinguishable angular distributions of the ground vdW state. The well at $\theta = 180^\circ$ follows the same trend as the secondary well of Ar–HCl, increasing its depth from $D = 160.41 \text{ cm}^{-1}$ to $D = 181.7 \text{ cm}^{-1}$ when v is excited from $v = 0$ to $v = 1$. As commented above, this causes that the well at $\theta = 180^\circ$ becomes the main potential well of Ar–HBr($v = 1$). The increase of the well depth at $\theta = 180^\circ$

for $\text{Ar-HBr}(v = 1)$ has the effect that the angular distribution of the $(n, b) = (0, 1)$ state becomes appreciably more concentrated at orientations associated with the Ar-Br-H isomer.

The distributions of Fig. 1 show that, while their global shape is determined by the bending state b , excitation of the HX vibration causes further variations of this shape. Such variations occur in the sense of either increasing or decreasing the degree of localization of the angular distribution in its corresponding potential well. Thus, HX vibrational excitation allows a higher degree of control on the angular shape of a specific (n, b) vdW state, and consequently on the photolysis reaction products. In this sense, excitation of the vdW stretching vibration n plays a similar role. We find that excitation of the n state has the effect of increasing the delocalization of the angular distribution over the whole range of orientations. As a result, angular distributions with a shape in between the two limiting cases of localization either in the primary or in the secondary potential well, can be prepared. Some of these intermediate situations are briefly discussed next.

In Fig. 3 the angular distributions of the $(n, b) = (4, 0)$, $(n, b) = (0, 2)$, and $(n, b) = (1, 2)$ vdW states of $\text{Ar-HF}(v = 0)$, $\text{Ar-HCl}(v = 0)$, and $\text{Ar-HBr}(v = 0)$, respectively, are shown. Similar distributions are found for $v = 1$ and $v = 2$ (in the case of Ar-HF). The distributions spread over the entire angular range, and they are not localized in one of the two potential wells of the cluster. In fact, a large amount of the angular intensity concentrates in the middle region $30^\circ < \theta < 130^\circ$ (particularly in the case of the $(n, b) = (4, 0)$ state). Thus, excitation of the vdW stretching and bending (for $b > 1$) modes makes possible to prepare initial distributions of intracluster orientations which are in between those essentially associated with the Ar-H-X and Ar-X-H isomeric species. This provides an additional degree of control on the Ar-HX UV photolysis reaction.

4. Conclusions

The bound state spectrum of the Ar-HX ($\text{X}=\text{F}, \text{Cl}, \text{Br}$) vdW clusters is investi-

gated. It is shown that the ultraviolet photolysis reaction in these clusters is affected to a large extent by the shape of the initial distribution of intracluster orientations prepared prior to the ultraviolet excitation. This dependence can be used to control the yield and final state distribution of the photolysis products. The change in the shape of the distribution of intracluster orientations prepared when the different cluster modes are excited is analyzed, focusing on the possible implications for photolysis reaction control.

For the three clusters studied, the angular distributions associated with the lowest vdW states with no bending excitation ($b = 0$) and with one quantum of bending excitation ($b = 1$), correspond mainly to the Ar-H-X and Ar-X-H isomer geometries, respectively. Upon cluster photolysis the initial angular distribution associated with the Ar-X-H isomer leads to a higher yield of Ar-X radical products than that of the Ar-H-X isomer. Excitation of the lowest stretching vibrational states of the HX moiety does not modify the global shape of the angular distributions, although it increases or decreases the localization of the distribution around the geometries of the corresponding isomer. Such excitation provides the possibility of a more selective control within the distributions associated with a specific isomer geometry. Similarly, it is found that excitation of the vdW stretching and bending modes (this latter for $b > 1$) leads to distributions with an angular shape in between those associated with the limiting cases of the Ar-H-X and Ar-X-H isomers. To conclude, this study shows that the lowest vdW state spectrum of the Ar-HX clusters provides a wide range of angular geometry distributions, in which the cluster can be initially prepared in order to selectively control the subsequent photolysis reaction products.

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TABLE CAPTIONS

Table 1. Energies of the first vdW states (in cm^{-1}) of $\text{Ar-HF}(v = 0, 1, 2)$, $\text{Ar-HCl}(v = 0, 1)$, and $\text{Ar-HBr}(v = 0, 1)$. The energies are relative to the $\text{HX}(v)$ vibrational energy level. Quantum numbers n, b corresponding to the vdW stretching and bending modes, respectively, have been assigned to the states. Ambiguous assignment in some cases is denoted by a question mark to the right of the corresponding number.

FIGURE CAPTIONS

Fig. 1. Angular distributions associated to the ground vdW state $(n, b) = (0, 0)$, and the first excited Σ bend state $(n, b) = (0, 1)$ of $\text{Ar-HF}(v = 0, 1, 2)$, $\text{Ar-HCl}(v = 0, 1)$, and $\text{Ar-HBr}(v = 0, 1)$. All the distributions are normalized to unity. See the text for details.

Fig. 2. Ratio between the probability of Ar-Br radical products, $P_{\text{Ar-Br}}$, and the total probability of $\text{Ar-HBr}(v = 1)$ photodissociation, P_{total} , vs the cluster excitation energy E , calculated quantum mechanically for the initial ground $[(n, b) = (0, 0)]$ and first excited Σ bend $[(n, b) = (0, 1)]$ vdW states of $\text{Ar-HBr}(v = 1)$.

Fig. 3. Angular distributions associated to the $(n, b) = (4, 0)$ vdW state of $\text{Ar-HF}(v = 0)$ (solid line), the $(n, b) = (0, 2)$ vdW state of $\text{Ar-HCl}(v = 0)$ (long dashed line), and the $(n, b) = (1, 2)$ vdW state of $\text{Ar-HBr}(v = 0)$ (short dashed line). All the distributions are normalized to unity.

Table 1

(n, b)	Ar–HF($v = 0$)	Ar–HF($v = 1$)	Ar–HF($v = 2$)
(0, 0)	-101.238	-110.800	-121.941
(1, 0)	-62.402	-69.383	-77.739
(0, 1)	-49.008	-53.281	-57.361
(2, 0)	-34.429	-39.126	-44.768
(1?, 1)	-16.684	-20.416	-24.559
(3, 0?)	-15.611	-18.937	-22.410
(4, 0)	-5.637	-7.157	-9.038
(5, 0)	-1.092	-1.564	-2.173
(n, b)	Ar–HCl($v = 0$)	Ar–HCl($v = 1$)	
(0, 0)	-115.179	-116.936	
(0, 1)	-91.556	-93.363	
(1, 0)	-82.724	-84.159	
(1, 1)	-65.434	-67.419	
(2, 0)	-56.954	-58.909	
(0?, 2)	-46.626	-48.303	
(2, 1)	-39.987	-42.173	
(3, 0)	-33.752	-34.896	
(2, 2?)	-23.715	-25.840	
(n, b)	Ar–HBr($v = 0$)	Ar–HBr($v = 1$)	
(0, 0)	-121.255	-121.611	
(0, 1)	-110.454	-112.470	
(1, 0)	-96.342	-95.835	
(1, 1)	-87.059	-90.046	
(2, 0)	-76.211	-75.013	
(2, 1)	-65.887	-70.129	
(1?, 2)	-65.657	-60.198	
(3, 0)	-56.562	-53.902	
(3, 1)	-47.533	-50.063	