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Citation: *J. Chem. Phys.* **117**, 9423 (2002); doi: 10.1063/1.1514980

View online: <http://dx.doi.org/10.1063/1.1514980>

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# Cage effect for the photodissociation of H<sub>2</sub>O molecules in argon clusters embedded inside neon clusters

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(Received 13 March 2002; accepted 27 August 2002)

A study of energy relaxation processes of H<sub>2</sub>O-doped rare gas clusters excited with vacuum ultraviolet synchrotron radiation is presented. An enhanced quenching of electronically excited fragment OH\*(A) is observed in Ar<sub>m</sub>Ne<sub>N</sub> clusters ( $m < 10^2$ ,  $N \approx 7.5 \times 10^3$ ). The doping of interior of small argon clusters has been achieved by using a "sequential pick-up" technique (Ne<sub>N</sub> + H<sub>2</sub>O + mAr). Due to a low temperature of the Ne host cluster the Ar atoms are fixed around the H<sub>2</sub>O molecule prohibiting structural rearrangements. A strong decrease of the OH\*(A) fluorescence yield has been observed for  $m > m_1 = 12$ . This effect is attributed to a formation of the second ( $m_2 = 54$ ) and higher shells of Ar atoms around the water molecule. The principal contribution from a noncomplete second shell ( $m_2^* = 32$ ) after a closure of 20 triangular windows in the first shell is suggested. Due to a finite size of the cluster matrix and fast sample renewal, the cage exit and reentry processes can be investigated. © 2002 American Institute of Physics.

[DOI: 10.1063/1.1514980]

## INTRODUCTION

Investigations on the electronic properties and dynamics of single molecules isolated in solids are of fundamental interest since they differ considerably from those in gases. Over the last decade a series of studies have been devoted to the photodissociation of water molecules isolated in rare-gas matrices of Ne, Ar, Kr, and Xe excited at the first water absorption continuum at  $\sim 7.5$  eV.<sup>1-3</sup> A cage effect has been observed depending on the kinetic energy of the OH(X) + H fragments. It has been found that matrix atoms introduce a barrier of  $E_b \approx 1.7$  eV, which can prevent molecular dissociation. Unfortunately, the experimental uncertainties in these measurements were larger than the expected variations of the barrier height for different rare gases. Moreover, microscopic reversibility and multiple barrier crossing are non-negligible factors, which are difficult to consider explicitly in bulk matrix experiments. The use of doped cluster beams is especially useful because this technique offers a fast sample renewal and the possibility of a detailed analysis of cluster size effects on chemical reactivity and dynamics of embedded atoms, molecules, or radicals.<sup>4,5</sup>

In recent experiments, we studied the caging of elec-

tronically excited fragments OH\*(A) after VUV excitation of rare-gas clusters (He, Ne, and Ar) doped with H<sub>2</sub>O molecules. We believe that these experiments can give useful information about the cage formation, which can be compared with that obtained in the studies of the H<sub>2</sub>O( $\tilde{A}$ ) → OH + H photodissociation dynamics in rare-gas matrices. This point can be justified by the following: (1) OH\*(A) is not quenched in the light rare-gas matrices, (2) photodissociation reactions H<sub>2</sub>O( $\tilde{B}$ ) → OH\*(A) + H and H<sub>2</sub>O( $\tilde{A}$ ) → OH + H proceed by repulsive potential curves in a generally similar way (a sketch of the relevant potential curves of the water molecule is presented in Fig. 1; and (3) the most rapid product of both reactions, H(1s) atom, loses its kinetic energy or escapes the cage on a very short time scale, which allows disregarding the interaction dynamics between the Ar cage and the heavier OH\*(A) or OH(X) radicals.

Initially in our experiments, the rare-gas cluster atoms are excited. This is followed by an energy transfer to the embedded H<sub>2</sub>O molecule and its dissociation. Important in these studies is that (i) the excitation energy ( $h\nu_{exc} = 17.70$  eV in case of Ne induces an excess of kinetic energy in a light fragment H, which is well above the cage barrier  $E_b$  earlier determined from bulk matrix experiments, and that (ii) the average cluster size  $N$  is controlled. We have observed that the He<sub>N</sub> cluster environment influences only the

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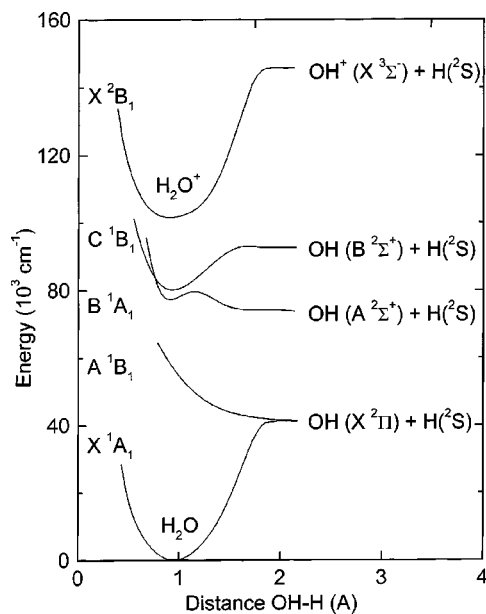


FIG. 1. A sketch of the relevant potential curves of the water molecule.

photoelectron yield;<sup>6</sup>  $\text{Ne}_N$  clusters modify the relaxation processes and strongly reduce the rotational temperature of the  $\text{OH}^*(A)$  molecules.<sup>7</sup> In pick-up experiments of free  $\text{Ar}_N$  clusters prepared in a supersonic expansion and  $\text{H}_2\text{O}$  molecules from a cross-jet, the molecules preferentially take a position in the surface layer, which results only in a partial rotational cooling of the  $\text{OH}^*(A)$  fragment.<sup>7</sup>

Using a three-beam doping technique, which consists of a sequential pick-up of  $\text{H}_2\text{O}$  molecules in a first step and Ar atoms in a second step from two cross-jets by large Ne clusters prepared in a supersonic expansion, we were able to build a shell of up to approximately 100 Ar atoms around the  $\text{H}_2\text{O}$  molecule.<sup>8,9</sup> Small cold  $\text{H}_2\text{O}@Ar_m$  clusters ( $m \leq 10^2$ ) were stabilized inside large  $\text{Ne}_N$  clusters ( $N \approx 7.5 \times 10^3$ ). Fluorescence of the  $\text{OH}^*(A)$  fragments has been studied as a function of the number of deposited Ar atoms  $m$ . As a result, the cage effect has been observed for the first time in doped rare-gas clusters with a shell-like structure.

## EXPERIMENT

The measurements were performed at the experimental station CLULU at the synchrotron radiation laboratory HASYLAB in Hamburg.<sup>10</sup> Our previous results indicate that by using a standard “pick-up” technique for doping free Ar clusters prepared in a supersonic expansion with  $\text{H}_2\text{O}$  molecules from a cross-jet, we were not able to embed molecules on the inside of the clusters.<sup>9</sup> This is apparently related to the difference in Ar–Ar and Ar– $\text{H}_2\text{O}$  interaction potentials. To surmount this limitation, we have employed a “sequential pick-up” technique.<sup>8</sup> A conical nozzle ( $D = 200 \mu\text{m}$ ,  $2\theta = 4^\circ$ ) is the source of large clusters made out of light atoms (Ne in our case). The nozzle is mounted on a liquid helium cryostat and was operated at typical temperatures down to 30 K and stagnation pressures up to 200 mbar, which assured the creation of large  $\text{Ne}_N$  clusters. The average cluster size  $N$  was determined using well-known scaling laws according to the

formula<sup>11–13</sup>  $N = 33 \cdot (\Gamma^*/1000)^{2.35}$ , with  $\Gamma^* = K_{\text{ch}}[(p \cdot d_{\text{eq}}^{0.85})/T^{2.2875}]$ ,  $K_{\text{ch}}(\text{Ne}) = 185$ , and  $p$  is in mbar,  $T$  in K, and  $d$  in  $\mu\text{m}$  are used. In a first pick-up process  $\text{Ne}_N$  clusters are doped with single water molecules, which are embedded inside the clusters. The cluster size distribution in the nozzle expansion experiments has a width (FWHM) of  $\Delta N \approx N$ . In a second step the  $\text{H}_2\text{O}@Ne_N$  clusters interact with Ar atoms from an additional cross-jet. Because of the low temperature of Ne clusters ( $\sim 10$  K) compared to Ar clusters ( $\sim 37$  K),<sup>14</sup> the Ar atoms “freeze” around the  $\text{H}_2\text{O}$  molecule and build a shell-like structure inside the large host Ne clusters. The low cluster temperature and the rapid cooling mechanism due to the evaporation of neutral Ne atoms prohibits any structural rearrangement of the embedded  $\text{H}_2\text{O}@Ar_m$  clusters. Typically,  $\text{Ne}_N$  clusters with an average size of  $N \approx 7.5 \times 10^3$  and solute  $\text{Ar}_m$  clusters (with a Poisson distribution) of an average size  $m \leq 10^2$  were produced in these experiments.

Monochromatized synchrotron radiation ( $\Delta\lambda = 0.05$  nm) in the spectral range of 100–140 nm (Al grating) or 40–100 nm (Pt grating) was focused on the doped cluster beam 10 mm downstream from the nozzle. Fluorescence excitation spectra in the VUV-UV ( $\lambda \leq 300$  nm) and in the UV-visible-IR ( $200 \leq \lambda \leq 900$  nm) were recorded by two photomultipliers containing CsI and GaAs(Cs) photocathodes. Additionally,  $\text{OH}^*(A \rightarrow X)$  fluorescence excitation spectra have been measured using a UG-11 large-band filter (bandpass  $\lambda = 320 \pm 40$  nm) in front of the photomultiplier. Energy-resolved fluorescence spectra in the UV and visible spectral range were collected over 600 s with a liquid nitrogen-cooled CCD camera (Princeton Instruments) installed after a Czerny–Turner-type monochromator ( $f = 275$  mm, 150 or 1200 l/mm gratings, 250  $\mu\text{m}$  slits). The background pressure was kept below  $10^{-3}$  mbar during the experiments by continuous pumping of the interaction volume.

## RESULTS AND DISCUSSION

Compared with studies on embedded impurities in solid rare-gas matrices, doped cluster beams offer several advantages for investigating molecular dynamics. First, the fast sample renewal and the control of the mean number of doped atoms, molecules, or radicals create working conditions similar to those of gas-phase experiments, where photochemistry is not affected by the presence of the reaction products. In a specific application to investigate the cage effect, the use of doped cluster beams allows us to consider the so-called reentry processes in detail. The balance between exit and reentry processes is of importance in  $\text{H}_2\text{O}@Rg$  matrices, at least for light dissociation products, like H atoms.<sup>1,2,15</sup> Second, the study of size effects enables us to observe the building process of the cage.

Because of the low density of doped clusters in the beam, the excitation energy was tuned to the first excitonic band of the large host  $\text{Ne}_N$  clusters at 70.05 nm. The energy rapidly transfers onto the impurity center after the excitation. This is shown in Fig. 2, in which UV-visible-IR fluorescence excitation spectra of the  $\text{Ar}_m@Ne_N$  and  $\text{H}_2\text{O}@Ar_N$  clusters are displayed. In this series of experiments the clusters are excited around 70.05 and 102.8 nm, respectively. The exci-

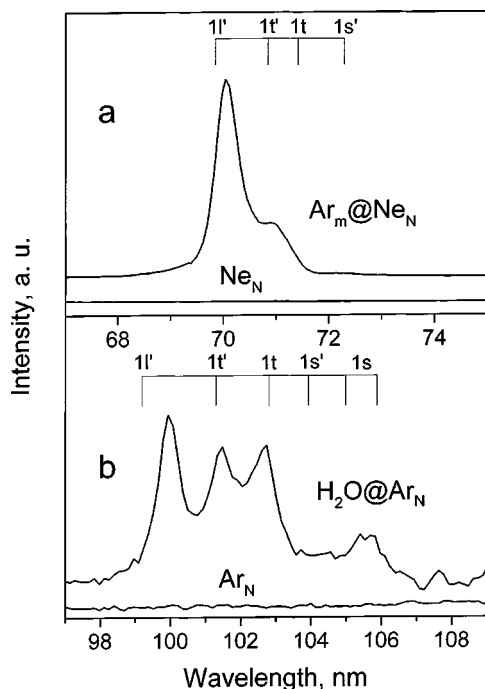
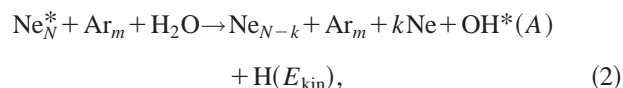
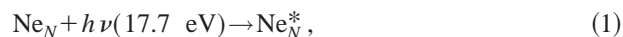


FIG. 2. UV-visible-IR fluorescence excitation spectra of Ne<sub>N</sub> and Ar<sub>m</sub>@Ne<sub>N</sub> clusters ( $m \leq N \approx 7.5 \times 10^3$  atoms/cluster) (a) and of Ar<sub>N</sub> and H<sub>2</sub>O@Ar<sub>N</sub> clusters ( $N \approx 400$  atoms/cluster) (b).

tonic absorption bands of the corresponding rare gas solids are indicated. Since pure Rg<sub>N</sub> clusters excited in the energy range of the first absorption bands do not emit UV-visible-IR photons, the excitation spectra in Fig. 2 are a fingerprint for a strong energy transfer to the embedded Ar clusters or else to the H<sub>2</sub>O molecules: Ne<sub>N</sub> → Ar<sub>m</sub> → H<sub>2</sub>O. Moreover, as this has been discussed in our recent paper,<sup>7</sup> large Ne clusters completely absorb impurity centers Ar<sub>m</sub> and H<sub>2</sub>O. This can be seen, in particular, by the absence of the surface exciton band in the excitation spectrum presented in Fig. 2(a).

To analyze the observed fluorescence in more detail, energy-resolved spectra of H<sub>2</sub>O@Ne<sub>N</sub> and H<sub>2</sub>O@Ar<sub>m</sub>Ne<sub>N</sub> clusters were recorded and are shown in Fig. 3. Emission bands are assigned to Ar\*(4p) atomic and OH\*(A) molecular transitions. These experiments ensure that via initial Ne cluster excitation one can deposit energy in the water molecule.

The UV fluorescence signal in Fig. 3 is due to OH\*(A) fragments produced in the following reactions:



Simultaneously, fluorescence of desorbed Ar\*(4p) atoms in the visible and near-infrared spectral range ( $\lambda_{\text{flu}} \geq 700 \text{ nm}$ ) is also observed:

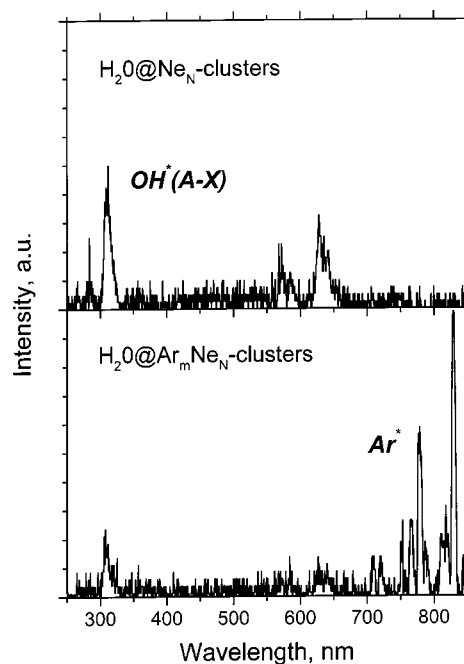
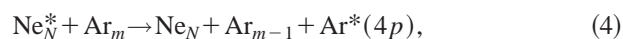
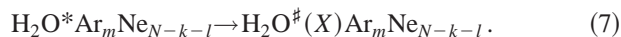
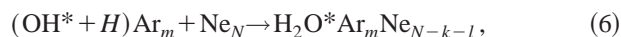


FIG. 3. Fluorescence spectra of H<sub>2</sub>O@Ne<sub>N</sub> and H<sub>2</sub>O@Ar<sub>m</sub>Ne<sub>N</sub> clusters ( $\lambda_{\text{exc}} = 70.05 \text{ nm}$ ). Fluorescence bands at  $\sim 620 \text{ nm}$  belong to the second-order grating reflection of the UV emission of OH(A  ${}^2\Sigma^+ \rightarrow X {}^2\Pi$ ).

This effect has been recently observed in small Ar<sub>m</sub> clusters solvated in large Ne<sub>N</sub> clusters.<sup>8</sup> This process is similar to the exciton-induced desorption in pure rare gas solids.<sup>16</sup> In the so-called “cavity-ejection mechanism,” the interaction of the electronically excited atomic Ar\*(4p) centers with surrounding neutral Ar atoms (whether it is repulsive or attractive) is correlated to the sign of the  $V_0$  value (electron affinity) of the respective solid. Detailed investigations show that the correlation not only holds for the undoped but also for doped materials.<sup>17</sup> A repulsive interaction between the excited atom and the surrounding neutrals is expected for positive  $V_0$ . These results show that the Ne cluster is a relatively soft matrix and does not cage the electronically excited species, even if their kinetic energy is low ( $\sim 0.04 \text{ eV}$  in the case of Ar\*<sup>18</sup>).

On the other hand, the deposition of Ar atoms in a shell around the H<sub>2</sub>O molecule can prohibit the exit of the rapid hydrogen atom (in the ground electronic state). This can result in the recombination of the dissociation products and the quenching of OH\*(A) fluorescence. This quenching tentatively occurs through the ground-state  $\tilde{X}$  potential, which is the main predissociation channel ( $\geq 90\%$ ) for water molecules excited in the VUV spectral region:



H<sub>2</sub>O<sup>#</sup>(X) in (7) denotes the ground-state water molecule with a high excess of kinetic energy above the dissociation limit, which behavior we do not consider in the following. Comparing the UV-visible-IR fluorescence spectrum of H<sub>2</sub>O@Ne<sub>N</sub> clusters with the spectrum of the shell-like H<sub>2</sub>O@Ar<sub>m</sub>Ne<sub>N</sub> clusters in Fig. 3, the quenching of the OH\*(A) fluorescence is clearly observable.



In our recent article<sup>7</sup> we characterized the dissociation/ionization products of the H<sub>2</sub>O molecule after the excitation of neon clusters. This case appears to be similar to that of H<sub>2</sub>O-doped helium clusters:<sup>6</sup> in both cases the ionic exit channel is found strongly suppressed. This is expected because of a negative electron affinity of helium, neon, and at least small argon clusters (see in Ref. 19). Therefore, we disregard ionization processes in our discussion. The only observed excited fragment in H<sub>2</sub>O-doped neon clusters is OH\*(A) with a very low rotational temperature of ~10 K, which is a characteristic temperature of neon clusters.<sup>7</sup> Moreover Ne<sub>N</sub>Ar<sub>m</sub> cluster experiments show that the energy transfer from a large host neon cluster to a small embedded argon cluster results principally in the Ar\*(4p) atom desorption,<sup>8</sup> which emits in the IR spectral region. As a consequence, the competitive channel in the energy relaxation process might be the Ar\*(4p) atoms desorption. This is not the case, because as one can see later from Fig. 5 the IR-line intensity linearly increases with *m* and do not account for an almost stepwise decrease of the OH\*(A) fluorescence intensity.

Moreover, in our recent experiments,<sup>7</sup> where Ar<sub>N</sub> host clusters were doped by water molecules from the crossbeam, we did not succeed observing any fluorescence quenching of OH\*(A). We showed that in such case a H<sub>2</sub>O molecule does not penetrate inside the Ar<sub>N</sub> cluster and takes the site on its surface. Thanks to a successive doping technique used in the present experiments, we succeeded freezing argon atoms around the water molecule. Apparently, a confinement of the predissociation products OH\*(A)+H(1s) in the cage formed by argon atoms is a reason of the observed fluorescence quenching.

The dissociation excess energy can be efficiently transmitted to the host Ne clusters. The doped clusters were excited in the first excitonic absorption band at 17.70 eV. The gas phase dissociation energy of H<sub>2</sub>O( $\tilde{X}$ )→OH(X)+H is 5.118 eV and the transition energy of OH(A→X) is  $T_e = 4.053$  eV. Therefore, the energy transfer to the water molecule releases 17.70-(5.12+4.05)=8.53 eV, which is distributed between vibrational, rotational (OH\*), and translational (mainly H) degrees of freedom. The binding energy of a Ne atom in the solid is 26.5 meV. Our estimations show that if caging takes place the Ne<sub>N</sub> cluster ( $N \approx 7500$ ) may lose only a small part of its atoms, approximately  $k \approx 320$ , during the energy relaxation process. The desorption of neutral Ne atoms leads to the stabilization of the solute water molecule and the buildup of a small solute Ar cluster around it.

It was shown recently that with the “sequential pick-up” technique it is possible to prepare clusters with a well-defined multishell structure containing an Ar core, an inner shell of Kr atoms, and an outer shell of Ne atoms.<sup>8</sup> Using the same experimental setup, one can *a priori* expect in our case the formation of an atomic Ar shell around the solute H<sub>2</sub>O molecule. In our experiments we attempted the fixing of *m* Ar atoms around the H<sub>2</sub>O molecule by varying the argon cross-jet pressure. The mean size of the solute Ar<sub>*m*</sub> cluster in the cross-beam experiments at CLULU has been previously estimated by Laarmann *et al.*<sup>8</sup> based on theoretical and experimental work by Lewerenz *et al.*<sup>20</sup> It has been shown that the absorption lineshape of the first exciton of the solute Ar<sub>*m*</sub>

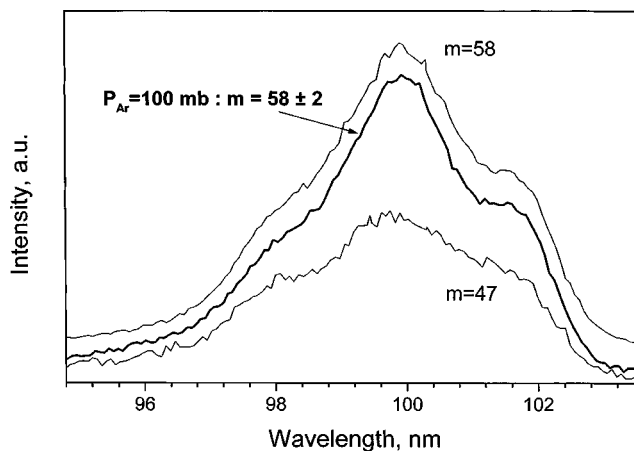


FIG. 4. A size calibration of multishell H<sub>2</sub>O@Ar<sub>*m*</sub>Ne<sub>*N*</sub> clusters ( $N \approx 7.5 \times 10^3$ ) in present experiments corresponding to the Ar cross-beam pressure of 100 mbar. The mean size *m* of embedded Ar<sub>*m*</sub> clusters is estimated from the calculations and measurements in pure rare-gas Ar<sub>*m*</sub>@Ne<sub>*N*</sub> clusters by Laarmann *et al.*<sup>21</sup> (for an explanation see the text).

cluster in a large Ne cluster changes with its size *m* according to a Frenkel exciton model.<sup>21</sup> A comparison of excitation spectra of Ar<sub>*m*</sub>@Ne<sub>*N*</sub> clusters obtained in our experiments (when a water cross-beam is switched off) with the results of Ref. 21 allows a cluster size *m* calibration. This is shown in Fig. 4 for the Ar cross-beam pressure of 100 mbar, which corresponds to a mean size of  $m = 58 \pm 2$  atoms/cluster. Because the cluster size *m* of the embedded Ar cluster is proportional to the cross-beam pressure, we obtain the calibration relation of  $m(\text{atoms}) \approx 0.58 \cdot p_{\text{Ar}}(\text{mbar})$  in our experimental geometry.

We have measured the fluorescence excitation spectra of the  $A^2\Sigma^+ \rightarrow X^2\Pi$  transition of the OH dissociation fragments. Each scan has been carried out through the absorption band of the large host neon clusters ( $\lambda_{\text{exc}} \approx 70$  nm). At the same time to avoid any contribution from another spectral region, the fluorescence has been collected through a broadband spectral filter ( $\lambda = 320 \pm 40$  nm). The UV band intensity at  $\lambda_{\text{exc}} \approx 70$  nm as a function of the mean number *m* of embedded Ar atoms is presented in Fig. 5 (we estimate the error bars as an  $m \pm 2$  atom/cluster). The experimental results show that the OH\*(A) emission only slightly weakens up to  $m \geq 12$  (~10%) and it is strongly reduced in intensity for approximately  $m \geq 17$  deposited Ar atoms. The analysis of experimental data in Fig. 5 shows that in this size domain ( $m \geq 17$ ), the intensity follows an almost exponential decrease with *m*:  $I_{\text{fluo}} = I_0 \exp(-m/m^*)$ . The least mean square fit results in  $m^* = 19 \pm 3$ .

It is well known that small rare gas clusters have a polyicosahedral structure with a five fold symmetry. The first shell is built of  $m_1 = 12$  atoms around one atom in the center. In case of H<sub>2</sub>O-doped Ar clusters, an extraordinary stability of Ar<sub>12</sub>H<sub>2</sub>O has been earlier reported in theoretical work by Liu *et al.*<sup>22</sup> Surprisingly, the deposition of approximately 12 Ar atoms around the water molecule does almost not lead to a quenching of the OH\*(A) emission. On the other hand, filling of the second shell ( $12 < m < 54$ ) induces a strong reduction of the OH\*(A) fluorescence yield. The decrease by  $1/e$

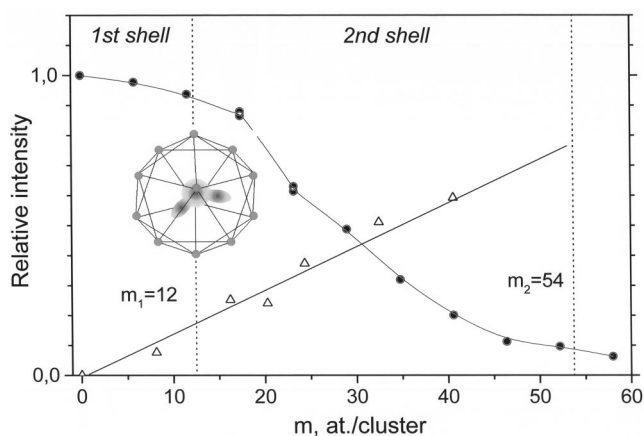


FIG. 5. Normalized integral intensity of the OH( $A\ 2\Sigma^+ \rightarrow X\ 2\Pi$ ) emission as a function of the mean size of the embedded argon cluster  $m$  (calibrated with error bars of  $\pm 2$  atom/cluster):  $I_{m=0}=1$ . H<sub>2</sub>O@Ar <sub>$m$</sub> @Ne <sub>$N$</sub>  clusters ( $N \approx 7.5 \cdot 10^3$ ) are excited at 70.05 nm.

and  $1/e^2$  correspond to the size  $m$  of  $\sim 32$  and  $\sim 54$ . Interestingly, the geometry of Ar<sub>32</sub>H<sub>2</sub>O is characterized by a non-complete second shell after a closure of 20 triangular windows in the first shell. Ar<sub>54</sub>H<sub>2</sub>O cluster has a completed two-shell polyicosahedral structure.

Before discussing the nature of this effect, one has to make some remarks on the nature of the cage effect under discussion. A caging reported in Refs. 1–3 is related to the competition between the dissociation and the recombination of the ground state products. In contrast to this, the present experiments describe the cage effect in terms of the quenching process of the excited fragment OH\*(A). This is quite different, because the fluorescence efficiency is determined not only by a total exit probability from the cage but also by an exit probability during the quenching lifetime. Therefore, even in the case where the H atom loses kinetic energy not very rapidly and possesses energy sufficient to exit the cage, trajectories of OH\* and H can undergo multiple crossing and the efficient caging (cage-induced quenching) may be observed. A numerical estimation is given below to clarify this point.

As we have already mentioned, the quenching event can occur if the H atom stays inside the cage. We now consider the atom losing its kinetic energy in collisions with surrounding Ar atoms. First, we estimate the energy loss pathlength before its energy decreases below the cage exit barrier of  $E_b = 1.7$  eV. The energy transfer from the Ne <sub>$N$</sub> \* cluster and the predissociation of the solvated water molecule results in dissociation fragments that carry out a high amount of the kinetic energy,  $E \approx 8.5$  eV [reaction (3)]. We assume that the H atom takes roughly half of it  $E_H \approx 4.3$  eV (another half belongs to the OH rotation). We make our estimations using the continuum model proposed in Ref. 2. The energy decrease of the H atom in the Ar cage can be described by  $E(t) = (E_0^{-1/2} + \gamma t / l \sqrt{2m_H})^{-2}$ , where  $\gamma = 2m_H m_{Ar} / (m_H + m_{Ar})^2 \approx 0.05$ ,  $l \approx d(\text{Ar} - \text{Ar}) = 0.375$  nm is the mean-free pathlength and  $E_0 = E_H$  is the initial energy of the H atom. The full pathlength of the atom inside the cage before it loses the energy  $E_H - E_b$  will be  $L_0 = l \gamma^{-1} \cdot \ln(E_H/E_b)$

$\approx 7$  nm. On the other hand, we can estimate a free pathlength of the hydrogen atom inside the cage before it undergoes a quenching collision with OH\*(A),  $L_q$ . Roughly, taking the H–OH\* interaction distance to be equal to the equilibrium one in H<sub>2</sub>O( $\tilde{C}$ ):  $r \approx 0.10$  nm, the quenching cross-section is estimated as  $\sigma_q \approx 0.03$  nm<sup>2</sup>. We also estimate the accessible cage volume as  $V_{\text{cage}} \approx 0.1$  nm<sup>3</sup>. Finally, we obtain the quenching pathlength from  $\sigma_q \cdot L_q \approx V_{\text{cage}}$ , to be  $L_q \approx 3$  nm. We see that the quenching pathlength is smaller than the energy loss pathlength of the hydrogen atom inside the cage of argon atoms:  $L_q < L_0$ . This means that in our experimental conditions the quenching of OH\*(A) by H atoms occurs efficiently when it is still hot and possesses kinetic energy above the cage barrier.

We attribute the observed effect (see Fig. 5) to the caging of the H<sub>2</sub>O photodissociation fragments by argon cluster atoms: being confined in a small volume, OH\*(A) and H have a high probability to be quenched through the left repulsive branch of the H<sub>2</sub>O( $\tilde{X}$ ) potential. We believe that the first shell of argon atoms  $m_1^* = 12$  is not sufficient for the formation of the stable cage. The present experimental results indicate that the perfect cage is formed by the filling by Ar atoms of the second icosahedral shell around the H<sub>2</sub>O molecule. In the process of the cage formation the cluster structure Ar<sub>32</sub>H<sub>2</sub>O may play an important role, as it is transparent for the  $e^{-1}$  of reaction fragments. It is formed by argon atoms taking a top position above triangular windows of the first shell. This special geometry is due to the condensation process in cold Ne clusters. This structure becomes efficiently screening the exit reaction products with a high amount of kinetic energy.

As we have seen, the cage is almost formed by 32 Ar atoms (transparency of  $\sim 30\%$ ). Moreover, 54 Ar atoms form the cage with  $\sim 10\%$  transparency. We believe that at a low neon host cluster temperature of 10 K, the melting of this solute Ar<sub>54</sub> cage is negligible and the exit probability of the H atom is low, even at large excess kinetic energies. On the other hand, we see from Fig. 5 that if the first shell is closed ( $m = 12$ ), the cage is not formed, and the quenching of the OH\*(A) fragment in collisions with a H atom can be almost neglected. In the intermediate size domain with the first shell closed and the second shell forming ( $12 < m < 54$ ), a non-trivial mechanism is responsible for the high probability of the fragments exit. Indeed, a simple geometrical model based on the cage coating by argon atoms failed, explaining the regime crossover, which occurs at  $m \approx 17$ : in that framework the UV intensity should decrease linearly monotonically with  $m$ , which is not the case (see Fig. 5).

In the following we consider two possible mechanisms, which are capable of explaining the experimental results: (1) model of the cage melting, and (2) model of the cage window closure, which favor correspondingly the delayed and direct cage exits by a rapid H atom.

(1) Recently, Tarasova *et al.*<sup>2</sup> have shown using a continuum approximation that because of the dissipation of energy by rapid H fragments, the local temperature of first shell atoms can reach a melting point, which enables cage exit. Although the initial cluster temperature is rather low in our experiments (10 K, respectively, to 30 K of the solid argon in

Ref. 2), the heat exchange between the cage and the buffer (interaction  $\text{Ar}_m\text{-Ne}$ ) is slower and the total kinetic energy of the fragments is higher (4.3 eV). This can result in a thermal explosion of solute  $\text{Ar}_{12}(\text{OH}^* + \text{H})$  clusters. On the other hand, the thermal stability and the thermal exchange with the buffer increases for larger solute clusters. This could explain why the  $\text{Ar}_{54}(\text{OH}^* + \text{H})$  cluster is stable inside the Ne matrix. It would be interesting to compare our experimental results with numerical calculation of the cage stability as a function of cluster size.

(2) Another explanation can be proposed. According to theoretical calculations of the minimum energy structures for small  $\text{Ar}_m\text{H}_2\text{O}$  clusters ( $m=1-14$ ) by Liu *et al.*,<sup>22</sup> a small angular anisotropy has been found. The cage induces the potential barrier  $U_{\text{rot}} \sim 20 \text{ cm}^{-1}$ , which may slightly hinder a rotation of the centered water molecule. On the other hand, the temperature of solute  $\text{H}_2\text{O}@\text{Ar}_{12}$  clusters in present experiments is induced by large host neon clusters and it is as low as  $\sim 10 \text{ K}$ .<sup>14</sup> This corresponds to a thermal energy of  $kT \ll U_{\text{rot}}$  and the solute water molecule may not be considered as a free rotator in our experiments, but rather it is aligned in the cage. It may be that in these conditions the dissociation exit direction of the rapid hydrogen atom fits the cage window, which prevents the caging. In this case these are the second shell argon atoms, which close the cage. The experimental data show that the closure of the 20 triangular faces at surface of doped  $\text{Ar}_{12}\text{H}_2\text{O}$  clusters has a significant effect on the caging process. The coating with additional  $\sim 20$  Ar atoms ( $m=54$ ) almost closes the cage.

This second mechanism seems to be more realistic from our viewpoint. It does not contradict the earlier conclusion about the dominant prompt exit from the first cage, and it could explain the behavior of  $I_{\text{fluor}}(m)$  in the range of  $m \approx m_1 = 12$ . Moreover, our experimental finding (Fig. 5) sheds more light on balance between the prompt exit and the cage reentry processes, whose importance has been discussed over the last decade. In fact, we can conclude that the cage formed by the first shell of atoms aligns the solute water molecule inside the cage, but is not able to trap the exit fragment. The prompt exit probability from this first layer of atoms is  $p_1 \approx 90\%$ . As discussed above, an almost complete caging is observed after the deposition of approximately 54 atoms. The probability of prompt exit from the cage formed by two layers is roughly  $p_{12} \approx 10\%$  (Fig. 5). The probability of the first shell reentry ( $p_{r1}$ ) can be found from

$$p_{r1} = 1 - p_2$$

and

$$p_{12} = p_1 p_2 + p_1 p_2 \cdot p_1 (1 - p_2) + \dots + p_1 p_2 \cdot [p_1 (1 - p_2)]^i + \dots = \frac{p_1 p_2}{1 - p_1 (1 - p_2)} = 0.1,$$

where  $p_2$  is the prompt exit probability from the cage formed by the second layer atoms. We obtain  $p_2 \approx 0.012$  and that the hydrogen atom may undergo multiple barrier crossings  $i$  before leaving the cage:  $i \approx -1/\ln(p_1(1-p_2)) \approx 9$ . In the limit of the opposite extreme, if the hydrogen atom is disaligned with respect to the cage window after the first exit event, the first

cage exit probability may decrease for the second and higher exit events  $i$ :  $p_1^{(i)} < p_1$ . In this case the number of the barrier crossings is smaller. Assuming that  $p_1^{(i)} \ll p_1$ , one obtains  $p_2 \approx 0.10$ , and the number of the barrier crossings is  $i \approx 1$ . The real situation depends on the degree of the hydrogen atom disalignment with respect to the window of the first cage. One has to note that if the proposed hypothesis is true, the cage reentry processes involving the higher number shells can be disregarded because of that low probability.

## COMPARISON WITH EARLIER RESULTS

Our results suggest that the prompt exit of the H atom from the stable  $\text{Ar}_{54}$  cage of is of low probability:  $0.1 \ll p_1 p_2 \ll 0.01$ . This is a new result since absolute values of exit probabilities are difficult to obtain experimentally from bulk matrix experiments,<sup>1-3</sup> where (i) the dissociation fragments appear in their ground state configurations, (ii) the homogeneous matrix is of an infinite size, and (iii) cage reentry processes cannot be considered explicitly. As to the cage reentry processes, they principally occur between the first and the second cage layers formed correspondingly by 12 and 42 argon atoms. In the framework of the proposed mechanism, the number of the barrier crossings  $i$  depends on the reaction exit alignment with respect to the cage windows, and can be  $1 \leq i \leq 9$ . If the disalignment is strong ( $i=1$ ), the prompt exit dominates; and if the disalignment is negligible ( $i=9$ ), the cage exit by the H atom is delayed. The experimental results on the  $\text{OH}^*(A)$  fluorescence yield can be successfully treated within the framework of the model discussed above [ $p_{12}(m)$  dependence, Fig. 5). Nevertheless, this model is oversimplified and the accurate quantitative balance between the direct and delayed exit channels must be found in future experiments.

The absolute photodissociation quantum yield of  $\text{H}_2\text{O} \xrightarrow{h\nu} \text{OH}(X) + \text{H}$  has been measured earlier for argon matrices at a temperature of 5 K by Schriever *et al.*<sup>23</sup> The excitation at 160 nm corresponds to the excess kinetic energy of the hydrogen atom of  $\sim 2.8$  eV. The cage exit probability  $\eta \approx 20\%$  estimated in Ref. 23 is higher than the value of  $p_{12} = 10\%$  obtained here. One of the factors, which can account for this discrepancy, is the difference of the cage geometries in solid argon and in  $\text{Ar}_m$  clusters. Second, this difference may originate from the fact that the quenching rate of  $\text{OH}^*(A)$  by H (used in this work as a measure of the caging) is higher than the recombination rate of the ground state  $\text{OH}(X)$  and H inside the argon cage (earlier experiments). This has been already discussed in the present paper. In other words, at the moment the quenching occurs the hydrogen atom still possesses a high amount of the kinetic energy and is capable of escaping the cage on a longer time scale. As we can see, this difference may be related to the delayed exit processes and be responsible for up to  $1 - (p_{12}/\eta) \approx 50\%$  of the overall cage exit efficiency.

We have already seen in recent experiments that the predissociation of water molecules inside  $\text{Ne}_N$  clusters is followed by a thermalization of the  $\text{OH}^*(A)$  product at the cluster temperature of  $\sim 10 \text{ K}$ .<sup>7</sup> Whereas a rapid thermalization of the H atom can also be expected, no cage-induced



quenching of the OH\*(A) fluorescence has been observed in that case. The neon cage appears to be highly transparent for rapid hydrogen atoms. The presence of the solute Ar<sub>m</sub> cluster changes the situation and only approximately two layers of argon atoms ( $m_2=54$ ) are sufficient to observe the effect. This result seems to contradict to earlier publications where the cage effect has been observed in both neon and argon matrices with almost equal exit barrier heights.<sup>1-3</sup> This difference in the influence of neon and argon cluster environments on the predissociation of a solute water molecule requires an explanation. In fact, the following solution may be proposed: the cage effect may be hindered and it concerns highly electronically excited fragments, which possess a low amount of kinetic energy. Because of that, the dissociation process is strongly modified inside large neon clusters, as it has been reported in Ref. 7. Below we explain this point.

In fact, with excitation at 17.7 eV, free water molecules dissociate mainly into H\*( $n=3$ ), OH\*(C), and H\*( $n=2$ ) excited fragments. Those threshold energies are 17.203, 16.054, and 15.303 eV, respectively.<sup>24</sup> Assuming as earlier that the kinetic energy of the hydrogen atom is one-half of the reaction exit energy ( $E_{\text{kin}} \leq 1.2$  eV), we can see that it is below the cage barrier energy ( $E_b \approx 1.7$  eV). In agreement with these estimations no fluorescence of the above-mentioned excited states has been observed in our previous cluster beam experiments.<sup>7</sup> We believe that this is a manifestation of the cage effect in Ne clusters and explains the marked difference between the spectroscopy of free water molecules and that solute in clusters. On the other hand, the energy relaxation to the OH\*(A) excited fragment supplies the kinetic energy of  $\sim 4.3$  eV to the hydrogen atom. Ne clusters are softer than the Ar clusters and the Ne cage heating in collisions with hydrogen atoms is more efficient (because of the smaller mass difference). For these reasons the cage-induced quenching may not be observed in this case.

## CONCLUSION

In summary, we report the first results of spectroscopic studies on the molecular H<sub>2</sub>O reactivity in rare-gas clusters with a shell-like structure. Using a "sequential pick-up" technique small H<sub>2</sub>O@Ar<sub>m</sub> clusters ( $m \leq 10^2$ ) were embedded inside cold Ne<sub>N</sub> host clusters ( $N \approx 7.5 \times 10^3$ ). The first shell of Ar atoms ( $m_1=12$ ) around the dissociated H<sub>2</sub>O molecule is highly transparent and does not cage the rapid hydrogen atom (dissociation yield is 90%). A strong decrease of the OH\*(A) fluorescence yield has been observed for  $m > m_1$ . The effect is attributed to the formation of the second shell of Ar atoms ( $m_2=54$ ) around the water molecule. An important role of the H<sub>2</sub>O@Ar<sub>32</sub> cluster produced by the closure of 20 triangular windows of the first shell of Ar<sub>12</sub>H<sub>2</sub>O clusters is suggested in the cage formation. For a perfect cage the deposition of roughly 54 atoms is needed. In H<sub>2</sub>O@Ar<sub>54</sub> clusters the photodissociation yield of OH\*(A)

is as low as 10%. Our first results confirm that the excited state dissociation is dominated by a prompt exit of the H atom from the first-shell cage ( $m_1=12$ ), although the delayed exit from the second-shell cage ( $m_2=54$ ) may contribute, too. The study of the cage effect of excited OH\*(A) fragments in doped H<sub>2</sub>O@Rg<sub>m</sub>@Ne<sub>N</sub> clusters as a function of size can shed more light on the dissociation dynamics. Because of the small cluster size and fast renewal, the dissociation fragments do not influence the process. Moreover, multiple barrier crossing by rapid hydrogen atoms and the cage reentry can be explicitly considered in such experiments.

## ACKNOWLEDGMENT

This work was supported by the IHP-Contract HPRI-CT-1999-00040 of the European Commission.

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