Dissociation and suppressed ionization of H_2O molecules embedded in He clusters: The role of the cluster as a cage

A. V. Kanaev[a)]
Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, C.N.R.S., Institut Galilée, Univerité Paris-Nord, 93430 Villetaneuse, France

L. Museur
Laboratoire Physique des Lasers, C.N.R.S., Institut Galilée, Univerité Paris-Nord, 93430 Villetaneuse, France

T. Laarmann
Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronen Synchrotron DESY, Hamburg, Notkestr. 85, 22603 Hamburg, Germany

S. Monticone
Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, C.N.R.S., Institut Galilée, Univerité Paris-Nord, 93430 Villetaneuse, France

M. C. Castex
Laboratoire Physique des Lasers, C.N.R.S., Institut Galilée, Univerité Paris-Nord, 93430 Villetaneuse, France

K. von Haeften and T. Möller
Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronen Synchrotron DESY, Hamburg, Notkestr. 85, 22603 Hamburg, Germany

(Received 30 May 2001; accepted 11 September 2001)

Electronic structure and energy transfer in H_2O doped He_N clusters ($N \approx 10^4$) is studied with photoexcitation in the spectral range of 140–40 nm (9–30 eV). The reaction dynamics is investigated by fluorescence of neutral OH* and H* and ionic H_2O^{+*} fragments. The rotational temperature of embedded water molecules has been estimated from the 124 nm line shape ($3pa_1\, C\,^1B_1 \leftarrow 1b_1\, \tilde{X}\,^1A_1$ transition). Two different temperatures ($T_1 \leqslant 5$ K and $T_2 \approx 30$ K) have been found. We propose that the lower temperature (T_1) is due to completely thermalized water molecules trapped inside helium clusters, while the warmer molecules (T_2) are formed if they are first captured by helium clusters but then leave the clusters again. Predissociation of H_2O with excitation below the ionization limit ($\lambda_{exc} > 100$ nm) is found to be unaffected by the cluster environment. On the other hand, the ionization ($\lambda_{exc} < 100$ nm) seems to be suppressed inside helium clusters in favor of the fragmentation into neutral products. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1415434]

INTRODUCTION

Photochemistry of free molecules differs considerably from that of molecules embedded in solids, where the matrix cage plays an important role. For example, an increase of the threshold energy, a decrease of the photodissosiation yield, and even new reaction channels (formation of precursor isomers) could be observed.[1] A better understanding of the reaction dynamics may be achieved by following its evolution in clusters of different sizes. Another interesting aspect could be to study the competition between matrix relaxation and energy transfer processes.

The experimental approach is greatly facilitated if the reaction fragments fluoresce. This is the case for the water molecule, which yields different excited fragments such as OH*, H*, and H_2O^{+*}.[2] These emission bands in the UV-visible spectral range appear to be helpful in studying the reaction dynamics. For example, exhaustive studies have been devoted in the past to the $\tilde{C}\,^1B_1$ state, which predissociates via the repulsive $\tilde{B}\,^1A_1$ potential into $OH^*(A)/OH(X) + H(1s)$ fragments (see in Ref. 3 and references therein). Additionally, weak fluorescence of the predissociating $\tilde{C}\,^1B_1$ state has been observed too, which allowed refinement of the analysis of the heterogeneous $\tilde{C}\,^1B_1 \rightarrow \tilde{B}\,^1A_1$ predissociation.[4,5] A sketch of the relevant potential curves of the water molecule is presented in Fig. 1.

We are interested in photodissociation dynamics of H_2O trapped inside Rg_N clusters (*Rg*—light rare gas atoms: He, Ne, Ar). The corresponding cluster studies have been, up to now, limited to mixed Ar–H_2O and net $(H_2O)_N$ clusters.[6,7] In the first cited work a multiple resonance IR+UV (pump)+UV (probe) method has been used to investigate the state-selected dynamics of van der Waals Ar–H_2O clusters. Fluorescence excitation measurements on $(H_2O)_N$ clusters

a)Author to whom correspondence should be addressed; Electronic mail: kanaev@limhp.univ-paris13.fr

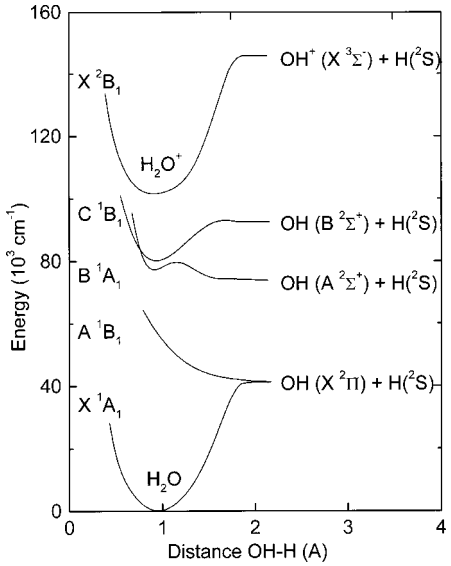

FIG. 1. A sketch of the relevant potential curves of the water molecule.

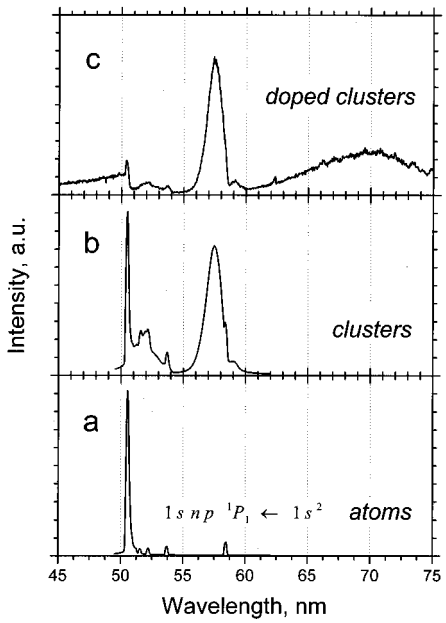

FIG. 2. VUV-UV fluorescence excitation spectra of: helium atomic beam (a), and He_N (b) and $He_N@H_2O$ (c) cluster beams ($N \approx 10^4$).

have been performed in the second cited work in the spectral region of 60–250 nm. At $\lambda_{exc}=140-100$ nm the fluorescence yield has been found to belong to the OH*(A) group ejected from surface states of water clusters. No other appreciable fluorescence has been observed in clusters with excitation out of this range. This is quite different from the case of free water molecules, where neutral OH*(A,C) and H*(ns), and ionized H_2O^{+*} species fluoresce under the excitation below 100 nm.[2] This important difference makes it possible to distinguish between clusters doped with single or several water molecules.

In the present communication we report first results on fluorescence photoexcitation of $He_N@H_2O$ clusters in the VUV spectral range of $\lambda_{exc}=140-40$ nm (9–30 eV). We have succeeded in exciting a single water molecule inside helium clusters or to excite helium clusters and to observe an energy transfer to the embedded water molecule.

EXPERIMENT

The measurements have been performed at the CLULU experimental station at HASYLAB/DESY.[8] Experiments with pure helium clusters have been previously described.[9,10] In the present experiments, helium clusters were prepared in a continuous free-jet expansion of pure helium gas at a stagnation pressure of 3000 mbar through an orifice-type nozzle of 40 μm diameter. The nozzle was mounted on a liquid He cryostat and then cooled down to temperatures of 10–12 K, which allows the preparation of large He_N clusters with $N \approx 10^4$.[10] $He_N@H_2O$ clusters were then prepared by a standard pick-up technique.[11] An effusive crossbeam of H_2O molecules intersected the cluster beam 5 mm downstream from the cryogenic nozzle. The doped clusters have been excited with synchrotron radiation (SR) and analyzed downstream of the intersection of the two beams. Tunable SR ($\Delta\lambda=0.05$ nm) in the spectral range of 100–140 nm (Al-grating) or 40–100 nm (Pt-grating) was focused on the cluster beam. Fluorescence excitation spectra (VUV-UV and UV-visible-IR) were recorded by two photomultiplier tubes with CsTe and GaAs(Cs) photocathodes, covering the wavelength range from 110–300 nm and 160–930 nm, respectively. UV-visible fluorescence spectra were collected over 600 s with liquid nitrogen cooled CCD camera (Princeton Instruments) installed behind a monochromator ($f=275$ mm, 150 or 1500 1/mm gratings, 250 μm slits, $\Delta\lambda=6$ and 0.6 nm, respectively). The background pressure (He) was kept below 10^{-3} mbar during experiments.

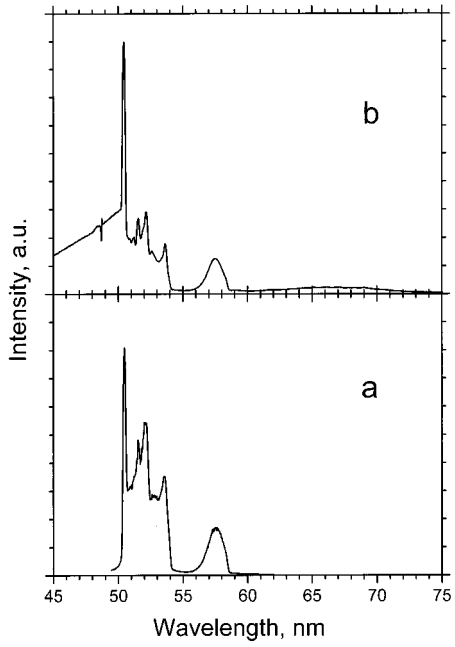

FIG. 3. UV-visible-IR fluorescence excitation spectra below 100 nm of: He_N clusters (a) and $He_N@He_2O$ clusters (b) ($N \approx 10^4$).

RESULTS AND DISCUSSION

Excitation spectra of the He atomic and cluster beams are shown in Figs. 2(a), 2(b) (VUV-UV fluorescence) and Fig. 3(a) (visible-IR fluorescence). The excitation spectrum of atoms (room temperature expansion) is dominated by the $1snp\,^1P_1 \leftarrow 1s^2$ transitions converging to the helium ionization limit at 24.59 eV. The width of these peaks is limited by the experimental spectral resolution. The sharp peak observed close to the ionization limit ($\sim$24.59 eV) is due to the congestion of many spectrally unresolved lines. In cluster beams the intensity of the atomic lines decreases and bands appear.[10] Relative intensities of the atomic lines and the bands change when clusters grow, which makes them useful for the mean size estimation.

Determination of a mean He_N cluster size N is a delicate procedure. In the experimental conditions where the stagnation pressure and temperature (p,T) correspond to Fig. 2(b), the expansion isentrope passes close to the critical point. Clusters either may grow by condensation from the gas or may be formed directly by fragmentation of the liquid. The last process results in much larger sizes than predicted by Hagena's scaling law.[12] For an evaluation of the mean cluster size we have compared our fluorescence excitation spectra with those earlier measured in He_N cluster beams produced in adiabatic expansion from the gas phase.[13] In the last case the scaling law is valid and can be used for a mean size determination according to a formula: $\langle N\rangle = 2.834 \cdot 10^5 (p^2 d^{1.7}/T^{5.07})$,[13] where p is in mbar, T in K, and d in μm are used. We obtain $N \approx 10^4$ atoms/cluster (or $R = \sqrt[3]{3N/4\pi\rho_{cl}} \approx 5.6$ nm, with $\rho_{cl} = 0.7\rho_{\text{liquid}}$ from Ref. 11). Our estimations show that clusters begin to condense from the gas phase at the nozzle temperature of $T_c \leqslant 25$ K. The decrease of the nozzle temperature may change the build-up mechanism and large helium clusters are produced at $T \leqslant 11$ K.

In the next section we discuss spectral measurements with initial excitation of both the water molecule and the helium cluster.

EXCITATION BELOW THE WATER IONIZATION LIMIT

First we consider the spectral range of $100 \leqslant \lambda_{\text{exc}} \leqslant 140$ nm, where helium clusters do not absorb. Water molecules absorb in this spectral region, predissociating into $OH(X) + H(1s)$ ($\sim$90%) and $OH^*(A) + H(1s)$ fragments ($\sim$10%). Fluorescence of $OH^*(A\,^2\Sigma^+ \rightarrow X\,^2\Pi)$ at $\sim$315 nm has been recorded. The excitation spectra of free water molecules and of $He_N@H_2O$ clusters are shown in Fig. 4. One has to note that free water molecules from the crossbeam partially penetrate into the excitation zone because of beam expansion, and this fluorescence could also be seen in our experiments. The helium beam was not switched off during the measurements, but its temperature has been kept above the condensation point T_c, which prevents cluster formation. The presence of the He atomic beam did not change the fluorescence intensity of free water molecules, which demonstrates that collisions with He atoms were negligible and/or they do not deviate considerably from the water crossbeam.

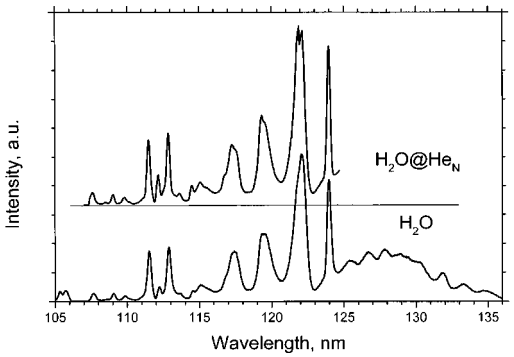

FIG. 4. UV fluorescence excitation spectra above 100 nm of $He_N@H_2O$ clusters ($N \approx 10^4$) and of free water molecules ($P_{\text{water}} = 33$ mbar in both cases).

Two spectra shown in Fig. 4 are generally similar, which indicate that the presence of the cluster environment does not change the water predissociation dynamics. They are dominated by the $3sa_1 \leftarrow 3a_1$, $np \leftarrow 1b_1$ and $nd \leftarrow 1b_1$ Rydberg transitions.[14] We have not observed in doped clusters neither a resonant VUV emission nor an intensified broad visible continuum related to the bound-free $\tilde{C}\,^1B_1 \rightarrow \tilde{B}\,^1A_1$ fluorescence of H_2O. This indicates that the surrounding He_N cluster atoms do not considerably prevent water dissociation and that the cage effect plays a minor role in helium clusters.

To be sure that water molecules are embedded inside helium clusters and that the observed fluorescence signal comes from doped clusters and not from free water molecules we have carefully examined the absorption line shape at $\sim$124 nm. It belongs to the $3pa_1\,\tilde{C}\,^1B_1 \leftarrow 1b_1\,\tilde{X}\,^1A_1$ transition and shows a partially resolved rotational structure, which is sensitive to the rotational level populations. The fluorescence product $OH^*(A)$ is not expected to be quenched under our experimental conditions ($p < 10^{-3}$ mbar). This allows us to obtain the rotational temperature of the water molecule from the excitation spectrum, if the Boltzman distribution in the ground state is assumed. The water molecule is an asymmetric rotor with rotational constants $(I_a > I_b > I_c)$ in the ground and excited states of $\tilde{X}(27.8778; 14.5092; 9.2869)$ cm^{-1} and of $\tilde{C}(25.67; 12.55; 8.55)$ cm^{-1}, correspondingly.[15] Additionally, it is known that rotational constants of light molecules are unaffected by the presence of liquid helium environment.[16] Taking into account the $\tilde{C} \leftarrow \tilde{X}$ electronic transition energy of $T_0 = 80\,624.7$ cm^{-1} we have numerically calculated the excitation spectra of the $OH^*(A \rightarrow X)$ fluorescence at different temperatures. The same formalism has been used to calculate the spectra of free and trapped molecules. The simulation includes the branching from $\tilde{C}$ to $\tilde{B}$ states $[\propto (0.35\langle J_a'^2\rangle/1 + 0.35\langle J_a'^2\rangle)$, where $\langle J_a'^2\rangle$ is the mean square momentum projection on the molecular axis $a]$ and that from $H_2O^*(\tilde{B}\,^1A_1)$ to $OH^*(A)[\propto \exp(-0.1\langle J_a'^2\rangle)]$ from Ref. 3, and an experimental spectral resolution of $\Delta\omega = 22$ cm^{-1}. The experimental and calculated spectra are shown in Fig. 5.

Two examples are presented. When the nozzle temperature is 300 K no helium clusters are produced. The numerical simulation with the rotational temperature of $T = 250$ K is in

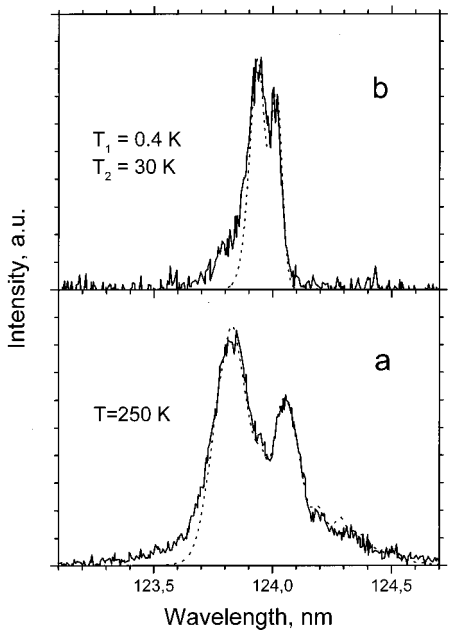

FIG. 5. Fluorescence excitation spectra near 124 nm: H_2O molecules from the crossbeam (a), and $He_N@H_2O$ clusters (b). Calculated excitation spectra of OH*(A) are given in (a) and (b) by the dotted line.

a good agreement with the experimental spectrum [Fig. 5(a)]. Under our experimental conditions the water cross-jet can be regarded as a laminar flow of molecules without considerable cooling due to the expansion, which explains this relatively high rotational temperature. When the nozzle is deeply cooled down ($\leqslant$12 K), large helium clusters are produced and can efficiently capture water molecules. Two fractional temperatures of $T_1 \leqslant 5$ K and $T_2 \approx 30$ K with almost equal relative populations were needed to describe the spectrum of doped clusters [Fig. 5(b)] at the nozzle temperature of 11–12 K (the calculated spectra were not sensitive to the rotational temperature below 5 K). No contribution from the room temperature fraction of water molecules has been observed. Because the helium cluster temperature is 0.4 K,[16] we assign this value to the lowest temperature $T_1 = 0.4$ K. Furthermore, cooling down the helium nozzle from room temperature and with an open water crossbeam, we saw no changes in the UV-fluorescence signal intensity until a nozzle temperature of $T^* \approx 30-40$ K was reached, where it began to grow. At $T_{\text{nozzle}} = 12$ K the fluorescence was almost four times higher in intensity than at room temperature. Taking into account that condensation of helium clusters begins at the temperature T_c (estimated above) which is close to the measured $T^*$of the signal build-up, we conclude that the fluorescence comes predominately from water molecules undergoing collisions with He clusters. While a temperature of $T_1 \leqslant 5$ K is reasonable, the temperature $T_2 \approx 30$ K is somewhat unexpected.

An unusual contribution from high rotational levels of the ground state water molecules $J_{Ka,Kc} = 1_{10}$ ($E_{10} = 42.4\,\text{cm}^{-1}$) and $J_{Ka,Kc} = 1_{11}$ ($E_{11} = 37.2\,\text{cm}^{-1}$), was earlier observed in IR absorption spectra in helium cluster experiments.[17] The authors have proposed that the signal may come from the partially relaxed $He_N@H_2O$ complexes at the time of the interaction with IR photons. Surprisingly, these energies E_{10} and E_{11} correspond to the fractional temperature $T_2 \approx 30$ K observed in the present experiments. We believe that T_2 characterizes free water molecules, which are cooled in collisions with clusters. This is due to the fact that the sticking coefficient (s) of the pick-up process is less than 1. A helium cluster is not rigid and an impinging molecule easily penetrates it on impact. As it has been discussed in Ref. 11, a fraction $f = 1 - s$ of molecules, which can amount up to $\sim$0.5 (SF_6), leaves the helium cluster after passing through it. This fraction acquires a temperature higher than the cluster temperature because of the small residence time inside.

The fact that two fractional temperatures can characterize H_2O molecules requires an explanation. The reason may be that collisions with clusters of the most abundant size ($N \approx 10^4$) do not result in the trapping (cooling until $T_1 = 30$ K), and only a second collision or collisions with large clusters in the tail of the size distribution traps water molecules ($T_2 = 0.4$ K). Another possibility may be an unusual bimodal cluster size distribution, different from the generally observed log-normal one. Such a bimodal size distribution indeed has been measured in helium clusters under supercritical source conditions:[16] large clusters (c_L) are formed directly from a fragmented liquid phase and small clusters (c_S) are condensed from gas atoms evaporated from large droplets.

We conclude that helium clusters should be sufficiently large to capture a hot water molecule and that a critical cluster size N^* exists for a given crossbeam condition. Large He_N with $N_1 \geqslant N^* > 10^4$ can trap water molecule and thermalize it at the cluster temperature of $T_1 \approx 0.4$ K. On the contrary, smaller clusters with $N_2 < N^*$ are transparent with respect to impinging water molecules and only slow down the rotational temperature to $T_2 \approx 30$ K.

These measurements of the H_2O excitation spectrum confirm that a considerable fraction of doped $He_N@H_2O$ clusters are prepared in our experiments.

EXCITATION ABOVE THE WATER IONIZATION LIMIT

In the spectral range below 100 nm both the helium cluster and H_2O molecules can absorb photons. Excitation of He_N results in discrete fluorescence of helium atoms and molecules in VUV and UV-IR spectral regions.[9] In large clusters, relaxation processes involving molecular states dominate. Following excitation of free H_2O molecules fluorescence of hydrogen atoms H*(ns),OH*(A,B,C) radicals, and $H_2O^{+*}(\tilde{A})$ ions is observed.[2]

VUV-UV fluorescence excitation spectra of doped clusters are given in Fig. 2(c). Comparison with the spectrum of a helium cluster [Fig. 2(b)] shows that helium bands, especially those in the 50–54 nm (23–25 eV) region, are strongly attenuated by the presence of water molecules inside helium clusters. On the other hand, water has little effect on helium bands in the visible-IR fluorescence excitation spectrum [shown in Fig. 3(a), 3(b)]. Up to now, no identification of these bands in large helium clusters has been given. Two continua related to the presence of water impurities are seen

in both VUV-UV and visible-IR spectra [Fig. 2(c) and Fig. 3(b)] at ~70 nm and $\lambda \leqslant 50$ nm. The band at 70 nm related to the $4sa_1,5sa_1 \leftarrow 1b_2$ electronic transitions in H_2O is already known,[2] while the second one below 50 nm with an asymmetric shape has not been reported before. It seems to fit to the helium photoionization continuum: with its maximum at the ionization threshold of $I(He^+)=24.59$ eV and gradually decreasing in intensity to shorter wavelengths.

Ionization of a helium cluster beam results in almost no fluorescence, although charge recombination $He_N^+ + e^-$ accompanied by a population of highly excited states is possible in the beam. In doped clusters an energy transfer can accompany electron exchange between the water molecule and the helium ion to water. Moreover, excitation of the helium cluster atoms is not possible because of the lack of energy: $I(He^+)-I(H_2O^+)=11.795(eV)<E(He_N^*)$. The visible-IR fluorescence [Fig. 3(b)] can be assigned to the $H_2O^{+*}(\tilde{A})$ and $OH^{+*}(A)$ excited ions produced in the following reactions:

$$He_N + h\nu \rightarrow He_N^+ + e^-,$$

$$He_N^+ + H_2O \rightarrow He_N + H_2O^{+*}(\tilde{A}),$$

$$He_N^+ + H_2O \rightarrow He_N + OH^{+*}(A) + H.$$

The ionization continuum of helium is also seen in VUV-UV fluorescence excitation spectra of doped clusters [Fig. 2(c)]. There are at least two possible explanations of this VUV-UV fluorescence:

(1) From energy considerations (thresholds of the $H_2O^+ + e^-$ and $OH^+ + H + e^-$ formation are correspondingly 12.615 eV and 18.05 eV) this emission may come from hypothetical highly excited states of ions H_2O^+ and OH^+. However, almost no fluorescence is expected under photoexcitation of free water molecules between 20 eV and 35 eV (62–35 nm),[18] which is in agreement with earlier experiments.[2]

(2) This may also be due to the $OH^*(C\,^2\Sigma^+)$ radical, whose emission in the VUV-UV spectral range at $170-190\,\text{nm}(C-X)$ and $225-260\,\text{nm}(C-A)$ falls into the sensitivity range of our detector. On the other hand, the yield of excited neutrals would require an increase of electron recombination in the doped clusters respectively to the pure helium clusters. More experiments are required to assign this band.

Finally, we compare fluorescence spectra of H_2O molecules and of $He_N@H_2O$ clusters. They are presented in Fig. 6 for excitation at 67.1 and 57.5 nm. These wavelengths correspond to particularities in the reaction exit channel. This spectral range is characterized by a competition between autoionization and the dissociation into neutrals. The yield of the $H_2O^{+*}(\tilde{A})$ ion is almost independent on the excitation wavelength; at the same time, formation of $H^*(n>1)$ is observed in the narrow spectral window (± 5 nm) in the vicinity of 65 nm.[2] Both characteristic emissions have been observed in our experiments: a broad band of H_2O^{+*} spans from 400 to 700 nm,[19] and the narrow H-Balmer β, γ, δ, ε lines appear at $\lambda^{-1}(\text{nm}) = 91.15 \cdot (1/2^2 - 1/n^2)^{-1}$.

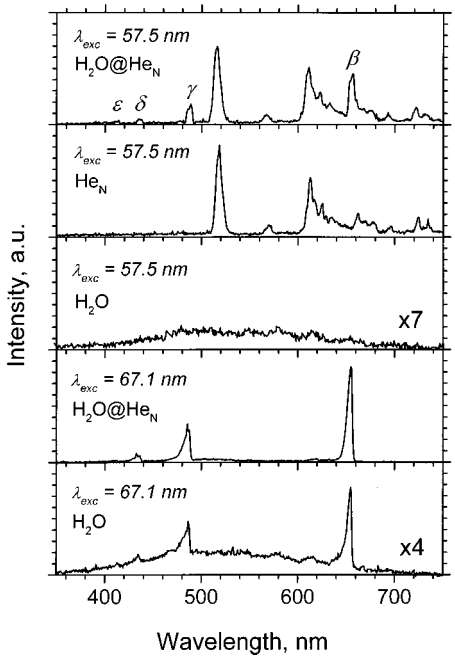

FIG. 6. Fluorescence spectra of H_2O molecular beam (a, c) and of $He_N@H_2O$(b,e) and He_N (d) clusters with excitation at 67.1 nm (a, b) and 57.5 (c–e). The spectra are normalized to the SR intensity. H-Balmer β, γ, δ, ε lines are indicated in the upper spectrum. In all these experiments the helium stagnation pressure is $P_{He}=3000$ mbar, the nozzle temperature varies from 300 K (atoms) to 12 K (clusters).

The fluorescence assigned to H_2O^{+*} is clearly presented in all recorded spectra with the initial energy deposition onto the H_2O molecule [Fig. 6(a)], which is in agreement with earlier observations.[2] $H^*(n>1)$ emission lines appear at $\lambda_{exc}=67.1$ nm and disappear at more short-wave excitation. On the other hand, H-Balmer lines are strongly intensified (on the background of the broad continuum of excited water ions) in $He_N@H_2O$ clusters [see Fig. 6(b). Moreover, the residual H_2O^{+*} fluorescence seems to come from the small fraction of free water molecules, which are always present as discussed above. This finding seems to indicate the suppression of the ionization channel in helium clusters in favor of the predissociation into electronically excited neutrals.

Another peculiarity can be observed if we deposit energy into the helium clusters. In this case the energy transfer to the embedded molecule is expected if the molecular states are located close to the cluster absorption bands (excited orbital overlap). In present experiments $\lambda_{exc}=57.5$ nm fits into the broad absorption band inherent to large He_N clusters. Excitation of pure He_N clusters result in a rich visible-IR fluorescence spectrum [Fig. 6(d)] with the strongest bands recently assigned to the $E\,^1\Pi_g \rightarrow A\,^1\Sigma_u^+(\sim 510\,\text{nm})$, $F\,^1\Sigma,\Pi,\Delta_u \rightarrow B\,^1\Pi_g$ (~610–630 nm) and $D\,^1\Sigma_u^+ \rightarrow B\,^1\Pi_g$ (~660 nm) transitions of molecular helium dimers.[10] Direct excitation of the H_2O molecule at 57.5 nm is followed by the broadband $\tilde{A}\,^2A_1 \rightarrow \tilde{X}\,^2B_1$ water ion emission [Fig. 6(c)]. But surprisingly excitation of $He_N@H_2O$ doped clusters at the same wavelength shows intense H-Balmer lines [Fig. 6(e)], which is inherent to the neutral decay channel. This confirms the above proposed hypothesis that the ionization channel is suppressed.

The last remark concerns the reason for preionization suppression. Is it an effect of the cluster environment or of the temperature? The case of temperature is easier to understand. Actually, the temperature influences the rotational level population of a water molecule. If the excited Rydberg state is bound, it may be *J*-coupled to another state undergoing a direct dissociation (as it has been disused before for the $\tilde{C}\,^1B_1$ state) or else to ionization. To understand this point we consider the fluorescence excitation spectra in the range of ~70 nm (18 eV) and the corresponding fluorescence spectra. The excitation spectra in the 16–19 eV range consist of a broad continuum superimposed with a weak structure. This broad excitation continuum has been earlier assigned to the $nsa_1 \leftarrow 1b_2$ ($n=4,5$) transitions to the repulsive Rydberg states,[2] which undergo a direct dissociation into $H^* + OH$ (visible fluorescence) or $H + OH^*$ (VUV-UV fluorescence). The structure, on the other hand, belongs to the excitation of bound Rydberg states. It dominates the absorption spectra and yields water ions in the ground state. Our results show that the structure observed in the fluorescence excitation spectra [Figs. 2(c) and 3(b)] is too weak to account for the almost equal intensities of the H^* and H_2O^{+*} fluorescence (see in Fig. 6). We assign both of these products to the unstructured continuum and we conclude that they are produced via direct dissociation/ionization processes. In this case both decay channels (into neutrals and excited ions) involve repulsive Rydberg states and cannot be *J*- and temperature-dependent. For the moment we have no available experimental data to discuss the cluster effect on the yield of ground state ions. Therefore, the dissociation channel into excited ions limits our interpretation. We conclude that the observed effect of the preionization suppression is due to the He-cluster environment. In other words, the He atoms can suppress the ionization, that means the escape of an electron, while the dissociation of the H_2O is not hindered. We believe that this unusual phenomenon can be understood on the basis that He is a very soft material in terms of mechanical properties, while on the other hand the atoms have a strong repulsive interaction with electrons.

CONCLUSION

In conclusion, electronic structure and energy transfer in H_2O doped He_N-clusters ($N \approx 10^4$) is studied with synchrotron radiation excitation in the range of 9–30 eV. The rotational temperature of water molecules has been estimated from the 124 nm line shape. Two different temperatures of water molecules, <5 K (which we assign to 0.4 K) and 30 K, have been found in the H_2O doped clusters. The low temperature $T_1 \leqslant 5$ K is due to H_2O embedded in He_N, while we propose that warmer molecules $T_2 \approx 30$ K are formed if H_2O are first captured by the clusters and then leave the clusters. Excitation of clusters above the helium ionization limit results in intense VUV-UV and visible-IR fluorescence, tentatively assigned to ionic and neutral water fragments. Simultaneous charge and energy transfer processes may be responsible for it. In contrast to the free water molecule, the yield of H_2O^{+*} excited ions is suppressed in He_N-clusters, and the main excited products are $H^*(ns)$ atoms.

ACKNOWLEDGMENT

Financial support of Project No. II-98-026EC by the EU program is kindly acknowledged.

[1] *Chemistry and Physics of Matrix-Isolated Species*, edited by L. Andrews and M. Moskovits (Elsevier, Amsterdam, 1989).
[2] O. Dutuit, A. Tabche-Fouhaile, I. Nenner, H. Frohlich, and P. M. Guyon, J. Chem. Phys. **83**, 584 (1985).
[3] A. Hodgson, J. P. Simons, M. N. R. Ashfold, J. M. Bayley, and R. N. Dixon, Mol. Phys. **54**, 351 (1985).
[4] V. Engel, G. Meijer, A. Bath, P. Andresen, and R. Schinke, J. Chem. Phys. **87**, 4310 (1987).
[5] M. P. Docker, A. Hodgson, and J. P. Simons, Mol. Phys. **57**, 129 (1986).
[6] D. F. Plusquellic, O. Votava, and D. J. Nesbitt, J. Chem. Phys. **101**, 6356 (1994).
[7] M. Ahmed, C. J. Apps, C. Hughes, and J. C. Whitehead, J. Phys. Chem. **98**, 12530 (1994).
[8] R. Karnbach, M. Joppien, J. Stapelfeldt, J. Wörmer, and T. Möller, Rev. Sci. Instrum. **64**, 2838 (1993).
[9] K. Von Haeften, A. R. B. de Castro, M. Joppien, L. Moussavizadeh, R. von Pietrovski, and T. Möller, Phys. Rev. Lett. **78**, 4371 (1997).
[10] M. Joppien, R. Karnbach, and T. Möller, Phys. Rev. Lett. **71**, 2654 (1993).
[11] M. Lewerenz, B. Schilling, and J. P. Toennies, J. Chem. Phys. **102**, 8191 (1995).
[12] O. F. Hagena, Phys. Fluids **17**, 894 (1974); Surf. Sci. **106**, 101 (1981); Z. Phys. D: At., Mol. Clusters **4**, 291 (1987).
[13] K. von Haeften, Ph.D. thesis, University of Hamburg, Germany (1999).
[14] P. Gürtler, V. Saile, and E. E. Koch, Chem. Phys. Lett. **51**, 386 (1977).
[15] J. W. C. Johns, Can. J. Phys. **41**, 209 (1963); *ibid.* **49**, 944 (1971); M. N. R. Ashfold, J. M. Bayley, and R. N. Dixon, Chem. Phys. **84**, 35 (1984).
[16] J. P. Toennies and A. F. Vilesov, Annu. Rev. Phys. Chem. **49**, 1 (1998).
[17] R. Fröchtenicht, M. Kaloudis, M. Koch, and F. Huisken, J. Chem. Phys. **105**, 6128 (1996).
[18] G. H. F. Diercksen, W. P. Kraemer, T. N. Rescigno, C. F. Bender, B. V. McKoy, S. R. Langhoff, and P. W. Langhoff, J. Chem. Phys. **76**, 1043 (1982).
[19] H. Lew, Can. J. Phys. **54**, 2028 (1976).