CLUSTERS

Ionic chromophores Xe_p^+ ($p \leq 4$) in multishell rare-gas clusters $\text{Xe}_m(\text{NF}_3)_k\text{Ne}_{7500}$ ($m, k \leq 100$) studied with fluorescence spectroscopyA. Kanaev^{a)}*Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, C.N.R.S., Institut Galilée, Université Paris-Nord, Villetaneuse 93430, France*

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We have studied fluorescence spectra of small Xe_m and $\text{Xe}_m(\text{NF}_3)_k$ clusters ($m, k \leq 10^2$) embedded in large host Ne_{7500} clusters, excited with SR excitation in the VUV spectral region above the $\text{Xe}^+(^2P_{1/2})$ atomic limit. The IR emission bands due to ionic chromophores Xe_p^+ ($p=2,3,4$) as well as UV ($B-X$) and visible ($C-A$) bands due to desorbed Xe^+F^- excimer molecules have been observed. The triatomic Xe_2F excimer emission has only been observed under low-energy excitation close to the lowest xenon exciton absorption band. A competition between ionic and charge-transfer reaction channels is followed as a function of the cluster sizes m and k . © 2006 American Institute of Physics. [DOI: [10.1063/1.2389018](https://doi.org/10.1063/1.2389018)]

INTRODUCTION

There is a well-known fundamental difference between neutral and ionized rare-gas clusters. The neutral clusters are bound by the weak van der Waals pairwise interaction, while polarized forces induced by the ionized core strongly increase the cluster solidity. This has a consequence on the atomic desorption process, accompanied by the cluster cooling. Another point of difference is that while in the neutral cluster the representative “building block” is the rare-gas dimer, in the ionic cluster a larger unit can be produced due to a charge delocalization process. For example, Xe_p^- ($p=2-4$) units have been observed experimentally from analysis of absorption and fluorescence spectra¹⁻³ and theoretically predicted in free xenon clusters.⁴⁻⁶ The IR fluorescence of self-trapped holes in rare-gas solids has been studied recently in Refs. 7–9. There has been steady interest in rare-gas ionic clusters on account of their role as model systems for understanding charge-transfer and solvation processes in bulk media. The use of clusters offers the possibility of studying the evolution from the atomic limit towards the bulk material as a function of cluster size, which is an important issue of the fundamental physics. Moreover, because of the large percentage of surface atoms, small clusters are extremely interesting objects for interface studies.

Recently, the so-called “pickup” technique has allowed the growth of small guest rare-gas clusters inside large host rare-gas clusters, and the investigation of embedded clusters

with a shell-like geometric structure.^{10,11} This method has the advantage of controlling the temperature, the surface or bulk localization and the size of the guest cluster, as well as the size of the host cluster. Neon is a good solvent system for such experiments for several reasons: $\text{Ne}_{N>1000}$ clusters are soft enough and easily pick up atoms or molecules. They efficiently thermalize the dopant molecules at a characteristic cluster temperature of ~ 10 K.¹² Moreover, the surrounding neon cluster atoms hardly perturb the energy levels of embedded molecules. Since neon clusters are transparent within the VUV spectral range, they are well suited to the study of electronic properties of molecules and heavier rare-gas clusters made of Ar, Kr, and Xe atoms. Recently, investigation of Ar_mNe_N (Ref. 11), Kr_mNe_N (Ref. 13), and Xe_mRg_N clusters ($\text{Rg}=\text{He, Ne}$)¹⁴ ($m \leq 100 \leq N \approx 7500$) have given insight into the tightly bound bulk interface excitons in small rare-gas clusters. It has been shown that a large penetration depth of the interface exciton into the bulk of the embedded cluster, induced by the surrounding neon matrix, prohibits a formation of the electronic structure inherent to the corresponding bulk solids.

However, the solvation effect on ionic cations Xe_p^+ ($p=2-4$) inside multishell clusters has never been the subject of experimental study. In that way one could inspect for influence of the surrounding medium on the ionization, charge delocalization, and charge transfer processes.

In the present paper we report on the spectroscopy of small ionized clusters ($m \leq 100$) embedded inside large

FIG. 1. Schematic potential curves of the relevant states related to $5p^5 2P_{1/2}$ and $5p^5 2P_{3/2}$ atomic xenon ion limits.

(7500) Ne clusters. Using the multiple cross-beam technique, we have also prepared multishell $\text{Xe}_m(\text{NF}_3)_k\text{Ne}_N$ clusters ($m, k \leq 100$), where a competition between the charge delocalization onto the Xe_p^- ($p=2-4$) units and charge transfer reaction leading to the rare-gas halide excimer formation is expected. The experiments were carried out using the energy-resolved fluorescence technique. As in our previous studies, we make use of the IR fluorescence of ionic chromophores^{2,3} on transitions down to the lowest bound and first excited unbound states (Fig. 1). We have followed the evolution of the IR band shape and relative IR and UV band intensities as a function of the number of picked-up Xe atoms and NF_3 molecules. From a detailed analysis of the experimental data we gain new information on the charge delocalization in the solvated xenon clusters.

EXPERIMENT

The measurements have been performed at the CLULU experimental station¹⁵ at the DESY synchrotron. Neon clusters were prepared in a supersonic expansion of the gas neon at 200 mbar pressure through a conical nozzle (200 μm , $2\theta=4^\circ$) cooled down to 30 K. The average cluster size $7500 \approx N$ was determined using well-known scaling laws according to the formula:^{16,17} $N=33(\Gamma^*/1000)^{2.35}$, with $\Gamma^*=K_{\text{ch}}pd_{\text{eq}}^{0.85}/T^{2.2875}$, $K_{\text{ch}}(\text{Ne})=185$, and p in mbar, T in K, and d in μm are used. The width of the cluster size distribution (FWHM) is $\Delta N \approx N$. Using a successive “pickup” technique, these large neon clusters were doped first with NF_3 molecules and second with Xe atoms from two cross jets. The embedded clusters are cold: their temperature of 10 K is defined by that of the neon host cluster.¹⁸ The Poisson statistic determines the average number of picked-up molecules (k) and atoms (m). The mean sizes of the embedded Xe_m and $(\text{NF}_3)_k$ clusters have been estimated by measuring the VUV-fluorescence excitation spectra of the Ar_m clusters inside large neon clusters in the range of 12.4 eV, prepared by expanding the argon gas correspondingly through xenon (m) and nitrogen trifluoride (k) nozzles, as is explained in Ref. 13. Laarmann *et al.*¹¹ have shown that the absorption line shape of tightly bound excitons in Ar_m clusters changes with their size m according to the Frenkel exciton model. By comparing the experimental spectra line shapes with those from

Ref. 11, one obtains a relation between the cross-jet pressure and the average number of embedded atoms. Since the probability for a Ne cluster to pick up atoms is dependent mainly on the Ne cluster size and the average cross-jet particle density along the beam axes, the calibration is also valid in the case of Xe and NF_3 doping.

Monochromatized synchrotron radiation ($\Delta\lambda=0.25$ nm bandpass) in the spectral range of 100–140 nm (Al grating) or 40–100 nm (Pt grating) was focused on a doped multishell $\text{Xe}_m\text{Ne}_{7500}$ and $\text{Xe}_m(\text{NF}_3)_k\text{Ne}_{7500}$ cluster beam 10 mm downstream from the nozzle. Generally, we excited the cluster beam in the lowest excitonic band of the host neon clusters at 17.7 eV (70 nm). After the excitation the energy is efficiently transferred onto an impurity center, a small embedded xenon cluster. Fluorescence excitation spectra in the VUV-UV ($\lambda \leq 300$ nm) and in the UV-visible-IR (200 nm $\leq \lambda \leq 900$ nm) were recorded by two photomultipliers with CsI and GaAs(Cs) photocathodes, respectively. The background pressure was kept below 10^{-3} mbar during the experiments.

Before presenting experimental results, let us remark on the cluster composition. The pickup of atoms and molecules by large Ne_{7500} clusters results in a release of energy. Neon atoms are weakly bound and evaporate from the Xe_mNe_N cluster by heating. In fact, the binding energies per atom of rare-gas neon and xenon solids are 26.5 meV and 172.3 meV.¹⁹ Therefore, doping may decrease the initial cluster size by ~ 6.5 Ne atoms per adsorbed Xe atom if the kinetic energy of the free atoms is neglected. Therefore, doping by $m \leq 10^2$ xenon atoms does not change the neon cluster size considerably. It can be shown that the same conclusion is valid for the doping by a small number of NF_3 molecules. The conclusion that host neon clusters with $N=7500$ are stable under the experimental doping conditions ($m, k \leq 100$) has been confirmed by measurements of the luminescence excitation spectra in the spectral range of neon absorption, $h \approx 17.7$ eV.

RESULTS AND DISCUSSION

The fluorescence spectra of xenon clusters excited above the atomic ionization limit originate from molecular states related to the $5p^5 2P_{1/2} \rightarrow 5p^5 2P_{3/2}$ transitions in ionic chromophores Xe_p^- ($p=2-4$).^{2,3} The relevant potentials of the two-atomic ions are schematized in Fig. 1. Because of a low barrier between the trimer and tetramer ionic cores, the corresponding transitions are not resolved in relatively hot ($T=79 \pm 8$ K)¹⁸ free xenon clusters. Experimental results on the fluorescence of Xe_N^+ ($N \leq 2 \times 10^4$) have been reported in Refs. 2 and 3. However, Laarmann *et al.*³ have remarked that because of two main radiation channels associated with $2(1/2)_g \rightarrow 1(1/2)_u$ and $2(1/2)_u \rightarrow 1(1/2)_g$ transitions and three possible ion cores (Xe_2^+ , Xe_3^+ , and Xe_4^+), six fluorescence bands can be resolved in fluorescence spectra at sufficiently low temperatures. These new spectral bands have been demonstrated in small, Xe_{40} clusters embedded in large neon clusters using the pickup method:³ the temperature of such cluster is defined by the host neon temperature, which is about 10 K.¹⁸ The size dependence of the IR fluorescence spectra of these embedded Xe_m clusters ($m \leq 10^2$) is studied in the present work.

FIG. 2. Fluorescence spectra of $\text{Xe}_m\text{Ne}_{7500}$ excited at 17.7 eV.

$\text{Xe}_m\text{Ne}_{7500}$ clusters

The IR fluorescence spectra of $\text{Xe}_m\text{Ne}_{7500}$ clusters excited at $\lambda_{\text{exc}}=70$ nm are presented in Fig. 2. The multi-peak Gaussian fit has been used to resolve the contributions of the six bands labeled by *a*, *b*, *c*, *d*, *e*₁, and *e*₂. They have been assigned by Laarmann *et al.*³ to radiative transitions in the ionic dimer (subbands *e*₁, *e*₂), trimer (*b*, *d*) and tetramer (*a*, *c*) cores inside xenon clusters.

According to the scheme in Fig. 1, the bands *e*₁, *b*, and *a* originate from the higher-positioned (more shallow) electronic *g* state, whereas the bands *e*₂, *c*, and *d* originate from the more strongly bound *u* state: the corresponding dimer ion states are $2(1/2)g$ and $2(1/2)u$ (Ref. 20). As one can see from this figure, bands *d* and *c* dominate the fluorescence of very small xenon clusters, $m \leq 5$. Bands *b* and *a* appear at $m \geq 30$ and became stronger in clusters larger than $m \geq 50$. With further increase of the size, $m \geq 70$, the spectral shape of the IR fluorescence remains almost unchanged. Their integrated relative intensities issued from the multi-peak Gaussian fit are shown in Fig. 3. As their contribution is small, the dimer bands are not shown in this figure.

The different state origin of the two groups of bands *d/c* and *b/a* is evidenced from fluorescence decay measurements, presented in Fig. 4. All these curves can be well approximated by two-exponent fits, resulting in excited state lifetimes of $t_1=1.5 \mu\text{s}$ and $t_2=150$ ns. On the other hand, the corresponding decay amplitudes *A*₁ and *A*₂ vary with the cluster size *m*: only the long-lived decay component is present at $m \leq 20$, while the short-lived decay component intensifies in larger xenon clusters (see Fig. 4a). Its relative intensity as a function of the size *m* is shown in Fig. 4b. A

FIG. 3. Relative intensities of the IR emission bands due to ionic chromophores ($p=2,3,4$).

correlation between relative intensity of the bands *b/a* and short-lived fluorescence decay allows their straightforward identification. We assign the longer lifetime of $t_1=1.5 \mu\text{s}$ to the fluorescence bands *d/c* appearing in small xenon clusters, and the shorter lifetime of $t_2=150$ ns to the fluorescence bands *b/a* appearing in the larger clusters. This assignment is in general agreement with the dimer ion state structure dis-

FIG. 4. IR fluorescence decay (a) and the fast component relative intensity in $\text{Xe}_m\text{Ne}_{7500}$ clusters as a function of the size *m* ($E_{\text{exc}}=17.7$ eV).

cussed in the theoretical paper by Wadt.²¹ Similar repartitioning of the excited electronic states is expected in xenon ion trimers and tetramers and can explain our finding.

In contrast to the ionic chromophore subbands, relative fluorescence intensity originated from different chromophores Xe_4^+ and Xe_3^+ does almost not change in the cluster size range $m \leq 10^2$. This result follows directly from Fig. 3 if we sum, respectively, the band intensities $d+b$ and $c+a$: each chromophore accounts for about 50% of the IR intensity. Our measurements confirm the charge localization on ionic trimer and tetramer cores in small xenon clusters. Recently, Laarmann *et al.*³ have shown that in free Xe_N clusters the charge is preferentially repartitioned on Xe_4^+ and Xe_3^+ cores when $N \leq 200$, and localized on Xe_2^+ only when $N \geq 400$. This explains in particular why only the dimer ionic core is observed in the bulk solids in both absorption²¹ and fluorescence.²² Theoretical and experimental studies by Gascón *et al.*²³ have shown that tetramer and trimer cores coexist in small xenon clusters $N \leq 30$, the relative population of which undergoes oscillatory variation with size. The interconversion of these two isomers was also suggested at temperatures of ~ 60 K. The temperature of our embedded Xe_m clusters is considerably lower, and the interconversion may be prohibited. This may in particular explain the fact that the subband intensity variation within each isomer with size is not accompanied by an intensity variation between the two isomers. The last is determined by the energy-relaxation dynamics and not by the thermodynamic equilibrium between the relaxed ionic cores. The isolation of Xe_4^+ and Xe_3^+ ionic isomers at the low temperature of 10 K makes their population independent on cluster size, in contrast to what is observed in hotter free xenon clusters ($T=79$ K).³ We also remark that clusters with preferential isomer population cannot be resolved in our experiments because of a broad cluster size distribution: Poisson distribution of the embedded xenon clusters is convoluted with that lognormal of the host neon clusters, issued of the nozzle expansion, resulting in a width somewhat larger than $\sqrt{m}$.

Our results show the importance of the small cluster environment. Indeed, comparing with free xenon clusters Xe_4^+ and Xe_3^+ isomers contribute in fluorescence spectra with almost equal weightings. Moreover, the upper state population within each ionic core sensitively depends on the cluster size m shown in Fig. 3. This cannot be an effect of the cluster temperature, which is fixed at 10 K. Moreover, the temperature would be expected to decrease with size m , leading to population of the deeper $2(1/2)u$ excited state. As a consequence, the intensity of the $2(1/2)u \rightarrow 1(1/2)g$ transition would increase, and that does not happen. A preferential population of the lower excited state related to $2(1/2)g$ of Xe_2^+ in small clusters may be explained by an effect of the interface formation similar to that discussed in Refs. 13 and 14 or by the embedded atoms compression 14. According to Refs. 13 and 14, exciton formation in embedded rare-gas clusters depends on the electron affinity. In the particular case of Xe_mNe_N clusters a perturbation of the Xe–Ne interfacial layer is strong, and the bulk exciton of Xe_m only appears at sufficiently large $m \geq 50$. The second case seems less probable, since an effect of compression was observed only in small neon clusters, about $40 < N < 90$.¹⁴ However, the

FIG. 5. Fluorescence spectra after excitation of multispherical $\text{Xe}_{50}(\text{NF}_3)_k\text{Ne}_{7500}$ clusters at 17.7 eV.

case of embedded ionized cluster atoms is different from that of neutral isolated xenon atoms studied in Ref. 14, and further studies are required.

$\text{Xe}_m(\text{NF}_3)_k\text{Ne}_{7500}$ clusters

A competition between the ionization and charge-transfer reaction can be studied in multispherical $\text{Xe}_m(\text{NF}_3)_k\text{Ne}_{7500}$ clusters. In fact, excitation of the neon cluster activates two reaction mechanisms. (1) Ionization of the internal Xe_m cluster takes place following the energy transfer process. The electron leaves the cluster, whereas the hole is localized on excited chromophores Xe_p^{+*} ($p=2,3,4$) that give rise to the characteristic IR fluorescence bands shown in Fig. 2. (2) The energy transferred from neon cluster triggers charge-transfer reactions resulting in excimer creation: XeF or Xe_2F . In bulk xenon XeF relaxes to Xe_2F , and therefore its observation would be an indication of the excited-state desorption process.^{24,25}

The fluorescence spectra recorded after excitation of multispherical $\text{Xe}_{50}(\text{NF}_3)_k\text{Ne}_{7500}$ clusters at 17.7 eV are shown in Fig. 5 for different sizes k . At $k=0$ only IR fluorescence of Xe_p^{+*} has been observed. However, with an increase of NF_3 doping the IR band shape changes. It seems to follow the opposite tendency to that earlier observed in the two-component $\text{Xe}_m\text{Ne}_{7500}$ clusters: with increasing k the intensity of the subbands a and b decreases relative to that of subbands c and d . Moreover, at $k \leq 30$ new XeF excimer emission bands appear: $B-X$ in the UV at 3.5 eV, and $C-A$ in the visible at 2.5 eV.

The observed excimer bands apparently belong to the desorbed excited fragments illustrating the importance of the excited-state stimulated desorption processes in cryogenic solids. The relatively weak spectral features at 3.65 eV and 3.15 eV do not correspond to the known NF₃ fluorescence products.²⁶ They indicate that a part of the expelled excited products is hot and possess significant vibrational excitation: correspondingly, $v'=2-3$ (*B* state) and $v'=6\pm 1$ (*C* state). The XeF excimers escape through the outer shell of Ne₇₅₀₀ cluster. However, according to Ref. 12 vibrational cooling of OF fragments can be particularly inefficient in neon clusters in view of the low Debye energy (6.4 meV) compared to the vibrational quantum (e.g., in the *C* state $\omega_e=346\text{ cm}^{-1}$). The main fluorescent bands however are narrower than those observed earlier in pure xenon clusters.^{24,25} This may be an effect of rotational cooling by the neon matrix.

The mechanism of the excimer state creation (channel (2)) may proceed as follows:

First, the ionization of the internal Xe_{*m*} cluster takes place. In Xe_{*m*}Ne_{*N*} clusters this results in Xe_{*p*}⁺* center creation (channel (1)). However in Xe_{*m*}(NF₃)_{*k*}Ne_{*N*} the electron may not escape and can be trapped by the first-shell cluster (NF₃)_{*k*}. This happens if the size *k* is above some critical value $k^* \approx 30$. The NF₃ molecule accommodating excess electron subjects to the dissociative attachment. However, it can be stabilized in clusters as NF₃[−] anion and larger cluster ion units (NF₃)_{*L*>1}[−] (Ref. 24). In such a case the Coulomb attraction between the localized hole Xe_{*p*}⁺* and (NF₃)_{*k*}[−] or lighter anionic fragment can result in XeF excimer formation. The excess energy of the electronically excited center is apparently so strong that the expulsion proceeds before the relaxation into Xe₂F takes place. Additionally, the binding energy of the Xe_{*p*}⁺* core is much smaller than that of the ground-state ion Xe_{*p*}⁺. This may prohibit Xe₂F formation from xenon core states related to the 5*p*⁵ 2*P*_{1/2} atomic limit. In fact, no signature of the of this trimer rare-gas halide emission has been observed with 17.7 eV excitation.

On the other hand, if the excitation energy is lowered below the onset of ionization, the broadband intracluster emission of Xe₂F appears, as shown in Fig. 6. It is centered at 1.48 eV (838 nm), which is lower than that reported in bulk solid Xe matrixes, 1.60 eV (775 nm),²⁵ and in small free xenon clusters, 1.54 eV (805 nm).²² The spectral width of this emission $\Delta E_{FWHM}=0.27\text{ eV}$ corresponds to that observed in solids and somewhat smaller than in free clusters (0.35 eV). A small red shift in the embedded xenon clusters and a narrower bandwidth may be due to the neon cluster compression. This issue requires verification.

The dependence of the Xe_{*p*}⁺* fluorescence intensity (*I*_{IR}) on the size *k* of the first-shell cluster (NF₃)_{*k*} is shown in Fig. 7. In this series the integral IR fluorescence of the excited chromophores (*p*=2,3,4) was recorded through the RG610 filter (red cut-off at $\lambda > 600\text{ nm}$), which allowed higher-sensitivity measurements in a large size domain. The observed semilogarithmic plot is characterized by two kinetics domains separated by a crossover region at $30 \leq k < 60$. This

FIG. 6. IR fluorescence spectra after excitation of multishell Xe50(NF₃)_{*k*}Ne₇₅₀₀ clusters at 8.551 eV for *k*=50 (a), 25 (b), 14 (c).

transient region apparently relates to an increase of the electron trapping rate by the NF₃ cluster after the critical size of $k \geq k^* = 30$. The fact that the critical size k^* does not depend appreciably on the size of the embedded xenon cluster *m* (see Fig. 7) indicates that the electron exit from the neon cluster may not be a direct but rather a delayed process: in case of the direct exit the electron trapping probability would be a function of the NF₃ shell width ($k^{2/3}$) and not of the size *k*. An increase of the neutral reaction channel relative to molecular ionization has recently been observed in large neon clusters doped with water molecules.¹²

Let us make an additional remark concerning the excited-state reactivity of Xe_{*p*}⁺*. The plot of ln(*I*_{IR}) versus cluster size *k* suggests an excited-states quenching process. Moreover, as we can see in Fig. 5, the spectral line shape of the IR band changes with growing *k*: subbands *b* and *a* weaken faster, and the subbands *d* and *c* dominate the fluorescence spectra at large *k*. As our results show, the short-lived excited state 2(1/2)*g* is at the origin of the subbands *b* and *a*, while the long-lived excited state 2(1/2)*u* is at the origin of the subbands *d* and *c*. This indicates a much higher reactivity of the 2(1/2)*g* state in comparison to the 2(1/2)*u* one. This may be related to its larger equilibrium distance, which enables more efficient potential curve-crossing be-

FIG. 7. Relative intensity of the IR fluorescence of Xe_{*m*}(NF₃)_{*k*}Ne₇₅₀₀ clusters as a function of the size *k*, $E_{\text{exc}}=17.7\text{ eV}$.

tween the chromophore and the anion. Indeed, the more localized state $2(1/2)u$ may be centered inside the embedded clusters while the more delocalized² one $2(1/2)g$ is readily set in contact with the negatively charged halogen donor.

CONCLUSION

The present spectroscopic study of multishell Xe_m and $\text{Xe}_m(\text{NF}_3)_k$ clusters ($m, k \leq 10^2$) embedded in large host Ne_{7500} clusters clears up the hole localization process in small xenon clusters and evidences a competition between the ionization and charge-transfer reactions. The IR emission bands due to ionic chromophores ($p=2,3,4$) as well as the UV ($B-X$) and visible ($C-A$) bands due to desorbed Xe^+F^- excimer molecules have been observed. The cluster size effect of m and k on the reaction dynamics was observed. The delocalization of hole on trimer and tetramer ionic cores is confirmed in xenon clusters of size $m \leq 10^2$. Because of a low cluster temperature of 10 K, configuration mixing is prohibited, resulting in almost equal relative ion isomer populations. However, the excited state distribution within each isomer changes with the size m , which may reflect the compression of the atoms or an Xe–Ne interface effect. The free XeF excimer emission shows the importance of the excited-state desorption processes in rare-gas clusters. The charge-transfer reaction takes place when the first-shell cluster size k is higher than the critical size $k^* \approx 30$. The triatomic Xe_2F excimer is not observed at 17.7 eV excitation; this emission has only been observed under low-energy excitation close to the lowest atomic $^3P_{1,2}$ states. This result shows that a large neon cluster is not a good cage for rapid reaction fragments, which readily escape it.

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