

# Ionic chromophores $\text{Xe}_p^+$ ( $p \leq 4$ ) in multishell rare-gas clusters $\text{Xe}_m(\text{NF}_3)_k\text{Ne}_{7500}$ ( $m, k \leq 100$ ) studied with fluorescence spectroscopy

A. Kanaev<sup>1</sup>, L. Museur<sup>2</sup>, T. Laarmann<sup>3</sup>, and T. Möller<sup>4</sup>

<sup>1</sup> *Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, C.N.R.S., Institut Galilée, Université Paris-Nord, Villetaneuse 93430, France*  
E-mail: kanaev@limhp.univ-paris13.fr

<sup>2</sup> *Laboratoire Physique des Lasers, C.N.R.S., Institut Galilée, Université Paris-Nord, Villetaneuse 93430, France*

<sup>3</sup> *Max-Born Institute, Max-Born Str. 2a, Berlin 12489, Germany*

<sup>4</sup> *Institut für Atomare Physik, Technische Universität Berlin, Hardenbergstr. 36, Berlin 10623, Germany*

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We have studied fluorescence spectra of small  $\text{Xe}_m$  and  $\text{Xe}_m(\text{NF}_3)_k$  clusters ( $m, k \leq 10^2$ ) embedded in large host  $\text{Ne}_{7500}$  clusters, excited with SR excitation in the VUV spectral region above the  $\text{Xe}^+(^2\text{P}_{1/2})$  atomic limit. The IR emission bands due to ionic chromophores  $\text{Xe}_p^+$  ( $p = 2, 3, 4$ ) as well as UV ( $B-X$ ) and visible ( $C-A$ ) bands due to desorbed  $\text{Xe}^+\text{F}^-$  excimer molecules have been observed. The triatomic  $\text{Xe}_2\text{F}$  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  $k$ .

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**Keywords:** ionic chromophores, excited state distributions, charge transfer reaction, doped rare-gas clusters, excimer molecule emission, fluorescence.

## Introduction

A fundamental difference between the neutral and ionized rare gas clusters is well known. 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 representing building unit is the rare gas dimer, a larger unit can be produced in the ionic cluster due to a charge delocalization process. For example,  $\text{Xe}_p^+$  ( $p = 2-4$ ) units have been experimentally observed from analysis of absorption and fluorescence spectra [1–3] and theoretically predicted in free xenon clusters [4–6]. IR fluorescence of self-trapped hole in

rare-gas solids has been recently studied in Refs. 7–9. A steady interest to the rare gas ionic clusters is explained by their role as model systems in understanding of the charge transfer and solvation processes in bulk media. The use of clusters offers a possibility to study its 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 «pick-up» technique 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 localiza-

tion 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 the characteristic cluster temperature of  $\sim 10$  K [12]. Moreover, the surrounding neon cluster atoms do almost not perturb the energy levels of embedded molecules. Since neon clusters are transparent within the VUV spectral range, they are well-suited to study electronic properties of molecules and heavier rare-gas clusters made of Ar, Kr and Xe atoms. Recently, investigation of  $\text{Ar}_m\text{Ne}_N$  [11] and  $\text{Kr}_m\text{Ne}_N$  [13] and  $\text{Xe}_m\text{Rg}_N$  clusters (Rg = He, Ne) [14] ( $m \leq 100 \ll N \approx 7500$ ) gave 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  $\text{Xe}_p^+$  ( $p = 2-4$ ) inside multishell clusters has never been a subject of experimental studies. Influence of the surrounding medium on the ionization, charge delocalization and charge transfer processes could be inspected in this way.

In the present paper we report on the spectroscopy of small ionized clusters ( $m \leq 100$ ) embedded inside large 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  $\text{Xe}_p^+$  ( $p = 2-4$ ) 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 ionic chromophores fluorescence [2,3] on the 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  $\text{NF}_3$  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 station [15] at synchrotron DESY. Neon clusters were prepared in a supersonic expansion of the gas neon at 200 mbar pressure through a conical nozzle (200  $\mu\text{m}$ ,  $2\theta = 4^\circ$ ) cooled down until 30 K. The average cluster size  $7500 \approx N$  was de-

termined 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  $\mu\text{m}$  are used. The width of the cluster size distribution (FWHM) is  $\Delta N \approx N$ . Using a successive «pick-up» technique these large neon clusters were doped firstly with  $\text{NF}_3$  molecules and secondly 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  $\text{Xe}_m$  and  $(\text{NF}_3)_k$  clusters have been estimated by measuring the VUV-fluorescence excitation spectra of the  $\text{Ar}_m$  clusters inside large neon clusters in the range of 12.4 eV, prepared by expanding the argon gas correspondingly through xenon ( $m$ ) and nitrogen trifluorine ( $k$ ) nozzles, as it is explained in Ref. 13. Laarmann et al. [11] have shown that the absorption lineshape of tightly bound excitons in  $\text{Ar}_m$  clusters changes with their size  $m$  according to the Frenkel exciton model. By comparing the experimental spectra lineshapes 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 mainly depending 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  $\text{NF}_3$  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 the 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 used to excite 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 impurity center, that is a small embedded xenon cluster. Fluorescence excitation spectra in the VUV-UV ( $\lambda \leq 300$  nm) and in the UV-visible-IR ( $200 \text{ nm} \leq \lambda \leq 900$  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, a remark on the cluster composition can be made. The pick-up atoms and molecules by large  $\text{Ne}_{7500}$  clusters results in a release of energy. Neon atoms are weakly bound and evaporate from the  $\text{Xe}_m\text{Ne}_N$  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  $\sim 6.5$  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 do not change considerably the neon cluster size. It can be shown that the same conclusion is valid for the doping by a small number of  $\text{NF}_3$  molecules. This conclusion about stability of the host neon clusters with  $N = 7500$  in the experimental doping conditions ( $m, k \leq 100$ ) has been confirmed by measurements of the luminescence excitation spectra in the spectral range of the neon absorption of  $h \approx 17.7$  eV.

## Results and discussion

Fluorescence spectra of xenon clusters excited above the atomic ionisation limit originate from molecular states related to the  $5p^5 \ ^2P_{1/2} \rightarrow 5p^5 \ ^2P_{3/2}$  transitions in ionic chromophores  $\text{Xe}_p^+$  ( $p = 2-4$ ) [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 fluorescence of  $\text{Xe}_N^+$  ( $N \leq 2 \cdot 10^4$ ) have been reported in Refs. 2, 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 ( $\text{Xe}_2^+$ ,  $\text{Xe}_3^+$ , and  $\text{Xe}_4^+$ ), six fluorescence bands can be resolved in fluorescence spectra at sufficiently low temperatures. These new spectral bands have been demonstrated in small  $\text{Xe}_{40}$  clusters embedded in large neon clusters using the pick-up method [3]: the temperature of such cluster is defined by the host neon temperature, which is about 10 K [18]. Size-dependence of the IR fluorescence spectra of

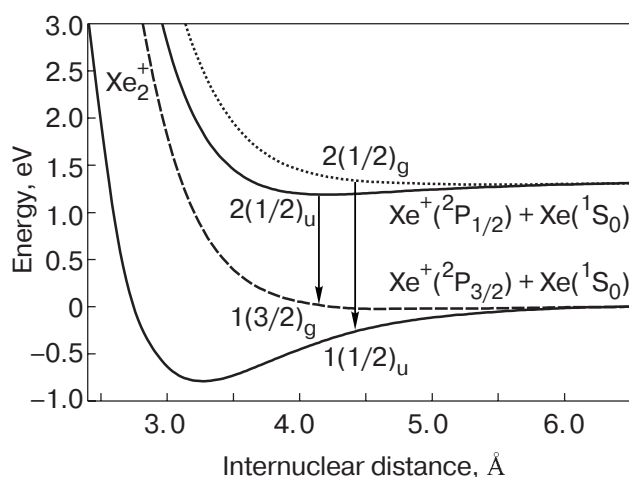


Fig. 1. Schematic potential curves of the relevant states related to  $5p^5 \ ^2P_{1/2}$  and  $5p^5 \ ^2P_{3/2}$  atomic xenon ion limits.

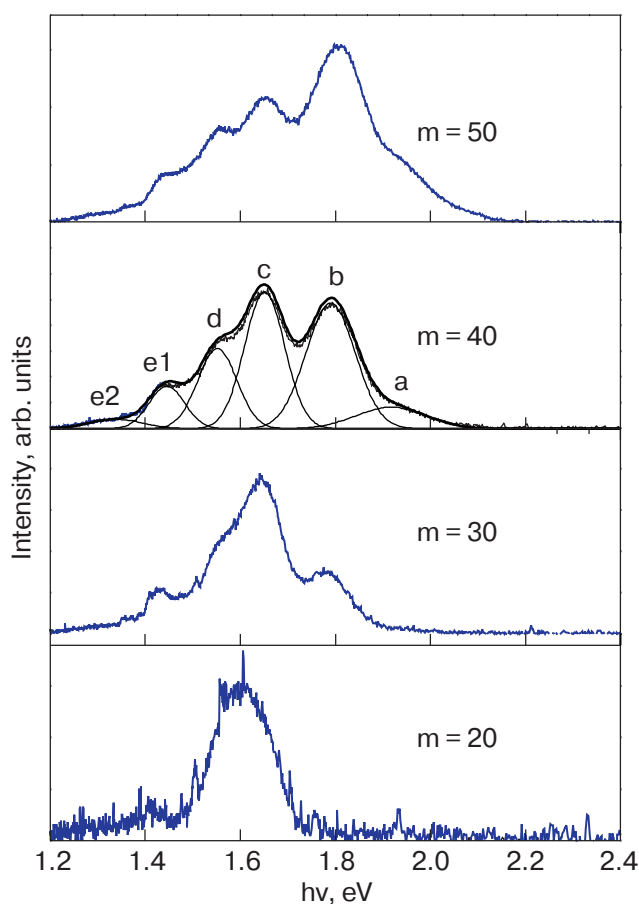


Fig. 2. fluorescence spectra of  $\text{Xe}_m \text{Ne}_{7500}$  excited at 17.7 eV.

these embedded  $\text{Xe}_m$  clusters ( $m \leq 10^2$ ) is studied in the present work.

### $\text{Xe}_m \text{Ne}_{7500}$ 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-peaks gaussian fit has been used to resolve the contributions of six bands labelled 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 schema in Fig. 1, the bands  $e_1$ ,  $b$ ,  $a$  originate from the higher positioned (more shallow) electronic  $g$ -state, whereas the bands  $e_2$ ,  $c$ ,  $d$  originate from the stronger bound  $u$ -state: the corresponding dimer ion states are  $2(1/2)g$  and  $2(1/2)u$  [20]. As one can see from this figure, the bands  $d$  and  $c$  dominate the fluorescence of very small xenon clusters  $m \leq 5$ . The 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-peaks

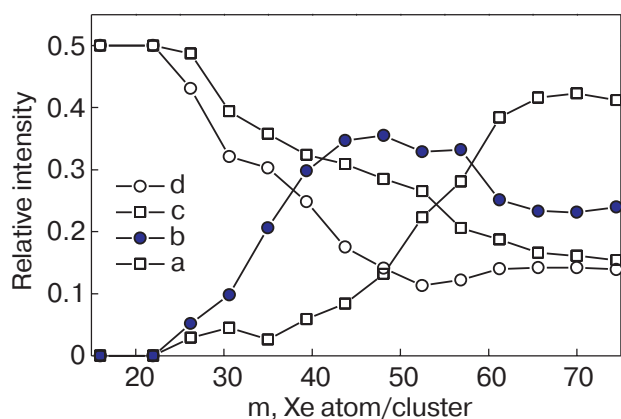


Fig. 3. Relative intensities of the IR emission bands due to ionic chromophores ( $p = 2, 3, 4$ ).

gaussian fit are shown in Fig. 3. Because of a low contribution, the dimer bands are not shown in this figure.

Different state origin of the two groups of the bands  $d/c$  and  $b/a$  can be evidenced from fluorescence decay measurements, presented in Fig. 4. All these curves can be well fitted by two-exponents resulting in excited-state lifetimes of  $t_1 = 1.5 \mu\text{s}$  and  $t_2 = 150 \text{ ns}$ . 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. 4,a). Its relative intensity as a function of the size  $m$  is shown in Fig. 4,b. A correlation between relative intensity of the bands  $b/a$  and shortlived fluorescence decay allows their straightforward identification. We assign the longer lifetime of  $t_1 = 1.5 \mu\text{s}$  to the fluorescence bands  $d/c$  appeared in small xenon clusters, and the shorter lifetime of  $t_2 = 150 \text{ ns}$  to the fluorescence bands  $b/a$  appeared in the larger clusters. This assignment is in general agreement with dimer ion state structure discussed in theoretical work by Wadt [21]. Similar repartitioning of the excited electronic states is expected in xenon ion trimers and tetramers that explains our finding.

In contrast to the ionic chromophore subbands, relative fluorescence intensity originated from different chromophores  $\text{Xe}_4^+$  and  $\text{Xe}_3^+$  does almost not change in the cluster size range  $m \leq 10^2$ . This result is directly followed 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  $\text{Xe}_N$  clusters the charge is preferentially repartitioned on  $\text{Xe}_4^+$  and  $\text{Xe}_3^+$  cores when  $N \leq 200$ , and localized on  $\text{Xe}_2^+$  only

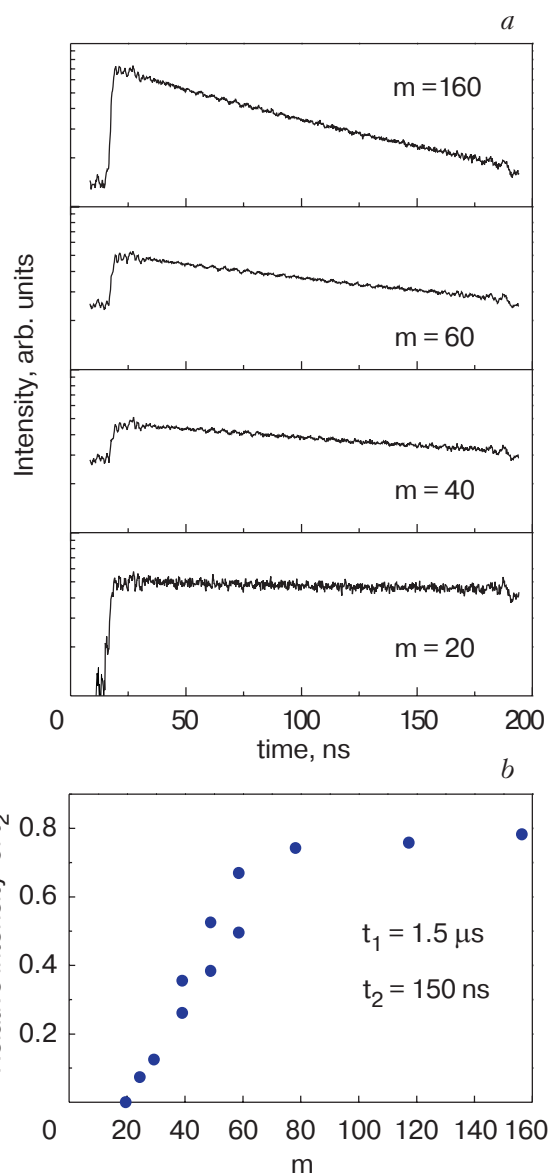


Fig. 4. IR fluorescence decay (a) and the fast component relative intensity in  $\text{Xe}_m\text{Ne}_{7500}$  clusters as a function of the size  $m$  (b) ( $E_{\text{exc}} = 17.7 \text{ eV}$ ).

when  $N \geq 400$ . This explains in particular why only dimmer ionic core is observed in the bulk solids in both absorption [21] and fluorescence [22]. Theoretical and experimental studies by Gascón et al. [23] have shown that tetramer and trimer cores coexist in small xenon clusters  $N \leq 30$ , which relative population undergoes oscillatory variation with size. The interconversion of these two isomers was also suggested at temperatures of  $\sim 60 \text{ K}$ . The temperature of our embedded  $\text{Xe}_m$  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 the intensity variation between 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  $\text{Xe}_4^+$  and  $\text{Xe}_3^+$  ionic isomers at 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 somewhat larger width than  $\sqrt{m}$ .

Our results show an importance of the small cluster environment. Indeed, comparing with free xenon clusters  $\text{Xe}_4^+$  and  $\text{Xe}_3^+$  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 that is fixed at 10 K. Moreover, the temperature would be expected to decrease with size  $m$  leading in population of a 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 that is not the case. A preferential population of the lower excited state related to  $2(1/2)g$  of  $\text{Xe}_2^+$  in small clusters may be explained by an effect of the interface formation similar to that discussed in [13,14] or by the embedded atoms compression [14]. According to Refs. 13, 14, the exciton formation in embedded rare-gas clusters depends on the electron affinity. In particular case of  $\text{Xe}_m\text{Ne}_N$  clusters a perturbation of the interface Xe-Ne layer is strong and the bulk exciton of  $\text{Xe}_m$  only appears at sufficiently large  $m \geq 50$ . The second case seems less probable since the effect of compression was only observed in small neon clusters about  $40 < N < 90$  [14]. However, the case of embedded ionized cluster atoms is different from that of neutral isolated xenon atom studied in Ref. 14 and requires further studies.

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

A competition between the ionization and charge-transfer reaction can be studied in multishell  $\text{Xe}_m(\text{NF}_3)_k\text{Ne}_{7500}$  clusters. In fact excitation of the neon cluster activates two reaction mechanisms. (1) Ionization of the internal  $\text{Xe}_m$  cluster takes place following the energy transfer process. The electron leaves the cluster, whereas the hole is localized on excited chromophores  $\text{Xe}_p^{+*}$  ( $p = 2, 3, 4$ ) 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 the excimer creation: XeF or  $\text{Xe}_2\text{F}$ . In bulk xenon XeF relaxes into  $\text{Xe}_2\text{F}$ , therefore its observation would be an indication of the excited-state desorption process [24,25].

The fluorescence spectra recorded after excitation of multishell  $\text{Xe}_{50}(\text{NF}_3)_k\text{Ne}_{7500}$  clusters at 17.7 eV are shown in Fig. 5 for different sizes  $k$ . At  $k = 0$  only IR fluorescence of  $\text{Xe}_p^{+*}$  has been observed. However, with an increase of  $\text{NF}_3$  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: intensity of the subbands  $a$  and  $b$  decreases relatively to that of the subbands  $c$  and  $d$  when  $k$  increases. Moreover, at  $k \leq 30$  new XeF excimer emission bands  $B-X$  in the UV at 3.5 eV and  $C-A$  in the visible at 2.5 eV appear.

The observed excimer bands apparently belong to the desorbed excited fragments illustrating the importance of the excited-state stimulated desorption processes in cryogenic solids. Relatively weak spectral features at 3.65 eV and 3.15 eV do not correspond to the known  $\text{NF}_3$  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  $\text{Ne}_{7500}$  cluster. However, according to [12] vibrational fragments cooling can be particularly ineffi-

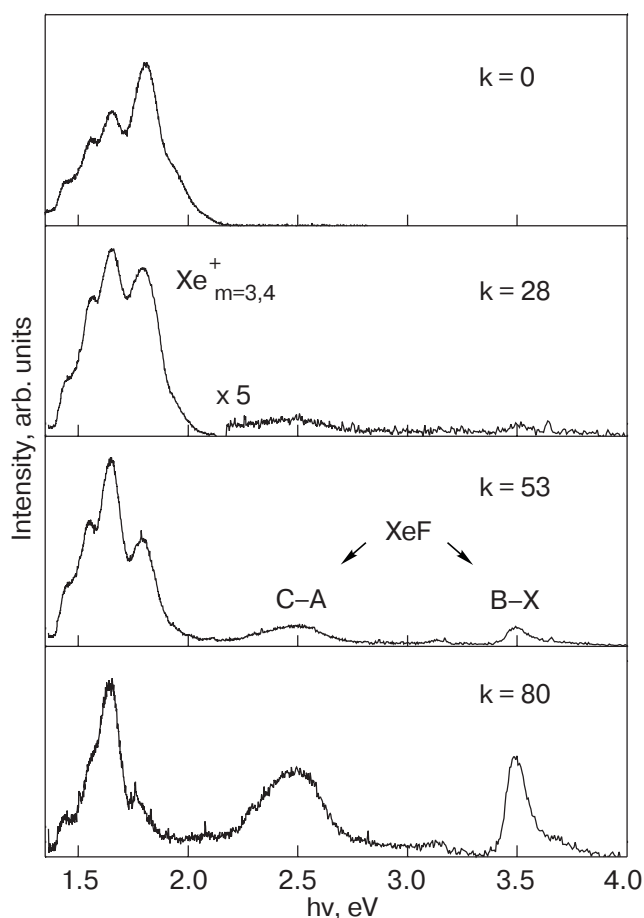
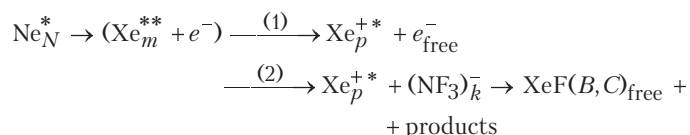


Fig. 5. Fluorescence spectra after excitation of multishell  $\text{Xe}_{50}(\text{NF}_3)_k\text{Ne}_{7500}$  clusters at 17.7 eV.



cient in neon clusters in view of a low Debye energy (6.4 meV) compared to the vibration quantum (e.g., in the C-state  $\omega_e = 346 \text{ cm}^{-1}$ ). The main fluorescent bands however are narrower than those earlier observed 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 following:



Firstly, the ionization of the internal  $\text{Xe}_m$  cluster takes place. In  $\text{Xe}_m\text{Ne}_N$  clusters this results to the  $\text{Xe}_p^{+*}$  center creation (channel (1)). However in  $\text{Xe}_m(\text{NF}_3)_k\text{Ne}_N$  the electron may not escape and can be trapped by the first-shell cluster  $(\text{NF}_3)_k$ . This happens if the size  $k$  is above some critical value of  $k^* \approx 30$ . The  $\text{NF}_3$  molecule accommodating excess electron subjects to the dissociative attachment. However it can be stabilized in clusters as  $\text{NF}_3^-$  anion and larger cluster ion units  $(\text{NF}_3)_{l>1}^-$  [24]. In such case the Coulomb attraction between the localized hole  $\text{Xe}_p^{+*}$  and  $(\text{NF}_3)_k^-$  or lighter anionic fragment can result in the  $\text{XeF}$  excimer formation. The excess energy of the electronically excited center is apparently so strong that the expulsion proceeds before the relaxation into  $\text{Xe}_2\text{F}$  takes place. Additionally, the binding energy of the  $\text{Xe}_p^{+*}$  core is much smaller than that of the ground-state ion  $\text{Xe}_p^+$ . This may prohibit the  $\text{Xe}_2\text{F}$  formation from xenon core states related to the  $5p^5 2P_{1/2}$  atomic limit. In fact, no signa-

ture 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 ionization onset, the broad-band intracuster emission of  $\text{Xe}_2\text{F}$  appears, as shown in Fig. 6. It is centered at 1.48 eV (838 nm) that is lower compared to 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  $\text{Xe}_p^{+*}$  fluorescence intensity ( $I_{IR}$ ) on the size  $k$  of the first-shell cluster  $(\text{NF}_3)_k$  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 the cross-over region at  $30 \leq k < 60$ . This transient region apparently relates to an increase of the electron trapping rate by the  $\text{NF}_3$  cluster after the critical size of  $k \geq k^* = 30$ . The fact that the critical size  $k^*$  does not appreciably depend on the size of the embedded xenon cluster  $m$  (see Fig. 7) indicate that the electron exit from the neon cluster may not be direct but rather delayed process: in case of the direct exit the electron trapping probability would be a function of the  $\text{NF}_3$  shell width ( $k^{2/3}$ ) and not of the size  $k$ . An increase of the neutral reaction channel relatively to molecular ionisation has

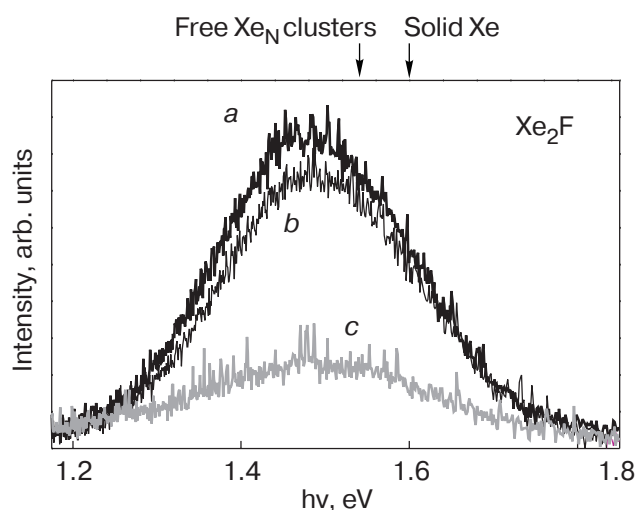


Fig. 6. IR fluorescence spectra after excitation of multi-shell  $\text{Xe}_{50}(\text{NF}_3)_k\text{Ne}_{7500}$  clusters at 8.551 eV for  $k = 50$  (a), 25 (b), 14 (c).

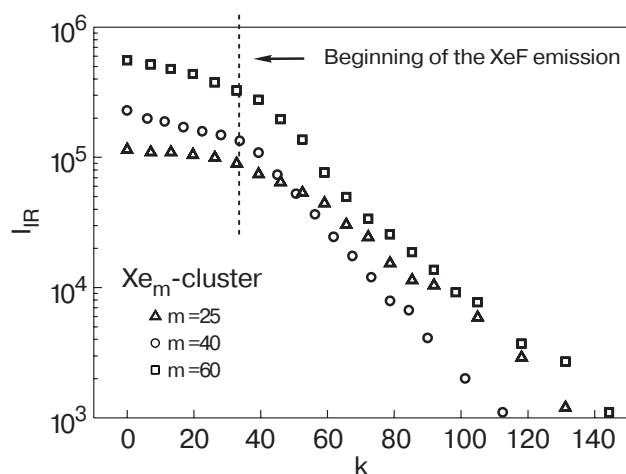


Fig. 7. Relative intensity of the IR fluorescence of  $\text{Xe}_m(\text{NF}_3)_k\text{Ne}_{7500}$  clusters as a function of the size  $k$ ,  $E_{\text{exc}} = 17.7 \text{ eV}$ .

been recently observed in large neon clusters doped with water molecules [12].

Additional remark concerns the excited-state reactivity of  $\text{Xe}_p^+*$ . The plot of  $\ln(I_{IR})$  vs cluster size  $k$  suggests the excited-states quenching process. Moreover as we can see in Fig. 5, the spectral lineshape of the IR band changes with growing  $k$ : subbands  $b$  and  $a$  weaken faster and the subbands  $d$  and  $c$  dominate 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 respect to the  $2(1/2)u$  one. This may be related to its larger equilibrium distance that enables more efficient potential curve-crossing between the chromophore and the anion. Indeed, more localized state  $2(1/2)u$  may be centered inside the embedded clusters while more delocalized one  $2(1/2)g$  [2] is readily set in contact with the negatively charged halogen donor.

### Conclusion

The present spectroscopy study of multishell  $\text{Xe}_m$  and  $\text{Xe}_m(\text{NF}_3)_k$  clusters ( $m, k \leq 10^2$ ) embedded in large host  $\text{Ne}_{7500}$  clusters clear up the hole localization process in small xenon clusters and evidences a competition between the ionization and charge-transfer reaction. The IR emission bands due to ionic chromophores ( $p = 2, 3, 4$ ) as well as UV ( $B-X$ ) and visible ( $C-A$ ) bands due to desorbed  $\text{Xe}^+\text{F}^-$  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 the configuration mixing is prohibited resulting in almost equal relative ion isomer populations. However, excited state distribution within each isomer changes with the size  $m$ , which may reflect the atoms compression either Xe-Ne interface effect. The free XeF excimer emission shows an 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  $\text{Xe}_2\text{F}$  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 that readily escape it.

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