

Photochemical processes in doped rare gas clusters studied with luminescence spectroscopic methods

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Photochemical processes in Xe and NF₃ doped rare gas clusters Rg_N (Rg = Ar, Kr, Xe) are investigated with luminescence spectroscopy using photo-excitation with synchrotron radiation. Relaxation processes in Xe doped Ar_N clusters depend considerably on the location of the Xe atom in the cluster. Following excitation of surface sites desorption of electronically excited Xe atoms in the ³P₁ state is a dominant decay channel. Xe atoms in the interior of the cluster emit inside bubbles. The results are discussed in view of recent molecular dynamics (MD) simulations. Electronically excited Rg_N clusters doped with NF₃ emit luminescence bands attributed to RgF* and Rg₂F*. This result gives strong evidence for the first charge transfer reactions in clusters.

Introduction

The investigation of photochemical processes in molecular and condensed matter has been a topic of interest for many decades.^{1,2} Photochemical processes are of considerable importance in various branches of research and are therefore investigated in great detail. Studies on clusters which could fill the gap between the traditional branches of molecular and condensed matter physics and chemistry were only started recently. One of the unique characteristics of clusters is their large surface to bulk ratio.³ This allows the investigation of photochemical processes in different environments, *e.g.* at the surface, in interior sites or in very small clusters in which the atoms are coordinated by only a few other atoms. In this context, the following aspects are important: (i) photochemical processes are either reactive (bond breaking and formation of new bonds) or non-reactive (*e.g.* radiationless transitions); (ii) dissociation is very common in small molecules but can be hindered in a matrix; (iii) in general photochemical processes in condensed matter involve the excitation of phonons which is equivalent to the excitation of vibrations in free molecules; this can lead to substantial heating of the cluster; (iv) desorption processes at surfaces might be of considerable importance in clusters since surface atoms make up a large fraction of the cluster.

In this article we present a study of photochemical processes in doped rare gas clusters. These clusters were chosen because rare gases are the most common materials in matrix spectroscopy. Furthermore, rare gas clusters can be generated quite easily with nozzle expansion. Two different systems will be discussed. (i) Rare gas clusters doped with atoms of a heavier rare gas are prototypes for systems with non-reactive relaxation dynamics. Here, interesting aspects include the site and size dependence of the processes.

In addition, these systems are of special interest because the relaxation dynamics of XeAr_N clusters have been investigated very recently with molecular dynamics (MD) simulations.⁴ (ii) The formation of rare gas halides which are the most common media in excimer lasers is taken as an example for reactive processes.

Experimental

The measurements were performed at the experimental set-up Clulu at HASYLAB/DESY. A detailed description has been given elsewhere.⁵ Therefore, the important components are here described only in brief. The set-up consists of a cluster beam, an atomic cross-jet for doping of the clusters, a time-of-flight mass spectrometer and several detectors for the registration and analysis of the luminescence light.

Usually, large conical (convergent-divergent) nozzles (diameter between 80 and 500 μm , opening cone angle $2\theta = 8\text{--}30^\circ$) are used for the generation of clusters in the size range $\langle N \rangle = 2\text{--}10^5$. Mixed clusters were generated by a co-expansion of a gas mixture, typically 30–300 ppm of the guest material (Xe or NF_3) in Kr, Ar or Ne, or by using a pick-up technique with a cross-jet. At these low concentrations only single guest atoms or molecules are embedded in the clusters. The size of the clusters can be varied by changing the nozzle temperature or the stagnation pressure. The size distribution in the cluster beam is analysed with a time-of-flight mass spectrometer and by using scaling laws.^{5,6} In order to reduce the background pressure in the main experimental chamber the cluster beam is skimmed and only the central part of the cluster beam enters the mass spectrometer. Typically the width ΔN (FWHM) of the size distribution corresponds to the average number $\langle N \rangle$ of atoms per cluster.

For luminescence spectroscopy monochromated synchrotron radiation (bandpass 0.05–0.25 nm; $3 \times 10^{10}\text{--}1 \times 10^{12}$ photons s^{-1} within the bandpass in the spectral range 40–160 nm) intersects with the cluster beam approximately 10 mm downstream of the nozzle opening. The fluorescence light is either analysed with two different grating monochromators or detected spectrally undispersed with different types of photomultipliers. For the visible and IR spectral range a commercial 0.275 m Czerny-Turner type monochromator equipped with three gratings (150 l mm^{-1} for overview spectra, 1200 l mm^{-1} for high resolution) is used. The monochromator is coupled to the experimental chamber with a lens system consisting of two LiF lenses. In order to detect weak signals from clusters in a molecular beam a liquid nitrogen cooled CCD camera is attached to the monochromator. With the 1200 l mm^{-1} grating the spectral resolution can be varied between 0.1 and 3 nm. Fluorescence in the vacuum-ultraviolet (VUV) spectral range is analysed with a home-built 0.69 m Pouey type monochromator. A position sensitive detector allows the recording of a complete spectrum simultaneously. As a result of the large grating (110 mm diameter) the monochromator produces slightly asymmetric line-shapes. Typically, the resolution is 0.7 nm corresponding to approximately 60 meV at 10 eV.

Excitation spectra of VUV and visible luminescence can be recorded with a solar blind photomultiplier (Hamamatsu R1460, CsTe cathode) and a photomultiplier with a GaAs(Cs) cathode (Hamamatsu R 94-02).

Results and Discussion

Xe doped rare gas clusters: site specific excitation and decay

Xe doped Ar clusters can be viewed as a model system for doped clusters.^{7–9} Fig. 1 displays a fluorescence excitation spectrum of XeAr_N clusters containing on average 500 atoms, covering the spectral range around the first atomic resonance of Xe. Since the fluorescence yield in this spectral range is close to 100% it corresponds to the absorp-

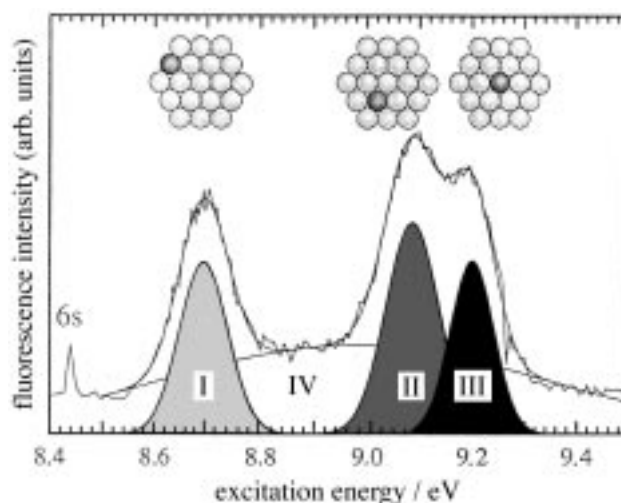


Fig. 1 Fluorescence excitation spectrum of XeAr_N clusters containing approximately 500 atoms. The identification of different sites is illustrated at the top of the figure.

tion of the clusters. Apart from the weak sharp line ($5p \rightarrow 6s\ ^3P_1$) of free Xe atoms which are always present in the beam, three bands are seen which can be assigned to Xe atoms inside the cluster surface (band I), one monolayer below the surface (band II) and deep inside the interior of the cluster (band III).[†] Note that one can distinguish between atoms deep inside the cluster and one monolayer below the surface because Xe atoms in substitutional sites deep inside the Ar cluster are considerably compressed by the surrounding Ar atoms.¹⁰ All absorption bands are blue-shifted relative to the resonance line of atomic Xe. The blue shift can be regarded as a consequence of a cage effect. Upon excitation the size of the electronically excited orbital increases. If the Xe atom is embedded inside a cluster the available space is restricted and the excitation energy is shifted towards higher energies, similar to the energy of a particle in a small box. Molecular dynamics calculations⁹ have underlined this picture and provided a quantitative understanding of the spectral features. According to these calculations the blue shift is proportional to the number of nearest neighbours (NN). This gives us a tool at hand to study the relaxation process in doped clusters with selective excitation of Xe atoms in well defined sites.

Spectrally resolved luminescence spectra of XeAr_N clusters are presented in Fig. 2. These spectra are recorded following excitation of Xe atoms deep inside the cluster with 9.20 eV (band III). The most dramatic general feature is that the spectral shift of the prominent emission band is rather small, at least up to $\langle N \rangle = 10\,000$, in contrast to the large shift in absorption. Five emission bands labelled as A, B, C, D and E can be seen. Band E is resonant with the excitation and visible only in rather large clusters. Since the cross-section for scattering¹¹ is proportional to N^2 it can be assigned to light scattered from the cluster. The energy shift either to the emission of the free atom at 8.437 eV or relative to the excitation at 9.20 eV, the so-called Stokes shift, contains information on the site of the emitting atom. A small shift relative to the free atom points towards a low coordination of the Xe atom. For the smallest clusters ($\langle N \rangle = 900$) only one emission band at 8.437 eV and a width of 50 meV is observed. If the size of the cluster is further reduced to $\langle N \rangle = 350$ (not shown here¹²) the fluorescence spectrum is almost

[†] It should be noted that this assignment differs slightly from the original one in ref. 8; the position of the Xe atom is shifted by one monolayer towards the center of the cluster. In addition a fourth band can be seen which is due to weak congested bands.

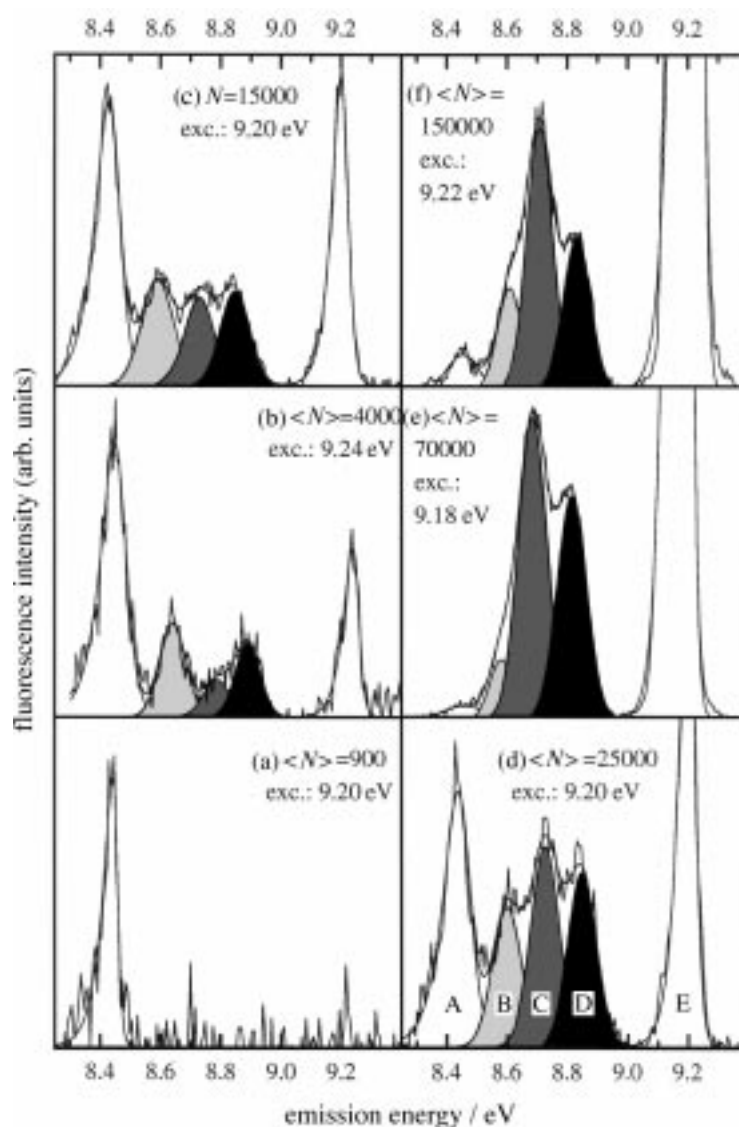


Fig. 2 Fluorescence spectra of XeAr_N clusters as a function of the cluster size. The excitation energy of approximately 9.2 eV (band III in absorption) populates sites deep in the interior of the cluster.

unchanged. Since the width of the band is slightly broader than the emission of the free atom and the spectral shift is less than 100 meV we conclude that the emitting Xe atoms are either very weakly bound at the cluster surface, as seen in the solid,¹³ or inside a bubble. The formation of the bubble can be explained in the following way. If the Xe atom inside the cluster is excited the size of the atom is increased and a strong repulsive force of the excited electron acts on the surrounding Ar atoms. If the cluster is sufficiently small the Ar atoms can be pushed away and a bubble is formed around the electronically excited Xe atom. Furthermore, one can expect that the cluster can melt, since an excess of energy of approximately 0.8 eV is transferred to the cluster. According to MD calculations⁴ the latter process takes place up to $N \approx 55$.

Our experimental results can be compared with recently performed calculations by Goldberg and Jortner.⁴ According to their work the configurational relaxation process in XeAr_{146} occurs on a time-scale of $t < 20$ ps, whereupon the fluorescence quantum yield during this process is negligible. They have calculated fluorescence spectra for a single Xe atom in different sites of Ar clusters ($N = 54$ and 146). For the excitation of the central site corresponding to an excitation into band III they obtained one rather sharp line [$\Delta E(\text{FWHM}) = 62$ meV at 30 K, $N = 146$] blue-shifted by 87 meV for $N = 146$ relative to the atomic resonance line. These findings are in reasonable agreement with our experimental results for somewhat larger clusters. In the work by Goldberg and Jortner the sharp emission line is interpreted as fluorescence of Xe inside a bubble. The formation of the bubble takes place on a time scale of a few hundred fs while the expansion of the bubble occurs in 2 ps. The average size of the bubble, defined as the increase of the nearest neighbour distance, is 0.08 nm. As a result of this large dilatation the spectral shift relative to the free atom nearly vanishes and the line becomes rather sharp. Finally, the relaxation is accompanied by movement of the Xe atom towards the surface. In view of the similarity of the measured and calculated spectra we conclude that in the size range $\langle N \rangle = 350\text{--}900$ Xe atoms enclosed in bubbles emit if sites deep in the interior of the cluster are excited.

If the cluster size is increased additional bands appear, which are labelled B, C, and D (band E is due to scattered light). Since the emission bands are considerably blue-shifted relative to the emission of the free atom we attribute them to Xe on different sites inside the cluster. The origin of the blue shifts is visualised in a potential relaxation scheme of the XeAr molecule in Fig. 3. The minimum in the potential energy curve of XeAr in the first electronically excited states is located at larger internuclear separations than the minimum in the ground state. This explains the strong blue shift in absorption and the smaller blue shift in emission. In a similar way the spectral shifts can be explained in the configuration coordinate model used in the discussion of electron–phonon interactions in matrix spectroscopy.¹⁴

The band labelled D at 8.85 eV corresponds to the prominent emission band in Xe doped solid argon¹⁵ and exhibits the strongest blue shift. It is accordingly assigned to Xe in substitutional sites (twelve nearest neighbours). With time resolved measurements¹⁶ a emission at 8.78 eV in the solid could be attributed to the emission of Xe atoms in the $6s\ ^3P_2$ state in substitutional sites. Thus we conclude that band C at 8.78 eV is due to emissions from the 3P_2 state. Band B is rather strong in clusters containing 4000 atoms. In this size regime emissions from $6s\ ^3P_1$ are very strong (bands A and D). Therefore, we assume that band B which is also strong is due to emissions from the 3P_1 state; in view of the small blue shift the coordination number must be less than 12. Using this assignment the following trends can be established for decay processes following excitation of Xe atoms deep inside Ar clusters: (i) in very small clusters ($N < 13$ theoretical;^{4,7} $\langle N \rangle < 100$ experimental, this work) the Xe atom desorbs from the cluster; (ii) up to the cluster size $\langle N \rangle = 25\,000$ the formation of a bubble around the Xe atom and subsequent emission from the $6s\ ^3P_1$ is the dominant relaxation process; (iii) above 50 000 atoms per cluster the clusters become big enough in order to prevent the formation of bubbles. With a simple statistical model and the measured intensity ratio between bands A and D the number of shells around a bubble can be estimated to be less than six. If the number of shells is larger the bubble can not withstand the pressure from the Ar atoms and collapses. Furthermore, the appearance of band B gives evidence that in some cases Xe sites with coordination numbers less than twelve are populated; (iv) in very large clusters ($N > 50\,000$) simultaneously with the disappearance of the bubble emissions the intensity of luminescence from the $6s\ ^3P_2$ state becomes dominant. This is reasonable because emissions from the dipole-forbidden 3P_2 state are not expected to occur from a bubble state because the weak coupling to the surrounding Ar atoms can weaken the selection rule.

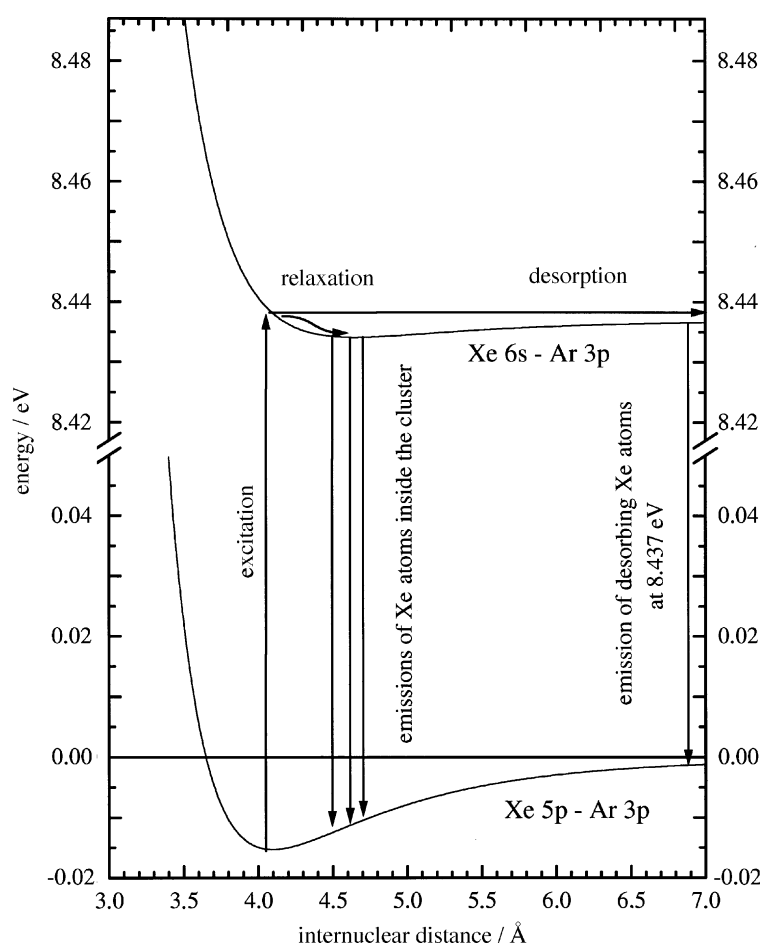


Fig. 3 Relaxation scheme and potential energy curves of XeAr

In the next paragraph we discuss the dependence of the relaxation process of the initially excited site. Luminescence spectra of XeAr_N clusters containing 1400 and 130 000 atoms are presented in Fig. 4. If Xe atoms in one monolayer below the surface are excited [band II at 9.08 eV, Fig. 4 (b) and (e)], apart from scattered light (9.08 eV), an emission band at 8.44 eV is observed. The spectral shift relative to the free atom is very small and therefore it is attributed to the emission of Xe atoms inside a bubble. This result is in agreement with the calculations.⁴ Within the size range under investigation no variation with the cluster size is observed. This behaviour is reasonable because the vicinity of the surface of the cluster determines the relaxation process. If Xe atoms inside the surface are excited [band I, Fig. 4 (c) and (f)] a very sharp emission is observed, which is within the error bars, identical with the emission of free atoms. As mentioned before the asymmetry of the lineshape is due to the aberration of the monochromator. Thus, we attribute this emission to Xe atoms desorbing from the cluster. Again, within the size range investigated, no variation with the cluster size is observed. From the potential curves in Fig. 3 the desorption of free Xe atoms is not unexpected. The first electronically excited state which is dipole allowed from the ground state has a very shallow minimum at large internuclear distances. At the equilibrium distance in the ground state the excited state is strongly repulsive. Hence dissociation and desorption

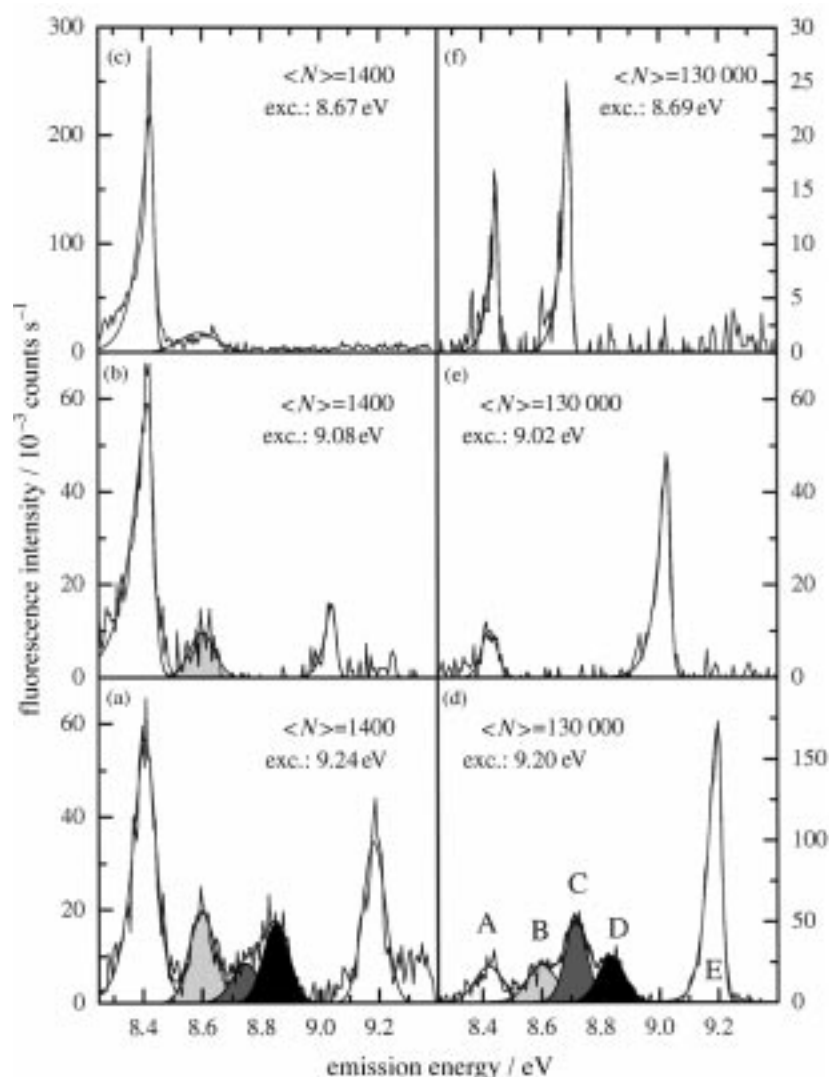


Fig. 4 Fluorescence spectra of XeAr_N clusters recorded following different sites: (a) and (d) deep interior sites; (b) and (e) interior; (c) and (f) surface

can in principle occur if it is not hindered by surrounding Ar atoms. If the Xe atom is inside the surface it is not completely coordinated and desorption can occur. One monolayer below the surface the Xe atoms are surrounded by a complete shell and instead of desorption a bubble is formed around the Xe atom. In this description no variation with the cluster size is expected. This is in agreement with the experimental findings.

While our results for Xe atoms in all different interior sites are in agreement with the MD calculations,⁴ there seems to be a discrepancy for surface sites. Here the MD calculations predict that electronically excited Xe atoms remain at the surface in so-called spring sites while the internuclear distance is increased by 0.061 nm. On the other hand, desorption of electronically excited Xe atoms in the $6s\ ^3P_1$ state is observed in Xe doped solid Ar in coexistence with emissions of Xe atoms at large internuclear separations in spring sites.¹⁷ The spectral shift between the two emissions is 40 meV and should be

detectable with our set-up. Thus, we conclude that the relaxation processes at the surface depend in a subtle way on the properties of the surface, *e.g.* the exact shape of the potential.

Reactive photochemical processes in NF_3 doped clusters: the formation of rare gas halides

Charge transfer reactions between excited rare gas atoms (Rg^*) and halogen containing molecules (MX), so-called 'harpoon' reactions, are well characterised in the gas phase.^{18,19} RgX^* excimer formation proceeds through curve crossing of a covalent Rg^* entrance potential with a Rg^+-MX^- ion pair potential and a subsequent dissociation of the complex along the $\text{R}-\text{X}^-$ coordinate. These reactions constitute an important class of chemical reaction which play a key role in excimer lasers. Analogous reactions were investigated in great detail in liquid²⁰ and solid samples.²¹ Usually, the reaction dynamics in the liquid and the solid differ considerably from those in the gas phase. In the gas phase the excimers are formed directly by charge transfer in a collision complex while in liquid and solid samples the dissociation of the fluorine containing molecule usually takes place in the first step.²¹ This raises the question whether analogous reactions can be observed in clusters and how they proceed.

Fluorescence spectra of Xe_N , Kr_N , and Ar_N clusters doped with 0.1% NF_3 recorded following excitation in the first absorption band of the pure clusters at 8.38 eV (Xe), 10.33 eV (Kr) and 12.11 eV (Ar) are presented in Fig. 5. Several broad and narrow

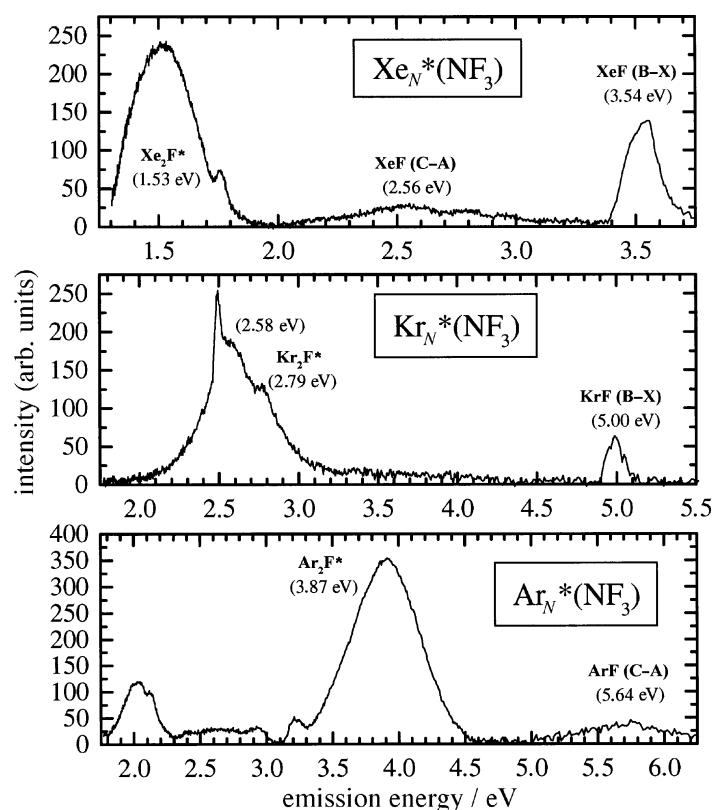


Fig. 5 Fluorescence spectra of NF_3 doped rare gas clusters. Assignments of different emission bands are labelled. Some very sharp bands at 1.79 eV (Xe), 2.50 eV (Kr), 2.0 eV and 3.22 eV (Ar) are due to the second order light of the monochromator from the B—X emissions.

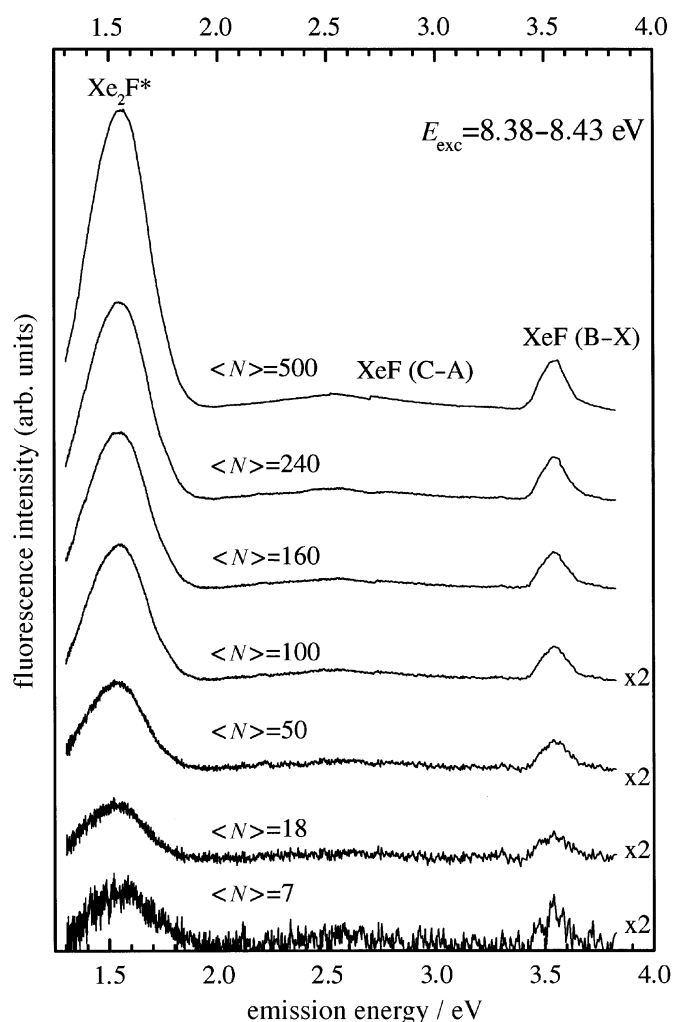


Fig. 6 Fluorescence spectra of NF_3 doped Xe_N clusters as a function of cluster size N

emission bands can be seen. The narrow bands at 3.54 eV (Xe) and 5.0 eV (Kr) are attributed to the $\text{B} \rightarrow \text{X}$ transition of XeF^* and KrF^* . A similar band at 6.4 eV is observed for NF_3 doped Ar clusters.^{22,23} These bands are the prominent emissions in the gas phase and provide intense UV light in excimer lasers.¹⁹ Weak broad emissions at 2.56 eV (Xe) and 5.64 eV (Ar) are assigned to the corresponding $\text{C} \rightarrow \text{A}$ transitions. Within the error bars the measured transition energies in the cluster agree with the gas phase values. The broad intense emissions at 1.53 eV (Xe), 2.58 eV and 2.79 eV (Kr), and 3.87 eV (Ar) are shifted by less than 100 meV from the well known $4\Gamma \rightarrow 1,2\Gamma$ transition of the triatomic Rg_2F^* excimers in the solid. Similar broad bands emitting at somewhat higher energies are observed in the gas phase at high pressure.¹⁹ Therefore, we attribute the strong broad emission bands in clusters to triatomic excimers. Interestingly, diatomic excimer emissions are only observed in liquid and solid samples if ternary mixtures, *e.g.* Xe, Kr and F_2 , are prepared.²⁰

The simultaneous appearance of diatomic and triatomic emissions from clusters can be explained in the following way. Diatomic emissions are not shifted relative to the gas

phase values and are accordingly attributed to diatomic RgF^* excimers desorbing from the cluster. The large spectral red shift of approximately 0.5 eV of the Rg_2F^* fluorescence relative to the gas phase indicates that the triatomic excimers do not desorb from the cluster. Thus, Rg_2F^* emissions are due to triatomic excimers at the surface or in the interior of the cluster.

Size dependent fluorescence spectra of NF_3 doped Xe_N clusters are displayed in Fig. 6. The increase in fluorescence intensity reflects the increase in cluster density. This has been checked by comparing the luminescence intensity of emissions from Xe excimer centres in the VUV and from the XeF^* and X_2F^* excimers in the UV. With increasing cluster size the contribution of XeF^* decreases. Thus, we conclude that the desorption rate of XeF^* decreases with increasing cluster size.

Conclusions

The relaxation dynamics in electronically excited Xe doped Ar_N and NF_3 doped Xe_N , Kr_N and Ar_N clusters have been investigated. In the case of an atomic impurity like Xe the relaxation pathway is determined by the position of the Xe atom in the argon cluster. It turned out that a bubble is formed around the Xe^* atom if the Xe atom is located inside the cluster as a consequence of the repulsive interaction between Xe^* and the surrounding atoms. The emissions of Xe atoms from bubbles are prominent up to a cluster size of 25 000 indicating that the bubbles are rather stable against compression by the surrounding Ar atoms. The relaxation processes in clusters differ considerably from those in the solid even up to $\langle N \rangle = 10\,000$. Emission from substitutional sites becomes very strong in the size range $\langle N \rangle = 10^4$ – 10^5 .

RgF^* and Rg_2F^* excimer fluorescence is observed following photo-excitation of NF_3 doped rare gas clusters. To the best of our knowledge this is the first report on charge transfer reactions in clusters. The excimers are formed in photon induced charge transfer reactions inside the clusters following excitation into the first excitonic absorption band of the clusters. While the triatomic excimers emit in the interior or at the surface of the cluster, diatomic $\text{B} \rightarrow \text{X}$ fluorescence is due to desorption of RgF^* from the cluster surface. The results show that relaxation processes in clusters differ considerably from those in the gas phase and in solid samples.

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Paper 7/06123D; Received 21st August, 1997