Photochemistry with fast sample renewal using cluster beams: formation of rare-gas halides in charge-transfer reactions in NF₃-doped rare-gas clusters

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Abstract

Charge transfer reactions in free clusters are observed in a photoluminescence study on doped rare-gas clusters (Rg clusters, Rg = Ar, Kr and Xe). Following photoexcitation into the first absorption bands of Rg clusters, fluorescence from free RgF excimers ejected from the clusters and from Rg,F excimers localized in the interior of the clusters is observed. The results show that the reaction dynamics in clusters differs considerably from that in the gas and solid phase.

1. Introduction

Photochemical processes in gas-phase and solid samples differ considerably in various aspects. One particular observation, which is often observed in matrix studies, is the presence of long-lived radicals and highly reactive atoms being formed in photodissociation processes [1,2]. Due to their low mobility in solid samples, these species are metastable against recombination. This makes the detailed investigation of relaxation dynamics and reaction pathways in condensed matter often rather difficult because the composition of the sample changes during the experiment. Thanks to the fast sample renewal in cluster beams (typically clusters spend only 10⁻⁶ s in the interaction region with the photon beam) photochemical processes in clusters are not affected by the presence of reaction products. This allows the investigation of photochemical processes in condensed matter under conditions similar to gas-phase experiments.

In this Letter, we report on the observation of charge transfer (CT) reactions in clusters covering a large-size range, namely the formation of RgF and Rg,F excimers in NF₃-doped Rg clusters (RgN = Ar, Kr, Xe; N = 2–500). Analogous reactions are very well characterised in the gas [3–5] and solid...
phase [6–11]. Based on their single, weakly-bound valence electron, excited Rg\(^+\) atoms can be regarded as pseudo-alkalis. In the gas phase, the reactions between excited rare-gas atoms (Rg\(^+\)) and halogen (X) containing molecules (MX), so-called ‘harpooning’ reactions, proceed through a curve crossing of a covalent Rg\(^+\)–XM entrance potential with an Rg\(^+\)–X\(^-\) ion-pair potential. Subsequent dissociation of the complex leads to the formation of RgX\(^+\) excimers [4]. Previous attempts to study CT reactions in small clusters, e.g. in Xe\(_n\)Cl\(_2\) [12–14] or Ar\(_n\)O\(_2\), have shown that the characteristic excimer fluorescence which is emitted after the CT reaction takes place is only observed for small complexes with \(N = 1\) or \(2\). This already gives strong evidence that photochemistry in clusters and solids differs considerably.

2. Experiment

The experiments were performed at the CLULU (cluster luminescence) arrangement at HASYLAB (DESY) [15]. In short, Rg\(_N\) clusters (\(N = 2–500\)) are prepared in a continuous free-jet expansion of pure Ar, Kr or Xe gas at a stagnation pressure up to 5 bar and a temperature between 120 and 300 K through a conical nozzle (\(d = 100\) \(\mu\)m, \(2\varphi = 30^\circ\)). A beam of NF\(_3\) molecules, prepared in an expansion through a 300 \(\mu\)m nozzle, intersects the cluster beam 15 mm downstream. Mixed clusters were formed by two different techniques. NF\(_3\)-doped Ar and Kr clusters are prepared by a co-expansion of 0.1% NF\(_3\) in Ar or Kr gas or by a pick-up technique. Doped Xe clusters are only formed by a pick-up technique. On the basis of our results for Xe-doped Ar clusters [16], we assume that the clusters are solid if they are prepared by co-expansion. In view of the results presented in the next paragraph, we assume that the clusters are also solid if they are prepared by the pick-up technique. The background pressure was kept below 10\(^{-4}\) mbar during the experiment by a continuous pumping of the interaction-volume. Tunable synchrotron radiation in the vacuum ultraviolet (VUV) range (\(\Delta\lambda_{vac} = 0.25\) nm) was focused on the cluster beam. The UV–visible (UVV) fluorescence was analysed by a Czerny–Turner-type monochromator (\(f = 275\) mm, 150 1/mm grating, 300 \(\mu\)m slits) equipped with a liquid nitrogen cooled CCD camera (Princeton Instruments). Spectra were collected over 300 s. Simultaneously, the total VUV fluorescence was detected by a channelplate detector coated with CsI behind a LiF window (energy range, 7–11.5 eV). Excitation spectra of UV–IR fluorescence (2–6 eV) covering the RgF\(^+\) and Rg\(_2\)F\(^+\) fluorescence were recorded with a photomultiplier (Hamamatsu R943-02) with a GaAs (Cs) photo cathode and a quartz window. For a given stagnation pressure and temperature of the gas before expansion, the mean cluster size \(N\) was calculated using the experimental calibration curve [15].

3. Results and discussion

Fluorescence spectra of NF\(_3\)-doped Xe\(_N\), Kr\(_N\) and Ar\(_N\) clusters recorded after 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. 1. Under our experimental conditions, the clusters are doped with only one NF\(_3\) molecule. This has been checked by measuring the excitation spectra for different NF\(_3\) densities in another set of measurements [17]. At sufficiently low densities, spectral features due to NF\(_3\) dimers are absent. Several broad and narrow emission bands can be seen in Fig. 1. The narrow bands at 3.54 eV (Xe) and 5.0 eV (Kr) are attributed to the B \(\rightarrow\) X transition of XeF\(^+\) and KrF\(^+\). A similar band at 6.4 eV is observed for NF\(_3\)-doped Ar clusters (the small band at 3.2 eV in Fig. 1 is due to the second order of the monochromator of this band) [17,18]. These bands are the prominent emissions in the gas-phase NF\(_3\)/Rg mixtures providing intense UV light in excimer lasers [4]. The emissions are due to bound free fluorescence from the lowest electronically excited CT Rg\(^+\)F state labelled B to the repulsive ground state X. Weak broad emissions at 2.56 eV (Xe) and 5.64 eV (Ar) are assigned to the corresponding gas-phase C \(\rightarrow\) A transitions [4]. Within the error bars, the measured transition energies in the cluster agree with the gas-phase values (see Table 1). The broad and intense emissions at 1.53 eV (Xe), 2.58 eV as well as 2.79 eV (Kr) and 3.87 eV (Ar) are energetically close (<100 meV) to the well known \(^2\)I \(\rightarrow\) \(^2\)\(^\text{I}^\text{'}\) transi-
Fig. 1. Fluorescence spectra of NF$_2$-doped Rg clusters (cluster size $N = 100$ (Xe); $N = 30$ (Kr); $N = 150$ (Ar)). Assignments of different emission bands are labelled. Some very sharp bands at 1.79 eV (Xe), 2.50 eV (Kr), 2.0 and 3.22 eV (Ar) labelled by arrows are due to the second order of the monochromator.

Table 1

<table>
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<tr>
<th></th>
<th>ArF</th>
<th>Ar$_2$F</th>
<th>KrF</th>
<th>Kr$_2$F</th>
<th>XeF</th>
<th>Xe$_2$F</th>
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<td>$\Delta E$ (eV)</td>
<td>$E$ (eV)</td>
<td>$\Delta E$ (eV)</td>
<td>$E$ (eV)</td>
<td>$\Delta E$ (eV)</td>
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<td>0.1$^a$</td>
<td>4.3$^a$</td>
<td>0.68$^a$</td>
<td>5.0$^a$</td>
<td>0.1$^a$</td>
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<tr>
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<td>0.52$^b$</td>
<td></td>
<td></td>
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<tr>
<td>Solid</td>
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<td></td>
<td>2.74$^d$</td>
<td>0.37$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cluster</td>
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<td>0.1$^c$</td>
<td>3.9$^c$</td>
<td>0.61$^c$</td>
<td>5.0$^c$</td>
<td>0.1$^c$</td>
</tr>
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</table>

$^a$From Ref. [27].
$^b$From Ref. [6].
$^c$This work.
$^d$From Ref. [2].
$^e$In the case of Kr$_2$F$^+$, the $4^2\Gamma_{1,2} \rightarrow 2^1\Gamma$ transitions is split into two components.
emissions are due to triatomic excimers at the surface or in the interior of the cluster.

Cluster size-dependent fluorescence spectra of NF₃-doped Xeₙ clusters are displayed in Fig. 2. The excitation energy was tuned to the first excitonic absorption band of Xeₙ clusters at approximately 8.4 eV [19]. The increase in fluorescence intensity reflects the increase of the particle density of clusters in the interaction region. This has been checked by comparing the luminescence intensity of intrinsic fluorescence of the clusters in the VUV (Xe₂⁺ centres inside the cluster [19]) and from the XeF⁺ and Xe₂F⁺ excimers in the UV. With increasing cluster size, the contribution of XeF⁺ decreases. The intensity ratio $J_{1,2}$ of XeF⁺ and Xe₂F⁺ excimer fluorescence can be described by $J_{1,2} = 0.25 \times N^{-1/3}$ [17].

Furthermore, the intensity ratio $J_{1,2}$ between XeF⁺ and Xe₂F⁺ depends on the excitation energy. We have measured the ratio for bulk and surface excitations. It turned out that the ratio for surface and bulk excitations (here labelled $J_{s,b}$) can be described by [17] $J_{s,b} = 1.05 \times N^{-1/3}$ which is characteristic for the surface to bulk ratio [20]. Since XeF⁺ is due to desorbing excimers while Xe₂F⁺ is due to excimers in adsorbed states, we conclude that the desorption rate of XeF⁺ decreases with increasing cluster size. The $N^{-1/3}$ of $J_{s,b}$ indicates that excimers formed at the surface desorb. Furthermore, it gives evidence that NF₃ molecules are present in the surface as well as being solvated in the interior sites of the cluster. Here we assume that the clusters are solid for the following reason: there is no significant difference between the measured fluorescence spectra and fluorescence excitation spectra of NF₃-doped Ar and Kr clusters prepared either by co-expansion or by the pick-up technique (see below). If the clusters were melted upon collisions with NF₃, we would expect significant differences between the spectra. The same argument should hold for Xe clusters which are more tightly bound. Which site in Xe clusters is preferentially populated depends on the strength and the bond length of the Xe–NF₃ interaction in comparison with the Xe–Xe interaction [21]. Unfortunately, there are no data available for the interaction potentials between Xe and NF₃. In view of the small size, large polarizability and the dipole moment ($\alpha = 3.62 \times 10^{-24}$ cm$^3$, $p = 0.235$ debye, [28]) of NF₃ we expect that it can stay at the surface as well as be solvated in the interior of Xeₙ clusters. In the case of Krₙ clusters, we have performed measurements on NF₃-doped clusters prepared by either a pick-up technique or conventional co-expansion. Fluorescence spectra recorded after excitation of clusters prepared by either method [17] show no significant difference, indicating that NF₃ molecules can, to a certain extent, migrate inside the clusters.

Fluorescence excitation spectra of the intrinsic Krₙ cluster fluorescence in the VUV and of Kr-halide excimer fluorescence in the energy range 2–5 eV are compared in Fig. 3. The strongest bands are due to the well-known excitonic absorption bands [22] of Krₙ clusters ($N \approx 500$) labelled 1s, 1t and 1l and the corresponding spin–orbit states 1's, 1't and 1'l. The suffix ‘s’ denotes surface states, ‘t’ and ‘l’ longitudi-

![Fluorescence spectra of NF₃-doped Xeₙ clusters as the function of size.](image-url)
Fig. 3. (a) Fluorescence excitation spectra of intrinsic luminescence (energy range, 7–11.5 eV) of Kr$_3$ clusters (full line) and of KrF$^+$ and of Kr$_2$F$^+$ excimer fluorescence (dashed line, energy range 2–6 eV) formed in a photochemical reaction inside the clusters. Surface and bulk excitons of the clusters labelled s,s' (surface) and t,t' and l,l' (transverse and longitudinal bulk states) [22,23], the atomic resonance lines (5s,5s') and dimer absorption bands (B$^1\Sigma_u^+$ and C$^1\Sigma_u^+\text{I}_{u}$) [26] are indicated. Experimental conditions: coexpansion of 0.1% NF in Kr; $N = 500$. (b) The intensity ratio of the sum of KrF$^+$, Kr$_2$F$^+$ fluorescence to the intrinsic fluorescence of Kr$_3$ clusters for $N \approx 500$. It is clearly visible that bulk states contribute significantly more to the formation of krypton halide excimers than surface states. The dashed lines are only to guide the eye.

The sharp lines in the excitation spectrum of VUV radiation (7–11.5 eV) are due to Kr atoms and dimers which are always present in the beam. In the fluorescence excitation spectrum of KrF$^+$ and Kr$_2$F$^+$ these lines are absent, while the excitonic absorption bands of Kr$_3$ are prominent. This demonstrates that KrF$^+$ and Kr$_2$F$^+$ are formed after excitation of Kr$_3$ clusters, localization of the excitation on the Kr–NF$_3$ complex and subsequent dissociation into CT states of the type Kr$^+–F^–$ or Kr$_2^+$F$^-$. The absence of the sharp lines due to Kr atoms and dimers in the fluorescence excitation spectrum of KrF$^+$ and Kr$_2$F$^+$ fluorescence can be interpreted in two different ways. (i) Under our experimental conditions, namely with a low concentration of NF$_3$, molecular complexes containing one NF$_3$ molecule and one or two Kr atoms are not formed or their absorption is substantially shifted relative to the absorption of bare Kr atoms and dimers. (ii) Larger complexes favour the formation of the Rg halides. On the other hand, it is well known that Rg halide formation from gas-phase Kr and NF$_3$ enclosed in a gas cell is very efficient [4]. Thus, we conclude that under collision-free conditions, namely with a low concentration of NF$_3$, a minimum cluster size of three to five Kr atoms [17] is required for the formation of van der Waals Kr$_3$–NF$_3$ complexes and subsequent formation of Rg halides. Interestingly, the opposite has been observed for the Xe$_{18}$–Cl$_2$ system [14]. In this case, only monomers and dimers led to the formation of XeCl$^+$.

From spectrally resolved measurements of bare Kr$_3$ clusters, it is well known that the trimer and larger clusters emit fluorescence from vibrationally relaxed Kr$^+$ [24]. Moreover, the ratio of the sum of Kr$_2$F$^+$ and KrF$^+$ emission versus Kr$^+$ fluorescence increased almost linearly with $N^{1/3}$ for $N > 5$ (see Fig. 4) [17]. In other words, the formation of Rg halide excimers increases linearly with the radius of the cluster. This gives evidence that their formation is considerably larger in the interior of the cluster than at the surface. In view of the fast relaxation of the primary excited states into Kr$^+$, it seems to be likely that Kr$_3$F$^+$ is formed in a two step process. After excitation, Kr$_3^+$ is formed inside the clusters. In a second step, Kr$_2$F$^+$ is formed in a reaction with NF$_3$.

The intensity of the KrF$^+$ and Kr$_2$F$^+$ fluorescence, normalised to the intrinsic Kr$_3$ fluorescence, is presented in the lower part of Fig. 3. The increase with increasing excitation energy indicates that there is an energy threshold for the formation of the halides. A threshold energy of 9.9 ± 0.05 eV was derived from the data in Fig. 3 by a linear fit of the data between 10 and 10.4 eV. Furthermore, one can see that surface and bulk excitons of the clusters...
Fig. 4. The intensity ratio between the sum of KrF\(^*\) and Kr\(_2\)F\(^*\) fluorescence in the UV and visible and the intrinsic luminescence of Kr\(_x\) clusters in the VUV spectral range as a function of \(N^{1/3}\). The increase with \(N^{1/3}\) gives evidence that the formation of krypton halide excimers is more favourable in the interior of the cluster than at the surface. The dashed lines are only to guide the eye.

labelled s,s' (surface) and t,t' and l,l' (transverse and longitudinal bulk states), respectively, both contribute to the formation of the halides. In agreement with the results discussed before, the yield of surface states is 35% lower.

Finally we compare the reaction dynamics in clusters with corresponding processes in the gas and solid phase. Studies in the gas phase show that photoreactions starting with Rg\(^*\) or MX\(^*\) lead depending on the pressure with high efficiency, to the formation of RgF\(^*\) or Rg\(_2\)F\(^*\) [4]. Triatomic excimers are preferentially formed at high pressure. On the other hand, it is now well established that in the solid a two-step process is usually required [1,2]. First the MX molecule is dissociated by a photon of sufficient energy and, in a next step induced by a second photon, the photochemical reaction between a halogen atom and the matrix leads to the formation of Rg\(_2\)F\(^*\) excimers.

This raises the question: how do the reaction dynamics in clusters differ from those in the solid? Firstly, we like to point out that, at least under our experimental conditions, two-step processes involving two photons are extremely unlikely because of the low photon flux and the fast sample renewal. Therefore, we can assume that the photo reactions are due to one-step processes, while in the solid a two-step process is required. At present, we can only speculate as to why in the solid the two-step process is much more efficient than the one-step process. One plausible explanation could be that fast, radiationless transitions depopulate very efficiently electronically excited states. In the cluster, these processes may be not as efficient as in the solid, allowing the harpooning reaction to take place.

In the cluster, it may happen as already discussed that the excitation of the clusters becomes localized on Rg\(_2\)\(^*\) self-trapped molecular centres [19,23] before the energy is transferred to the NF\(_3\) molecule. In addition, the branching ratio between formation from Rg\(^*\) or Rg\(_2\)\(^*\) can depend on the excitation energy. This could, e.g. explain the observed energy dependence in Fig. 3b. If the formation of Rg halides proceeds via Rg\(_2\)\(^*\) the available energy is considerably reduced by the energy needed for the relaxation into Rg\(_2\)\(^*\) and might not be sufficient in order to allow the formation of the halide excimers. At present, we cannot make a definite statement if the formation of Rg halides proceeds via Rg\(_2\)\(^*\) or Rg\(_2\)\(^*\)\(^*\).

Time resolution may help to solve this problem, since the lifetime of the long-lived Rg\(_2\)\(^*\) is (depending on the rare gas) 10–100 times longer than that of Rg\(^*\) [23].

The Rg fluorine systems are characterized by a large excess energy between excitation ( \(\approx 10\) eV for Kr) and emission (2.5 eV for Kr\(_2\)F\(^*\) and 5 eV for KrF\(^*\)). If the total relaxation energy is less than 5 eV, the formation of KrF\(^*\) and Kr\(_2\)F\(^*\) is energetically possible. From this viewpoint, Rg fluorides are good candidates for the formation of halide excimers in clusters. These findings may explain why previous attempts to observe excimer emission from large Cl\(_2\)- or O\(_2\)-doped Rg clusters failed [12–14]. On the other hand, in a study on F\(_2\)-doped liquid krypton with femtosecond multiphoton excitation, evidence is given that Kr\(_2\)F\(^*\) excimers can also be formed in a direct reaction between F\(_2\) Kr\(^*\) centres formed in the relaxation process of krypton excitons [25]. From the time evolution, it could be concluded that the dissociation of the F\(_2\) into two F atoms is not required in the first step of the reaction. This indicates that under certain conditions a reaction pathway similar to the one reported here in clusters can be observed in liquid rare gases.
4. Conclusions

The first CT reactions in clusters containing up to 500 atoms are reported. The fluorescence of RgF⁺ excimers desorbing from the cluster and of Rg₂F⁺ excimers emitting inside the cluster are observed following photoexcitation in the first strong absorption bands of NF³-doped Rg clusters. The strongest emissions can be attributed to the B→X RgF and 2²Σ⁻→1²Σ⁺ Rg₂F⁺ transitions. In the case of Kr₅ clusters, the energy threshold of the reaction was determined to be 9.9 eV. The reaction dynamics in the clusters differs considerably from that in the gas-phase and solid samples. In contrast to gas-phase experiments performed in a gas cell, RgF⁺ emissions dominate the fluorescence spectra, at least for large clusters (N > 100). In a similar way, measurements on solid samples show dominant Rg₂F⁺ fluorescence. However, in the clusters a one-step excitation process involving one photon is established while in the solid a two-step excitation with two photons is needed for the formation of Rg₂F⁺ excimers. Thanks to fast sample renewal in cluster beams, photoreactions can be studied without complications due to the presence of reaction products.

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References