



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 Rg₂F^{*} 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. © 1999 Elsevier Science B.V. All rights reserved.

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 Rg₂F^{*} excimers in NF₃-doped Rg clusters (Rg_N = Ar, Kr; Xe; N = 2–500). Analogous reactions are very well characterised in the gas [3–5] and solid

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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_NCl_2 [12–14] or Ar_NO_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 ($d = 100 \mu\text{m}$, $2\varphi = 30^\circ$). A beam of NF_3 molecules, prepared in an expansion through a $300 \mu\text{m}$ 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 ($\Delta\lambda_{\text{exc}} = 0.25 \text{ nm}$) was focused on the cluster beam. The UV-visible (UVV) fluorescence was analysed by a Czerny–Turner-type monochromator ($f = 275 \text{ mm}$, 150 l/mm grating, $300 \mu\text{m}$

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_2F^* 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 $\text{B} \rightarrow \text{X}$ transition of XeF^* and KrF^* . A similar band at 6.4 eV is observed for NF_3 -doped Ar clusters (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 $\text{C} \rightarrow \text{A}$ 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 ($< 100 \text{ meV}$) to the well known $^2\Gamma \rightarrow 1,2^2\Gamma$ transi-

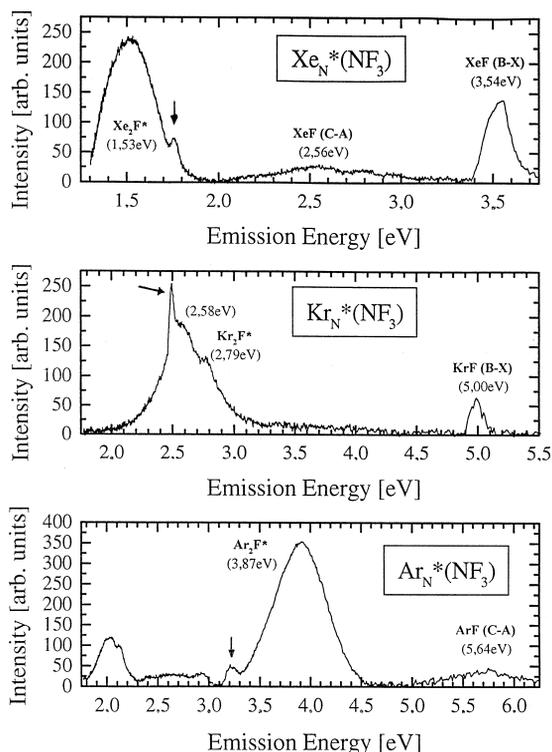


Fig. 1. Fluorescence spectra of NF_3 -doped Rg clusters (cluster size $N \approx 100$ (Xe); $N \approx 30$ (Kr); $N \approx 150$ (Ar)). Assignments of different emission bands are labelled. Some very sharp bands at 1.79 eV (Xe), 2.50 eV (Kr), 2.0 and 3.22 eV (Ar) labelled by arrows are due to the second order of the monochromator.

tion of the triatomic Rg_2F^* excimers in liquid and solid samples. Similar broad bands emitted at some-

what higher (0.3–0.5 eV) energies are observed in the gas phase at high pressure [4]. The width of these emission bands from clusters is in good agreement with the values for the gas and the condensed phase (see Table 1). Therefore, we attribute the intense broad emission bands in clusters to triatomic excimers. The large spectral shift of the triatomic excimer emission with respect to the diatomic one is due to the extra binding energy of Rg_2^+F^- relative to Rg^+F^- which is approximately the binding energy of Rg_2^+ . Interestingly, diatomic RgF^* excimer emissions are only observed in liquid and solid samples if ternary mixtures, e.g. Xe, Kr and F_2 are prepared [6]. In the case of NF_3 -doped Ar_N clusters, a few weak yet unassigned bands between 2.1 and 3.0 eV are observed (the intense band at 1.95 eV is presumably due to the second order from the Ar_2F^* fluorescence at 3.9 eV).

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 absence of RgF^* fluorescence in an adsorbed configuration is not surprising since in the adsorbed configuration RgF^* can easily be converted into Rg_2F^* excimers which are considerably lower in energy [4]. 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^*

Table 1

Comparison between the emission energy E and the width ΔE (FWHM) of diatomic B–X transitions and triatomic $4^2\Gamma-1,2^2\Gamma$ transitions of Rg halides under various conditions

	ArF		Ar_2F		KrF		Kr_2F		XeF		Xe_2F	
	E (eV)	ΔE (eV)	E (eV)	ΔE (eV)	E (eV)	ΔE (eV)	E (eV)	ΔE (eV)	E (eV)	ΔE (eV)	E (eV)	ΔE (eV)
Gas	6.43 ^a	0.1 ^a	4.3 ^a	0.68 ^a	5.0 ^a	0.1 ^a	2.95 ^a	0.5 ^a	3.55 ^a	0.15 ^a	2.0 ^a	0.3 ^a
Liquid			4.0 ^b	0.52 ^b			2.79 ^b	0.38 ^b			1.8 ^b	0.16 ^b
Solid							2.74 ^d	0.37 ^d			1.6 ^e	0.29 ^e
Cluster	6.43 ^c	0.1 ^c	3.9 ^c	0.61 ^c	5.0 ^c	0.1 ^c	2.79 ^c	0.27 ^c	3.55 ^c	0.15 ^c	1.54 ^c	0.35 ^c
							2.59 ^c	0.19 ^c				

^aFrom Ref.[27].

^bFrom Ref. [6].

^cThis work.

^dFrom Ref. [2].

^eFrom Ref. [10]. In the case of Kr_2F^* , the $4^2\Gamma-1,2^2\Gamma$ 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 NF_3 -doped Xe_N clusters are displayed in Fig. 2. The excitation energy was tuned to the first excitonic absorption band of Xe_N 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 (Xe_2 centres inside the cluster [19]) and from the XeF^* and Xe_2F^* excimers in the UV. With increasing cluster size, the contribution of XeF^* decreases. The intensity ratio $J_{1,2}$ of XeF^* and Xe_2F^* excimer fluorescence can be described by $J_{1,2} = 0.25 \times N^{-1/3}$ [17].

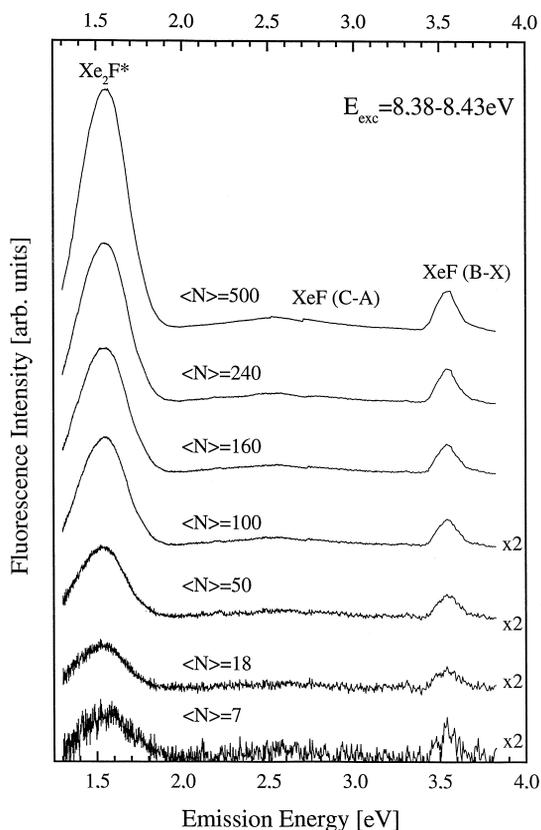


Fig. 2. Fluorescence spectra of NF_3 -doped Xe_N clusters as the function of size.

Furthermore, the intensity ratio $J_{1,2}$ between XeF^* and Xe_2F^* 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 Xe_2F^* 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 NF_3 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 NF_3 -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 NF_3 , 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– NF_3 interaction in comparison with the Xe–Xe interaction [21]. Unfortunately, there are no data available for the interaction potentials between Xe and NF_3 . In view of the small size, large polarizability and the dipole moment ($\alpha = 3.62 \times 10^{-24} \text{ cm}^{-3}$, $p = 0.235$ debye, [28]) of NF_3 we expect that it can stay at the surface as well as be solvated in the interior of Xe_N clusters. In the case of Kr_N clusters, we have performed measurements on NF_3 -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 NF_3 molecules can, to a certain extent, migrate inside the clusters.

Fluorescence excitation spectra of the intrinsic Kr_N 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 Kr_N clusters ($N \approx 500$) labelled 1s, 1t and 1l and the corresponding spin-orbit states 1s', 1t' and 1l'. The suffix 's' denotes surface states, 'l' and 't' longitudinal

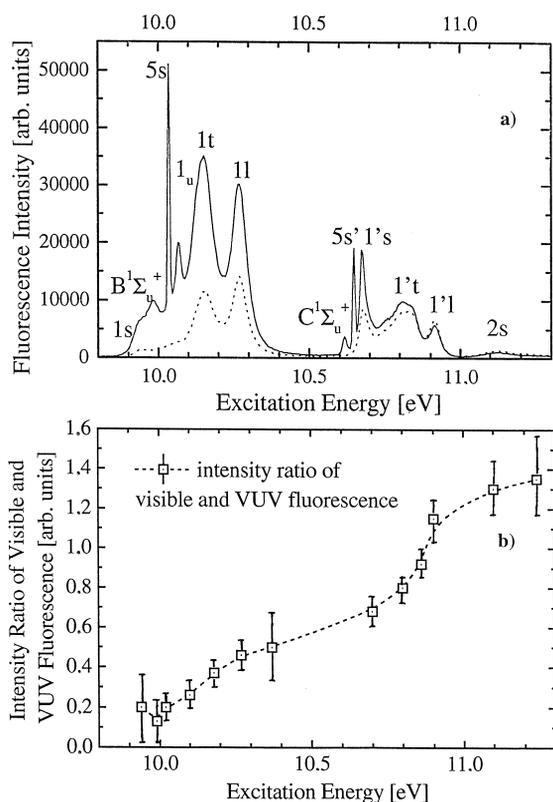


Fig. 3. (a) Fluorescence excitation spectra of intrinsic luminescence (energy range, 7–11.5 eV) of Kr_N clusters (full line) and of KrF^* and of Kr_2F^* excimer fluorescence (dashed line, energy range 2–6 eV) formed in a photochemical reaction inside the clusters. Surface and bulk excitons of the clusters 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 ($\text{B}^1\Sigma_u^+$ and $\text{C}^1\Sigma_u^+$, 1_u) [26] are indicated. Experimental conditions: coexpansion of 0.1% NF_3 in Kr; $N \approx 500$. (b) The intensity ratio of the sum of KrF^* , Kr_2F^* fluorescence to the intrinsic fluorescence of Kr_N 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.

nal and transverse bulk exciton states, respectively [23]. The rather 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_2F^* these lines are absent, while the excitonic absorption bands of Kr_N clusters are prominent. This demonstrates that KrF^* and Kr_2F^* are formed after excitation of Kr_N clusters, localization of the excita-

tion on the $\text{Kr}-\text{NF}_3$ complex and subsequent dissociation into CT states of the type $\text{Kr}^+ - \text{F}^-$ 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_2F^* 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_N-NF_3 complexes and subsequent formation of Rg halides. Interestingly, the opposite has been observed for the Xe_N-Cl_2 system [14]. In this case, only monomers and dimers led to the formation of XeCl^* .

From spectrally resolved measurements of bare Kr_N clusters, it is well known that the trimer and larger clusters emit fluorescence from vibrationally relaxed Kr_2^* [24]. Moreover, the ratio of the sum of Kr_2F^* and KrF^* emission versus Kr_1^* 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_2^* , it seems to be likely that Kr_2F^* is formed in a two step process. After excitation, Kr_2^* is formed inside the clusters. In a second step, Kr_2F^* is formed in a reaction with NF_3 .

The intensity of the KrF^* and Kr_2F^* fluorescence, normalised to the intrinsic Kr_N 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

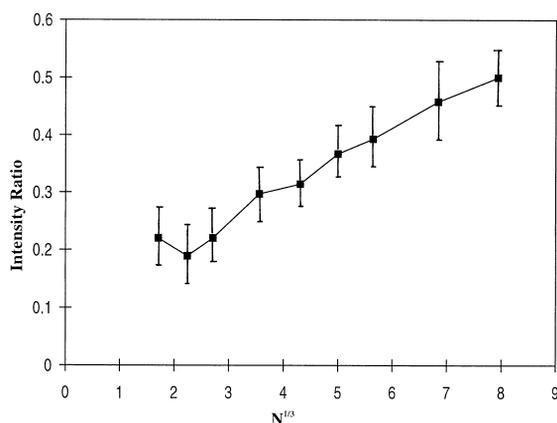


Fig. 4. The intensity ratio between the sum of KrF^* and Kr_2F^* fluorescence in the UV and visible and the intrinsic luminescence of Kr_N clusters in the VUV spectral range as a function of $N^{1/3}$. The increase with $N^{1/3}$ gives evidence that the formation of krypton halide excimers is more favourable 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_2F^* [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_2F^* excimers.

This raises the question: how do the reaction dynamics in clusters differs 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 excitation 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^* 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 (≈ 10 eV for Kr) and emission (2.5 eV for Kr_2F^* and 5 eV for KrF^*). If the total relaxation energy is less than 5 eV, the formation of KrF^* and Kr_2F^* 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_2F^* 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 Rg_2F^* excimers emitting inside the cluster are observed following photoexcitation in the first strong absorption bands of NF_3 -doped Rg clusters. The strongest emissions can be attributed to the B-X (RgF^*) and $4^2\Gamma-1,2^2\Gamma$ (Rg_2F^*) transitions. In the case of Kr_N 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, Rg_2F^* emissions dominate the fluorescence spectra, at least for large clusters ($N > 100$). In a similar way, measurements on solid samples show dominant Rg_2F^* 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 Rg_2F^* excimers. Thanks to fast sample renewal in cluster beams, photoreactions can be studied without complications due to the presence of reaction products.

Acknowledgements

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