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Photochemistry in rare gas clusters

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Abstract. In this contribution photochemical processes in pure rare gas clusters will be discussed. The relaxation dynamics of electronically excited He clusters is investigated with luminescence spectroscopy. After electronic excitation of He clusters many sharp lines are observed in the visible and infrared spectral range which can be attributed to He atoms and molecules desorbing from the cluster. It turns out that the desorption of electronically excited He atoms and molecules is an important decay channel. The findings for He clusters are compared with results for Ar clusters. While desorption of electronically excited He atoms is observed for all clusters containing up to several thousand atoms a corresponding process in Ar clusters is only observed for very small clusters ($N < 10$).

PACS. 36.40.-C Atomic and molecular clusters – 82.50.-m Photochemistry and radiation chemistry – 78.55.-m Photoluminescence

1 Introduction

Rare gas clusters have attracted considerable interest for many years since they have many unique properties. As clusters with a large band gap they can be regarded as model systems for insulators. The stability [1], geometric [2] and electronic structure [3] of the heavier rare gas clusters has been investigated in great detail. Recently, several research group have begun to study the properties of He clusters [4]. These studies are in part devoted to the properties of pure He clusters. They exhibit many unusual and fascinating thermodynamic, electronic and dynamical properties. In contrast to most other materials He clusters are liquid, clusters of the isotope ^{4}He are even superfluid for a cluster size larger than $N = 70$ [5]. As a result of a very small van der Waals binding He clusters can be regarded as very soft and diffuse agglomerates of atoms. Several aspects of the electronic structure of He clusters were recently investigated with fluorescence excitation spectroscopy utilising synchrotron radiation SR [6]. Of particular interest is the development of electronically excited levels with cluster size. He clusters can be regarded as a model system since the electronic structure of He atoms is very simple. The absorption spectrum from the $1s$ ground state is characterised by transitions into dipole allowed np ($n = 2, 3, 4, \dots$) transitions. In the context of the dynamics and the relaxation processes of He clusters two questions are particularly interesting: (i) How are the atomic excitations modified in the cluster? (ii) What are the relaxation processes following electronic excitation?

In this paper various aspects of photochemical processes in rare gas clusters will be addressed. Radiative relaxation processes following photoexcitation of He clusters will be discussed and compared with results for Ar clusters. In order to get a deeper insight radiative cascades in the visible and infrared (IR) spectral range are investigated. It turns out that the desorption of electronically excited atoms and molecules plays an important role in the relaxation dynamics. The efficiency of desorption can be related to the electron affinity of the cluster and the time scale of radiationless relaxation into the lowest excimer states of rare gas dimers.

2 Experimental

The measurements are performed at the experimental station Clulu at HASYLAB. He clusters are prepared in a free jet expansion of cold He gas (4–30 K) at a stagnation pressure of 2000–4000 mbar through flat nozzles with a orifice of 0.03–0.006 mm diameter. For the preparation of Ar clusters a conical nozzle (0.2 mm diameter, opening cone angle $2\theta = 30°$) was used. With a stagnation pressure of 400–900 mbar and a nozzle temperature 100–300 K the size of Ar clusters could be varied between 2 and 2000. The beam consisting of atoms and clusters is photo-excited with monochromatized synchrotron radiation in the energy range between 20–25 eV (He) and 12–16 eV (Ar). Fluorescence light emitted from the clusters is detected with two different photomultipliers covering a spectral range from 8–30 eV and 2–6 eV. Luminescence spectra in the visible and infrared spectral range are recorded with a 0.275 m Czerny–Turner spectrograph equipped with a liquid nitro-

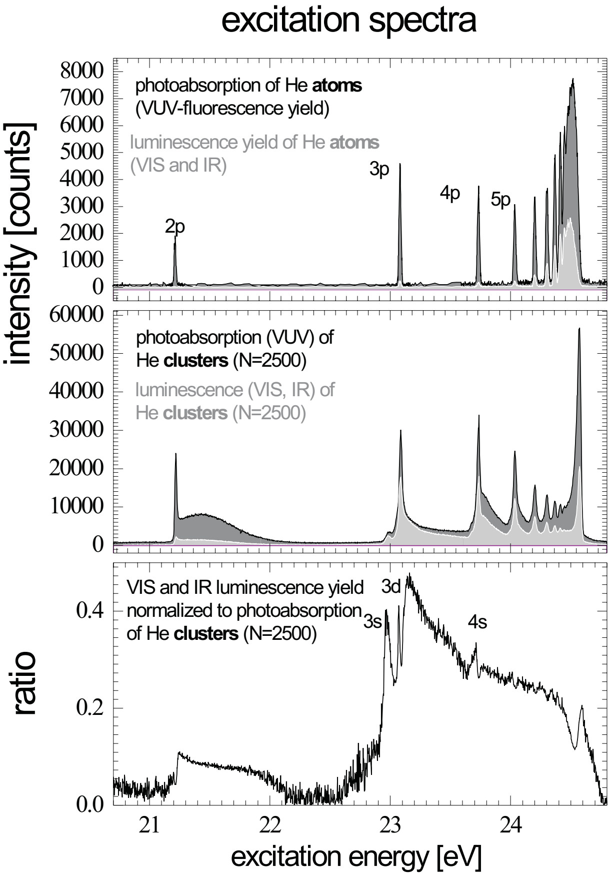

Fig. 1. Excitation spectra of the VUV (dark grey) and visible/ infrared (light grey) fluorescence of He atoms (top) and He clusters (middle). The ratio of visible/infrared fluorescence and VUV fluorescence of He clusters ($N \approx 2500$) is shown in the lowest part.

gen cooled CCD camera. In the case of He clusters a precise determination of the cluster size is very difficult because they are very fragile. Here we give estimates based on results for heavier rare gas clusters and well known scaling laws [7].

3 Results and discussion

Fluorescence excitation spectra of He atoms and of a cluster beam are presented in Fig. 1. Here it is assumed that the yield of the vacuum ultraviolet (VUV) fluorescence is a measure for the absorption. For He atoms this is certainly a very good approximation and based on the results for the other condensed rare gases it is expected that it holds also for He clusters [7]. Therefore, if we refer in the following to absorption spectra in a more precise sense fluorescence excitation spectra of VUV radiation are meant. One important advantage of fluorescence excitation spectroscopy is that the absorption can even be measured in beams which are optically very thin.

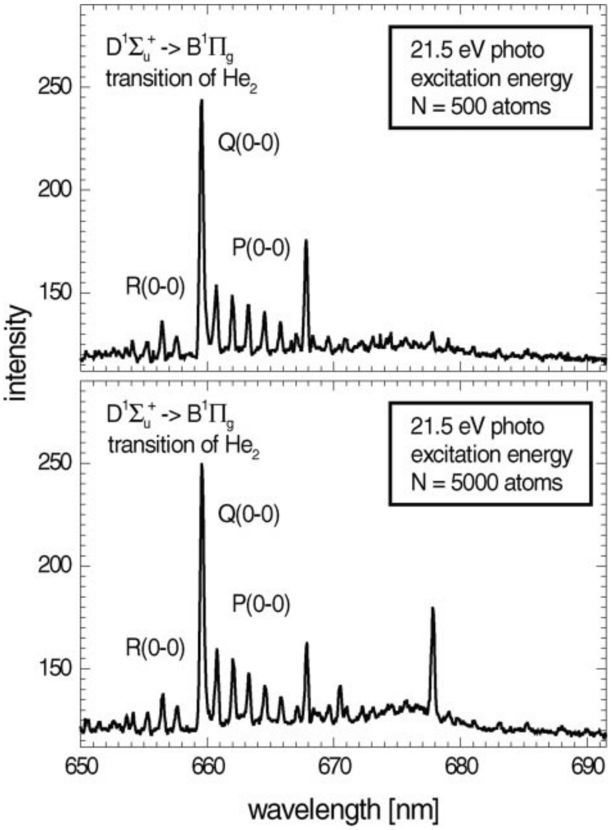

Fig. 2. Fluorescence in the visible spectral range following photo excitation of He clusters excited at 21.5 eV measured with high spectral resolution. Rotational resolved lines of the (0,0) D→B transition of He_2 can be seen. The P, Q and R branches are indicated in the figure.

The strong lines in the atomic absorption can be attributed to transitions from $1s$ into np states ($n = 2, 3, \ldots, 10$). The absorption spectrum of a cluster beam consists of two different components. The sharp lines are due to He atoms which are always present in the beam. Rather broad bands blue-shifted with respect to the atomic resonance lines are due to cluster absorption [6]. Up to a cluster size of a few thousand atoms the cluster absorption bands can be interpreted as atomic like transitions perturbed by the presence of surrounding atoms [6]. For larger clusters we have evidence that excitonic type excitations contribute to the absorption in the energy range 23–24 eV. In this energy range the absorption cannot be directly related to one of the resonance transitions of atomic He. One of the main results obtained from the absorption measurements is that the bands of large clusters are very broad despite the small van der Waals interaction in the ground state. The large spectral width of the bands is a direct consequence of the strong interaction of He atoms in electronically excited states with surrounding ground state atoms. As a result of this strong interaction the excimer states of He_2 are bound by approximately 2.5 eV [8]. Apart from the excitonic effects the absorption of He clusters can be explained on the basis of molecular pair potentials. The blue-shift with respect to the atomic resonance lines is due to a repulsive interaction at intermediate internuclear distances [9, 10] which gives rise to so-called 'humps' (see also Fig. 3) [8].

In contrast to many other materials condensed He emits a rich spectrum in the visible and infrared spectral range [11]. The fluorescence yield in the visible and infrared range of He atoms and clusters is shown in Fig. 1 (in light grey). Since the infrared and visible transitions of He atoms are in competition with fast transitions in the VUV the yield is very low. Surprisingly, the yield of visible and infrared fluorescence emitted from clusters is rather high (see Fig. 1). In the lowest part of Fig. 1 the ratio of visible/infrared and VUV emission of clusters is presented. At approximately 23 eV pronounced structures can be seen and the ratio is particularly high. The distinct peaks at ~ 22.95 eV match with the atomic $3d$ and $3s$ levels which are dipole forbidden from the $1s$ ground state. In the cluster these transitions become allowed, presumably due to a symmetry breaking at the cluster surface. Nevertheless, the transition moment to the ground state is small while the decay rate to dipole allowed states with $2p$ character is rather high (see the discussion of the spectrally resolved fluorescence below). This explains why there is an enhancement of the IR-fluorescence.

In order to get more insight into the relaxation dynamics spectrally resolved fluorescence spectra are recorded in the VUV and visible/infrared spectral range [10, 12] The dominant decay channel is a radiative transition from excimer states to the ground state which gives rise to a very broad continuum in the VUV [10]. Fluorescence spectra in the visible spectral range are presented in Fig. 2. The excitation energy was tuned to 21.5 eV which is a particular strong absorption band of He clusters containing more than 100 atoms. He atoms and molecules do not absorb at this energy. In contrast to the VUV fluorescence many sharp lines can be seen. They coincide within the error bars with the well-known emission lines of free He atoms and of He_2 molecules [13] and can therefore be assigned to the fluorescence of He atoms and molecules ejected from the cluster since He atoms and molecules in the beam can not be excited at 21.5 eV. This gives evidence that the desorption of electronically excited atoms and molecules is an important path way in the relaxation process of He clusters. In addition to the sharp lines a somewhat broader emission at 675 nm is observed for large clusters containing on average 5000 atoms. The broadening is an indication that the radiative process takes place in the interior of the cluster, e.g. He_2 inside the cluster or close to the surface. Since this band is weaker for smaller clusters (mean size $N = 500$, see Fig. 2) we assume that there is a size dependent competition between desorption and relaxation inside the cluster. Relaxation inside the cluster or close to the surface is more pronounced in larger clusters. On the basis of spectrally resolved measurements the large yield of visible and infrared luminescence can be understood in the following way. After excitation of He clusters electronically excited He atoms and molecules are formed inside the cluster in various states correlated with ns, np, and nd levels. Electronically excited atoms and molecules are then ejected from the cluster. Since the s- and d-symmetric levels cannot directly decay to the $1s$ ground state by the emission of a VUV photon the probability of radiative cascades in the visible and infrared spectral range is rather high. The excitation and relaxation scheme is illustrated in Fig. 3.

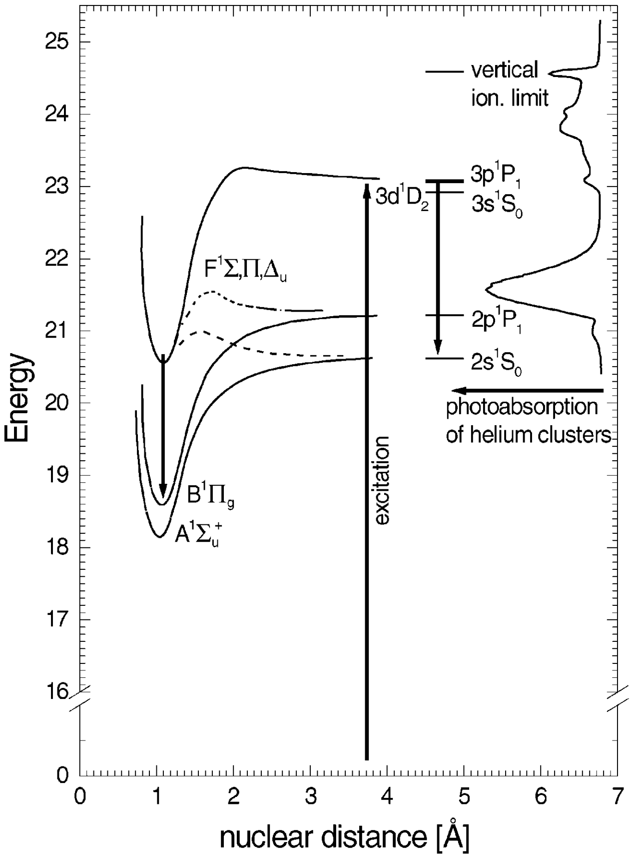

Fig. 3. Schematic illustration of excitation and relaxation processes in He clusters. The potential curves are drawn using the potentials in [8].

These findings for He clusters can be compared with corresponding measurements for Ar clusters. Spectrally resolved fluorescence emitted from a Ar cluster beam (mean cluster size $N = 150$) is presented in Fig. 4. Many sharp lines can be seen and identified with fluorescence of free Ar atoms in various $4p$ levels. Visible fluorescence from electronically excited Ar_2 similar to that of He_2 could not be observed. This is very reasonable because highly excited Ar_2 molecules are known to predissociate [14]. Similar fluorescence of free atoms was observed for Ne, Kr and Xe clusters [15]. However, there is an important difference in the relaxation process in the heavier rare gas clusters (Ar, Kr, Xe) compared to the He clusters. For Ar, Kr and Xe IR-fluorescence of free atoms can only be observed following excitation of very small clusters containing less than ten atoms. This can be concluded from the excitation spectra of VUV and IR-fluorescence of Ar clusters presented in Fig. 5. For small clusters (mean size $N = 4$) the IR-luminescence yield shows some similarity with the VUV yield – at least above 14 eV – indicating that these clusters emit in the IR. The increase of the IR-yield towards

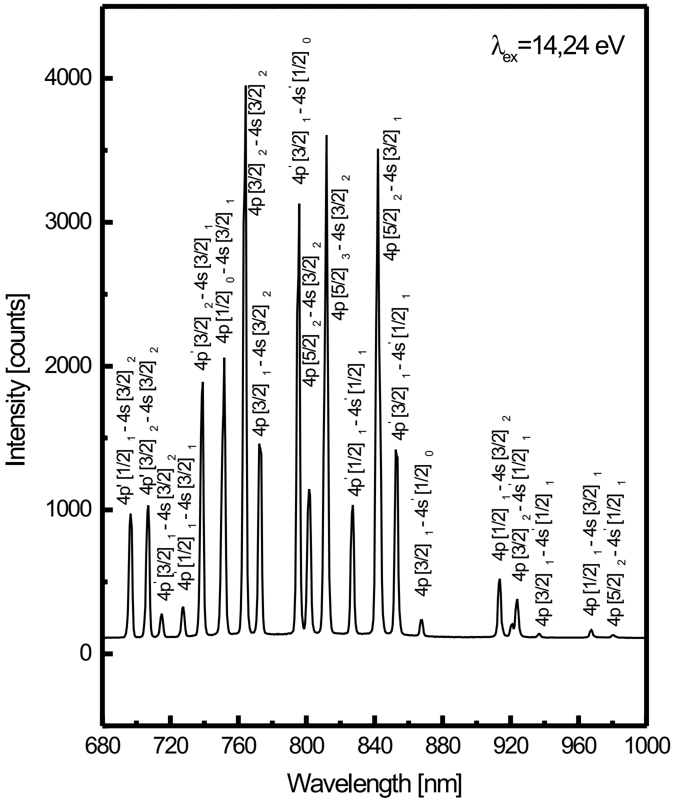

Fig. 4. Fluorescence in the visible and IR spectral range following photoexcitation of a beam of Ar clusters ($N \approx 500$). All lines can be identified with transitions of free Ar atoms. The assignment is given in the figure.

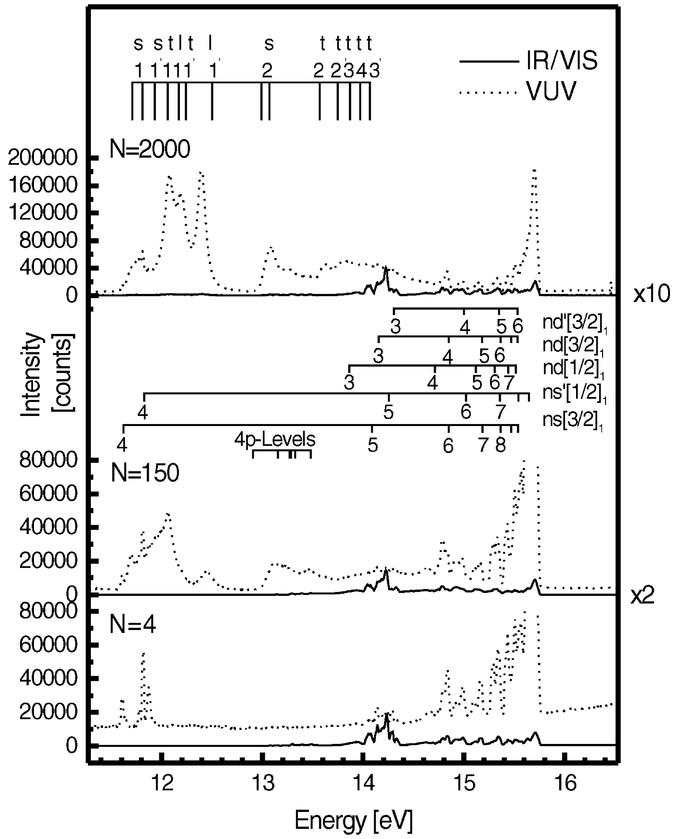

Fig. 5. Excitation spectra of the VUV (dotted line) and visible/infrared (full line) fluorescence of Ar clusters. The mean size of the clusters is indicated in the figure.

the ionisation energy at ~ 15.7 eV can be explained in the following way. With increasing energy loosely bound states with extended orbitals are excited. Since the overlap of their wave function with the ground state wave function is rather small the decay rate to the ground state is small while cascades in the IR are getting rather strong.

If the mean size of clusters in the beam is increased the VUV excitation spectra are considerably altered while the IR excitation spectra are almost unchanged. Especially the well known exciton states [16] between 13 and 14 eV do not contribute to the IR luminescence. Thus, we conclude that Ar atoms, molecules and small clusters which are always present as a small admixture in the cluster beam are responsible for atomic IR fluorescence.

Ne clusters on the other hand exhibit a similar behaviour [15] as He clusters. IR fluorescence of atoms desorbing from the clusters is observed in the whole size range up to $N \approx 5000$. These findings are consistent with results obtained for rare gas solids. IR fluorescence of desorbing atoms from the surface of rare gas solids is only observed for solid Ne [17]. The key feature for understanding the different behaviour is the interaction between an electronically excited atom and the surrounding rare gas atoms. If the interaction is repulsive one can expect that desorption takes place. It is widely accepted that the character of the interaction is related to the electron affinity. If the electron affinity is negative, it is assumed that the interaction is repulsive [17]. In this simple picture, one should expect that desorption should be observed for He, Ne and Ar clusters regardless of their size, while it should be suppressed for Kr and Xe clusters, because the electron affinity of He, Ne and Ar is negative [18]. The observed trend follows this expected behaviour except for Ar clusters. On the other hand, it is well known that Ar atoms in the energetically lowest electronically excited 4*s* levels desorb from solid Ar [17]. One possible explanation could be that a very fast radiationless relaxation due to a curve crossing with a repulsive molecular state takes place. In the case of the dimers of the heavy rare gases Ar, Kr, Xe the crossing with repulsive states seems to favour predissociation and population of low lying states (see Fig. 6). Furthermore, fast vibrational relaxation can depopulate the primary excited states. As a consequence, low lying states are populated which can only emit in the VUV. In other words, it is likely that the desorption of electronically excited Ar atoms is not prevented, but low lying states are populated which do not emit in the IR. For He the situation is different. The binding energy of He_2 is so large that the minima of the electronically excited states are lower than the atomic dissociation limit. As a result tightly bound excimer states are formed with a barrier at intermediate internuclear separations (see Fig. 3). This prevents a fast radiationless population of low lying states by a curve crossing mechanism.

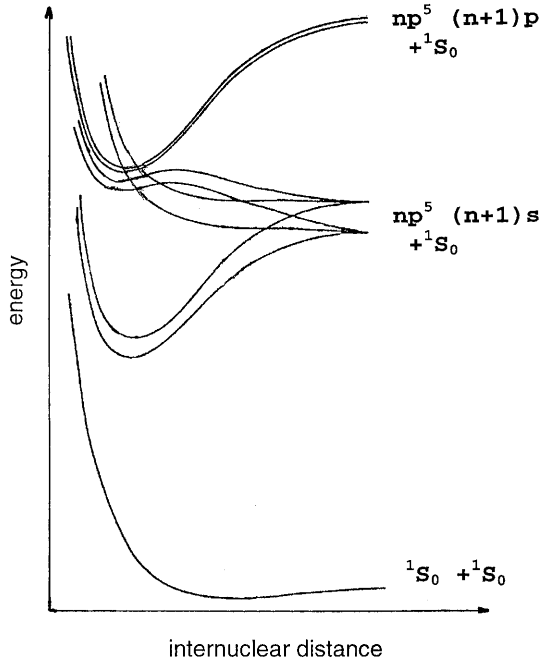

Fig. 6. Schematic potential energy curves of Ar_2. From [19].

4 Conclusion

In this paper photochemical processes in rare gas clusters are discussed. The relaxation dynamics of electronically excited He clusters is investigated with luminescence spectroscopic methods. Many sharp lines are observed in the visible and IR spectral range after electronic excitation of He clusters with synchrotron radiation in the VUV spectral range. The lines can be attributed to He atoms and molecules desorbing from the cluster in electronically excited states. Some weak and broad features are shifted with respect to atomic and molecular emission giving evidence that radiative relaxation can also take place inside the cluster or close to the surface.

It turned out that the desorption of electronically excited He atoms and molecules is an important decay channel. The findings for He clusters are compared with results for Ar clusters. Desorption of electronically excited Ar atoms emitting in the infrared spectral range is only observed for very small clusters ($N < 10$). We assume that fast non-radiative processes lead to a very efficient population of low lying states which can emit only in the VUV spectral range. The desorption of electronically excited atoms from Ne clusters indicates that non-radiative relaxation processes in Ne clusters are much slower than in Ar clusters.

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