Electronic structure and excited state dynamics of clusters: What can we learn from experiments with synchrotron radiation?

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Abstract

The investigation of the electronic structure and dynamics of clusters is a topic of current interest. Spectroscopy with vacuum ultraviolet (VUV) photons has two aspects: (i) systems with a large band gap can be studied and (ii) excitation of inner shell electrons allows us to obtain element-specific information. This paper gives an overview of recent developments in the field of cluster research with VUV radiation. Two topics will be discussed in detail: (i) Electronic excitation and relaxation dynamics in helium clusters studied with fluorescence spectroscopy. It turned out that desorption of electronically excited atoms and molecules is an important relaxation process. (ii) Inner shell photoionisation of NaCl clusters produced with a new pick-up cluster source. The near edge absorption structure (XANES) at the Cl 2p edge contains information on the geometric structure of the clusters. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Spectroscopy with synchrotron radiation (SR) has developed in the last twenty years into a very powerful tool for the investigation of electronic and geometric structure of atoms, molecules and solids. Absorption and fluorescence, ultraviolet (UPS) and X-ray photoelectron spectroscopy (XPS) have contributed considerably to our knowledge of electron correlation, chemical bonding and the electronic structure of various kinds of samples, ranging from simple atoms to rather complex systems like high-Tc superconductors. Thanks to the high energy of the photons, SR allows the element-specific excitation of inner shell electrons, which simplifies the interpretation of spectroscopic data. SR-based experimentation on clusters consisting of up to a few hundred atoms is still in its infancy. By far the largest number of studies on clusters make use of intense laser or electron impact excitation because the particle density in cluster beams is small. Pioneering experiments with SR were performed on rare gas clusters in the '80s [1–3]. There are however two classes of experiments that can only be done with high energy photons. The electronic structure and dynamics of materials with a large band gap can exclusively be probed with photons in the ultraviolet (UV) or vacuum ultraviolet (VUV) range. Helium clusters, which have many fascinating properties, belong to this class of samples. A study

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of the electronic structure and the dynamics of electronically excited states will be presented in the first part of this paper. Element-specific excitation on the other side of inner shell electrons requires excitation energies in the range from 30 to 1000 eV, depending on the material. Element-specific excitation is particularly helpful for the analysis of clusters containing different elements, especially tightly bound clusters, invoking strong bonds between different elements. At present, there is considerable effort to build cluster sources that are capable of producing such clusters with sufficient particle density for SR-based experiments. The first results of a photoionisation study on alkali halide clusters produced with a new cluster source will be presented in the second part of this paper.

2. Excited state dynamics of helium clusters

Helium clusters have attracted great interest in the last decade [4]. They exhibit many unusual and fascinating thermodynamic, electronic and dynamic properties. In contrast to most other materials, He clusters are liquid, clusters of the isotope $^4\text{He}$ 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 diffuse agglomerates of atoms. Several aspects of the electronic structure of He clusters were recently investigated with fluorescence excitation spectroscopy utilising SR [6]. Of particular interest is the development of electronically excited levels with cluster size. He clusters can be regarded as a model systems 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 ($n=2,3,4\ldots$) transitions. In the context of the electronic structure and dynamics of He clusters, two questions are particularly interesting: (i) How are the atomic excitations modified, in particular, can exciton states be observed as in the case of rare gas solids? And (ii) what are the relaxation processes following electronic excitation? As will be shown below, luminescence spectroscopy is ideally suited to address these questions.

The measurements were 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 mbar through flat nozzles with an orifice of 0.03–0.006 mm diameter. The beam consisting of atoms and clusters is photo-excited with monochromatized synchrotron radiation in the energy range between 20 and 25 eV. Fluorescence light emitted from the clusters is detected with two different photomultipliers, covering a spectral range from 8–30 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 nitrogen-cooled CCD camera. In the case of He clusters, precise determination of the cluster size is very difficult because they are very fragile. Here, we give only estimates based on results for heavier rare gas clusters and well-known scaling laws [7].

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 VUV fluorescence is a measure of 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 to absorption spectra in a more precise sense, fluorescence excitation spectra of VUV radiation are meant. From an experimental point of view, it is much easier to measure the absorption via fluorescence excitation than by transmission because the cluster beam is optically very thin. 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
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 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 a symmetry breaking takes place at the cluster surface.

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]. A fluorescence spectrum in the visible spectral range is presented in Fig. 2. 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. This provides evidence that the desorp-
tion of electronically excited atoms and molecules is an important pathway in the relaxation process of He clusters. In addition to the sharp lines, a somewhat broader emission at $\sim 14800 \text{ cm}^{-1}$ is observed for large clusters containing on average 5000 atoms. The broadening is an indication that it is due to a radiative process from the interior of the cluster, e.g. He$_2$ inside the cluster. Since this band is absent for clusters containing 250 atoms or less (not shown here), we assume that there is size-dependent competition between desorption and relaxation inside the cluster. On the basis of the 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 than ejected from the cluster. Since the s- and d-symmetric levels cannot decay directly 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.

3. Inner shell photoionisation of free and embedded alkali halide clusters

The connection between the electronic and geometric structures of molecules, surfaces and solids has been studied extensively using core level spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy. Unlike valence levels, core levels even in solids are atomic-like and highly localised. Core level spectra therefore reflect local properties and the surrounding of individual atoms can be probed. This makes core level spectroscopy highly interesting for the investigation of clusters.

So far, only very few studies utilising core level spectroscopy have been performed on clusters, most of them pertaining to the properties of rare gas clusters [14–16]. The lack of suitable cluster sources compatible with the requirements for spectroscopy with SR have prevented studies on tightly bound clusters in a free jet. The laser vapourisation cluster sources [17], which are probably the most widely used, are not suitable for experiments with SR since it is a pulsed source with a duty cycle of typically a few per cent. Over the last few years, we have put considerable effort into the construction of cluster sources for SR-based experiments. Apart from different types of gas aggregation sources [17], we have developed a new type of source that is based on a pick-up process [18,19]. A beam of large rare gas clusters passing through an oven picks up atoms or molecules, which are evaporated in the oven. The material condenses inside the rare gas cluster and forms a new cluster. The heat of condensation is taken away by evaporating the rare gas atoms. In analogy with the gas aggregation source, which uses cold gas for the nucleation process, this new source is called cluster aggregation [19].

Free and mixed clusters containing up to 100 atoms can be produced with the new source. At present, apart from alkali halides, CdS, Al and Ge clusters have been produced successfully. In the region of intersection with the synchrotron radiation beam, a density of the clustered material of more than $10^{10}$ atoms/cm$^2$ could be obtained, depending on the material. In the following, an inner shell photoionisation study on alkali halide clusters, namely NaCl, will be presented. The measurements were performed at the SX700 undulator beamline BW3 at Hasylab [20,21]. NaCl clusters are produced by passing a beam of large Ar clusters through an oven in which NaCl is evaporated. The size distribution of the NaCl clusters can be controlled by varying the size of the primary Ar cluster and the vapour pressure in the oven. The clusters are ionised with monochromatized SR between the apertures of a short time of flight mass spectrometer of just 10 mm length. This compact design allows us to make direct use of the time structure of synchrotron light without the need for electron ion coincidences.

Mass spectra recorded following photoionisation at $h\nu=254$ eV are shown in Fig. 3. At low oven temperatures, only Ar clusters can be seen. It should be noted that the size distribution of the Ar clusters is centred around $N=400$. This has been checked by additional measurements with a reflectron time of flight mass spectrometer using electron impact ionisation. Small Ar-cluster ions as observed in Fig. 3 are presumably fragments of larger clusters [22]. With increasing oven temperatures, the density of NaCl increases and mixed clusters of the type...
Na\textsuperscript{+}Ar\textsubscript{x} and in addition Na\textsubscript{x}Cl\textsuperscript{+}\textsubscript{N−1} clusters show up. On increasing the NaCl vapour pressure further, the Ar clusters completely disappear while the NaCl clusters become dominant. It should be noted that during the ionisation process, alkali clusters lose a halogen atom [23]. The intensity variation of different species in the beam is given in the left part of Fig. 3. While the intensity of Ar\textsuperscript{+}, which is a measure of the intensity of Ar clusters in the beam, decreases monotonically with increasing NaCl pressure, the intensity of Na\textsubscript{x}Cl\textsuperscript{+} first increases with NaCl pressure and then drops steeply. From mass spectra taken at different energies, we know that at low NaCl pressure, primary mixed clusters containing a large number of Ar atoms are formed. There is strong evidence that small Na\textsubscript{x}Cl\textsuperscript{+}\textsubscript{N−1} ions are ejected from the cluster. The steep drop in the Na\textsubscript{x}Cl\textsuperscript{+}\textsubscript{N−1} intensity at high pressure is due to the loss of Ar atoms, which provide a large photoionisation cross section. As outlined in the left part of Fig. 3, there are three different regimes. At low NaCl pressure, predominantly pure Ar clusters are present in the beam. In the intermediate pressure regime of ~10\textsuperscript{−3} mbar, mixed clusters are produced. Pure NaCl clusters are only formed in a very narrow pressure range. As a result by carefully controlling the vapour pressure, NaCl clusters can be prepared bare or embedded inside Ar clusters.

Partial ion yield spectra of different Na\textsubscript{x}Cl\textsuperscript{+}\textsubscript{N−1} ions in the energy range of the Cl 2p edge are presented in Fig. 4. For comparison, an ion yield spectrum of Na\textsuperscript{+} and the total electron yield (TEY) of a thin film of NaCl are given. The ion yield of Na\textsuperscript{+} reflects the absorption of NaCl molecules. A few weak but sharp structures between 200 and 210 eV are due to excitations into unoccupied levels with ns and nd character. The absorption of the 2p electrons into the continuum is delayed. Even the smallest clusters investigated showed some structure in the continuum, while there was no clear structure visible below the onset of the continuum. Three peaks, labelled by A, B and C, seemed to have counterparts in the TEY of a thin film. The labelling a,b,c . . . in the TEY spectrum is taken from the literature [24]. The maxima above 210 eV are XANES multi-scattering structures. By comparison
dynamics of electronically excited He clusters were investigated with luminescence spectroscopic methods. It turned out that the desorption of electronically excited He atoms and molecules is an important decay channel. In order to study inner shell excitations of tightly bound clusters, a new cluster source was developed that was based on a pick-up technique with a rare gas cluster beam. It allows the production of various kinds of cluster, either free or embedded inside rare gas clusters. As an example, results for NaCl clusters are presented. The ionisation process of mixed clusters shows some similarities with the decay processes in He clusters. Single NaCl ions are ejected from the primary argon cluster. By measuring XANES spectra of NaCl clusters, information on the geometric structure, e.g. the bond length between Na and Cl, could be obtained. The results presented here show that spectroscopy with SR is a very promising method for the investigation of clusters. In particular, cluster research will benefit considerably from the development of even brighter light sources, e.g. VUV free electron lasers, which are now under construction [25,26].

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