One more attempt on ArXe

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Abstract

Introduction

Electron spectroscopy can make important contributions to the research on composition and structure of free nanoparticles.[?] Besides by photoionization, free electrons emerging from nanoparticles can also be produced by the relaxation of electronically excited states. One such process, which is of particular importance in weakly bonded systems, is the Interatomic or Intermolecular Coulombic Decay (ICD).[?] In ICD, an electronic excitation decays by energy transfer to one of its neighbour atoms or molecules, thus releasing a free electron from the latter site. ICD is an important relaxation channel e.g. for inner-valence holes in elements C-Ne, and also for core levels vacancies e.g. in H_2O, where it competes with Auger decay[?] .

By definition, ICD is particularly sensitive to the chemical environment of the atom or molecule in which the primary excitation has taken place. We suggest that this property of ICD decay spectra can be used to derive information on a nanoparticle or a solvation system, for example. We report here about studies in which we produced heterogeneous clusters of the noble gases Ar and Xe with different sizes, and compositions ranging from a few Xe dopant atoms in an Ar matrix to clusters containing an equal amount of both species. By the use of electron, electron coincidence spectroscopy and of *ab initio* calculations on prototypical systems we show how the radiationless decay spectrum of Ar inner valence (3s) ionized states connects to the structure of the clusters.

Intermolecular Coulombic Decay initially was predicted from theoretical considerations of the energy levels in singly vs. doubly ionized, and doubly vs. triply ionized, hydrogen bonded clusters.[?] First experimental work some years later used Ne clusters,[?,?] but quickly was followed by demonstrations of ICD in a diverse range of other systems. Experimental and theoretical progress has been reviewed.[?,?,?] ICD proceeds by an initial ionization producing an ion in an excited state, followed by a transfer of energy to a neighbouring site, and an electron emission process therefrom. In the final state a positive charge remains at the site of ionization, and another was created at another atom or molecule. Soon after, related autoionization processes were discovered that proceed via a charge transfer instead of an energy transfer. We find that both energy and charge transfer induced autoionization plays a role in Ar-Xe, and will detail the relevant processes below.

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The notion of ICD requires that the electronic orbitals of the two sites can be distinguished, which typically is the case in weakly bonded systems, held together by hydrogen bonds or van-der-Waals bonds. In the case of strong (covalent or metallic) bonding, there is no distinction between ICD and Auger decay.[?]

First experiments on ICD in heterogeneous systems were on Ne-Ar clusters.[?] Those were followed by studies of ICD-like inner-shell decays in aqueous solution.[?][?][?] Pioneering work also showed the potential for studies of the interface between a substrate and an adsorbate by ICD.[?] More detailed work on Ne-Ar clusters was recently presented by some of the authors.[?] For this system, a detailed analysis of photoelectron spectra with respect to structural features of the mixed clusters is also available.[?] In Ref. [?] it was shown that an analysis of the ICD spectra allowed to decide between structural alternatives for which the photoelectron data were indiscriminate.

Rare gas clusters are suitable prototype systems for studies of (e.g.) ICD, as they can easily be produced by supersonic expansion. Mixed rare gas clusters easily form by coexpansion of the two gases through a cooled nozzle. The size of the clusters can be changed by varying the expansion parameters, although for heterogeneous clusters some uncertainty remains with respect to the cluster size, as empirical scaling laws[?] apply to expansion of pure gases only. Early studies of Ar-Xe clusters mostly focussed on the extreme cases of a single Xe atom embedded in an Ar cluster (e.g. Ref. [?]). Different sites of the dopant atom (on top of a surface, integrated in an Ar surface, inside the cluster) were distinguished by three separate bands in the fluorescence yield recorded as a function of excitation wavelength.[?] Increasing the Xe concentration in the expansion lead to changes in the fluorescence excitation spectrum that were interpreted as formation of Xe_2 and larger Xe complexes inside the clusters.[?] Experiments on Xe-rich mixed clusters were also conducted, and concluded that increasing the Xe content in a coexpanding ArXe mixture leads to the formation of Xe-core, Ar-shell systems with a sharp interface between the two species.[?][?] This finding was confirmed by electron diffraction experiments.[?] Always, the observed Xe content in the clusters is above the Xe content in the expanding gas mixture, as Xe can be condensed much easier than Ar.

Most recently, on the experimental side photoelectron spectra of small Ar-Xe clusters were analyzed, adding to the findings in earlier work.[?] We will discuss this paper in connection with our results below. Theoretical work on Ar-Xe was also published, and had a focus on the radiationless decay of Ar inner valence vacancies in these systems.[?][?] Interestingly, it was found that Ar $3s^{-1}$ is stable against autoionization in an ArXe dimer, but is destabilized by adding further Xe atoms, or an Ar solvation shell, to the system. Again, we will detail these results in conjunction with our current work.

The plan of our paper is as follows: ...

Experimental

Theoretical Approach

Experimental coincidence spectra are given by the kinetic energies E_{sec} of the secondary electron and the intensities of the peaks. The latter is proportional to the probability of the decay as well as the theoretically determinable decay width $\Gamma = \frac{\hbar}{\tau}$, which is inverse proportional to the lifetime τ. The manifold of these energies and decay widths will therefore compose the electron-electron coincidence spectrum. In case of noble gas clusters with given structures three aspects have to be taken into account: different decay mechanisms, the possibility to decay with multiple interaction partners and different decay channels within each decay mechanism. At the current stage of development we need to neglect the nuclear dynamics which additionally might play an important role.

Decomposing every system into pairs and triples of atoms is a very useful first order approximation to both the investigation of energies and decay widths of a larger system. Pairs and triples are combinations of two and three atoms, respectively. These atoms do not necessarily need to form bonds between each other

or even be close, but they are characterized according to fixed internal coordinates. Each pair and triple can be described by its properties which are in first order of approximation independent of further, eventually present, atoms. In the following, this approach is going to be called model of pairs and triples.

In case of the electronic decay processes one is interested in the energies of the initial E_{in} and the final states E_{fin} of the corresponding processes in order to determine, whether a channel β is open, i.e., in accordance with energy conservation, or not. When the channel is open, the excess energy is carried away by the emitted electron E_{sec} in form of its kinetic energy. These energies can in the model of pairs and triples be approximated to be

$$E_{in}^{\beta} = SIP(X_{in}^{\beta}) \tag{1}$$

$$E_{fin}^{\beta} = SIP(X_{fin1}^{\beta}) + SIP(X_{fin2}^{\beta}) + \frac{1}{d} \tag{2}$$

$$E_{sec}^{\beta} = E_{in}^{\beta} - E_{fin}^{\beta} \tag{3}$$

where X_{in} denotes the initially ionized atom and X_{fin1} and X_{fin2} describe the two ionized atoms in the final state. β denotes the decay channel characterized by the quantum numbers of the ionized atoms in the pairs and triples and d denotes the interatomic distance between the atoms X_{fin1} and X_{fin2}. The initially ionized atom X_{in} can coincide with one or both of the final state atoms X_{fin1} and X_{fin2}. As explained in chapter **??**, the distribution of the vacancies over the different atoms determines the kind of electronic decay process at hand. Hence, in an Auger process all three atoms would coincide, for an ICD X_{in} would coincide with one of X_{fin1} and X_{fin2} and for an ETMD3 all ionized states are located on different atoms.

In all autoionization processes considered, a second electron is emitted with the kinetic energy E_{sec}. If $E_{sec} < 0$, then the final state energy is higher than the initial state energy and the process is energetically not accessible. Hence, the corresponding channel is closed.

This ad hoc approach easily allows to correct for energetic shifts of ionization potentials as observed in larger clusters.

$$\Gamma_{ICD} = \sum_{i,\beta} N_{ICD,i}\Gamma_{ICD,i,\beta} \tag{4}$$

$$\Gamma_{ETMD} = \sum_{j,\beta} N_{ETMD,j}\Gamma_{ETMD,j,\beta} \tag{5}$$

$$\tag{6}$$

$$N_{ICD} = N_{in} \cdot N_{fin} = N_{Ar} \cdot N_{Xe} = \sum_{i} N_{ICD,i}$$

$$N_{ETMD} = N_{in} \cdot N_{fin}(N_{fin} - 1) = N_{Ar} \cdot N_{Xe}(N_{Xe} - 1) = \sum_{j} N_{ETMD,j}$$

$N_{ICD,i}$ and $N_{ETMD,j}$ depend on the structure

$$\Gamma_{\beta}(E_{res}) = 2\pi \left| \langle \Phi_{in} | H_f | \chi_{\beta} \rangle \right|^2 \tag{7}$$

$$\Gamma_{ICD,i,\beta} = 2\pi \frac{\sigma^{(X_E)}(\omega_{vp,\beta})}{R_i^6 \omega_{vp,\beta}^4 \tau_{in,\beta}} \tag{8}$$

$$\Gamma_{ETMD,j,\beta} = 2\pi \sum_{m,M'_{in},D} \frac{a_m \Theta_m(\alpha_i)\sigma^{(X_E)}(\omega_{vp,\beta})\tilde{D}_{m,j,\beta}(M_{in,D}}{R_j^6 \omega_{vp,\beta}} \tag{9}$$

$$\tag{10}$$

$$\tag{11}$$

$$\tag{12}$$

$$\tag{13}$$

$$\tag{14}$$

$$\tag{15}$$

Experimental Results

Discussion of Experimental Results

Theoretical Results

Discussion

Summary

Supporting Information Available: This will usually read something like: "Experimental procedures and characterization data for all new compounds. The class will automatically add a sentence pointing to the information online: This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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