Interface identification by non-local autoionization transitions

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We use an autoionization process that involves ultrafast energy transfer to neighbouring sites to characterize the formation of NeAr van der Waals bonds in clusters formed by a coexpansion of both gases. This autoionization process, the so-called Interatomic or Intermolecular Coulombic Decay (ICD), is ubiquitous in weakly bonded systems. The energy of the electron being emitted in 10 the ICD process is shown to be characteristic for the two neighbouring entities and is therefore suggested as a new means for structural investigation, such as interface identification, of weakly bonded complexes.
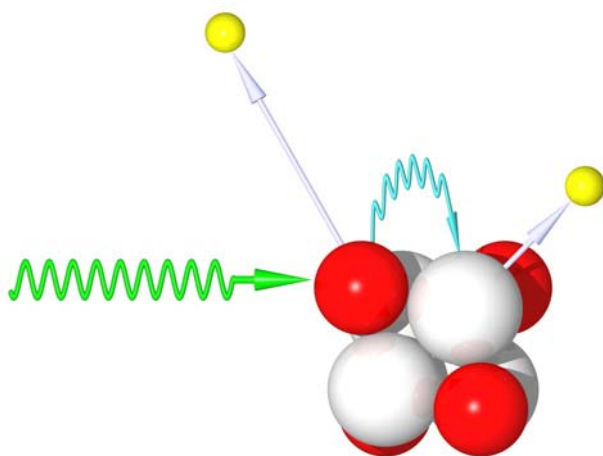
Introduction

15 Non-covalently bonded species are of great importance in chemistry and biochemistry. Since non-covalent bonds, e.g. via hydrogen bridge bonds or van der Waals interactions, are weak, the properties of the subsystems are relatively 20 unperturbed compared to the isolated atoms or molecules. Structural determination of such complexes has relied a lot on indirect methods, such as comparison of the results of various spectroscopies with quantum chemistry calculations.[1] More specifically, these works often addressed the vibrational 25 spectrum of the complex under study, be it in the IR or far IR frequency range. Size selectivity and isomer selection in these experiments were achieved by combining excitation with an IR and a UV photon.[2] As a prerequisite for the application of any such method, the complex to be studied must have IR 30 active modes of vibration, and in the case of two-color experiments, contain molecules with a suitable chromophore.

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For systems which lack these prerequisites, much less about their structure is known. On van der Waals clusters, experiments using electron spectroscopy,[3,4] surface scattering 35 with subsequent mass spectrometry,[5] and electron diffraction[6] have been carried out. Simulated results show far more detail than currently is experimentally accessible.[7,8]

In this article we introduce a method that directly identifies the two atomic or molecular species forming an interface in a 40 weakly bonded complex. As an example we use van der Waals clusters of Ar, which are partially covered by a single layer of Ne atoms. We observe a signal easily detectable by electron spectroscopy, which only is present due to the fact that a weak bond between Ne and Ar atoms was formed in the cluster 45 condensation process, and which is specific for the two kinds of atoms forming the interface. It occurs as the result of a recently discovered electronic deexcitation process of inner-valence vacancies in the Ne layer, which involves an energy transfer to a neighboring site. This process, now termed 50 Interatomic/Intermolecular Coulombic Decay (ICD), is predicted to be generally present in weakly bonded systems of lighter atoms and molecules.

Electronic relaxation processes, such as Auger decay and analysis of X-Ray Fluorescence, have been used to determine 55 elemental compositions of matter for a long time. The first step in the application of any such technique, which is

creation of a deep core hole, does not assume any special property of the target being probed. Since these decay processes, however, are not sensitive to the chemical neighborhood of the site which is probed, they are not suited for the investigation of the subtle changes in energy and structure brought about by non-covalent complex formation. In contrast, the ICD process potentially depends very sensitively on the environment of the initially excited site. It proceeds as follows: After creation of a vacancy in an inner valence orbital, e.g. by photoionization with VUV radiation, electronic energy is released by filling the vacancy from an outer valence shell. This energy is transferred to a neighboring site, where in turn ionization of an outer valence electron occurs. Emission of an electron by Auger decay, on the other hand, is a local process, which occurs from the site that was initially ionized. After having been predicted on theoretical grounds,[9] the existence of ICD and the graphical description outlined above were recently verified experimentally for free van der Waals clusters of Ne.[10-12]

Contrary to intuition ICD does not require a chemical bond between the two sites involved in the energy transfer. Its existence was first inferred from a consideration of the energy levels of doubly charged states in weakly bonded systems. Compared to the constituent monomers, the double ionization potential in an extended system is always lower, since in states with two positive charges distributed to two different sites their Coulomb repulsion is significantly smaller compared to a doubly charged monomer. This potentially renders inner valence vacancy states unstable against autoionization, which could only decay via fluorescence otherwise.[9] Consequences of this simple fact were, however, not investigated until recently, since it is not self-evident that an efficient transition mechanism, which directly links a singly ionized to a delocalized doubly ionized state, is viable. Example systems, for which explicit calculations have meanwhile been presented, are $2s^{-1}$ states in $(H_2O)_x$, $(HF)_x$ (Ref. 9), Ne_{2-13} (Ref. 13) and NeAr (Ref. 14). In a recent investigation of the decay mechanism ICD was interpreted as an exchange of a virtual photon in the limit of long bond lengths (weak bonds), this picture being modified by an increasing role of orbital overlap for shorter bonds.[15] The ICD rate was shown to depend on the bond length R by an R^{-6} law in the long R limit. In this respect, ICD resembles the well-known Förster Resonance Energy Transfer,[16] but contrary to the latter it can occur by involving atomic subunits of the investigated system and energy conservation is not limiting the possible combinations of 'donor' and 'acceptor' sites. It is therefore a phenomenon of much greater generality.

Eventually, the system is left in a state with two opposing positive charges. A weakly bonded dimer will then disintegrate because of the Coulomb repulsion, and this signature of ICD was directly observed in Ne_2.[11] From the conservation of energy, the total kinetic energy of the ions and the ICD electron has to match the energy difference between the inner valence ionized and the asymptotic, doubly charged final state.

The sensitivity of ICD to the environment of the ionized site was not investigated so far yet, since all experiments on ICD reported so far were carried out on homogenous clusters.[10-12] From the above, however, it is clear that ICD involves a simultaneous change of the electronic structure at two different sites, as the result of which one electron will be emitted into the continuum. A sketch of the ICD process in heterogeneous clusters is shown in Fig. 1. Obviously the energy of the secondary electron emitted in this process depends on the energies of inner and outer valence orbitals at the initial site of excitation and at its nearest neighbors.

Here, we report on the ICD signal from a coexpansion of Ne and Ar gas into a free molecular beam, by which van der Waals clusters are formed. Determining the composition of these clusters is intricate, and usually requires molecular dynamics simulations for the given expansion parameters.[5,8] In our work, we will demonstrate the appearance of an ICD signal due to the transition

$$(Ne\ 2s^{-1})Ar \rightarrow (Ne\ 2p^{-1})(Ar\ 3p^{-1}) + e^{-}_{ICD}\ , \qquad (1)$$

which is uniquely related to the formation of a weak bond between Ne and Ar atoms and which thus signals expansion conditions suitable for the formation of heteroclusters. Additional insight underpinning this interpretation comes from an analysis of the photoelectron spectra, which are well known for both pure Ne and Ar clusters.[12,17]

Experimental

The experimental set-up has been described earlier.[18] Here we report only an outline and some details that have changed with respect to these references. Clusters were formed by supersonic expansion of a gas mixture of Ne and Ar (99.999% purity) through a small opening in a copper nozzle. The data displayed in this article were measured using a conical nozzle with a smallest diameter of 80 µm, a cone length of 1100 µm and a full opening angle of 30°. To achieve clustering of inert gases, the nozzle can be cooled down to liquid He temperatures. Gases expanded into a first chamber that is separated from the main experimental chamber by a conical skimmer. The main vacuum chamber was pumped by a cryopump of 900 l/s capacity mounted opposite to the inlet of the cluster beam and a smaller turbo pump of 360 l/s. Photons were produced by the UE52-SGM undulator beamline of the BESSY synchrotron radiation source (Berlin, Germany). The photon energy resolution amounted to approx. 85 meV. Electrons were detected in a commercial hemispherical analyser (Scienta ES 200). Linearly polarized synchrotron radiation was used, and the analyser was mounted at an angle of 54.7° with respect to the electric field vector, and perpendicular to the beam propagation direction. We have set the pass energy of the electron analyzer to 20 eV, and the analyzer resolution to approx. 134 meV. For the experiments on clusters with less Ar content, which are mentioned in the discussion but not displayed, a copper nozzle with a short conical section of 100 µm diameter and a full opening angle of 30° was used, and the measurements were done at the U125/1-PGM and U125/2-SGM beamlines of BESSY. Here, typical settings for the photon bandwidth and the analyzer resolution were 100 meV and 80 meV, resp. The electron energy analyzer was used at a pass energy of 5 eV.

Results

Photoexcited electron spectra from NeAr clusters recorded at a photon energy sufficient for ionization of the Ne 2s orbital are shown in Fig. 2. The Figure shows spectra taken at two different temperatures of the nozzle used for the gas expansion (top and bottom row of panels). The ICD transition energy can roughly be calculated from the known atomic ionization potentials involved and the Coulomb repulsion for two positive charges separated by the distance of the NeAr van der Waals bond. This simple estimate results in a kinetic energy of 7 eV,[‡] same as a more elaborate quantum-mechanical calculation for the NeAr dimer.[20] Inspecting the leftmost panels in Fig. 2 we see a peak at about the predicted energy, which is present only at the lower of two expansion temperatures chosen. ICD into a $(Ne^+)_2$ final state, which is also possible in principle, is expected at a much smaller kinetic energy, since the ionization energy of the Ne outer valence level is several eV larger than for the respective level in Ar. In experiments on pure Ne clusters, ICD was observed at around 1.6 eV kinetic energy.[10] As argued below, we suppose that in our gas beam, at the expansion conditions characterized by this lower temperature, cold Ar clusters covered with a single layer of Ne atoms form. In contrast to that, at the higher of two temperatures only the Ar atoms may condense, such that we have Ar clusters seeded in an atomic Ne beam. Thus, the ICD signal can be used as a monitor for formation of weak NeAr bonds.

A more careful inspection of Fig. 2 shows a second, weaker structure at a kinetic energy about 1.2 eV higher than the main mixed ICD peak. This is in beautiful agreement with simulations of Scheit *et al.* on mixed ICD in the NeAr dimer that include the final state nuclear dynamics.[20] There, the higher kinetic energy peak is explained as the combined result of decays from the ν=1 and ν=2 vibrationally excited dimer states.

Discussion

The kinetic energy we observe for the NeAr mixed ICD is larger in our experiment than in the estimates and calcula-tions, because the latter were carried out for a NeAr dimer while in the experiment we probe larger clusters. In the latter, a larger part of the excitation energy is available for the ICD electron because the Coulomb explosion in the final state is hindered by the surrounding atoms, thus less energy is transferred into kinetic energy release of the ionic fragments.

The formation of mixed NeAr clusters at an expansion temperature of 66 K is also plausible from a consideration of the binding energies of van der Waals dimers. For NeAr, the binding energy is 5 meV, corresponding to a temperature of 58 K.[14] Thus, at 66 K a sufficient fraction of atoms is slow enough to form bonds with the Ar clusters, which act as nuclei for the condensation process. In contrast, the Ne-Ne bond with 3.7 meV binding energy (43 K) is weaker, such that bonding of the Ne to other Ne atoms is unlikely.

Ne and Ar photoelectron spectra taken in the same experiment corroborate our inference on the cluster structure. At the higher of two temperatures, the Ar 3s spectrum shows two distinct peaks corresponding to bulk and surface sites of Ar clusters, as can be seen from their binding energy.[17] At higher binding energy the atomic 3s peak from a small amount of uncondensed gas is visible. In the region of binding energies pertaining to Ne 2s photoionization, only a signal from atomic species is visible. In contrast to that, at the lower expansion temperature, the distinction between the two components of the Ar peak is less clear, and in the Ne binding energy range a new peak appears, the binding energy of which is in-between the values for Ne 2s surface and bulk sites.[12] Both of these changes can be explained by the formation of a third peak corresponding to NeAr interface sites, which has in a similar manner been observed in ArXe clusters.[4]

We can infer further information on the composition of the clusters we probe from the photoelectron spectra. A comparison of the area of Ne 2s and Ar 3s photoelectron lines, normalized by the respective cross sections,[21] gives an approximate measure of the relative Ar content, and for the pure Ar clusters at the higher expansion temperature the bulk/surface ratio gives an approximate measure of the cluster size.[22] For the spectrum shown in Figure 2, these analyses give an Ar fraction of 0.48(5) and a mean Ar cluster size of 100(20) atoms. It should be noted that the clusters exhibit a size distribution ranging from the monomer to values above the mean size. A simple numerical simulation by relaxing 108 Ne atoms from random positions atop of a core of 100 Ar atoms, the structure of which was taken from the Cambridge Cluster Database,[23] gives an Ar core, which is densely but not completely covered by a single layer of Ne atoms. It can be seen that all Ne atoms have more Ar than Ne nearest neighbors. That is, although ICD to states with two Ne 2p vacancies, as seen in earlier work,[10-12] may compete with the mixed IC decay demonstrated in this article, the latter will be the dominating relaxation mode.

Recent adiabatic simulations of the lowest energy isomers of mixed A, B clusters resulted in inverted structures, that is in our case in Ne clusters covered with Ar.[24] In contrast to the conditions in our experiment, identical Lennard-Jones parameters for both species A and B were used for these calculations, as only atom size effects, independent of energe-tic effects, were of interest. We think that the formation of such structures in a coexpansion of the two gases, when the mixture is taken to a low temperature in a short time, is rather unprobable. The formation process of the clusters could be taken into account in a molecular dynamics simulation, but to our knowledge for mixed van-der-Waals-clusters formed in a coexpansion no such simulations are available. However, for mixed cluster formation by pick-up simulations have been carried out,[25,26] and for pick-up of Kr atoms by Ar clusters evidence has been presented that the simulated structure is similar to one that was experimentally obtained by coexpan-sion.[25] There, different than in Ref. 24 a homogeneous distribution of the Kr atoms in a $Ar_{880}Kr_{120}$ cluster was found. For the pick-up of Ne atoms by Ar clusters these simulations support our idea of an Ar core with Ne layers around it. Only immediately after the time of pick-up, Ne might temporarily penetrate into the Ar core on a ps timescale.[26] The dimer binding energies (NeNe: 3.7 meV[27], NeAr: 5 meV[14], ArAr: 10.5 meV[28]) illustrate this behavior. In an experimental study of the cluster composition for a coexpansion of nitrogen and

argon, seeding of nitrogen condensation by Ar cores was found as well.[29]

In a series of additional experiments we have probed clusters with a lower fraction of Ar atoms. The Ar photoelectron signal in these experiments was less intense and neither the Ne nor the Ar photoelectron signals were showing a clear distinction between bulk and surface sites. The ICD signal appeared at the same kinetic energy as shown in figure 2. Its intensity relative to the Ne 2s photoelectron line was reproducible for repeated experiments with the same Ne/Ar ratio of the clusters, and stayed constant or increased with increasing Ar content. It can therefore be expected that the strength of the ICD signal, in comparison to the initial inner valence signal, can be used not only as a qualitative but also a quantitative monitor for the elemental surroundings of the ionized site.

In bulk metal oxides, recently a non-local resonant electron emission process was discovered and termed MARPE (Multi-atom Resonant Photoemission).[30,31] Although the strength of MARPE is now established to be smaller than expected in first experiments,[30] its existence doubtlessly has been demonstrated.[31] In comparison to ICD, the same type of quantum mechanical matrix elements is responsible for this effect. However, MARPE is a resonant scattering process involving inner shells and transition energies of several hundred eV, which compete with strong local relaxation channels. The similarity to ICD is therefore mainly formal.

Conclusions

The Interatomic/Intermolecular Coulombic Decay demonstrated in this article should be prevalent for inner-valence vacancy states in weakly bonded systems. It can be understood as a relaxation within the electronic structure, which is mediated to the surroundings of the decaying site. Since information on nearest neighbors is thus imprinted into the electron energy spectra resulting from the decay, and since the vacancy creation and decay processes are entirely general, we expect this process to readily find applications in the analysis of clusters, large, hydrogen-bridge bonded molecules, and solutes.

Notes and references

‡ Ne 2s atomic binding energy: 48.5 eV, Ne 2p outer valence binding energy: 21.65 eV (average of $2p_{1/2}$, $2p_{3/2}$), Ar 3p outer valence binding energy: 15.8 eV (average of $3p_{1/2}$, $3p_{3/2}$), final state internuclear distance: 3.5 Å.[14,19]

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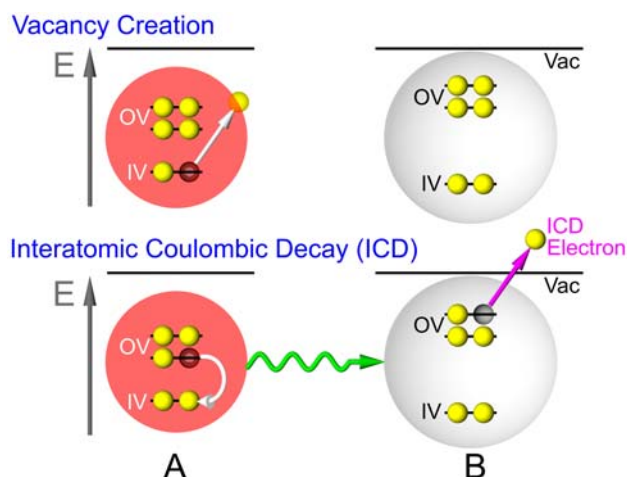## Single column figure/scheme (below)

Fig. 1 The Interatomic Coulombic Decay. Creation of a vacancy in an inner-valence level, e.g. by photoionization, disposes energy into a weakly bonded system, here a dimer AB. In the subsequent decay process, the initial vacancy is filled from an outer valence level; energy released by this process is transferred to a neighbouring site B, which in turn is ionized. This process typically proceeds on a fs time scale.[12,13]
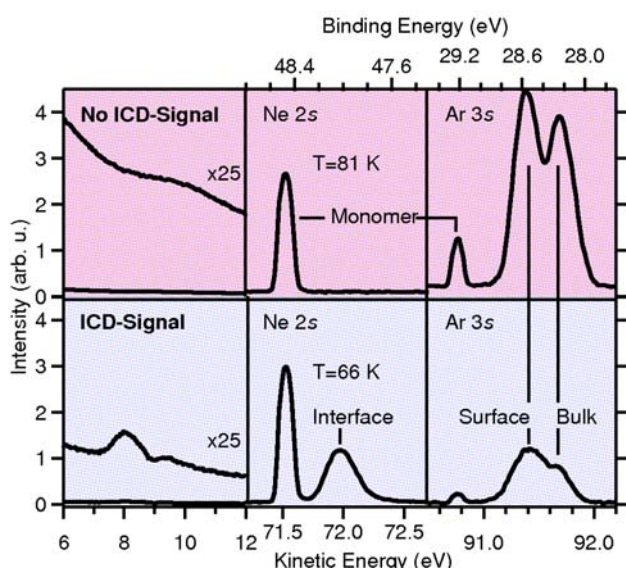
Single column figure/scheme (below)

Fig. 2 Spectra of photoelectrons and subsequently emitted ICD electrons from a NeAr coexpansion. In the bottom row of panels, conditions suitable for formation of mixed NeAr clusters were selected. The photoelectron spectra show the presence of Ar bulk, surface and interface sites (right) and of Ne interface sites (middle). Consequentially a signal from ICD can be detected (left). At a higher expansion temperature, Ne atoms cannot condense and the molecular beam consists of pure Ar clusters and atomic Ne (top row). From Ne, only the monomer photoelectron signal can be seen (middle) and the ICD signal vanishes (left). The photon energy was at 120 eV for both expansion temperatures. The intensity scale is in arbitrary units but the range is the same for all panels.