Size Effects in van der Waals Clusters Studied by Spin and Angle-Resolved Electron Spectroscopy and Multi-Coincidence Ion Imaging

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Abstract. We have studied the valence and inner-shell photoionization of free rare-gas clusters by means of angle and spin resolved photoelectron spectroscopy and momentum resolving electron-multi-ion coincidence spectroscopy. The electron measurements probe the evolution of the photoelectron angular distribution and spin polarization parameters as a function of photon energy and cluster size, and reveal a strong cluster size dependence of the photoelectron angular distributions in certain photon energy regions. In contrast, the spin polarization parameter of the cluster photoelectrons is found to be very close to the atomic value for all covered photon energies and cluster sizes. The ion imaging measurements, which probe the fragmentation dynamics of multiply charged van der Waals clusters, also exhibit a pronounced cluster size dependence.

1. Introduction
Atomic and molecular clusters are ideal model systems to study the transition of electronic properties from individual atoms and molecules to the bulk behavior of condensed matter [1, 2, 3]. Rare gas van der Waals clusters are particularly well-suited due to their easy scalability and the extent to which the properties of their atomic constituents are known. In order to obtain the most complete information possible from our experiments, we have studied the valence and inner-shell photoionization of free Ar, Kr, and Xe clusters by spin and angle-resolved time-of-flight photoelectron spectroscopy as well as multi-coincidence ion momentum imaging.

2. Angle-resolved photoelectron spectroscopy
Angle-resolved photoelectron spectroscopy is a well established technique for the study of the electronic structure of atoms, molecules as well as condensed matter [4, 5]. However, while photoelectron spectroscopy of clusters, and in particular rare gas clusters, has been a growing field since the late 1980s [6, 7, 8, 9, 10, 11, 12, 14, 13, 15], there is a paucity of angle-resolved measurements. In addition to first qualitative studies on rare gas clusters by Öhrwall et al. [10] and our recent quantitative studies [16, 17], measurements of the photoelectron angular distribution parameter are only available for small metal clusters (e.g. [18]).
Figure 1. Schematic diagram of the experimental setup with two time-of-flight (TOF) electron spectrometers mounted to a rotatable vacuum chamber [20]. The incident synchrotron radiation crosses the interaction region perpendicular with respect to the drawing plane.

For quantitative measurements of the electron angular distribution parameter $\beta$ [19] of a cluster target, it is crucial to detect the photoelectrons at two (or more) angles simultaneously, so the measurement is independent of temperature and density fluctuations of the cluster beam.

In our setup, shown in Fig. 1, the photoelectrons are detected using two electron time-of-flight (TOF) analyzers situated in the plane perpendicular to the light propagation direction at the "magic angle" ($54.7^\circ$) and at $0^\circ$ with respect to the light polarization [20]. In order to achieve sufficient spectral resolution, suitable retarding voltages can be applied to the drift tube of the TOF spectrometers. A beam of rare gas van der Waals clusters is produced by an adiabatic expansion cluster source and crossed with a beam of linearly polarized synchrotron radiation (bandwidth $\approx 100 - 150$ meV) from the undulator beamlines 8.0.1, 9.0.2, and 10.0.1 of the Advanced Light Source (ALS). For the present experiment, xenon and krypton gas with a stagnation pressure, $P_0 = 60 - 200$ kPa, was expanded through a 100 $\mu$m nozzle cooled to $170 - 240$ K in order to produce clusters with average sizes $\langle N \rangle$ between 60 and 8000 atoms [21]. For the smaller clusters, up to $\langle N \rangle = 1000$, a simple pinhole orifice was used, while the larger clusters were produced with a conical nozzle with half opening angle of $7^\circ$. The pinhole aperture has the advantage that the scaling laws used to determine the average cluster size are generally more accurate, but the maximum cluster size is limited by the high stagnation pressure required and the resulting load on the turbo pumps. A conical nozzle with small opening angle allows the production of much larger clusters, whose sizes, however, are known less accurately [11].

The cluster size dependence of the angular distribution parameter for Xe 4d surface and bulk photoelectrons, measured at a photon energy $h\nu = 150$ eV, where the 4d photoelectron angular anisotropy is highest, is presented in Fig. 2(a). A significant decrease of the angular distribution parameter of the bulk component is observed for average cluster sizes larger than $\langle N \rangle = 1000$, while the angular distribution of the surface component is only slightly smaller than the atomic value and stays constant within the range of the experimental error. These observations are consistent with the qualitative findings by Öhrwall et al., who reported a more isotropic angular distribution of photoelectrons from clusters with average sizes $\langle N \rangle = 1000 - 4000$ compared to photoelectrons from free atoms, and also noted significant differences in the behavior of surface and bulk components [10]. This effect was attributed to elastic scattering of the photoelectrons by neighboring atoms in the cluster, leading to more isotropic angular distributions for electrons from the interior of the cluster than for those from the surface or a free atom.

In order to investigate the role and effects of electron scattering in more detail, we have
performed multiple scattering (MS) model calculations (for a detailed description of the formalism applied, see Ref. [22]) and compare them to the experimental data in Fig. 2(b) and 3(a). The calculations start from atomic transition matrix elements, which reproduce the experimental angular distribution of atomic Xe 4d and 5p photoelectrons as shown in Fig. 2 and 3. The cluster potential is treated in a muffin-tin approximation, and the results are averaged for random orientations of the cluster with respect to the incident light. In order to reduce the computation time, the calculations were performed for small clusters of 55 atoms in icosahedral geometry, and 53 atoms in a fcc structure (not shown here). To model the surface component, electron emission from the outermost layer was considered, while only electrons emitted from the innermost 10 atoms were taken for the bulk component. Our model calculations clearly reproduce the experimentally observed trends and confirm that the increased isotropy of the cluster photoelectrons can be attributed to elastic scattering of the ejected electrons by the neighboring atoms in the cluster. For the 4d photoelectrons, they seem to slightly overemphasize the effect of electron scattering and show deviations from the atomic distribution already for small clusters, where the experimental results are still close to the atomic value. A possible explanation may lie in an inadequate definition of bulk emitters in the calculation, where some intermediate atoms closer to the surface, whose electrons experience much less scattering, are left out. When extrapolating the calculated results to larger clusters, the finite escape depth of the photoelectrons also has to be taken into account. It effectively limits the influence of elastic scattering in larger clusters, since electrons emitted from the deepest atoms can no longer escape from the cluster [11, 23].

Fig. 3 compares the angular distribution parameters \( \beta \) of the outer-valence photoelectrons from Xe and Kr clusters, as a function of photon energy, to those of the free atoms. We find pronounced differences between the cluster and atomic photoelectrons in the first 30-40 eV above threshold, where the angular distributions of the cluster photoelectrons is much more isotropic than the corresponding distributions of atomic photoelectrons. For higher photon energies (not shown here), the angular distributions of cluster valence photoelectrons follow more closely those of free atoms [16].
Figure 3. (color online) Xe 5p and Kr 4p cluster photoelectron angular distribution parameter (symbols) compared to multiple scattering (MS) calculations for icosahedral Xe clusters of 55 atoms (dashed and dash-dotted lines). The energy axis in the calculation is scaled to match calculated and experimental atomic $\beta$ curves (dotted and solid lines).

3. Spin-resolved photoelectron spectroscopy

With the advent of synchrotron radiation as an intense source of circularly polarized light in the early 1980s, energy and angle-resolved measurements of the spin polarization of photoelectrons became possible [24, 25]. For atomic and molecular targets, it was mostly the promise of so-called complete experiments determining all dynamical quantities, i.e. matrix elements and phases, of the photoionization process that motivated these experiments [24, 25, 26, 27, 28, 29, 30, 31], while the possibility of a more detailed investigation of the band structure and magnetic properties motivated the pioneering solid state and surface physics studies [32, 33, 34, 35, 36]. Complementing these studies on atoms, molecules, surfaces and solids, we were now able to measure, for the first time, the spin polarization of photoelectrons emitted from rare gas clusters in the gas phase. Our experiments were performed at the Advanced Light Source (ALS) using elliptically polarizing undulators (EPU) at beam line 4.0.2 and 11.0.2 set to deliver 100% circularly polarized light. The experimental setup shown in Fig. 4 was similar to the one

Figure 4. Schematic diagram of the experimental setup for the spin-resolved photoelectron spectroscopy [30]. The inset shows the geometry of the experiment.
used previously to measure the spin polarization of atomic and molecular targets [30, 37, 38, 31].
An electron time-of-flight (TOF) detector combined with a spherical Mott polarimeter of the Rice type, operated at 25 kV, carried out the spin-resolved analysis. The geometry of the experiment was selected to measure the polarization of the spin component of the electrons along the photon propagation direction for electrons emitted in the plane perpendicular to the photon propagation direction and at 45° with respect to the horizontal plane (see inset in Fig. 4). Instrumental asymmetries of the Mott polarimeter were eliminated by inverting the helicity of the circularly polarized light approximately every hour and later recombining the results.

From the backscattered intensities $I_1$ and $I_2$ counted in the MCP detectors 1 and 2 of the Mott polarimeter (see Fig. 4), the electron spin polarization $P$ can be calculated by

$$ P = \frac{1}{S_{eff}} \times \frac{A}{1} $$

where $A$ is the counting asymmetry between $I_1$ and $I_2$ and $S_{eff}$ is the analyzing power of the polarimeter (effective Sherman function) [30].

Fig. 5 depicts a typical photoelectron spectrum of Xe clusters with average size $\langle N \rangle = 1000$ measured at 115 eV photon energy. The black spectrum (dashed line) shows the spin-unresolved photoelectron spectrum, measured with a regular electron TOF analyzer (without a Mott detector), while the red (solid) and blue (dotted) curves show the spin-resolved spectra in MCP detector 1 for positive and negative light helicity. A preliminary analysis of our data shows only very small differences between the counting asymmetries of the atomic and cluster peaks and hence very similar spin polarizations for atomic and cluster photoelectrons for all cluster sizes (from $\langle N \rangle = 200$ to $\langle N \rangle = 1500$) and all photon energies (from 110 to 170 eV) considered. However, a detailed, quantitative analysis of the spin polarization according to eq. (1) is under way and will be discussed in a forthcoming publication [39].

4. Multi-coincidence ion momentum imaging
The recent discovery of Interatomic Coulombic Decay (ICD) as an ultra-fast electron decay mechanism in van der Waals clusters [40], and the unexpected results of cluster
photoionization experiments with a Free Electron Laser [41] have sparked renewed interest in the photofragmentation of free rare gas clusters. Especially for larger clusters, the existing experimental results are sparse and focus almost exclusively on Ar clusters (see e.g. [42, 43]), with the exception of very recent work the fragmentation of Kr clusters after K-shell ionization [44]. Hence, we have performed an extensive investigation of the fragmentation of Ar, Kr and Xe clusters after valence and innershell photoionization by means of multi-coincidence momentum imaging spectroscopy. Photoelectron-photoion-photoion coincidence (PEPIPICO) spectra, kinetic energy releases, ion angular distributions, and momentum correlations are determined for all fragmentation channels as a function of photon energy and cluster size for clusters between 10 and 5000 atoms.

The data was taken with our recently developed coincidence momentum imaging setup, shown in Fig. 6. The details of our apparatus are described in detail elsewhere [46, 47], and only a brief description is given here. The system is based on a modified velocity map imaging spectrometer (VMI) [45], which provides high detection efficiency and good focusing properties for an extended interaction region. High collection efficiency and simultaneous detection of particles with different velocity and at all emission angles without the need to rotate the detector makes VMI ideally suited to study angular distributions and kinetic energy release in dilute targets such as clusters.

Ions created in the interaction region, defined by the crossing of the supersonic cluster beam with the photons from Beamline 8.0.1 or Beamline 10.0.1 of the Advance Light Source at the Lawrence Berkeley National Laboratory, are focused onto a position-sensitive detector (an 80 mm hex-anode delay line detector purchased from Roentdek [48]) by a set of open electrostatic lenses. The lens voltages are chosen such that all ions with equal kinetic energy and emission direction hit the anode at the same position independent of their starting point. The impact position on the detector thus provides their momentum in the directions parallel to the detector surface. For the given lens voltages, indicated in Fig. 6, the extraction field provides a full 4 \pi collection efficiency for ions with \( E_{\text{kin}} < 8 \text{ eV} \). The coincidence between ions and electrons, detected in a double-stack MCP detector situated close to the interaction region opposite to the VMI, provides the ion time-of-flight and allows determination of the ion momentum in the direction perpendicular to the detector surface. The data are collected in the list mode (i.e. event by event), and can be sorted off-line.

Fig. 7 shows exemplary ion time-of-flight spectra for fragmentation of Xe clusters of different sizes at 216 eV photon energy. Depending on the initial cluster size, singly charged fragments with sizes between 1 and up to 10 or more atoms per fragment are detected, often in coincidence with other singly charged fragments (see Fig. 8). Further details about the underlying fragmentation mechanisms may be revealed by an analysis of the kinetic energies and momentum correlations of coincident fragments, which is currently under way.
5. Conclusions
Our present study of the valence and inner-shell photoionization of free rare-gas clusters by means of angle and spin resolved photoelectron spectroscopy and momentum resolving electron-
multi-ion coincidence spectroscopy provides a very comprehensive experimental data set that poses a formidable challenge to theory. We find a cluster size dependence of the inner-shell photoelectron angular distributions that can be attributed to elastic electron scattering, but detect only small differences between the spin polarization of cluster and atomic photoelectrons. Our ion momentum imaging measurements show a pronounced cluster size dependence of the cluster fragmentation and provide a wealth of further information that may allow identifying specific fragmentation mechanisms.

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