Supporting Online Material for

Probing the Angular Momentum Character of the Valence Orbitals of Free Sodium Nanoclusters

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Materials and methods

Experimental setup

A schematic of the experimental setup is shown in Figure S1. Sodium cluster anions were produced by gas aggregation. For this purpose, sodium atoms were evaporated from a crucible, condensed to clusters in a liquid-nitrogen cooled helium gas flow, and ionized by a pulsed electric discharge. Afterwards the clusters were guided to a cold (6 K) 12-pole radio-frequency trap. The clusters thermalized with helium buffer gas with a density of about $4\times10^{14}$ cm$^{-3}$ inside the trap before they were transferred to a time-of-flight mass spectrometer. Mass selection with a multi-wire mass gate took place at the first time-focusing point of the mass spectrometer. After mass selection, the ions either entered the imaging spectrometer or they were deflected by the ion mirror to record the cluster intensity with a Daly-type ion detector ($S1$).

The imaging spectrometer uses an optimized velocity map imaging design with three acceleration zones instead of the two zones in the original design by Eppink and Parker ($S2$). The photoelectrons are amplified by a multi-channel plate (MCP) and then converted to visible light by a phosphor screen, which is monitored by a high-sensitivity, 1.4 megapixel CCD camera from outside the vacuum system. For suppression of surface-generated electrons, all surfaces are covered with a thin graphite film. The spectrometer is surrounded by a mumetal tube in order to reduce stray magnetic fields. The imaging spectrometer was energy calibrated using the well-known electron affinity of atomic oxygen ($S3$).

Data recording

The positions of electron impacts on the detector screen were determined by an event counting technique ($S4$). A single spectrum consists of approximately 300,000 data points. Events were separated from the background by brightness thresholding and noise filtering, and their centroids were calculated and stored.

After data recording was complete, the center point of the projection was determined either manually or by the algorithm described by Bordas et al. ($S5$). Normally, manual determination of the center point was more precise.

Reconstruction algorithm

The original 3-dimensional photoelectron angular distribution was reconstructed by a modified version of the phasex algorithm ($S6$), where the input data is described not by a cartesian-coordinates matrix but by an energy-angle-coordinates matrix with $200 \times 40$ pixels. The key advantage of this approach is that the input image consists of only 8,000 pixels instead of the typically $500 \times 500 = 250,000$ pixels of a high-resolution cartesian input. A homogeneous background signal of approximately 10% (30,000 events) distributed over 8,000 pixels gives good enough statistics ($\sim 4$ events
per pixel) to be compensated by subtracting a fixed value from the input matrix before any reconstruction routines are applied. This approach is not possible using the cartesian representation, where the background signal corresponds to less than one event per pixel.

We used a basis set with 100 Gaussian peak functions for the radial coordinate, and with the Legendre polynomials $P_0$, $P_2$, $P_4$ and $P_6$ for the angular coordinate. The polynomials of 4th and 6th order were included to absorb non-physical contributions to the signal in order to avoid artefacts in the $P_2/P_0$ ratio. Their intensity was normally less than 1%.

Our implementation was compared to the original pbasex program by reconstructing data from simulated projections. The results are essentially identical, but due to the possibility of background subtraction in the input image our approach is significantly less sensitive to noise ($S7$).

**Extraction of anisotropy parameters for individual transitions**

The reconstruction routine yields the intensity and the anisotropy parameter $\beta$ as a function of electron kinetic energy. For most cluster sizes, the intensity spectra consist of well-separated peaks, but the corresponding $\beta$ parameters are not perfectly constant over the range of a given peak due to experimental noise. We found that the most reliable way of extracting $\beta$ parameters for the individual contributions is to fit the 2-dimensional PAD with a reasonable number of peaks,

$$\sum_j a_j \exp\left(-\frac{E - E_j}{2w_j}\right) \times \left(1 + \beta_j P_2(\cos \theta)\right),$$  \hspace{1cm} (1)

where $a_j, E_j, w_j, \beta_j$ are the intensity, position, width and asymmetry parameter of each peak, and the sum runs over all peaks in the spectrum.

**Supporting text**

**The Bethe-Cooper-Zare formula**

Within the Bethe-Cooper-Zare theory ($S8$–$S10$), the anisotropy parameter $\beta$ is given by

$$\beta = \frac{l(l-1)R_-^2 + (l+1)(l+2)R_+^2 - 6l(l+1)R_- R_+ \cos \delta}{(2l+1)(R_-^2 + (l+1)R_+^2)}$$  \hspace{1cm} (2)

where

$$R_{\pm} = \int \psi_{f \pm}^*(r) \psi_i(r) r^3 dr$$  \hspace{1cm} (3)

are the radial matrix elements, $\psi_i$ and $\psi_{f \pm}$ are the initial and final state wave functions, $l$ is the angular momentum of the initial state, and $\delta = \delta_+ - \delta_-$ is the difference of the Coulomb phase shifts of the final state wave functions $\psi_{f \pm}$, defined by the asymptotic behavior ($S11$):

$$R_{\pm} \approx \sqrt{\frac{2}{\pi k}} \frac{1}{r} \cos(kr - (l \pm 1)\pi/2 + \delta_\pm) \quad \text{for} \quad r \to \infty$$  \hspace{1cm} (4)
The value of $\beta$ depends critically on the ratio $R_+/R_-$ and on $\delta$ (Figure S2). Strongly negative values can only appear for phase shift differences close to 0 or $2\pi$ and matrix element ratios on the order of 1.

The “interference term” $-6l(l+1)R_+R_-\cos\delta$ is the only term in the Bethe-Cooper-Zare formula that can assume negative values. It originates from the coherent superposition of partial waves with $l' = l - 1$ and $l' = l + 1$ and identical $m$. For incoherent superposition, this term would not be present, and negative $\beta$ parameters would not occur.

**Numerical details**

For the calculation of the angular distributions for single-electron-model potentials, we have solved the radial Schrödinger equation using the appropriate boundary conditions for the values and derivatives of the wave functions at the origin $r = 0$. The integration was performed numerically using Mathematica’s NDSolve with the “Automatic” setting for the integration method.

For the bound states, the eigenenergies $E_i$ were determined by a nested-intervals method to an accuracy better than $10^{-10}$ eV. The continuum states were then calculated by solving the same Schrödinger equation with $l' = l \pm 1$ and with the (positive) energy $E_i + \hbar\omega$ (“unrelaxed core” approximation) (SI2). The bound states were normalized by the standard condition that

$$
\int |\psi_i(r)|^2 r^2 dr = 1,
$$

and the continuum states were normalized by their asymptotic behavior for large radii (equation 4). The phase shifts $\delta_{\pm}$ were extracted by least-squares fitting. From the initial and final state wave functions, the radial matrix elements were integrated numerically, and the $\beta$ parameters were calculated according to equation (2).

**Self-consistent single particle potentials**

The “wine bottle” potentials given by Ekardt (SI3) for neutral clusters with 20 and 58 atoms were used as a starting point for the calculations of $\beta$ parameters for the clusters Na$_{19}^-$ and Na$_{55}^-$. Na$_{19}^-$ has 20 valence electrons, and its effective single-particle potential is assumed to be essentially identical to Ekardt’s result for Na$_{20}^-$. Na$_{55}^-$ has 56 valence electrons and is 2 electrons short of completion of the 2g shell (with 18 electrons); its effective single-particle potential is expected to be similar to Ekardt’s potential for Na$_{58}^-$. In order to compensate for different cluster sizes, the radial coordinate was scaled by $(n/N)^{1/3}$, where $n = 19, 55$, and $N = 20, 58$, respectively. The potential depths were scaled such that the binding energies of the highest occupied orbitals are in reasonable agreement with the experimentally determined detachment thresholds.
The long-range polarization interaction was incorporated by extrapolating Ekardt’s potentials by the following terms: At distances of approximately $4 \ldots 10 a_0$ ($a_0$: Bohr radius) from the surface, the cluster was treated as a classical metal sphere of radius $r_0 = r_S n^{1/3} + \sigma$, with $r_S = 4 a_0$ and $\sigma = 1 a_0$ ($S13$–$S15$). By the method of image charges, it can be shown that the electron is subject to the force ($S16$)

$$F(r) = \frac{r_0^2 (2r^2 - r_0^2)}{r^3 (r^2 - r_0^2)^2},$$

represented by a potential

$$V(r) = -\frac{r_0^3}{2r^2 (r^2 - r_0^2)}.$$  \hspace{1cm} (7)

At smaller distances, the image-charge potential goes over into the self-consistent effective single-particle potential from the jellium theory ($S17$). At large distances, this potential is replaced by the potential of an induced dipole,

$$V(r) = -\frac{\alpha}{2r^4}$$  \hspace{1cm} (8)

where $\alpha$ is the electric dipole polarizability. The polarizabilities of sodium clusters have been measured for several sizes ($S18$, $S19$). We have used the values $\alpha = 1591 a_0^3$ for Na$_{19}$ and $\alpha = 4261 a_0^3$ for Na$_{55}^-$. The potentials were smoothly interpolated, and the resulting effective potentials are shown in Figure S3.

**Variation of the single particle potentials**

Simple analytically describable potentials were also used to calculate $\beta$ parameters. We have tested square-well potentials,

$$V(r) = \begin{cases} V_0 & \text{for } r \leq r_0 \\ 0 & \text{for } r > r_0 \end{cases}$$  \hspace{1cm} (9)

and Woods-Saxon potentials,

$$V(r) = \frac{V_0}{1 + \exp(a(r - r_0))}.$$  \hspace{1cm} (10)

The potential depths were adjusted to match the detachment threshold energies. In the Woods-Saxon potentials, the steepness of the edge at $r = r_0$ is adjusted by the parameter $a$. The $\beta$ parameters calculated for different model potentials are shown in Figure S4. Except for stronger deviations close to threshold and some quantitative differences, the results are qualitatively similar, and they exhibit a rather typical behavior for each cluster size and state.

In addition, the parameters that specify the shape of the Woods-Saxon potentials were systematically varied by approximately $\pm 10\%$ around the optimum values determined from a fit to the potentials given by Ekardt ($V_0 = 4.63 \pm 0.5$ eV for Na$_{19}$, $V_0 = 4.90 \pm 0.5$ eV for Na$_{55}^-$; $\sigma = 1.7 \pm 0.2 a_0$; $a = 0.7 \pm 0.1 a_0^{-1}$). The resulting curves are presented in Figure S5. No good match with the experimental data is obtained for any set of parameters.
Supporting figures

Figures S6 and S7 are similar to Figures 1 and 2 of the main article. Instead of the reconstructed photoelectron angular distributions, they show raw experimental data. For clarity, the intensity has been scaled by $\sqrt{E}$, where $E$ is the electron kinetic energy. This scaling partially compensates the distribution of electrons towards smaller radii (energies), which is due to projection, and enhances the visibility of the peaks at higher energies.

Figure S1: Schematic of the experimental setup.
**Figure S2:** The $\beta$ parameters calculated using the Bethe-Cooper-Zare formula (equation 2) as a function of the relative difference of the matrix elements, $x = (|R_+| - |R_-|) / (|R_+| + |R_-|)$, and for different values of angular momentum $l$. The black, red and blue curves correspond to phase shift differences of $\delta = 0$, $\pi/2$ and $\pi$ for $R_+R_- > 0$, and to $\delta = \pi$, $\pi/2$ and 0 for $R_+R_- < 0$.

**Figure S3:** The effective single-particle potentials used in the calculation of $\beta$ parameters for the clusters $\text{Na}_{19}$ and $\text{Na}_{55}$, combined from the potentials given by Ekardt (red), the image-charge potentials (blue), and the polarization potentials (cyan).
Figure S4: The $\beta$ parameters calculated using the potentials given by Ekardt, extrapolated by the interaction of the electron with the polarizable residual (blue solid line), square-well potentials (red, dotted line), and Woods-Saxon potentials (blue, dash-dotted line).

Figure S5: The $\beta$ parameters calculated using Woods-Saxon potentials, with the parameters for depth, spill-out and surface thickness varied by approximately $\pm 10\%$ around the optimum values determined from a fit to the potentials given by Ekardt. The curve that results from the optimum parameters is emphasized by a darker shade. The experimental data are shown for comparison.
**Figure S6:** Complement to Figure 2 of the main article.

**Figure S7:** Complement to Figure 3 of the main article.
References