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Orientation averaged angular distributions of photo-electrons from free Na clusters

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ABSTRACT

We explore, from a theoretical perspective, photo-electron angular distributions (PAD) of small Na clusters using the time-dependent local-density approximation (TDLDA). We assume an isotropic ensemble of free clusters and develop, for the case of one-photon emission, analytical formulae for the orientation averaged PAD which require only six TDLDA calculations in properly chosen reference frames. All information in the averaged PAD is contained in one anisotropy parameter. This parameter varies little with system size, but is crucially influenced by the detailed ionic structure.

Photo-induced reactions have been used for decades as key tools to explore cluster properties. Optical absorption unraveled rich information on structure and dynamics of clusters [1–4]. More information can be gathered when also resolving reaction products. Particularly informative are observables from electron emission following laser irradiation: Photo-Electron Spectroscopy (PES) which provides the kinetic energy of the emitted electrons [5,6] and Photo-Angular Distributions (PAD). More recently, measurements of PAD usually combined with PES, were performed for a variety of systems, W_N^-, $N = 4$–11 [7,8], Hg_N^-, $N = 3$–20 [9], C_{60} [10] and medium sized Na_N^- clusters [11,12].

The theoretical description of PAD has a long history in atomic physics [13] and is treated usually in perturbation theory [14]. The details for PAD from atoms are worked out in [15–17]. There also exists a large body of PAD from molecules, some even time-resolved [18–20]. These methods require a good knowledge of the continuum states for the outgoing electrons which is an always delicate matter to handle and which becomes awfully involved in situations without any symmetry where a full 3D description is required. On the other hand, there exist well developed methods to describe the dynamics of molecules and clusters in terms of time-dependent density-functional theory, actually at the level of the time-dependent local-density approximation (TDLDA) [21–23]. They also allow to describe correctly electron emission by employing absorbing boundary conditions [24,25] and a careful bookkeeping delivers a convenient TDLDA evaluation of PAD [26,27] without the need of constructing explicitly the cumbersome outgoing states. This procedure is simple for molecules/clusters with fixed orientation. Free molecules, however, come along as an ensemble with arbitrary orientations thus requiring orientation averaging (OA). Such OA is straightforward in the context of perturbation theory [19], but calls for a large number of calculations for different orientations in case of TDLDA. The aim of this Letter is to develop, for the first time, an OA for TDLDA with a minimum of TDLDA calculations. This is achieved by starting from the formal result of one-photon perturbation theory and relating its matrix elements to PAD from TDLDA. This will allow to come down to only six TDLDA calculations for an exact OA in the one-photon regime. The exact OA will be used as a benchmark to develop a direct OA in TDLDA (by simply summing over a proper sample of orientations) which then is applicable beyond the one-photon regime.

The electronic state of a system is given by the set of occupied single-electron states $|\phi_i\rangle$, $i = 1 \ldots N$. Exciting these states by a laser pulse leads to electron emission with a PAD $A(\vartheta, \varphi)$. (For simplicity, we prefer here the notation A rather then the often used $d\sigma/d\Omega$.) The ϑ, φ are the emission angles in the laboratory frame which is aligned such that ϑ, φ are the angles with respect to the laser polarization axis. One particular orientation is characterized by the Euler angles $\alpha\beta\gamma$ needed for the rotation from the laboratory frame to the system frame. The rotated state is $|\phi_{\alpha\beta\gamma,i}\rangle = e^{i\alpha \hat{J}_z} e^{i\beta \hat{J}_y} e^{i\gamma \hat{J}_z} |\phi_i\rangle$. Laser excitation of this rotated state

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yields a PAD $A^{(i)}_{\alpha\beta\gamma}(\vartheta,\varphi)$ in the laboratory frame. The OA-PAD is then

$$\overline{A^{(i)}}(\vartheta,\varphi) = \int \frac{d\alpha\, d(\cos\beta)\, d\gamma}{8\pi^2} A^{(i)}_{\alpha\beta\gamma}(\vartheta,\varphi). \tag{1}$$

A formally closed expression for the OA-PAD can be derived in one-photon perturbation theory [17,14,19]

$$\overline{A}^{(i)} = C^{(i)}_0 Y_{00}(\vartheta,\varphi) + C^{(i)}_2 Y_{20}(\vartheta,\varphi), \tag{2}$$

$$C^{(i)}_0 = \frac{1}{3}\sum_\mu a^{(i)}_{\mu\mu,00},$$

$$C^{(i)}_2 = \sum_\mu a^{(i)}_{\mu\mu',2m'} (-)^\mu \begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & 2 \\ -\mu & \mu' & m' \end{pmatrix},$$

$$a^{(i)}_{\mu\mu',lm'} = \int d(\cos\vartheta)\, d\varphi\, Y^*_{lm'} A'^{(i)}_{\mu\mu'}(\vartheta,\varphi), \tag{3}$$

$$A'^{(i)}_{\mu\mu'}(\vartheta,\varphi) = \mathcal{N}\langle\psi_{k\vartheta\varphi}|\hat{r}_\mu|\phi_i\rangle\langle\phi_i|(\hat{r}_{\mu'})^*|\psi_{k\vartheta\varphi}\rangle,$$

where $\mathcal{N} = 4\pi^2 e^2\omega/\hbar c$ accounts for the normalization of the photon field, $\psi_{k\vartheta\varphi}$ is an outgoing wave which asymptotically becomes a plane wave traveling in direction (ϑ,φ) with wave number $k = \sqrt{2m\varepsilon_{\text{out}}}$ where $\varepsilon_{\text{out}} = \varepsilon_i + \hbar\omega$ with ε_i being the single-electron energy of the initial state and ω the photon frequency. Note that we will use vectors in spherical representation r_0, r_+, r_- [28]. The laser pulse is represented by the dipole operator in direction $\hat{r}_0 \equiv \hat{z}$. The above formula probes all directions $\hat{r}_\mu$. The total PAD is simply the sum over initial states $\overline{A} = \sum_i \overline{A}^{(i)}$ and similarly for the coefficients $C_l = \sum_i C^{(i)}_l$. The OA-PAD has a very simple form which can be characterized by one parameter, the anisotropy β as

$$\overline{A} \propto 1 + \beta P_2(\cos\vartheta), \qquad \beta = \sqrt{5}\frac{C_2}{C_0}. \tag{4}$$

Limiting values for β are $+2$ (pure $\cos^2$ shape related to dominant forward–backward emission) and -1 (pure $\sin^2$ shape related to dominant sideward emission). The anisotropy parameter β is what remains after all: just one parameter characterizing the pattern of the OA-PAD in the one-photon regime.

We see from the above perturbative expression that all information is contained in the few coefficients $a^{(i)}_{\mu\mu',lm'}$ for $l = 0$ and 2. The idea is now to determine these coefficients by TDLDA calculations for a minimum amount of different cluster orientations. What TDLDA can deliver are the PAD for fixed (but arbitrary) orientations, i.e. the $A^{(i)}_{\alpha\beta\gamma}(\vartheta,\varphi)$, see Eq. (1). The key to success is the connection with the matrix $A^{(i)}_{\mu\mu'}$ given by

$$A^{(i)}_{\alpha\beta\gamma} = \sum_{\mu\mu'} D^{(1)*}_{0\mu}(\alpha,\beta,\gamma) D^{(1)}_{0\mu'}(\alpha,\beta,\gamma) A^{(i)}_{\mu\mu'}, \tag{5}$$

$$A^{(i)}_{\mu\mu'} = \sum_{lmm'} D^{(l)}_{mm'}(\alpha,\beta,\gamma) a^{(i)}_{\mu\mu',lm'} Y_{lm} \tag{6}$$

where the $D^{(l)}_{\nu\mu}$ are the well known rotation matrices [28]. We need to determine 3 coefficients $a^{(i)}_{\mu\mu,00}$ for $l = 0$ and 6 coefficients $a^{(i)}_{\mu\mu',2\mu-\mu'}$ for $l = 2$ (using symmetry $\mu \leftrightarrow \mu'$). Both $l = 0$ and $l = 2$ coefficients are projected with Eq. (3) from $A'^{(i)}_{\mu\mu'}(\vartheta,\varphi)$. We thus need only 6 different angular distributions in sufficiently different orientations. We take orientations along the axis of the cluster frame, namely, in symbolic way (100), (010), (001), (110), (101), and (011). For each orientation, we compute the PAD in the cluster frame and project onto $a^{(i)}_{\mu\mu,l0}$ for $l = 0$ and 2. Thus we have 6 linearly independent pieces of information from which we can compute the wanted coefficients $a^{(i)}_{\mu\mu',l\mu-\mu'}$ by solving a simple linear equation. The result is inserted into Eq. (2) which finally yields the averaged PAD. This procedure involves the calculation of PAD in the cluster frame which is done by full TDLDA. Perturbation theory was only invoked for deriving the averaging scheme.

An alternative to the above "exact OA" is a "direct OA" with Eq. (1). Rotation about the laser polarization axis (Euler angle α) does not require additional TDLDA runs. This leaves averaging over the Euler angles β, γ. Integration is approximated by finite summation, dividing the surface of the unit sphere into segments and adding up the results with a weight proportional to the area of the segment. This direct OA is conceptually simpler, but may require a rather large number of PAD evaluations. We will test that in comparison to the exact OA.

The numerical solution of the TDLDA equations for the cluster electrons uses standard techniques [25,29]. The electronic wave functions and spatial fields are represented on a grid in 3D coordinate space with spacing of $0.8a_0$ and box size of $(96 \times 0.8a_0)^3$. The kinetic energy is evaluated in Fourier space. Dynamical propagation for the wave functions is done by TV-splitting [30]. The cluster ions are frozen which is legitimate for the short time span used here. The laser excitation is described by an external dipole field with frequency ω and a $\sin^2$ envelope of total pulse length of 60 fs, i.e. a FWHM of 20 fs. We will use a moderate intensity $I = 10^{11}$ W/cm^2 to stay in the perturbative regime. We propagate until $t = 120$ fs to collect all emitted electrons.

Emission is accounted for by absorbing boundary conditions. High quality PAD are obtained by using spherical bounds with a radially symmetric mask function $\mathcal{M}(|\vec{r}|)$ [27]. The mask is active only in the absorbing zone $R_{\text{cut}} \leqslant |\vec{r}| \leqslant R_{\text{box}}$ (with $2R_{\text{cut}} = 72a_0$, $2R_{\text{box}} = 76.8a_0$) near the bounds of the numerical box and it switches gently from 1 to 0 to minimize unwanted reflections [31]. The Kohn–Sham time step is augmented by an absorbing step in which $\mathcal{M}(|\vec{r}|)$ is multiplied to the just propagated wave function.

To compute the PAD, the absorbed density is recorded and accumulated for each grid point yielding after all $\Gamma_i(\vec{r})$, the amount of electrons absorbed at site $\vec{r}$ from state ϕ_i. The $\Gamma_i(\vec{r})$ is non-zero only in the absorbing zone. The PAD is finally gathered by dividing the absorbing zone into radial segments S_ν, and integrating $\Gamma(\vec{r})$ over those segments. The PAD for fixed orientation in the cluster frame thus becomes

$$A'^{(i)} \propto \frac{1}{\|S_\nu(\vartheta,\varphi)\|} \int_{S_\nu} d^3r'\, \Gamma_i(\mathbf{r}'), \tag{7}$$

where $\|S_\nu(\vartheta,\varphi)\|$ is the area of the segment S_ν on the surface of a unit sphere. Finite sampling sizes induce some uncertainties. For the anisotropy β, we estimate an uncertainty of $\delta\beta \sim 0.05$.

What single electron energies ε_i is concerned, the ionization potential (IP) is for Na^+_N cluster cations ≈ 6 eV and for neutral Na_N clusters ≈ 3.5 eV. The span between lowest active state and IP is about the same for all clusters. The density of states increases with cluster size N. We use the laser frequency $\omega = 7.5$ eV for Na_N clusters and $\omega = 10$ eV for Na^+_N which both are safely in the regime of one-photon emission for all occupied states.

We first discuss Na_8. Its ions are arranged in two rings of four ions each, rotated relative to each other by 45°. The rings have a radius of $4.5a_0$ and a distance of $5.8a_0$. The ϕ_i orbitals group into two shells with $\varepsilon_{1s} = -5.8$ eV and $\varepsilon_{1p} \approx -4.3$ eV. Fig. 1 shows a couple of PAD. The three left panels are PAD for particular orientations. We see pronounced structures in ϑ and φ which depend very much on the orientations. The upper left panel (laser polarization along symmetry axis) indicates nicely the four-fold structure of the rings and their relative rotation by 45°. The next two snapshots below (polarization orthogonal to the first one) show a two-fold structure induced by the two rings of Na_8. The upper