Photoabsorption Spectra of Na$_n^+$ clusters: Thermal Line-Broadening Mechanisms

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Photoabsorption cross sections of small sodium cluster cations (Na$_n^+$, $n=3,5,7$, and 9) were calculated at various temperatures with the time-dependent local-density-approximation (TDLDA) in conjunction with \textit{ab initio} molecular dynamics simulations, yielding spectra that agree with measured ones without ad-hoc line broadening or renormalization. Three thermal line-broadening mechanisms are revealed: (I) lifting of level degeneracies caused by symmetry-breaking ionic motions, (II) oscillatory shifts of the entire spectrum caused by breathing vibrations, and (III) cluster structural isomerizations.

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Optical spectroscopy provides invaluable insights into the electronic structure, ionic configurations, thermal processes and dynamics in metal clusters, as well as about the size-dependent evolution of these properties. Indeed, investigations of these issues have been pursued rather intensively for over a decade both experimentally with photodepletion spectroscopy\cite{1,2} and theoretically\cite{3-9} with the main methodology employing the TDLDA\cite{3,5,10} in conjunction with \textit{ab initio} molecular dynamics simulations, yielding spectra that agree with measured ones without ad-hoc line broadening or renormalization. Three thermal line-broadening mechanisms are revealed: (I) lifting of level degeneracies caused by symmetry-breaking ionic motions, (II) oscillatory shifts of the entire spectrum caused by breathing vibrations, and (III) cluster structural isomerizations.

The Kohn-Sham (KS) equations with generalized gradient corrections (GGA)\cite{13} and non-local pseudopotentials\cite{14} were solved for Na$_n^+$ clusters ($n=3, 5, 7, 9$), and based on the Hellman-Feynman forces, finite temperature trajectories were generated by Langevin dynamics through the use of the BO-LSD-MD (with GGA) method\cite{12}. For each cluster size, starting from the (presumed) GGA-optimized ground state (GS) geometry and an equilibration of 10 ps duration, the system was allowed to evolve dynamically at the prescribed temperature for an additional period of $t_s=10$ ps. At each instant $t$, the excitation energies $\omega_{ij}$ were determined by solving the TDLDA eigenvalue problem\cite{10}

$$
\sum_{kl}(\epsilon_{ij}^t)^2 \delta_{ij}^t \delta_{kl}^t + 4 \epsilon_{ij}^t K_{ij,kl}^t F_{ij}^t F_{ij,kl}^t = (\omega_{ij}^t)^2 F_{ij}^t,
$$

where $i$, $j$ and $k$, $l$ denote particle-hole pairs\cite{15}, and $\epsilon_{ij}^t$ the corresponding KS orbital energy differences. The coupling matrix is given by

$$
K_{ij,kl}^t = \int d^3 r_1 d^3 r_2 \phi_{ij}^t(\mathbf{r}_1) \left( \frac{1}{r_{12}} - \delta(\mathbf{r}_{12}) \right) \frac{\partial^2 \rho(\mathbf{r}_1)}{\partial \rho(\mathbf{r}_2)} \phi_{kl}^t(\mathbf{r}_2),
$$
with the GS electron density $\rho^t$, the product of two (real) KS orbitals $\phi_{ij}^t$, and the LDA exchange-correlation potential $v_{xc}$. The oscillator strength (OS)

$$f_i^t = \frac{4}{3} \sum_{\nu} \left| \sum_{ij} d^3r \phi_{ij}^t(r) n(r) \sqrt{\epsilon_{ij}} F_{ij}^t \right|^2$$

(1)

corresponding to the transition energies $\omega_i^t$, were accumulated in bins of width $\Delta \omega=0.025$ eV yielding the absolute photoabsorption cross section per valence electron

$$\sigma(\omega) = \frac{1}{n-1} \frac{2\pi^2}{c k_b T} \int_{0}^{\infty} \frac{dt}{\Delta \omega} \sum f_i^t e^{i \omega t} e^{i (\omega+\Delta \omega) t}$$

We note first the overall good agreement between the magnitudes and shapes of the calculated and measured photoabsorption cross sections (shown here for Na$_{n}^{+}$, $n=3, 5$ and 9); compare the red histograms with the black curves in Fig. 1, and note that neither (artificial) numerical broadening nor a renormalization of the spectra has been applied. The slight deviations in peak positions are within the known accuracy of the TDLDA ($\pm 0.2$ eV)$^{10}$.

The calculated Na$_{3}^{+}$ spectrum at $T=100$ K (Fig. 1a) exhibits a low energy peak originating$^{16}$ from two transitions $\omega_1=\omega_2=2.65$ eV, from the occupied s-like orbital to two empty p-like KS orbitals located in the plane of the Na$_{3}^{+}$ equilateral triangle (see grey insets 1, 2 and 3 at the left of Fig. 1a). The high energy peak at $\omega_3=3.41$ eV is due to an excitation to another p-like orbital that is perpendicular to the cluster plane (grey inset 4 in Fig. 1a). In the experiments $\sigma(\omega)$ is determined from the depletion of the Na$_{3}^{+}$ intensity due to dissociation following absorption of a photon $h\omega$. Excitation into the $\text{in-plane}$ anti-bonding orbitals (insets 2 and 3) promotes such dissociation and is accompanied by exhaustion of the OS for the first (lower energy) measured peak. Excitation into the $\text{out-of-plane}$ orbital (inset 4) has no direct destabilizing effect and in the measurements only 66% of the Thomas-Reiche-Kuhn sum rule (TRK)$^{10}$ is observed while the full TRK sum rule is found in the theoretical spectrum shown in Fig. 1a (as well as in all the calculated spectra that we show here).

Thermal motions distort the D$_{3h}$ symmetry of the Na$_{3}^{+}$ GS and the degeneracy of the low-energy transitions $\omega_1$ and $\omega_2$ is lifted. Indeed, the evolution of $\Delta\omega_{12}^{t}=\omega_2^{t}-\omega_1^{t}$ coincides with the temporal behavior of the standard deviation $\Delta\omega_{12}^{t}=\sqrt{\sum (b_i^{t} - b_i^{0})^2/3}$ of the three bond distances $b_i^{t}$ (see Fig. 2a). Additionally, the mean bond distance $\overline{b}$ is strongly anti-correlated with the mean frequency $\omega_{12}^{t}=(\omega_1^{t} + \omega_2^{t})/2$ as well as with the position of $\omega_3^{t}$ (compare the solid line with the lower and upper dashed curves in Fig. 2b) - that is, an increase of the ionic density (decrease of $\overline{b}$) results in a blue shift of the entire spectrum. Thus, the spectral line width of Na$_{3}^{+}$ can be fully understood in terms of line-splitting and spectral sweeping with the first caused by symmetry breaking (degeneracy

FIG. 1. Theoretical (red histograms) and experimental (black curves) photo absorption cross section for Na$_{3}^{+}$ at 100 K (a), Na$_{5}^{+}$ at 100 K (b) and 300 K (c), as well as for Na$_{9}^{+}$ at 100 K (d) and at 450 K (e). Grey insets in (a) display isosurfaces of the 4 lowest KS orbitals where yellow and purple distinguish the sign of the wave function and light blue spheres mark the position of the ions. The right top corner insets in (b-e) show static TDLDA spectra: (b) for the Na$_{5}^{+}$ GS (structure a), and for an instantaneous structure b with an elongated left triangle; (c) for an instantaneous bent planar geometry (γ). The calculated spectrum shown in (d) derives exclusively from configurations lying in the basin of the GS structure a whose oblate spheroidal electron density is depicted by the purple isosurface. The static spectrum of a is shown at the top inset in (d), and in the bottom inset we show the decomposition of that spectrum into the component along the z-axis (green sticks) and the perpendicular components (red sticks). The Na$_{9}^{+}$ isomer β is shown in (e), along with its electron density (purple isosurface) and its static spectrum (right top inset). To highlight the sensitivity of the experimental results to the temperature, we include in (e) the measured spectrum$^2$ at 540 K (grey curve).
lifting, mechanism I) and the latter by breathing vibrations of the cluster (density oscillations, mechanism II).

Similarly, the finite temperature dynamics of Na$_5^+$ distorts (even at $T=100$ K) the optimal D$_{3h}$ GS symmetry (see GS α in Fig. 1b where the perpendicular left and right triangles are equivalent, and compare to the instantaneous structure β shown in Fig. 1b with an elongated left triangle), resulting in fragmentation (I) of the GS line at $\omega_\alpha = 2.8$ eV into two separate spectral lines $\omega_\alpha$ and $\omega_\beta$ 17 (compare red and blue lines in the up-right inset of Fig. 2b). Consequently, the temporal variation of the absolute difference of the average bond lengths in the left and the right triangle ($\Delta_{lb} = |b_l - b_r|$), serving as a measure of the thermal structural distortion) correlates directly with the spacing $\delta_{ad} = \omega_\alpha - \omega_\beta$ between the frequencies of the spectral fragments (see solid and dashed curve in Fig. 2c).

While the relatively moderate structural distortions occurring at 100 K are not sufficient to lift the degeneracy of the states associated with the low energy absorption line of Na$_5^+$ (at ~2 eV, compare insets α and β at the upper right of Fig. 1b) which remains relatively sharp, increase of the temperature to 300 K results in bent configurations (see instantaneous structure γ on the left in Fig. 1c) where the low energy line is fragmented (see inset γ at the upper right of Fig. 1c), resulting in enhanced broadening of that spectral line (compare Figs. 1b and 1c). Further broadening of the lines is caused by the aforementioned breathing modes (spectral sweeping mechanism II) reflected in the direct correlation between the interionic Coulomb repulsion $E_{\text{cut}}$ (as a measure of the ionic density) and the average excitation energy $\tilde{\omega} = \frac{\sum I J \omega_I}{(n-1)}$ shown in Fig. 2d for the $T = 300$ K simulation.

For larger clusters, the occurrence of thermal isomerizations opens an additional line-broadening channel (III) 18. The GS structure of the Na$_5^+$ cluster 19 is shown at the left of Fig. 1d (marked α) and the TDLDA spectrum calculated for this static configuration exhibits several absorption lines distributed in a bimodal-like manner (see top inset at the upper right of Fig. 1d). This bimodality, which is in contradiction to the single-line spectrum predicted by the jellium model 5, originates from the “oblate shape” of the cluster with radii $R_z = 2.68$ Å along the D$_{3h}$ symmetry axis (α in Fig. 1d) and $R_{xy} = 3.22$ Å in the xy plane (these radii were determined from the diagonalized moment of inertia of the ionic GS structure α). The total electron density (see purple isosurface in Fig. 1d) is almost an ideal oblate spheroid. A decomposition of the OS of the D$_{3h}$ GS into a z ($\nu=3$ term in eq. 1) and the xy contribution ($\nu=1$ and 2 terms) shows clearly that, as expected 3, the smaller spatial dimension in the z direction is associated with a higher excitation energy (compare green and red line in bottom inset at the upper right of Fig. 1d). The bimodal character of the 100 K photoabsorption spectrum is evident in both the measured and calculated spectra (Fig. 1d), with further broadening caused by thermal motions through line-fragmentation and breathing vibrations of the cluster (mechanisms I and II).

The main thermal effect observed in the spectra of Na$_5^+$ is the conversion of the low temperature (e.g. $T = 100$ K, Fig. 1d) bimodal spectrum to one with a single broad maximum at higher temperatures (e.g. 450 K, Fig. 1e). This change in the spectrum is caused mainly by transformations between the GS geometry (α, Fig. 1d) and the structural isomer β (see configuration on the left of Fig. 1e). The static spectrum of the β isomer is shifted to lower energies with respect to that of the GS (α) structure (compare top insets marked α and β at the upper right corners of Figs. 1d and 1e). Thus, the high-temperature broad spectral feature (Fig. 1e) is due to contributions from both the α and β isomers to the phase-space trajectories generated by the Langevin MD simulation at 450 K 20,21.

The β-isomer may be characterized as having an octupolar shape, reflected in the shape of the electron density shown in Fig. 1e (see purple isosurface). To quantitatively analyze the spectral broadening caused by transitions (at high T) between the GS (α) and the β-isomer.
(which involve changes in shape-multipolarity) we calculate the dimensionless multipole shape parameters\(^2\),
\[ \alpha_{t,m} = -\frac{1}{2}\sum_{\ell=2}^{\infty} \sum_{m=-\ell}^{\ell} r_{i} Y_{\ell m}(\theta_{i}, \phi_{i}) \]
where \((r_{i}, \theta_{i}, \phi_{i})\) are the polar coordinates of the \(i\)th ion with respect to the center-of-mass of the cluster and \(r_{i}\) is the density parameter of bulk Na. We defined a parameter
\[ \Delta_{t} = \frac{1}{2} \sum_{\ell=2}^{\infty} \sum_{m=-\ell}^{\ell} |\alpha_{t,m}|^{2} \]
that measures the deviation from sphericity due to the multipole modes up to the order \(\ell\). Fig. 2e shows a remarkable correlation \((R^{2}=84\%)\), see ref.\(^{23}\), between \(\Delta_{t}\) and the width \(\Gamma\) of the spectrum at time \(t\) \((\Gamma^{t}\) is twice the standard deviation of \(\sigma^{t}(\omega)\) for \(2 < \omega < 3.5\) eV). Furthermore, including in such analysis only quadrupole and octupole deformations \((i.e. \Delta_{t,2}\) results in a similar high value of \(R^{2}(73\%))\), while limiting consideration to the quadrupole deformation alone \((i.e. \Delta_{t,2}^{4}\) yields a poor correlation \((R^{2}=19\%)\) pointing to the strong influence of octupolar deformations on the optical response of metal clusters (even closed shell ones \(i.e. Na_{2}^{3+}\)). This analysis confirms our conclusion pertaining to the importance of the isomerization mechanism \((\text{III})\) in explaining the thermal evolution of photoabsorption spectra \(\text{particularly at high temperatures.}\)

In summary, we demonstrated that calculations of absolute photoabsorption cross sections using the TDLD in conjunction with \textit{ab initio} MD simulations allow first-principles quantitative description and interpretation of optical spectra measured for sodium cations at various temperatures. Spectral line fragmentation resulting from symmetry-breaking ionic motions that lift electronic level degeneracies, frequency shifts \((\text{spectral sweeps})\) of the entire spectrum due to symmetry-conserving breathing vibrations, and structural isomerizations are identified as the main thermal line-broadening mechanisms with the first two operative for the smaller cluster \((Na_{3}^{+}\) and \(Na_{4}^{+}\)) and all three for larger ones.

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\(^{15}\) The convergence of \(\sigma(\omega)\) with respect to the size of the computational cell \((48 a_{0}\) in all three dimensions), and the number of orbitals (30-60) has been carefully checked.

\(^{16}\) For the smallest clusters \((Na_{3}^{+} \text{ and } Na_{4}^{+})\) an analysis of the largest elements in \(F_{\alpha \beta ij}\) \((\text{see eq. 1 and ref.}^{10})\) allows assignment of the particular particle-hole pairs \((i,j)\) that make a dominant contribution to a certain optical line \(I\). Such analysis is not fruitful for larger clusters whose level spectra are more dense.

\(^{17}\) The OS of the \(Na_{2}^{3+} \text{ 2.77 eV line stems mainly from the transition from the first occupied orbital (with an elongated s-like shape) to two degenerate orbitals spatially separated on one of the two triangles.}\)

\(^{18}\) While in the text we focus our discussion on the larger cluster \(Na_{3}^{+}\), we remark that isomerization broadening was found by us also for sodium \(Na_{7}^{2+}\), where at \(T=300 K\) we observed structural transitions between the \(D_{3h}\) pentagonal bipyramidal GS and a \(D_{4h}\) planar hexagonal isomer \((\text{lying } 141 \text{ meV above the GS})\) resulting in a bimodal spectral maximum for \(\omega \sim 2.4 \text{ eV}\), in addition to a broad absorption peak at \(3.5 \text{ eV}\) (see ref.\(^{7}\)).

\(^{19}\) The \(Na_{4}^{3+}\) GS structure \((\text{a tricapped trigonal prism, } \alpha \text{ in Fig. 1d})\) is lower by \(98 \text{ meV}\) than the \(Na_{3}^{+}\) GS reported in ref.\(^{7}\) and depicted as configuration \(\beta\) on the left of Fig. \(1e\) \((\text{a bicapped bipyramid with a } C_{2v}\text{ symmetry.})\)

\(^{20}\) We note that attempts to describe the simulated 450 K spectrum shown in Fig. \(1e\) by Boltzmann-weighted averaging of the broadened static 0 K spectra of the \(\alpha\) and \(\beta\) isomers \((\text{insets in Figs. } 1d \text{ and } 1e)\) do not lead to satisfactory agreement with our \textit{ab-initio} results and the experimental data, unless unphysically large broadening parameters are used. Furthermore, this procedure fails to describe the observed shift of the high-temperature spectrum to lower energies due to thermal expansion of the cluster.

\(^{21}\) From our simulations of \(Na_{5}^{3+}\) at 450 K, we observed a direct correlation between the ionic repulsion energy and the mean absorption frequency \((\text{similar to that shown in Fig. } 2d \text{ for } Na_{5}^{3+})\). The line broadening due to the breathing mode \((\text{mechanism } II)\) implied by such correlation, contributes merely \(66 \text{ meV}\) to the total width \((\sim 0.6 \text{ eV})\, \text{see Fig. } 1e)\).

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The coefficient \(\Gamma=\langle 1/t_{s} \rangle \int dt (\langle x(t) - \bar{x} \rangle (\langle y(t) - \bar{y} \rangle / (s_{y} s_{y}) \rangle) \langle x(t) + y(t) \rangle \langle x(t) + y(t) \rangle \text{measures the width of the distribution of } x(t) \text{ and } y(t) \text{ with means } \bar{x} \text{ and } \bar{y} \text{ and standard deviations } s_{y} \text{ and } s_{y}, \text{ respectively.}\)