Photoabsorption Spectra of Argon Cation Clusters: Monte Carlo Simulations Using Many-body Polarization

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Photoabsorption spectra of argon cation clusters: Monte Carlo simulations using many-body polarization

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A simple, semiempirical model that includes many-body polarization is used to study the ground and excited state properties of Ar5− clusters (N = 3−23) at 80 K. For purposes of comparison, a model that does not include many-body polarization is used to study clusters with N = 3−27. Monte Carlo simulations are used to calculate the average properties of these clusters. The model is similar to one previously used to study argon cation clusters without many-body polarization. The photoabsorption spectrum is in good agreement with experiment; in particular, the photoabsorption spectra for cluster sizes 4–10 do not show the blueshift that is seen with models that do not include many-body polarization. © 2000 American Institute of Physics. [S0021-9606(00)30141-6]

I. INTRODUCTION

The electronic and geometric structures of argon cation clusters have received both experimental1−12 and theoretical13−24 interest over the past few years. The focus has been to understand the extent of delocalization of the positive charge (hole) and the evolution of the photoabsorption cross section as a function of cluster size. Previous theoretical studies using a tight-binding model21 and a diatomics-within-molecules (DIM) approach13,14 have predicted a relatively large blueshift in the photoabsorption spectrum between three and seven atoms which is not seen in experiment. Neither model included many-body polarization (MBP), which may be important for polarizable atoms such as argon. Recent DIM calculations have included polarization effects through a three-body interaction in the simulation of photoabsorption spectra. Grigorov and Spiegelmann22 reported calculation for N = 3, 4, 8, 13, and 19 at finite temperature while Doltsinis et al.23 reported simulations at 0 K for N = 3. However, there has yet to be a study that includes polarization for all clusters from N = 3−23.

In this work, we use a semiempirical tight-binding Hamiltonian that includes many-body polarization to study Ar5− clusters at finite temperature. The form of the Hamiltonian is similar to the one previously used21 and includes simple, physically reasonable terms, which are either fixed using known properties such as the polarizability of neutral Ar or by fitting to the spectral and structural properties of Ar2, Ar2+, Ar3, and Ar3+. We calculate the thermally averaged electronic photoabsorption spectrum and charge distribution for clusters with N = 3−23 at a temperature of 80 K. We also calculate the photoabsorption spectra without using MBP for N = 3−27. Finally, we determine the minimum energy geometries at 0 K using MBP to investigate the most stable clusters in the range of N = 3−26.

II. MODEL HAMILTONIAN

Our Hamiltonian uses three basis functions per atom since the charge is in a p-type orbital and has the following form:

$$H = H_{Ar-Ar} + H_{Ar^+ - Ar} + E_{MBP} + t,$$  

where the first three terms give the diagonal elements and the last term gives the hopping matrix elements. $H_{Ar-Ar}$ is the short range repulsion interaction between neutral Ar atoms and is given by

$$H_{Ar-Ar} = \sum_{k,\mathbf{v}} |k,\mathbf{v}\rangle \left( \sum_{i,j \neq k} A e^{-B r_{ij}} \right) \langle k,\mathbf{v}|,$$  

where $|k,\mathbf{v}\rangle$ represents a p-type orbital on atom k with orientation $\mathbf{v}$ (representing the $\hat{x}$, $\hat{y}$, or $\hat{z}$ directions), and i and j label atoms. $H_{Ar^+ - Ar}$ is the short range repulsion between the atom with the charge and the neutral atoms:

$$H_{Ar^+ - Ar} = \sum_{k,\mathbf{v}} \sum_{i \neq k} |k,\mathbf{v}\rangle (A^+ e^{-B r_{iv}}) \langle k,\mathbf{v}|.$$

$E_{MBP}$ is the polarization energy of a system of N atoms in the presence of a charge:

$$E_{MBP} = \sum_{k,\mathbf{v}} |k,\mathbf{v}\rangle E_{MBP}(k) \langle k,\mathbf{v}|,$$

where the explicit form for $E_{MBP}(k)$, assuming a Drude oscillator model for the fluctuating dipoles on the argon atoms, is

$$E_{MBP}(k) = \sum_{i=1}^{3N} \frac{1}{2} \left( \sqrt{\lambda_i(k)} - \frac{X_i(k)}{\lambda_i(k)} - \omega_i \right).$$

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which was then used to estimate $B_v$ oscillators.

The form of the hopping term is estimated from its form for a two-atom cluster: $\langle \Psi_i | T + V_i + V_j | \Psi_j \rangle$, where $\Psi_i$ and $\Psi_j$ are the wave functions of the hole being localized in atoms $i$ and $j$, respectively, $T$ is the kinetic energy, and $V_i$ is the potential energy of the hole interacting with atom $i$. Assuming Slater $2p$-type orbitals we obtain

$$t_{ij}^{\gamma \eta} = -a e^{-b_{ij}} \left( e_{\gamma} \cdot e_{\eta} (1 + b_{ij} + \frac{1}{2} b_{ij}^2 r_{ij}^2) - \frac{b^2}{3} (e_{\gamma} \cdot r_{ij})(e_{\eta} \cdot r_{ij})(1 + b_{ij}) \right) + c s_{ij}^{\gamma \eta},$$

(6)

where $s_{ij}^{\gamma \eta}$ is the overlap matrix

$$s_{ij}^{\gamma \eta} = e^{-b_{ij}} \left( e_{\gamma} \cdot e_{\eta} (1 + b_{ij} + \frac{1}{2} b_{ij}^2 r_{ij}^2 + \frac{1}{3} b_{ij}^3 r_{ij}^3) - \frac{b^2}{5} (e_{\gamma} \cdot r_{ij})(e_{\eta} \cdot r_{ij})(1 + b_{ij} + \frac{1}{2} b_{ij}^2 r_{ij}^2) \right).$$

(7)

The parameters of the model are determined from known experimental values or by fitting the $Ar_N$ and $Ar_N^+$ ground and excited state properties for $N=1-3$. This is distinct from our previous work, in which only monomer and dimer properties were used to determine parameters. The polarizability and $C_6$ coefficient for Ar are taken from the literature. To determine $\omega_{Ar}$ and $\omega_{Ar^+}$, we use the relation given by Cao and Berne for a Drude oscillator model of the atoms, viz.

$$C_6 = \frac{2}{5} \frac{1}{\omega_{Ar}^2},$$

(2)

$$[2 \omega_1 \omega_2 / (\omega_1 + \omega_2)] \alpha_1 \alpha_2$$

for a mixture, where the $\alpha$'s are polarizabilities and the $\omega$'s are the frequencies of the Drude oscillators. $\omega_{Ar}$ is determined with knowledge of $C_6$ and $\alpha_{Ar}$. We consider $Ar_N^+$ as a mixture of Ar and $Ar^+$ and thus we need the frequency and polarization of Ar. We obtain $\alpha_{Ar^+}$ by using previously performed ab initio calculations of the polarizabilities of Ar and $Ar^+$ and scaling the literature value of $\alpha_{Ar}$ by the ratio of the polarizabilities determined in the ab initio calculations. We assume that the ratio of $\omega$'s is the same as the ratio of ionization potentials of Ar and $Ar^+$, which was then used to estimate $\omega_{Ar^+}$ from $\omega_{Ar}$.

We now discuss the inclusion of many-body polarization. We only include many-body polarization in the diagonal matrix elements of the Hamiltonian, which is consistent with our previous work. We follow the work by Cao and Berne and treat the polarizability of the atoms using a Drude model. Since the diagonal matrix elements correspond to the charge being localized on one atom, we can write the Hamiltonian for the Drude oscillators as

$$H = \sum_{i=1}^{N} \left( \frac{\mu_i^2}{2 \alpha_i \omega_i} + \frac{\mu_i^2}{2 \alpha_i} \right) - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \mu_i \cdot T_{ij} \cdot \mu_j$$

with $N=2-3$. The model Hamiltonian for the case without MBP is described in our previous work, except for a modification in the off diagonal terms that we present in this work. The parameters for the current models are shown in Table I.

<table>
<thead>
<tr>
<th>MBP parameters</th>
<th>$A$</th>
<th>$B$</th>
<th>$A^+$</th>
<th>$B^+$</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$\alpha$</th>
<th>$\alpha^+$</th>
<th>$\omega$</th>
<th>$\omega^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>180.845</td>
<td>1.8361</td>
<td>1514.41</td>
<td>2.1936</td>
<td>1.5949</td>
<td>1.9579</td>
<td>0.6495</td>
<td>11.09</td>
<td>6.5</td>
<td>1.1649</td>
<td>2.2045</td>
<td></td>
</tr>
<tr>
<td>Without MBP</td>
<td>172.520</td>
<td>1.8314</td>
<td>2164.39</td>
<td>2.2823</td>
<td>1.9159</td>
<td>0.9782</td>
<td>0.6172</td>
<td>95.310</td>
<td>107.448</td>
<td>5.4341</td>
<td></td>
</tr>
</tbody>
</table>

$\text{See Ref. 21 for its definition.}$

The parameters of the model Hamiltonian; all numbers are in atomic units.
where the charge is localized on atom $k$, $\mu_i$ is the dipole moment of atom $i$, $T_{ij}$ is the dipole–dipole tensor whose matrix elements are given by

$$T_{ij}^{\mu\nu} = 3r_{ij}^\mu r_{ij}^\nu - \delta_{\mu\nu} r_{ij}^2,$$

$\alpha_i$ is the polarizability of atom $i$, $\omega_j$ is the frequency of oscillator $i$, and $E_i(k)$ is the electric field at atom $i$ due to a charge on atom $k$. Making the substitution $\mu_i = \sqrt{\alpha_i}/\omega_i z_i$, the Hamiltonian becomes

$$\sum_{i=1}^N \frac{x_i^2}{2} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N z_i \cdot M_{ij} \cdot z_j - \sum_{i=1}^N \sqrt{\alpha_i}/\omega_i z_i \cdot E_i(k),$$

where the matrix $M_{ij}$ is defined by

$$M_{ij} = \omega_i^2 \delta_{ij} - \sqrt{\alpha_i}/\omega_i \omega_j T_{ij}(1 - \delta_{ij}).$$

Let us define

$$Z = (z_1, \ldots, z_N), \quad Q = (q_1, \ldots, q_N),$$

$$Y = [\sqrt{\alpha_1}/\omega_1 E_1(k), \ldots, 0, \ldots, \sqrt{\alpha_N}/\omega_N E_N(k)].$$

If $M$ is diagonalized via $Z = U \cdot Q$, where $U$ is a unitary transformation, the Hamiltonian becomes

$$\frac{1}{2} Q^2 + \frac{1}{2} Q \cdot M' \cdot Q - Y \cdot U \cdot Q,$$

where $M'$ is a diagonal matrix whose elements are the eigenvalues of $M$. If we define $X = Y \cdot U$, then the Hamiltonian becomes

$$\frac{1}{2} \sum_{i=1}^N Q_i^2 + \frac{1}{2} \sum_{i=1}^N \lambda_i \left( Q_i - \frac{X_i}{\lambda_i} \right)^2 - \frac{X_i^2}{\lambda_i},$$

where $\lambda_i$ are the eigenvalues of $M$. This is the Hamiltonian of $3N$ independent harmonic oscillators with a ground state energy

$$\sum_{i=1}^N \frac{1}{2} \left( \sqrt{\lambda_i} - \frac{X_i^2}{\lambda_i} \right).$$

To finally obtain the interaction energy we need to subtract the energy of $3N$ independent Drude oscillators:

$$E_{MBP} = \sum_{i=1}^{3N} \frac{1}{2} \left( \sqrt{\lambda_i} - \frac{X_i^2}{\lambda_i} - \omega_i \right).$$

**IV. RESULTS**

All calculations are performed at a temperature of 80 K. The initial configuration is obtained by combining a simulated annealing with a conjugate gradient minimization for the model without MBP. The starting geometry for this procedure is generated by randomly placing the $N$th atom around the cluster of $N-1$ atoms. The minimized geometry is then used as the initial configuration in the finite temperature calculations for both models, with and without MBP. A Monte Carlo (MC) simulation of 120,000 steps for small clusters (3–13) and 80,000 (14–23) for large clusters is performed to calculate the average properties.

**A. Photoabsorption spectrum**

In Fig. 1 we show the photoabsorption spectra as a function of the cluster size. Between $N = 3$–14 [Fig. 1(a)] we observe three peaks in the spectra. The first peak is located at about 260 nm. It was seen experimentally by Johnson and co-worker. Although this region is commonly referred to as a dimer remnant, the average charge for the ground state is distributed in a trimer core for $N > 3$. In terms of $\text{Ar}_3$ states, such energies correspond to states with nodes between the central atom and its two neighbors ($2\Sigma^+_u$). A second peak is located at about 425 nm and is characterized by the symmetry $2\Pi_u$. Although these transitions ($1\Sigma^+_u \rightarrow 2\Sigma^+_u, 2\Sigma^+_u$) are forbidden for a linear symmetric trimer, they emerge due to instantaneous vibrational symmetry breaking. A third and main peak is located at about 520 nm and is associated with the $\text{Ar}_3$ transition $1\Sigma^+_u \rightarrow 2\Pi^+_u$. At $N = 10$ this main peak redshifts to a final location around 570 nm for $N = 23$. From $N = 15$ [Fig. 1(b)] a high energy shoulder emerges and finally resolves at $N = 21$. This same trend occurs for the model without MBP for $N > 14$. However, without MBP, for $N \approx 14$ the spectra continue blueshifting and abruptly redshift at $N = 14$. For comparison with previous experimental and theoretical work, we calculate the...
wavelength \( \lambda_{\text{max}} \) at the maximum of the photoabsorption spectrum with a resolution \( \Delta \lambda = 5 \text{ nm} \). The results are shown in Fig. 2, along with results without using MBP and experiment. A particular feature of the experimental spectra is the absence of a blueshift for small clusters. Levinger et al.\(^\text{10}\) shown by open triangles in Fig. 2 reported spectra of \( \text{Ar}_N^+ \) for sizes \( N = 3 \) – 23. They claim that clusters between \( N = 4 \) and 15 present a similar spectrum to that of \( \text{Ar}_3^+ \) with a peak near 520 nm. Our spectrum for \( \text{Ar}_3^+ \) presents its peak at 525 nm and it is narrower than the spectrum obtained by Levinger et al. by about 30%. Consequently, the peak is higher by about 35%. We are not including spin–orbit coupling and zero-point energy effects which could lead to better agreement in terms of the width and height of the peak. Haberland et al.\(^\text{9}\) shown by open circles in Fig. 2 reported no blueshift from \( N = 3 \) – 6 after which they saw mainly a redshift and finally a constant value for \( N > 20 \). Our results using MBP agree very well with this trend. We find a maximum blue-shift of 5 nm from \( N = 3 \) – 7 which is smaller than the error bars presented in the experiment by Haberland et al. From \( N = 7 \) there is virtually no blueshift. It is important to mention that our calculations are based on fitting the excitation energy for \( \text{Ar}_3^+ \) to 520 nm, therefore our spectra are expected to agree better with the spectra obtained by Levinger et al., especially for small clusters. In summary, the evolution of the maximum peak as a function of the cluster size agrees very well with both experimental works. Although the qualitative results of the MBP model are similar to those without MBP for \( N > 14 \), it is clear that the inclusion of MBP is important for smaller clusters.

**B. Hole delocalization using MBP**

After each 10 Monte Carlo configurations the atoms are labeled in order of decreasing charge in the ground state. These configurations are saved for the calculation of the average charge for the different regions of the spectrum using the square of the transition dipole as a weighting factor. For all clusters, the average charge distribution in the ground state is localized in a trimer core. Figures 3 and 4 show the average charge in the excited states for different regions of the spectrum as a function of the \( n \)th atom \( (1 \leq n \leq N) \). Figures 3(a) and 3(b) show the excited state charge distribution for the ultraviolet (UV) region around 260 nm and the region around 425 nm for \( N = 4, 14, \) and 20. All cluster sizes follow the same trend, i.e., the hole is still localized in a trimer core. This is expected, since these two regions are already present in the photoabsorption spectrum for \( \text{Ar}_3^+ \). Figure 3(c) shows...
the excited state charge distribution for the main peak around 520 nm for $N \leq 14$. A common feature for these cluster sizes is the almost zero charge on the first atom (central atom). As $N$ increases, the hole is smoothly delocalized over the solvating atoms (atoms labeled $4-N$) accompanied by a decrease in charge on the core. This delocalization effect is correlated to the decreasing of the oscillator strength at the maximum of the peak and a consequent broadening of the photoabsorption spectrum. In our analysis of the main peak, we find contributions from three types of excited states. Two contributions are obvious for $N > 14$ and lead to the low and high energy peaks that become resolved by $N = 21$. A third contribution to the main peak comes from a large number of excited states with small transition moments; we refer to these states as the background.

To analyze the low and high energy regions of the main peak for $N > 14$ we only use those excited states whose values of the transition dipole are larger than a certain cutoff. We choose the cutoff such that states with $|\mu_{\omega}(l)|^2 < 0.5 \text{(a.u.)}^2$ are classified as the background. The cutoff value is chosen to resolve the low and high energy peaks and therefore to estimate the wavelength interval for each region. The intervals are 470 and 515 nm for the high energy peak and 515 and 650 nm for the low energy peak. Figures 4(a) and 4(b) show the average charge for the high/low energy regions, respectively. In the high energy region, about 60% of the charge is localized in the first five atoms, consistent with a higher kinetic energy for that relatively high localization. In the low energy region, the charge is a little more delocalized (50% over the first five atoms), consistent with a lower kinetic energy. For the background, the charge is completely delocalized over the entire cluster [Fig. 4(c)].

Since the trimer core and the next two solvating atoms are the carriers of at least 50% of the charge, we investigate the average location of atoms 4 and 5 relative to the ion core and the average nodal structure of the electronic states. For the analysis of atom 4, each saved configuration is translated and rotated so that atom 1 is at the origin and atom 2 is on the positive $\hat{x}$ axis. The cluster is then rotated about the $\hat{x}$ axis so that atom 4 lies in the $\hat{x}\hat{y}$ plane with its $\hat{y}$ coordinate greater than zero. Two types of configurations arise, one with atom 4 near atom 2 (70% of the configurations) and the other with atom 4 near atom 3. A similar analysis was applied to the location of atom 5. We do not attempt to determine the correlations between the locations of atoms 4 and 5 relative to the ion core and the average nodal structure of the electronic states. For the analysis of atom 4, each saved configuration is translated and rotated so that atom 1 is at the origin and atom 2 is on the positive $\hat{x}$ axis. The cluster is then rotated about the $\hat{x}$ axis so that atom 4 lies in the $\hat{x}\hat{y}$ plane with its $\hat{y}$ coordinate greater than zero. Two types of configurations arise, one with atom 4 near atom 2 (70% of the configurations) and the other with atom 4 near atom 3. A similar analysis was applied to the location of atom 5. We do not attempt to determine the correlations between the locations of atoms 4 and 5 the high and low energy regions. The average orientation of

FIG. 5. Average geometry of the trimer core for $N = 19$ with (a) the fourth solvating atom and (b) the fifth solvating atom. The average nodal structure is also shown.
the charge-carrying orbital on each atom is calculated by averaging the contributions from the three \(p\) orbitals on each atom and is indicated in Fig. 5. In the low energy region, atom 1 has almost no charge and the orbital on atom 4 overlaps constructively with the orbital on atom 2. In the high energy region atom 1 has about 13% of the charge and the orbital on atom 4 overlaps destructively with the orbital on atom 2, consistent with a higher energy. Figure 5(b) shows the average geometry for atom 5. In both the low and high energy regions the overlap between atom 5 and atom 2 seems to be constructive, although in the low energy region the overlap is more a \(\pi\) bond while in the high energy region is more a \(\sigma\) bond. In the high energy region, the orientation of atom 5 also appears to be correlated to the orientation of atom 1.

C. Energy optimization and magic numbers using MBP

We calculate the minimum energy geometry for the model with MBP by using the Powell minimization procedure over the saved configurations during the MC run for \(N<23\). The inclusion of MBP requires an \(N\times N\) diagonalization for each diagonal term of the Hamiltonian, thus using conjugate gradient minimization (which requires the calculation of the gradient) would be practically impossible. Even using the Powell method the time needed to achieve the optimized geometry is considerable. Therefore, for \(N=20–27\) we apply the Powell minimization to a single geometry which is obtained by conjugate gradient minimization over saved configurations using the model without MBP. This is justified as the optimized geometries with and without MBP are the same as those obtained in DIM calculations for the range of sizes \(N=20–27\).

There is no precise agreement among experiments, or between experiments and calculations in the assignment of magic numbers. In addition, there have been different ways to describe the stability of a cluster in the literature. Doltsinis et al. reported \(\Delta E_N = E_{N-1} - E_N \) and \(\Delta E = E_{N+1} - E_N = E_{N-1} - 2E_N\) as a function of cluster size while Ikegami et al. reported the relative binding energy \(\Delta E_N / \Delta E_{N+1}\) as a measure of the cluster stability. Magic numbers are somewhat dependent upon which definition is used. We find magic numbers at \(N=13, 17, 19, 23,\) and 25 using \(\Delta E_N / \Delta E_{N+1}\) and at \(N=13, 17, 19, 22,\) and 25 using \(\Delta E_N\) (Fig. 6). Doltsinis et al. found a similar ambiguity under these definitions at \(N=22\) and 23, although they found a magic number at \(N=16\) rather than 17. Interestingly, Ikegami et al. found magic numbers at \(N=13, 16, 19, 22,\) and 25 for all three definitions.

V. CONCLUSIONS

We presented a novel method in including many-body polarization interactions in the Hamiltonian model for \(A_{16}^+\) \((N=3–23)\). By comparing with experimental photoabsorption spectra we found very good agreement and noticed that inclusion of MBP is important for small clusters. We distinguished three components in the main peak of the spectra. In two of them, the low and high energy regions, the average charge for the excited states at 80 K is mainly localized on five atoms. These atoms are the trimer core and two solvating atoms. These are the carriers of greater than 50% of the total charge. In the third region, the background, the charge is completely delocalized over the entire cluster. We used the Powell method to calculate the optimized geometries at 0 K and found the most stable clusters to be at \(N=13, 17, 19, 23,\) and 25.
