I. INTRODUCTION

Neutral rare gas clusters and crystals are formed from closed shell atoms. Only one type of bond exists, given by the weak van der Waals interaction. This simplicity is destroyed upon ionization. An antibonding electron is removed, which leads to dramatic effects. For example, the binding energy of the neutral xenon dimer, Xe₂⁺, increases from 0.024 eV to about 1 eV upon ionization. It was at first conjectured¹ that also for the larger clusters the charge localizes on a dimer ion. Ab initio calculations showed that the charge is in effect spread over three or four atoms. One has thus three types of bonding for the rare gas cluster ions: (1) the strong chemical bond of the charged core, (2) the weaker interaction of the polarized atoms attracted to the charged core, and (3) the even weaker van der Waals interaction among atoms far removed from the charge.

Cluster science studies the transition from the atom/molecule to condensed matter. The charged atom and dimer are well known. Positively charged clusters are studied here, but what is their bulk counterpart? In fact, the charge localization process in condensed rare gases is well studied, as it dominates the electronic relaxation phenomena.²,³ In solid state language, this is a charged point defect, the antimorph of a Vₖ center. So that for charged rare gas clusters one does not study the transition to the perfect bulk, but rather to rare gas crystal or liquid containing a charged point defect.

For the clusters, there has been sustained interest in the structure and dynamics of rare gas cation clusters, Rₖ⁺, both as models for charge transfer and solvation and for their use in understanding ionization processes. Recent theoretical studies⁴⁻¹¹ have investigated the extent of charge delocalization by combining information obtained from photoabsorption experiments¹²⁻¹⁶ and from theoretical calculations of the charge density. Experiments using photoabsorption and photoionization experiments have studied He,¹⁶,¹⁷ Ar,¹²⁻¹⁵ and Xe clusters¹⁵,¹⁸ which are good representatives of the rare gases. An understanding of the spectral features requires a detailed understanding of the evolution of both ground and excited states as a function of cluster size.

The absorption spectrum of large clusters appears to evolve continuously from that of the trimer. For He₃⁺ the maximum of the absorption line has a very small redshift of approximately 16 nm from He₃⁺ to He₅⁺. Ab initio and diatomics-in-molecules calculations¹⁹⁻²¹ show He₅⁺ has a linear trimer ion core as its lowest energy geometry for N = 3–8. The small shift of the absorption line seen in the experiment suggests that the linear trimer core remains basically unperturbed by the solvating atoms. On the other hand, Knowles and Murrel²¹ found structures with a dimer ion core as the most stable geometries for N = 9–16. For Ar₅⁺, the redshift is about 90 nm¹⁵ for this same range of N. Simulations at 80 K suggest that the ground state of the cluster is a trimer core even for clusters as big as Ar₅⁺.¹¹ The shift of the absorption peaks results from a delocalization of charge density in the excited states over the solvating atoms.⁵,⁹,¹⁰,²² Simulations⁵,⁹,¹⁰ also revealed a second peak splitting from the main peak at around Ar₅⁺ and then shifting to higher energies. The excited states contributing to the higher energy peak differ little from those contributing to the low energy peak in terms of the relative amount of charge on the solvating atoms and the core atoms. The difference lies in different nodal structure.⁹,¹⁰,²² For Xe₅⁺, the redshift from Xe₃⁺ to Xe₅⁺ is 200 nm.¹⁵ The high energy peak is now clearly present and well resolved in the experimental absorption spectra of Xe₅⁺. Early discussions of these results suggested

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that these features were due to a development of a tetramer core.\textsuperscript{15} It was also suggested that two families of isomers could be coexisting, one with a linear trimer core and the other with a linear tetramer core.\textsuperscript{15} This hypothesis is quite plausible if we notice that the difference in energy between the T-shaped configuration for \( \text{Xe}^{4+}_3 \) (trimer core) and its linear isomer (tetramer core) is only 100 K, according to Kuntz and Vallrodor.\textsuperscript{23} This difference is in the range of the estimated temperature in the experiment. Such small differences in energy were actually predicted for \( \text{Ar}^{4+}_3 \). Kuntz and Vallrodor found a difference of just 10 K, while very recent calculations by Hrivnak and Kalus\textsuperscript{24} found a difference of 30 K. Recent experiments by Issendorff \textit{et al.}\textsuperscript{25} using photofragmentation show clear evidence of the coexistence of both isomers in \( \text{Xe}^{4+}_3 \) and \( \text{Ar}^{4+}_3 \). On the other hand, Doltinis\textsuperscript{7} has shown that a trimer core model can reproduce the experimental photoabsorption spectrum of \( \text{Xe}^{15}_3 \) in terms of positions of the peak maxima. In an earlier publication,\textsuperscript{15} only the absorption line shapes of \( \text{Xe}^{4+}_3 \) and \( \text{Xe}^{15}_3 \) were displayed. For the rest of the clusters in the range from 3 to 30, only the evolution of the maximum peak maxima with cluster size was shown.

In this work we will present experimental and theoretical photoabsorption cross sections for \( \text{Xe}^{n+}_N \) for the range 3 to 30. By combining simulation and experiment we will show that many of the features of the line shape are consistent with the coexistence of two families of isomers.

**II. EXPERIMENT**

Details of the experiment have been published earlier.\textsuperscript{15,26,27} Briefly, xenon clusters are produced by a supersonic expansion, and ionized by a pulsed electron beam. A first time-of-flight (TOF) mass spectrometer selects ions of a single mass. These are irradiated by photons from an excimer laser pumped dye laser. The photon induces an electronic transition in the charged core. The electronic excitation is rapidly converted into vibrational energy, which leads to an increase of the cluster’s vibrational energy followed by sequential ejection of several atoms. The overall process can be written as

\[
\text{Xe}^{n+}_N (\epsilon_0 + h\nu) \rightarrow \text{Xe}^{n+}_N (\epsilon_n + h\nu) \rightarrow \text{Xe}^{n+}_{N-1} + s \text{ Xe}.
\]  

(1)

The initial cluster energy \( \epsilon_0 \) is increased by the photon, making the cluster unstable with respect to atom emission. A second TOF spectrometer measures the distribution of the charged photofragments. The intensity of the cluster selected by the first TOF [\( \text{Xe}^{n+}_N \) in Eq. (1)] is measured with \( (I) \) and without \( (I_0) \) the photon flux. From the Lambert–Beer law one has for a good overlap of photon and cluster beam and a homogeneous linewidth:

\[
I/I_0 = \exp(-\sigma \phi \tau),
\]  

(2)

where \( \sigma \) is the cross section for photodestruction, and \( \phi \) and \( \tau \) are the laser fluence (photons per time and area), and pulse length, respectively. It is easy to measure the product \( \phi \tau \) with a calibrated light detector, so that one can obtain an absolute value for \( \sigma \) by measuring the ratio of two intensities as a function of laser fluence. If for each photon absorbed at least one Xe atom is emitted—which is true in the size and temperature range studied here—one can equate the measured cross section for photodestruction with the wanted one for photoabsorption.

**A. Estimate of the cluster temperature**

After ionization by electron impact, the positive charge localizes on a trimer or tetramer ion as these are the lowest energy structures. The energy liberated in the charge localization process heats the cluster, which subsequently cools by evaporation, similar to the process given by Eq. (1). At each evaporation step the cluster energy is reduced by the sum of the binding and recoil energy. The internal energy remaining in the cluster is determined mainly by the cluster dissociation energy and to a lesser degree by the time window of the experiment.\textsuperscript{27} The temperature \( T \) can be estimated as \( k_B T = D_n^a/24 \), where \( k_B \) is Boltzmann’s constant and \( D_n^a \) is the cluster ion dissociation energy. This gives an effective cluster temperature of 60 to 100 K.

**B. Interconversion of the isomers**

The calculations presented below show that at a very low temperature an interconversion between the trimer and tetramer structure is not possible, but at the rather high cluster temperatures employed in the experiment this is possible, and this can be verified experimentally. If there are two isomers, say \( A \) and \( B \) with fractions \( f_A \) and \( f_B \) in the beam, Eq. (2) has to be modified

\[
I/I_0 = f_A \exp(-\sigma_A \phi \tau) + f_B \exp(-\sigma_B \phi \tau).
\]  

(3)

One tunes the laser frequency to a position where isomer \( A \) absorbs (\( \sigma_A \) finite) and isomer \( B \) not (\( \sigma_B = 0 \)). A plot of \( I/I_0 \) versus laser fluence saturates at \( f_A \). If on the other hand, there are many interconversions between \( A \) and \( B \) during the 10 ns pulse length of the laser, one can reduce \( I/I_0 \) to arbitrary small values on increasing the laser power. This was observed experimentally, proving that the rate of interconversion between trimer and tetramer core is much faster than \( 10^5 \) per second.

**III. THE MODEL**

In a recent publication,\textsuperscript{10} Gascon and Hall presented a model Hamiltonian that includes many-body polarization for the study of \( \text{Ar}^{n+}_N \). In this section we describe the model introducing modifications that are relevant in treating Xe atoms. Our Hamiltonian uses six basis functions for each atom since the charge can be in a \( p \)-type orbital with spin-up or spin-down. The Hamiltonian has the following form:

\[
H = H_{Rg-Rg} + H_{Rg-Rg}^{+} + H_{MBR} + H_{SO}.
\]  

(4)

\( H_{Rg-Rg} \) is the short range repulsion interaction between neutral Rg atoms and is given by

\[
H_{Rg-Rg} = \sum_{r, \nu, \alpha} \sum_{k, j>i} A e^{-BR_{ij}} |k, \nu, \alpha\rangle \langle k, \nu, \alpha|,
\]  

(5)
where $|k, v, \alpha\rangle$ represents a $p$-type orbital on atom $k$ with orientation $v$ ($v = \hat{x}, \hat{y}, \hat{z}$) and spin $\alpha$ ($\alpha = \uparrow, \downarrow$), $i$ and $j$ label atoms, and $R_{ij}$ is the distance between atom $i$ and $j$. $H_{\text{Rg}^+ - \text{Rg}^-}$ is the short range repulsion between the atom with the charge and the neutral atoms,

$$
H_{\text{Rg}^+ - \text{Rg}^-} = \sum_{k, v, \alpha} |k, v, \alpha\rangle \sum_{i \neq k} A^+ e^{-B^+ R_{ki}} |k, v, \alpha\rangle.
$$

$H_{\text{MBP}}$ is the polarization energy of a system of $N$ atoms in the presence of a charge

$$
H_{\text{MBP}} = \sum_{k, v, \eta, \alpha} |k, v, \alpha\rangle D(k)^{\eta\eta} |k, \eta, \alpha\rangle,
$$

where the explicit form for $D(k)^{\eta\eta}$, assuming a Drude oscillator model of fluctuating dipoles on each atom, is

$$
D(k)^{\eta\eta} = \frac{3N}{2} \left[ \sqrt{\lambda}_i(k) - \frac{\langle \nu | X_i^2(k) | \eta \rangle}{\lambda_i(k)} - \omega \right],
$$

where $X_i(k)$ is the shift in the normal mode minimum due to the field from the charge on atom $k$, $\lambda_i$ is the normal mode frequency in the absence of electric field, and $\omega_k$ is the unperturbed atomic Drude frequency. Equation (8) is derived in detail in the next section. Note that the energy associated with $X_i(k)$ contributes to both diagonal and off-diagonal onsite elements.

The form of the hopping term $t$ is estimated from its form for a dimer ($\langle \Psi_i | (V_i + V_j)/2 | \Psi_j \rangle$, where $\Psi_i$ and $\Psi_j$ are the wave functions of the charge being localized in atoms $i$ and $j$, respectively, and $V_i$ is the potential energy of the charge interacting with atom $i$. Assuming Slater $2p$-type orbitals we obtain the off-diagonal matrix connecting atom $i$ and $j$.

$$
t_{ij} = t_{\sigma} + R_{ij} (t_{\pi} - t_{\sigma}),
$$

where $\delta^{\eta\eta} = (R_{ij} R_{ij})^{\eta\eta} = (R_i R_i)^{\eta\eta}$, and

$$
t_{\pi} = -ae^{-bR_{ij}} (1 + bR_{ij} + \frac{1}{2} b^2 R_{ij}^2),
$$

$$
t_{\sigma} = -ae^{-bR_{ij}} (1 + bR_{ij} - \frac{1}{2} b^3 R_{ij}^3).
$$

The hopping matrix between atom $i$ and $j$ is obtained by the direct product $t = t_{\pi} \otimes I_2$, where $I_2$ is the spin-dependent $2 \times 2$ identity matrix. It is interesting to notice that independent of the form of $t_{\pi}$ and $t_{\sigma}$, Eq. (9) is the general expression of the hopping matrix between $p$-type orbitals. In particular, it satisfies rotational invariance. One can take advantage of this by realizing that an atom produces a perturbation on a second atom so that the $\sigma$ and $\pi$ hopping terms are not strictly a result of the overlap of identical $p$ orbitals. One can therefore use a form for $t_{\pi}$ and $t_{\sigma}$ that has different $a$ and $b$ values in Eqs. (10) and (11) (i.e., $a_\pi$, $b_\pi$, $a_\sigma$, and $b_\sigma$).

For the inclusion of spin–orbit coupling we have followed the semiempirical atoms-in-molecule (AIM) scheme proposed by Cohen and Schneider\textsuperscript{29} in which the on-site off-diagonal elements only account for the spin–orbit coupling,

$$
H_{\text{SO}} = 2\delta \sum_k \sum_{\eta, \nu, \beta} |k, \nu, \alpha\rangle \langle k, \nu, \alpha| L_{k} \cdot S_{k} |k, \eta, \beta\rangle
$$

$$
\times \langle k, \eta, \beta|,
$$

where $\delta = -0.0160476$ (a.u.\textsuperscript{29}) is the spin–orbit coupling constant for a $5-p$ orbital of Xe$^+$. The matrix elements $\langle k, \nu, \alpha| L_{k} \cdot S_{k}| k, \eta, \beta\rangle$ are obtained by first evaluating the matrix elements $\langle k, m_{l} \alpha| L_{k} \cdot S_{k}| k, m'_{l}, \beta\rangle$, where $m_{l}$ ($l = 1$) represents the spherical harmonics basis set. Then the matrix is transformed by a change of basis from $|k, m_{l}, \alpha\rangle$ to $|k, \nu, \alpha\rangle$. Finally, the on-site matrix accounting for the spin–orbit coupling is

$$
H_{\text{SO}} =
$$

where $i = \sqrt{-1}$.

The procedure for calculating the photoabsorption spectrum is as follows: If $|a\rangle = \sum_{i, \nu} c_{i\nu} a_{i\nu} |i\rangle$, then the transition dipole between state 0 and $a$ for a given configuration is given by

$$
\mu_{0a}^{\xi} = \langle 0 | R^{\xi}_i a \rangle = \sum_{i, \nu} (c_{0\nu} a_{i\nu}) \langle R^{\xi}_i a | R^{\xi}_i a \rangle,
$$

where $R^{\xi}_i$ is the position vector of atom $i$, and $\xi = \pi, \sigma$, or $\pi$. For Eq. (13) we have adopted the simplified form used by Doltsinis et al.\textsuperscript{8} Finally, the photoabsorption cross section is reported as a function of the wavelength

$$
I(\lambda) = s_{0} \frac{\lambda^2}{\Delta \lambda} \sum_i \sum_a \sum_k \frac{1}{\lambda_{0a}} |\mu_{0a}(l)|^2
$$

$$
\times \Theta \left( \lambda_{0a} - \lambda + \frac{\Delta \lambda}{2} \right) \Theta \left( \lambda + \frac{\Delta \lambda}{2} - \lambda_{0a} \right),
$$

where $\Delta \lambda$ is the resolution in wavelength, $\Theta$ is the Heaviside step function, $N_c$ is the number of sampled configurations labeled by $l$, and

$$
s_{0} = \frac{1}{4\pi \varepsilon_0} \frac{4\pi^2}{3 c^2 \hbar^2}.
$$

IV. MANY-BODY POLARIZATION

We now present in detail the theory of many-body polarization (MBP). We follow the work by Cao and Berne\textsuperscript{30} 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
\[ H = \sum_{i=1}^{N} \left[ \frac{\mu_i^2}{2\alpha_i \omega_i^2} + \frac{\mu_i^2}{2\alpha_i} \right] - \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \mu_i \cdot T_{ij} \cdot \mu_j \]

\[ - \sum_{i=k}^{N} \mu_i \cdot E_i (k), \quad (15) \]

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

\[ T_{ij}^{\eta} = \frac{3R_i^2R_j^2 - \delta_{ij}R_i^2}{R_{ij}^2} \times \gamma_{\eta} (R_{ij}, \sigma), \quad (16) \]

\( \alpha_i \) is the polarizability of atom \( i \), \( \omega_i \) is the frequency of oscillator \( i \), and \( E_i (k) \) is the electric field at atom \( i \) due to a charge on atom \( k \), which for the moment is assumed a point charge. As a general idea proposed by Last and George \( \text{31} \) the dipole–dipole tensor in Eq. (16) is scaled by the damping term \( \gamma (R_{ij}, n) \) accounting for the overlap between two atoms. We propose here the form

\[ \gamma_{\eta} (R_{ij}, \sigma) = \left[ 1 + \left( \frac{\sigma}{R_{ij}} \right)^{12} \right]^{-1}, \quad (17) \]

with \( n = 4 \).

Making the substitution \( \mu_i \equiv \sqrt{\alpha_i \omega_i} z_i \), in Eq. (15) the Hamiltonian becomes

\[ \sum_{i=1}^{N} \frac{\dot{z}_i^2}{2} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} z_i \cdot M_{ij} \cdot z_j - \sum_{i=1}^{N} \sqrt{\alpha_i \omega_i} z_i \cdot E_i (k), \]

where the matrix \( M_{ij} \) is defined as

\[ M_{ij}^{\eta} = \omega_i^2 \delta_{ij} - \sqrt{\alpha_i \alpha_j \omega_i \omega_j} T_{ij}^{\eta} (1 - \delta_{ij}). \]

Let us define

\[ Z = (z_1, \ldots, z_k, \ldots, z_N), \]

\[ Q = (q_1, \ldots, q_k, \ldots, q_N), \]

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

where the \( 0 \) in the last definition is in the \( k \)th place. If \( M \) is diagonalized via \( Z = U \cdot Q \), where \( U \) is a unitary transformation, the Hamiltonian becomes

\[ H = \frac{1}{2} \dot{Q}^2 + \frac{1}{2} Q \cdot M' \cdot Q - Y \cdot U \cdot Q, \]

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

\[ H = \frac{1}{2} \sum_{i=1}^{3N} \dot{Q}_i^2 + \frac{1}{2} \sum_{i=1}^{3N} \lambda_i \left( Q_i - \frac{X_i^2}{\lambda_i} \right)^2 - \sum_{i=1}^{3N} \frac{1}{2} \sqrt{\lambda_i - X_i^2} / \lambda_i, \]

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

\[ \sum_{i=1}^{3N} \frac{1}{2} \sqrt{\lambda_i - X_i^2} / \lambda_i. \]

To finally obtain the interaction energy we need to subtract the energy of \( 3N \) independent Drude oscillators. The final MBP energy is obtained as

\[ D = \sum_{i=1}^{N} \frac{1}{2} \left( \sqrt{\lambda_i} - X_i^2 / \lambda_i \right). \quad (18) \]

We have assumed so far an electric field originated from a point charge. A more rigorous treatment assumes an angular charge distribution corresponding to the orbital containing the charge. This higher order approximation seems to be crucial for Xe. If it is not included there is a tendency to produce nondirectional forces resulting in structures like those of the neutral species. For instance, for Xe\(_4\) the lowest energy geometry would be a pyramid.

In the same spirit of the Born–Oppenheimer approximation we assume that the time scale for motion of the charge is much longer than that of the Drude oscillators. Therefore, we must evaluate the matrix elements of the ground state energy of the Drude Hamiltonian, this is, \( D^{\eta} = \langle \nu | D | \eta \rangle \). The only term that depends on orientation is \( X_i^2 (k) \). Its matrix element is approximated as follows:

\[ \langle \nu | X_i^2 | \eta \rangle = \sum_{\xi} \langle \nu | X_i | \xi \rangle \langle \xi | X_i | \eta \rangle, \]

where the sum is over the 3 \( p \) orbitals on the charged atom. It is clear that the evaluation of \( X_i^2 \) requires the evaluation of \( \langle \nu | E_q (p) | \eta \rangle \), where \( E_q (p) \) is the electric field on atom \( q \) produced by the charge on atom \( p \). Therefore, we must evaluate the term

\[ E_q (p)^{\nu} = - \nabla_{R_{qp}} \phi (R_{qp})^{\nu}, \quad (19) \]

which first requires

\[ \phi (R)^{\nu} = \int d r \; \psi_r (r) \psi_{\nu} (r) \frac{1}{|r - R|}, \quad (20) \]

We assume \( \psi_r \) is a 2–\( p \) orbital, \( \sqrt{3\tau^2} \) is the radius of the \( \tau \) electron and \( c \) is a fitting parameter. The last integral can be evaluated for \( R \gg 1/c \) and

\[ \phi (R)^{\nu} \approx \frac{1}{R} - \frac{3}{2c^2 R^3} \delta^{\nu} + \frac{9}{2c^2 R^5} R^2 R^{\nu}. \quad (21) \]

Taking the gradient in Eq. (21) we obtain,

\[ E^{\nu} = \left( \frac{R}{R^3} - \frac{9R^2}{2c^2 R^5} \right) \delta^{\nu} + \frac{45R}{2c^2 R^5} R^2 R^{\nu} \]

\[ - \frac{9}{2c^2 R^5} (e_x R^\nu + e_y R^\nu), \quad (22) \]

where \( e_x \) is the unit vector in the \( \nu \) direction. The first two terms in Eq. (22) already contain the expected effect of a charge distribution acting parallel and perpendicular to the interatomic axis. That is, it has the same form as Eq. (9), as a \( \sigma \) part and a \( \pi \) part. For computing simplification we only consider these two terms. We noticed that considering the extra term had a very small effect in the final results in the simulations. Finally, we also include a damping term on the contribution to the polarization energy coming from the electric
TABLE I. Parameters of the model Hamiltonian. All numbers are in atomic units.

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</tr>
<tr>
<td>$\sigma'$</td>
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</tr>
</tbody>
</table>

field. $E^{\gamma}(R)$ is scaled by $\gamma(R, \sigma^+)$. The value of $\sigma^+$ listed in Table I makes the contribution of $\gamma_0$ negligible. Nevertheless, it is included for completeness.

The parameters of the model are determined from known experimental values or by fitting the $Xe_N$ and $Xe_K^+$ ground and excited state properties (bond lengths, dissociation energies, and excitation energies) for $N = 1–3$. As we will discuss in detail in the next section, we also fit the difference in energy between the trimer and tetramer core structures of $Xe_4^+$ to be less than 100 K. The resulting parameters of the model are shown in Table I.

V. SIMULATIONS

All calculations are performed at a temperature of 60 K. A Monte Carlo (MC) simulation of 200,000 steps for small clusters (3–9), 100,000 for medium size clusters (10–15), and 60,000 for larger clusters (16–26) is performed to calculate statistical averages. In all cases an initial equilibration of 2000 steps is performed at 80 K. The starting geometry of each cluster is obtained by scaling the interatomic distances of the known minimum energy geometries of $Ar_N^+$ so that the lowest distance corresponds to the known experimental values of the trimer bond length of $Xe_3^+$.

As discussed in the introduction, the main hypothesis to test is whether the photoabsorption spectra can reveal the existence of two families of isomers. Therefore, one should expect the difference in energy between the trimer isomers for a given cluster to be such that both configurations are sampled at the temperature estimated in the experiment (60 K–100 K). Although there is no quantitative agreement between the calculated binding energies of both types of isomers, all models have given a difference in energy small enough so that after adding entropy effects it is conceivable that both types of isomers are present under experimental conditions.

The isomers seen in the simulations contain either a linear trimer core or a linear tetramer core. For instance, for $Xe_4^+$ the tetramer core and trimer core isomers are shown in Fig. 1 (darker shades represent more charge), they are referred to as “linear” and “T-shaped,” or $Xe_4^+$ and $(Xe_4^+)Xe$, respectively. For $Xe_5^+$ the tetramer core and trimer core isomers are shown in Fig. 2, these geometries are referred as $(Xe_4^+)Xe$ and $(Xe_4^+)Xe_2$, respectively.

In our model, in general, we use experimental data for $R_{g_1}$, $R_{g_2}$, $R_{g_3}$ to fit the parameters. Now, since $Xe$ presents a set of isomers whose difference in energy appears to be crucial in interpreting the experiment, we also fit the difference in energy between $(Xe_4^+)Xe$ and $(Xe_4^+)Xe_2$ to different values less 100 K. We found that a difference of 6 K ([$(Xe_4^+)Xe_2$ being lower in energy] presented the best agreement with the experiment. We chose the $Xe_5^+$ isomers rather than the $Xe_4^+$ isomers for this fitting because there is no experimental spectrum available for $Xe_4^+$. It is clear that this is a qualitative fitting, and that the detailed calculation of the energies goes beyond the scope of this work. The main idea is to perform a simulation in which both families of isomers are sampled and compare the resulting spectra with experimental spectra.

The existence of two isomers separated by a large energy barrier can lead to what is called “broken ergodicity” in the sampling process. In fact, we found that using a standard Monte Carlo (MC) technique the transition rate between the two isomers was very low. In order to generate transitions between the two isomers, we supplemented the standard Metropolis sampling with a method that attempts transitions from one isomer to another with appropriate trial transition probabilities so that detailed balance is satisfied. In our simulations, most moves are of the standard Metropolis MC type. Local moves are attempted with a probability $T(R \rightarrow R') = 1/\Delta$ within a local region, where $\Delta$ is the maximum step size in one direction. A second type of move is

![Figure 1](image1.png)

**FIG. 1.** (a) The tetramer core isomer of $Xe_4^+$ is linear, the color scheme represents charge distribution (0.08, 0.42, 0.42, 0.08). (b) The trimer core isomer of $Xe_4^+$ consists on a linear trimer (0.24, 0.52, 0.23) with one neutral atom attached to its side, usually referred to as T-shaped.

![Figure 2](image2.png)

**FIG. 2.** (a) $(Xe_4^+)Xe$, the tetramer core isomer of $Xe_4^+$ consists on a linear tetramer (0.08, 0.42, 0.42, 0.08) with one neutral atom attached to its side. (b) $(Xe_4^+)Xe_2$., the trimer core isomer of $Xe_4^+$ consists on a linear trimer (0.22, 0.52, 0.25) with two atoms attached to its side carrying together just 1% of the charge.
FIG. 3. The experimental photoabsorption cross section in Å$^2$ of hot Xe$_N$ for $N$ between 3 and 10, is plotted against the wavelength in nanometers. The error bars give the statistical error only. Only one peak is observed for $N=3$, which splits into two for increasing $N$.

FIG. 4. As in Fig. 3, but for $N=11–16$. 
attempted with a probability $P_J$ (approximately 10%) designed to jump from the energy basin of one isomer to the energy basin of the other isomer. The trial transition probability from a configuration $\{R\}$ in the initial basin to a configuration $\{R'\}$ in the second basin is defined as

$$T(\{R\} \rightarrow \{R'\}) = \frac{1}{2} \left[ e^{-C\Sigma_{j=1}^{N}(R'_j - R_j)^2} + e^{-C\Sigma_{j=1}^{N}(R''_j - R'_j)^2} \right].$$

$\{R^{(f)}\}$ represents the set of $3N$ coordinates of the minimum energy configuration of the initial (final) basin, and $C$ is an adjustable constant. It is chosen to obtain an appropriate acceptance ratio for the nonlocal moves. The underlying assumption in Eq. (23) is that the attempted configuration $\{R'\}$ is selected in the vicinity of $\{R\}$ with a probability

$$e^{-C\Sigma_{j=1}^{N}(R'_j - R_j)^2},$$

which assumes a very simplified harmonic approximation on each basin. The acceptance probability is then defined as

$$A(\{R\} \rightarrow \{R'\}) = \min[1, q(\{R\} \rightarrow \{R'\})],$$

where

$$q(\{R\} \rightarrow \{R'\}) = \frac{T(\{R\} \rightarrow \{R'\})\rho(\{R'\})}{T(\{R'\} \rightarrow \{R\})\rho(\{R\})},$$

FIG. 5. As in Fig. 3, but for $N$ between 17–30. The error in the absolute value of the photoabsorption cross section can be up to a factor of 2 for the two largest clusters.

FIG. 6. Oscillator strength as a function of clusters size for 13, 15, 19, 26. Experiment corresponds to hollow squares, simulations correspond to solid squares. Within the experimental uncertainty, good agreement is obtained between theory and experiment.
and $\rho(\{R\}) = \exp(-\beta U(\{R\}))$ is the Boltzmann probability. This method is similar to the scheme proposed by Rossky et al.\textsuperscript{33}

In Xe\textsubscript{N}\textsuperscript{+}, there are, actually, many local minima that are relevant at the temperatures of interest ($< 100$ K). However, they can be separated into two families that correspond to geometries where neutral atoms surround either a linear trimer core or a linear tetramer core. One member of each family is chosen for a given cluster size and used as the template in the trial transition probability for the nonlocal jumps. This does not prohibit the system from exploring other isomers within each family, as these isomers can be sampled simply by diffusion during standard Metropolis moves. Since transition among isomers within a family occurs relatively easy, any of these isomers can be used as template. For some cluster sizes we obtained templates by using the T-shaped and linear geometries for Xe\textsubscript{3}\textsuperscript{+} as seeds, then constructing larger clusters by adding atoms surrounding either core and finally locally minimizing these configurations. For other cluster sizes, we generated the templates by performing a high temperature Monte Carlo sampling and then locally minimizing stored configurations.

**VI. RESULTS**

**A. Experimental spectra**

Photoabsorption cross section for Xe\textsubscript{N}\textsuperscript{+} for most of the clusters in the range from 3 to 30 are presented in Figs. 3–6. For Xe\textsubscript{3}\textsuperscript{+} there is only one peak in this region, which can unambiguously be attributed to the absorption of the trimer ion. A splitting of the main peak begins at $N=5$, and two peaks are resolved for larger clusters. The low energy peak has roughly twice the intensity as the high energy peak, a point that will be important later in the discussion. It was tentatively concluded earlier\textsuperscript{15} that the second peak is due to the absorption of the tetramer ion. The story is a little bit more complicated, as discussed below. The cross sections exhibit another peak in the 200 to 500 nm range; part of the corresponding spectra have been reported earlier.\textsuperscript{15}

**B. Calculated spectra**

In Figs. 7 and 8 we present the spectra for most of the clusters from $N=3$ to $N=26$ in the range (200, 1200 nm). The agreement with the experiment in terms of position of all peaks and their relative heights is remarkable. The abso-
lute heights of the calculated spectra are larger by an average factor of 2, and the widths are comparable, except for the smallest clusters. The oscillator strengths must satisfy the Thomas–Reiche–Kuhn sum rule. This will manifest itself in our spectrum with the larger peak heights seen in our results. Another possibility for differences is the potential of different experimental “effective” temperatures for different cluster sizes. In addition, we have not included zero-point motion, which would tend to broaden our peaks.

A quantitative comparison of calculated and experimen-
tal spectral widths and heights is best done by comparing oscillator strengths. This is done for a few clusters in Fig. 6. Despite the expected larger calculated oscillator strengths, the trends are reasonably well reproduced, particularly in light of our estimated errors in experimental oscillator strengths of 75%. In light of the expected differences between the two sets of spectra, we deem the agreement between calculations and experiment to be very good. Figure 9 shows a general comparison of the maximum peaks as a function of cluster size including those peaks in the range (200, 500 nm) whose experimental values were reported in Ref. 15. The agreement between simulation and experiment is very good. From the experimental spectra, it can be observed that the maximum wavelength of the high energy peak reaches a value of 600 nm at $N=9$ and it remains approximately there. The high energy peak in the calculated spectra reaches that value more slowly and is not resolved until $N=10$. In order to analyze the possible contributions of the two isomers to the photoabsorption spectra, we performed simulations on each basin separately, making sure that there was no interconversion between the two isomers. Figure 10(a) shows the spectra for the two isomers of Xe$^+_5$, (Xe$^+_4$)Xe, and (Xe$^+_2$)Xe$_2$. The (Xe$^+_4$)Xe$_2$ isomer presents a maximum peak around 675 nm, while (Xe$^+_4$)Xe has a maximum around 775 nm. These two values agree quite well with the experimental values of the high and low energy peaks centered at 667 and 761 nm, respectively. The templates for each basin were presented in Fig. 2. The thermodynamic average in Fig. 10(b) exhibits a line shape very similar to the experimental line shape suggesting that both isomers are co-existing and that the isomer with a tetramer core is the most abundant. At this point, one might be tempted to assign the high energy peak to the trimer core and the low energy peak to the tetramer core. However, the same analysis on larger clusters shows that the isomer with a trimer core also develops a low energy peak whose intensity, as we will show below, becomes comparable to the intensity of the high energy peak at around $N=13$. The isomer with a tetramer core, however, appears to contribute mainly but not entirely to the low energy peak. All these observations can be brought together in the analysis of Xe$^{13}_1$. Figure 11(a) shows the spectra for the two isomers of Xe$^{13}_1$. The isomer (Xe$^+_3$)Xe$_{10}$ corresponding to the well-known icosahedral structure. This is the obvious choice for a template with a trimer core. The template for the isomer (Xe$^+_4$)Xe$_9$ is shown in Fig. 12. Simulations using the sampling technique described in the preced-
ing section show that both structures are very likely to be present at 60 K. In Fig. 11(a), it is important to observe that the (Xe₃⁺)Xe₁₀ presents both low and high energy peaks and that their maximum wavelength, 780 and 600 nm, respectively, agree well with the experimental values of 805 nm and 580 nm, respectively. This was already pointed out by Doltsinis who therefore suggested that the existence of a tetramer core isomer may not be necessary to describe the experimental results. However, the thermodynamic average [Fig. 11(b)], which includes both isomers, produces a line shape that matches the experimental line shape better not only in position of the peaks (810, 600 nm) but also in their relative heights suggesting again that both families of isomer coexist at 60 K.

C. Extent of charge delocalization

In order to analyze larger clusters than Xe₁₃⁺, it is important to emphasize the relationship between charge delocalization and geometry. Because of the directionality of the p orbitals, rare gas cation clusters tend to form linear subunits defined by the two atoms with the largest amount of charge. Regardless the structure of the surrounding atoms, delocalization of the charge appears to depend strongly on the overlap of the p orbitals in the direction defined by the linear subunit. With this in mind, it is clear whether a given structure will present a trimer, a tetramer or perhaps larger units of charge. By symmetry, the charge density in the ground state will be basically an even function about the center of mass of the linear core. That is, an even number of atoms on the linear core presents a tetramer core while an odd number of atoms presents a trimer core, and the amount of charge on each atom of the core depends on interatomic distances and dihedral angles in case the linear core is bent. For instance, the close shell structures of Xe₁₃⁺, Xe₁₉⁺, and Xe₂₅⁺ have a trimer, tetramer, and trimer core, respectively. Although the geometry of Xe₃₁⁺ with a linear core of six atoms may not be the one with the lowest energy, it will present a tetramer core. Therefore, any cluster in this range may present either of these two cores or, as in the case of smaller clusters than Xe₁₃⁺, a bimodal distribution of charge if both types of isomers are present at finite temperature. In order to investigate this distribution and whether a trimer core and a tetramer core may coexist or alternate in the sequence of cluster sizes, we have defined a simple quantity, $$\Delta q = q_1 - q_2 + q_3 - q_4$$, where $$q_1$$, $$q_2$$, $$q_3$$, and $$q_4$$ are the charges of the four atoms with the largest amount of charge in decreasing order. Structures with a trimer core have a $$\Delta q$$ close to 0.5 while for structures with a tetramer core it is close to 0. For instance, for Xe₁₁⁺, $$\Delta q=0.5$$ for (Xe₃⁺)Xe₈ and $$\Delta q=0.003$$ for (Xe₄⁺)Xe₇. In Fig. 13 we show the distribution of $$\Delta q$$, $$P(\Delta q)$$, at 60 K for the two isomers of Xe₃⁺. Notice that the distribution of $$\Delta q$$ for the tetramer core isomer is much broader than the distribution for the trimer core. This is probably due to the asymmetric stretching mode that leads to an instantaneous trimer structure. On the other hand, the structure (Xe₄⁺)Xe cannot have a small distortion in which the

![FIG. 13. Distribution of $$\Delta q$$ for the isomers Xe₄⁺ and (Xe₃⁺)Xe. $$\Delta q$$ is defined as $$q_1 - q_2 + q_3 - q_4$$, where $$q_1$$, $$q_2$$, $$q_3$$, and $$q_4$$ are the charges of the four atoms with the largest amount of charge in decreasing order.](image)

![FIG. 14. Distribution of $$\Delta q$$ for clusters in the range (4–11). In all cases, a bimodal distribution can be observed, consequence of the coexistence of isomers with a trimer and tetramer core.](image)
resulting geometry resembles a linear tetramer. Therefore, for any cluster we can expect for \( P(\Delta q) \) to exhibit a distribution similar to one of those in Fig. 13 or a combination of both. Figure 14 shows the distribution of \( P(\Delta q) \) for some clusters in the range (4–13). In all figures a bimodal distribution is apparent. This shows what the analysis of the photoabsorption had already suggested, that is, the coexistence of isomers with a trimer and tetramer core with more or less similar abundance. Figure 15 shows the distribution of \( P(\Delta q) \) for some clusters in the range (14–19). The distribution for \( \text{Xe}_{14}^+ \) shows that the most likely isomer is the one with a trimer core. On the other hand, for \( \text{Xe}_{19}^+ \), the most likely isomer is the one with a tetramer core. \( \text{Xe}_{15}^+ \) appears to mark the point of transition from trimer to tetramer core. For the clusters in the range (20–25) the transition is now from a tetramer to a trimer core (Fig. 16). Interestingly, the point of transition is \( \text{Xe}_{21}^+ \) whose structure is equivalent to that of \( \text{Xe}_{15}^+ \). That is, \( \text{Xe}_{15}^+ \) and \( \text{Xe}_{21}^+ \) both have two atoms in addition to the close shell structures of \( \text{Xe}_{13}^+ \) and \( \text{Xe}_{19}^+ \), respectively.

VII. CONCLUSIONS

We presented an experimental and theoretical study of the photoabsorption in \( \text{Xe}_N^+ \) clusters for \( N = 3 \) – 30. The theoretical model uses a finite temperature simulation, considering polarization and dispersion energies as many-body interactions. Two families of isomers coexist at 60 K for \( N \leq 13 \), where the charge is either localized on a linear trimer or tetramer core, respectively. This can be clearly seen in the line shapes of the spectra, which thus give information on the relative abundance of these two families of isomers. The transition between the two isomer basins is very unlikely to occur in this small \( N \) size range if the standard Metropolis
method is used. It was necessary to supplement it with a method that attempts non-local transitions from one isomer to another, in order to obtain reliable thermodynamicaverages.

For \(N = 14\)–\(19\), the structure of the charge core starts with a trimer for \(\text{Xe}_{14}^{+}\) and ends with a tetramer for \(\text{Xe}_{19}^{+}\), being \(\text{Xe}_{15}^{+}\) the point of transition. For \(N = 20\)–\(25\), the charge core presents now a transition from a tetramer core to a trimer one, being \(\text{Xe}_{21}^{+}\) the point of transition. It was pointed out that the structure of the charge distribution can be simply understood in terms of the number of atoms on the axis that contains the charge core.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. Erwin Poliakoff and Dr. Neil Kestner for stimulating and informative discussions. The calculations were performed on computers purchased using funds from NSF CHE9977124 and the Louisiana Education Quality Support Fund. The experiments were supported by the German Science Foundation (DFG) through SFB 276.
