Static Electric Polarizabilities as Evidence for Cluster Geometries

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We present self-consistent local-spin-density calculations of the static electric dipole polarizability tensor for several isomers of sodium clusters with up to nine atoms. We show how the comparison of the calculated polarizabilities with the experimental data can be used to identify which isomer is observed in the experiments. Our results indicate that sodium clusters with six atoms or less are planar and that the drop in the polarizability of Na₇ is related to the change from two-dimensional to three-dimensional geometries. We also present an analysis of recent measurements of photoabsorption resonance frequencies.

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The determination of the atomic geometrical arrangement is a fundamental problem in the study of very small metallic clusters, because a deep understanding of their electronic and chemical properties requires the knowledge of their atomic structure. Unfortunately, direct experimental evidence on the geometrical structure of small metal clusters is scarce and it is very difficult to obtain for unsupported clusters. Quantum calculations of the total energy of clusters can suggest plausible structures, but they often find isomers with similar energies, and therefore cannot predict with confidence which structure is the most stable because the accuracy of the calculations is limited. In this context, the measurements of the average static electric polarizability of clusters¹ are very interesting since the polarizability depends on both cluster shape and size. Furthermore, recent measurements of the total photoabsorption cross section of alkali clusters²⁻⁴ have been fitted to a collective resonance model, which uses the principal values of the static polarizability tensor as fit parameters. The anisotropy of the polarizability tensor provides additional information on the shape of the cluster.

The rotationally averaged static electric polarizabilities $\bar{\alpha}$ of sodium clusters with less than forty atoms were measured by Knight *et al.*¹ using a mclecular-beam deflection technique. The experimental results indicate that the general trend of the average polarizability per atom normalized to the atomic value $\bar{\alpha}/n\alpha_1$ is a slow decrease with increasing cluster size from the atomic value of unity to the bulk value of 0.4. They also found that clusters with a "magic number" of atoms corresponding to the closed electronic shells of spherical models have smaller relative polarizabilities. Finally, they observed a "fine structure" of the polarizability between two shell closings which was attributed to the deviation from sphericity of the geometry of the sodium clusters.⁵

The classical electrostatic polarizability of a perfect conducting sphere of radius R is $\alpha = 4\pi\epsilon_0 R^3$. Using a conducting sphere of radius $R = n^{1/3}r_s$, where r_s is the Wigner-Seitz radius, as a model for a Na_n cluster, the predicted normalized polarizability α/n is 40% of the measured atomic value α_1 , a good ballpark figure. Including the effect of the charge "spill out" present at the surface leads to the prediction that the polarizability of a spherical cluster is $\alpha = 4\pi\epsilon_0(R+t)^{3.6}$ Using the jellium value of t=0.5 Å for sodium clusters⁶ gives a good description of the trend of the measured polarizabilities with respect to cluster size. Several self-consistent calculations of the polarizability of a jellium sphere have been performed.^{6,7} They give similar trends as the spill out model, although with the added feature that they predict local minima of the average polarizability for closed-shell clusters.

All spherical models predict a structureless variation of polarizability between two electronic shell closings which disagrees with the experimental observations. The polarizabilities of a conducting ellipsoid along the principal axis *i* are given by⁸ $\alpha_i = \epsilon_0 V/n_i$, where *V* is the volume of the ellipsoid and $n_i \ge 0$ are the depolarization factors which satisfy the sum rule $\sum_{i=1}^{3} n_i = 1$. From this sum rule one can prove that the minimum of the average polarizability $\bar{\alpha} = \frac{1}{3} \sum_{i=1}^{3} \alpha_i$ at constant volume is obtained for a sphere $(n_i = \frac{1}{3})$. The fine structure observed in the average polarizability should therefore reflect the deviations of the true cluster geometry from a compact "spherical" shape.⁵

Here we present careful numerical calculations of the static electric polarizability of sodium clusters up to nine atoms, using a realistic description of their geometry. We show that the comparison with experiment of the polarizabilities calculated for different isomers can be used as evidence in the identification of their geometrical structures.

Our computational method is based on the local-spindensity approximation and the pseudopotential scheme.⁹ We use two nonlocal pseudopotentials, a norm-conserving *ab initio* pseudopotential [Bachelet, Hamann, and Schlüter¹⁰ (BHS)] and the empirical pseudopotential obtained by Bardsley.¹¹ We compute the total energy and the electron density of the molecules in the presence of the electric field by solving self-consistently the Kohn-Sham equations with a Gaussian basis set. The equilibrium geometries of the isomers are determined by minimizing their total energy. The polarizability tensor is obtained from the numerical derivative of the induced electronic density with respect to the perturbing external electric field. Details of the computational method will be described elsewhere.¹²

We show in Fig. 1 the calculated geometries for the isomers of Na₃ to Na₉. The bond lengths shown in the figure are calculated with the empirical Bardsley pseudopotential. The bond lengths calculated with the ab initio BHS pseudopotential are typically 7% shorter. The calculated geometries of the Na_n isomers agree in general with previous local-density⁹ and configuration-interaction¹³ (CI) calculations. The relation between the geometries and the underlying electronic structure have been discussed previously.⁹ For Na₆, Na₈, and Na₉ the difference in energy between the isomers shown in Fig. 1 is of the order of 1% or 2% of the binding energy of the cluster and theoretical calculations cannot predict with confidence which geometry is the true ground state. For Na_4 and Na_7 the difference in energies is sufficiently large (up to 700 meV in the case of Na_7) that we are confident that the equilibrium geometries are the diamond and pentagonal bipyramid. The T-shaped isomer of Na₄ and the planar isomer of Na₇ are included in our calculations only to test if the experimental polarizability can be used to identify the stable isomer. For Na₃ and Na₅ we only show in the figure the most stable geometry.

Na₃ is the Jahn-Teller system, and its Born-Oppenheimer surface has been studied extensively.¹⁴ The evidence from electron-spin resonance in a rare-gas matrix,¹⁵ and from the agreement of calculated¹⁶ and observed vibrational frequencies¹⁷ indicate that the stable geometry corresponds to an isosceles triangle with an apex angle larger than 60° (see Fig. 1). Evidence from electron-spin resonance shows that Na₇ in a rare-gas matrix¹⁸ has the pentagonal bipyramid shape shown in Fig. 1. For all other cluster sizes, there is no experimental evidence about their geometry.

We report in Fig. 2 the rotationally averaged polarizability $\bar{\alpha}$ and the normalized polarizability $\bar{\alpha}/n\alpha_1$ for the ground state (circles) and the most important isomers (triangles) of Na_n. The trends calculated with the BHS and Bardsley pseudopotentials are the same, and we will focus our discussion on the Bardsley pseudopotential. The empirical Bardsley pseudopotential gives better agreement with experiment because the atomic polarizability and molecular bond lengths are better described by that pseudopotential as was previously discussed in a detailed analysis of the polarizability of the dimer.¹⁹

The close agreement of the theoretical polarizabilities with the experimental values of Knight *et al.*¹ is clearly seen in Fig. 2. We find the odd-even alternation present in the experimental results for small clusters with less than six atoms and its disappearance for Na₇ and Na₈. The good agreement with experiment would disappear if we had used instead the polarizabilities of the highenergy isomers of Na₄ and Na₇, showing that we can



FIG. 1. Geometries of the most important isomers of Na_n . The interatomic distances are reported in Bohr radius and have been calculated with the empirical Bardsley pseudopotential.



FIG. 2. The rotationally averaged polarizabilities $\bar{\alpha}$ of the Na_n clusters are shown as a function of cluster size. (a) Absolute polarizability and (b) polarizability divided by the number of atoms and normalized to the atomic value. The two calculated curves correspond to the use of two different pseudopotentials. The lines are only a guide to the eye.

indeed use the matching of the theoretical and experimental trends to identify the equilibrium configurations. For Na₆ the calculations predict that the pentagonal pyramid (C_{5v}) is only 0.1 eV lower in energy than the planar (D_{3h}) geometry; however, the experimental trend is better reproduced if we assume that the D_{3h} geometry is the true ground state as indicated by the dashed lines of Figs. 2(a) and 2(b). With this assumption, we predict a stronger increase of $\overline{\alpha}$ from n=5 to n=6 and a *decrease* as we pass from six to seven atoms, in agreement with experiment. The analysis of the normalized polarizability $\bar{\alpha}/n\alpha_1$ also suggests that Na₆ has a planar geometry. For Na₈ the agreement with the experimental trend, i.e., the local minimum observed for the shell closing, is apparently better reproduced if we choose the polarizability value for the D_{2d} isomer of Na₈ (solid circles). However, if we notice that our calculations consistently underestimate the normalized polarizability for odd-atom clusters and is very accurate for even-atom clusters, a spurious local-spin-density effect, then we have a better agreement with the experimental trend if we assume the T_d geometry (solid triangles) to be the most stable. The averaged polarizabilities of the two Na₉ isomers are

478

practically identical and we cannot distinguish between them by comparing with the experimental values.

The observed drop in the normalized polarizability from Na_6 to Na_7 [Fig. 2(b)], and the associated small drop of the absolute polarizability [Fig. 2(a)] is surprising, because the polarizability is expected to be proportional to the volume of the cluster, and because the oddeven alternation present in the clusters with less than six atoms would lead us to expect an *increase* in the polarizability for Na7. We notice that odd-even oscillations are also present in the alkali ionization potentials⁹ but they persist for Na7 and Na8. This unexpected drop in polarizability can be explained by the change from the two-dimensional Na₆ structure to the three-dimensional Na7 structure. The averaged polarizability of a conducting ellipsoid is a minimum for a spherical shape and increases with increasing deviation from the compact spherical shape. More compact three-dimensional geometries should be expected to have lower average polarizabilities than the more anisotropic two-dimensional geometries. The calculations show (Fig. 2) that for Na₆ and Na7 the planar structures have higher polarizabilities, confirming that the decrease in the polarizability of Na7 is associated with a change of dimensionality.

Our discussion of the average polarizabilities shows that matching the experimental and theoretical patterns can be used to identify the geometries of clusters with seven sodium atoms or less. However, the evidence for Na₈ is questionable, and it is not possible to distinguish the isomers of Na₉ using the average polarizability. The values of the principal elements of the polarizability tensor α_i in Table I indicate that it is possible to distinguish between isomers with close average polarizabilities using the anisotropy of the tensor. Recent measurements of the photoabsorption cross section of small sodium clus-

TABLE I. Principal values in Å³ of the polarizability tensor of Na_n clusters, $\alpha_i/4\pi\epsilon_0$, calculated with the empirical Bardsley pseudopotential. The principal directions are indicated in Fig. 1, and coincide with the symmetry axis.

	a_{xx}	α_{yy}	azz
Na	22	22	22
$Na_2 - D_{\infty h}$	53	30	30
$Na_3-C_{2\nu}$	89	52	41
Na_4-D_{2h}	57	118	54
Na_4-C_{2r}	81	136	60
Na_5-C_{2c}	133	91	65
Na_6-C_{5v}	118	118	65
Na_6-D_{3h}	130	130	78
$Na_7 - D_{5h}$	114	114	86
$Na_7 - D_{2h}$	163	148	83
Na_8-D_{2d}	106	106	123
$Na_8 - T_d$	120	120	120
Na ₉ - C_{2c}	157	144	109
$Na_{9}-C_{2v}(D_{3h})$	172	109	125

ters^{2,3} have been interpreted with a surface-plasma resonance model, which predicts that peaks in the photoabsorption cross section of a cluster with n valence electrons should appear for the resonance frequencies

$$\omega_i^2 = \frac{e^2}{4\pi\epsilon_0} \frac{n}{m_e \alpha_i}$$

The published measurements² cover only the wavelength range of 452-515 nm and 560-604 nm, but since the absolute cross section is measured, the dipole sum rules can be used to infer the existence or absence of resonance peaks outside this range. The results for Na₈ indicate that there is a single resonance peak around 490 nm. The value, calculated from our numerical polarizabilities renormalized to the experimental atomic polarizability, is 475 nm in the case of the T_d geometry. For the D_{2d} geometry, we predict two resonances at 446 and 481 nm. Considering that the resonance width is about 70 nm, a line-shape analysis is required for a definitive conclusion, but the available data indicate that the T_d geometry may be the ground state. The experimental results² for Na₉ indicate that of the three resonance peaks two are quasidegenerate, and the third corresponds to a polarizability that is 1.7 times larger. That would agree with the calculated factor of 1.6 for the anisotropy of the polarizability of the capped triangular prism $[C_{2v}(D_{3h})]$ isomer. In the case of Na₄, the comparison of the calculated resonance frequencies with the experimental results³ is consistent with the diamond geometry.

In conclusion, we have calculated the polarizability of sodium clusters with nine atoms or less and have shown that the polarizability is a measurable property strongly sensitive to the clusters' shape. We compared the calculated polarizabilities with the measured average values and with the photoabsorption cross-section data. Our results indicate that the calculated *ab initio* geometries are correct, in particular, we find that for Na₆ the experimental ground state is the planar geometry. The strong decrease of \bar{a}/na_1 observed as we pass from six to seven atoms corresponds to the structural transition in the clusters.

ters' shape from two-dimensional to more compact three-dimensional geometries. Considering the difficulties traditionally encountered in the experimental determination of the geometry of microclusters, we expect that our approach of comparing calculated and experimental polarizabilities will be very useful in future determinations of the structures of very small clusters.

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