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Origin of spontaneous electric dipoles in homonuclear niobium clusters

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Surprisingly large spontaneous electric dipole moments recently observed in homonuclear niobium clusters below 100 K (Moro *et al.* **300**, 1265 (2003)) are explained using first-principles electronic structure calculations. The calculated moments for Nb_n ($n \leq 15$) closely follow the experimental data in which large dipole moments are seen for $n = 11$–14. We establish that the dipoles are strongly correlated with the geometrical asymmetry of the clusters. The magnitude of the dipole moment is roughly proportional to the spread in the principal moments of inertia and its direction tends to align along the axis of the largest principal moment. Charge deformation densities reveal directional, partially covalent bonds that enhance the formation of asymmetric geometries. Classical simulations of the deflection of a cluster in a molecular beam reveal that the electronic dipole may persist at higher temperatures, but is masked by the rotational dynamics of the cluster.

Though the response of nanoparticles to an external electric field has been actively studied for several years, the recent observation of permanent electric dipoles on the order of several debye (D) in free Nb_n clusters ($n \sim$10–100) has introduced an entirely new and unexpected dimension. That the intrinsic moment is only observed at temperatures $T(n \sim 10) \approx 100$ K[1] has led to speculation that the origin of large electric dipoles might be related to superconductivity in bulk Nb (rather robust at T_c=9 K) and that the dependence on temperature may signal a nanoscale "ferroelectric" transition. Permanent dipoles in mixed clusters and molecules, including canonical polar molecules like H_2O and HF, are well understood in terms of charge transfer between unlike atoms. However, it is more challenging to envision what forces could drive the underlying charge separation in homonuclear clusters of metal atoms. This unexpected and nonintuitive dielectric behavior in Nb clusters[1] has also attracted attention to the conceptually related question of quantum dipoles in symmetric clusters[2, 3].

A fundamental requirement for the occurrence of a permanent dipole is the lack of a center of inversion. For a homonuclear system, however, the issue is more complex because disproportionation into charged ions is energetically disfavored. These questions are more perplexing in clusters that are going to become metals (which support no charge separation) as their size increases. The calculations we discuss demonstrate that the origin of these large dipoles does not require a new state of matter related to superconductivity as suggested in Ref. 1, but is explained directly in terms of directional partially covalent bonds that favor the formation of clusters with low symmetry. The resulting charge separation, which implies internal electric fields on the order of 10^6 V/cm[1], is sustained by the chemical forces of the Nb bonding. By performing classical simulations of the rotational dynamics of the clusters in a molecular beam, we provide evidence that thermal averaging, instead of a loss of intrinsic moment, accounts for the observed temperature dependence.

The atomic and electronic structures of neutral Nb_n clusters ($n \leq 23$) have been extensively studied using first-principles electronic structure methods[4, 5, 6, 7], but there has been no theoretical study of their dielectric properties. In this Letter, the electric dipole moments of Nb_n clusters ($n \leq 15$) are analyzed in terms of their asymmetry and charge deformation using the electronic structure codes Gaussian98[8] and Abinit[9]. Calculations with Gaussian98 used Stuttgart-Dresden effective core potentials[10] and the B3PW91[11, 12] hybrid exchange-correlation functional. Calculations with Abinit[9] used the planewave (norm-conserving) pseudopotential method[20] and PBE96[13] GGA functional. The lowest energy structures as well as isomers close in energy (within 25 meV/atom) obtained by Kumar and Kawazoe[7] were used, except for Nb_{13}, for which a new structure lower in energy was found. Isomers of Nb_n^+ clusters have been observed in spectroscopic[14] and reactivity[15] experiments.

The calculated permanent electric dipoles (TABLE I) are compared in FIG. 1 with the reported values[1] for Nb clusters emitted after reaching thermal equilibrium with He gas at 50 K. Considering the many uncertainties in presenting such a comparison, the level of agreement is satisfying: moderate moments are found for $3 \leq n \leq 9$, large moments for $11 \leq n \leq 14$, and essentially zero moment for n = 4, 10, and 15. The only notable discrepancy is Nb_{10} for which experiments show significant dipole moment[21] while theoretically it is zero because of the symmetric nature of the lowest energy structure. A general feature in FIG. 1 is the larger calculated dipole moment in comparison to experiment. This difference may be due to the neglect of rotational dynamics in the experimental analysis[1]. Calculations on isomers, such

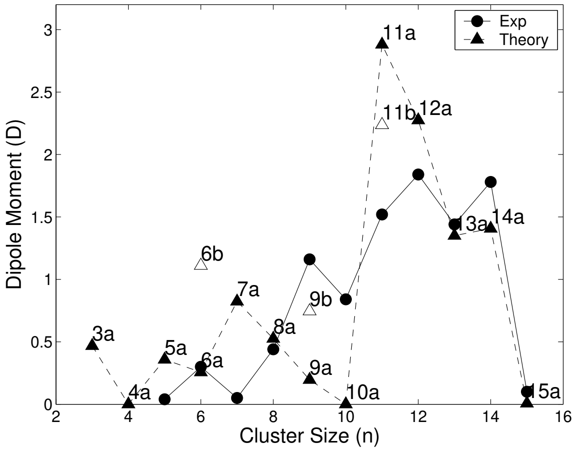

FIG. 1: Comparison of the calculated dipole moments and "low temperature" (50 K) experimental data from FIG. 2 of Ref. 1 (1 D = 0.20819 eÅ). Higher energy structures are labeled in alphabetical order, following the notation of Ref. 7.

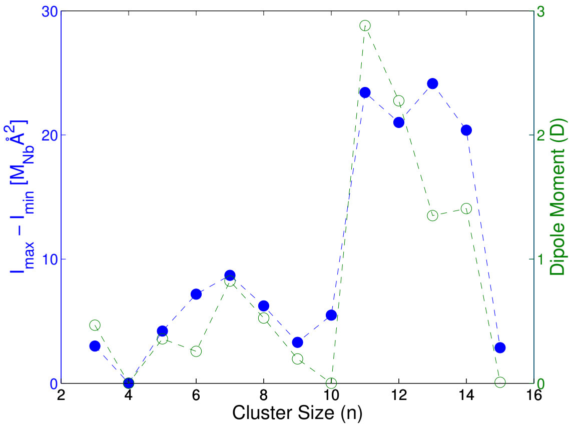

FIG. 2: The strong correlation between the dipole moment (green, right axis) and asymmetry of the cluster, as quantified by the difference between the largest and smallest principal moments of inertia (blue, left axis).

TABLE I: Principal moments of inertia I_1–I_3 ($M_{\rm Nb}$Å^2) and dipole moment μ (D) for Nb$_n$.

n	I_1	I_2	I_3	μ
2	0.00	2.21	2.21	0.0
3	2.57	3.00	5.56	0.5
4	6.33	6.33	6.33	0.0
5	7.49	11.15	11.69	0.4
6	10.51	16.06	17.69	0.3
7	17.69	20.96	26.38	0.8
8	21.37	23.36	27.61	0.5
9	28.76	29.08	32.05	0.2
10	32.54	38.03	38.03	0.0
11	34.32	48.32	57.74	2.9
12	43.05	55.11	64.06	2.3
13	51.28	61.35	75.42	1.4
14	61.29	66.71	81.68	1.4
15	73.59	76.44	76.45	0.0

as Nb$_{9b}$ and Nb$_{11b}$, whose binding energies are lower by 1 and 9 meV/atom respectively, show dipole moments closer to the experimental data[1], which may be an indication of isomers in the experimental conditions. However, Nb$_{6a}$ is in good agreement with experiment in comparison to Nb$_{6b}$, whose binding energy is also only moderately lower (20 meV/atom).

For $n > 2$ only in the case of Nb$_4$, which is a regular tetrahedron[7], does symmetry strictly forbid an electric dipole. Other cases of vanishing dipole moment, such as Nb$_{10}$ and Nb$_{15}$, are attributed to near symmetries. Nb$_{10}$ has an approximate D$_{4d}$ symmetry, whereas Nb$_{15}$ has near inversion symmetry with a cubic structure. These symmetries are reflected in the cluster's principal moments of inertia I_1, I_2, and I_3 (TABLE I). Nb$_4$, for example, is a spherical top ($I_1 = I_2 = I_3$), and Nb$_{10}$ and Nb$_{15}$ are symmetrical tops ($I_2 = I_3 \neq I_1$), although for Nb$_{15}$ the deviation from a spherical top is quite small. The rest of the clusters studied are asymmetrical tops ($I_1 \neq I_2 \neq I_3$). One measure of the degree of asymmetry is the spread $\Delta I = I_{\rm max} - I_{\rm min}$, where $I_{\rm max}$ ($I_{\rm min}$) is the largest (smallest) principal moment of inertia. Asymmetric clusters have correspondingly large values of ΔI. FIG. 2 shows the strong correlation between ΔI and the calculated electric dipole. Since the principal moments of inertia map the dynamics of a rigid body to that of an ellipsoid, ΔI can be interpreted as quantifying the existence of a preferred structural axis in the cluster. This interpretation is supported by the alignment of the electric dipole. In cases where ΔI is large (Nb$_{11}$–Nb$_{14}$), the direction of the dipole moment and the principal axis corresponding to $I_{\rm max}$ are close to collinear. The 26° deviation from collinearity of Nb$_{12}$ is the only exception to this otherwise near-perfect (within 5°) collinearity.

To understand the origin of the electric dipole we consider the charge deformation density due to bonding, that is, the difference between the charge density of the cluster and that of the isostructural spherical neutral atoms, for which the dipole moment vanishes. FIG. 3 shows the charge deformation for the simple and illustrative case of Nb$_3$[22], an isosceles triangle[7] with a dipole moment of 0.5 D. In FIG. 3, two isosurfaces are shown. The blue (red) surface corresponds to a negative (positive) isocontour of value -2.0 e/Å^3 (+2.0 e/Å^3). Taken together, these isosurfaces show how charge redistributes during the formation of bonds. Two general features can be discerned. First is the formation of a few specific covalent bonds as revealed by the charge build up between ions, which reflects charge being pulled in from elsewhere in the cluster. Second, some charge is pushed outward at each surface site due to Coulomb repulsion.

FIG. 4 shows the charge deformation for Nb$_{12}$ and Nb$_{15}$, which are representative of clusters with large

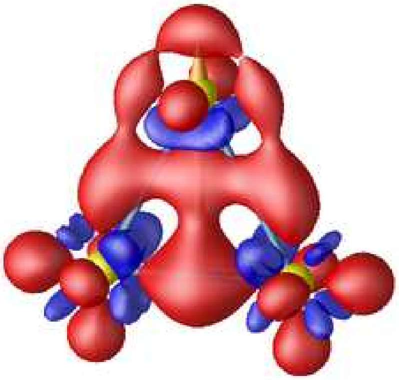

FIG. 3: Charge deformation of Nb_3 (0.5 D). Due to the mirror symmetry, the dipole moment (orange arrow) is restricted to lie on the symmetry axis.

dipole moment and no dipole moment respectively. The same color scheme and isocontour values are used as in FIG. 3 and the general features remain. Only in cases with a dipole moment, such as Nb_{12}, is there a strong asymmetric character to the deformation density. This reveals how strong directional bonding in isolated regions of the cluster leads to the intrinsic charge separation giving rise to asymmetry and the permanent dipole moment. We find however that the regions in the cluster in which the charge deformation shows this additional covalent character don't always coincide with the shortest bonds. Instead, directional bonding between *d*-electrons is important, driving the development of low-symmetry geometries.

An additional aspect of the experiments of Moro *et al.* is the disappearance of the dipole (*i.e.*, a change in the deflection of the cluster beam) when the clusters are formed at higher temperatures[1], which has been likened to a ferroelectric transition. One possible mechanism for the disappearance of the polarized electric state is the thermal excitation of vibrational modes within the cluster, which should be directly related to the temperature at which the clusters are formed. The charge response to vibrations might disturb the intrinsic charge separation in the static cluster at equilibrium. In addition, if the direction of the dipole moment were to fluctuate, this charge separation, if still in existence, could become unobservable if the time average of the dipole moment $\langle\vec{\mu}\rangle$ were sufficiently reduced. Such vibration-induced fluctuations of the dipole moment are known to be important in weakly bound molecules[16]. We suspect that such vibrations are responsible for the zero dipole moment observed in Nb_5 and Nb_7 which have distorted trigonal and pentagonal bipyramid structures respectively. In the symmetric structure of Nb_7, the highest occupied molecular orbital is doubly degenerate but occupied with one electron, which leads to a Jahn-Teller distortion. When formed and selected at a higher temperature, thermal motion may move the cluster through several structures with differing dipoles, the net effect of which would produce canceling deflections.

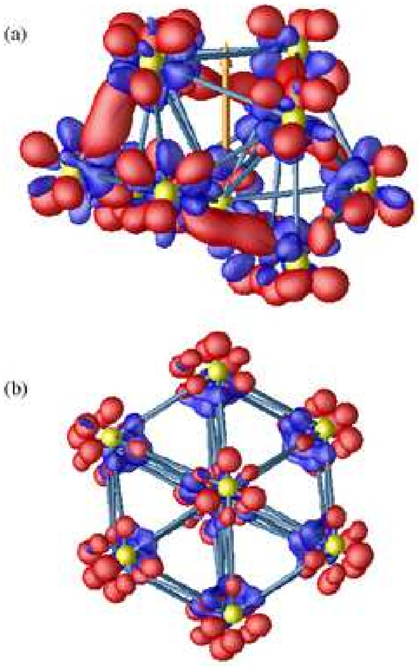

FIG. 4: Charge deformation for (a) Nb_{12} (2.3 D) and (b) Nb_{15} (no dipole). The direction of the dipole moment is represented by the orange arrow. Note the formation of strong covalent bonding. Unlike systems with a large dipole moment, no strong asymmetric covalency is seen in Nb_{15}. Instead the charge deformation density is entirely intra-atomic.

To quantify the influence of vibrations, we calculated the vibrational spectrum for Nb_{12}, a cluster with a large permanent electric dipole (2.3 D), and looked at the excitation of the 6 lowest energy vibrational modes between 60–105 cm^{-1}. These are in the range of those that would be excited during the experimentally observed transition, which occurs at a temperature on the order of 100 K. The atomic displacements associated with these vibrations are less than 0.1 Å and are unable to significantly alter the charge density or the permanent dipole, with relative changes of less than 3% or 0.1 D in magnitude and a few degrees in direction. This implies that another mechanism, beyond harmonic vibrations, is needed to explain the disappearance of the dipole moment.

Classical simulations by Dugourd *et al.*[17], using the thermal occupation of rotational states, were able to reproduce the molecular beam deflection of TiC_{60} clusters, but full temperature dependence was not studied. FIG. 5 shows the classical deflection of a representative niobium cluster (Nb_{12}) with a dipole moment of 2 D at 20 and 300 K when the homogenous electric field is on and off. These profiles were obtained by numerically evaluat-

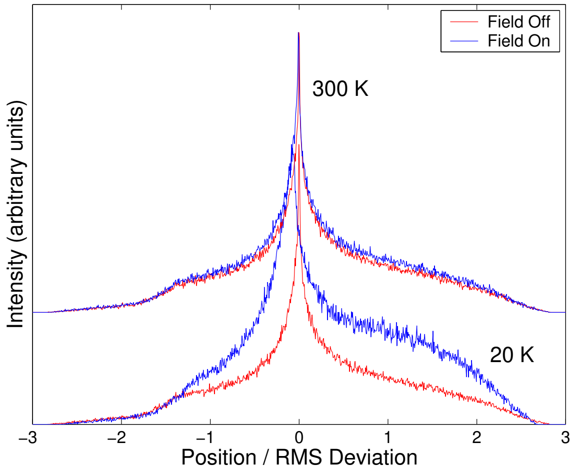

FIG. 5: Classical deflection of a model Nb_{12} cluster with a dipole moment $\mu = 2$ D at 300 K (top) and 20 K (bottom). At higher temperatures, the rotational dynamics masks the permanent dipole moment.

ing the deflection[17] of 10^6 random initial configurations (orientation and rotational energy) of a cluster with symmetric inertial moments $I_1 = I_2 = 45$ M_{Nb} Å^2 and $I_3 = 65$ M_{Nb} Å^2. The deflection due to the induced dipole, which would shift each profile a constant distance, has been ignored by setting the electric polarization $\alpha = 0$. In addition, the broadening of the profile due to the cluster's reduced translational velocity at lower temperature has been divided out.

The classical deflection profile FIG. 5 and the experimental profiles in Ref. 1 agree qualitatively. In particular, the asymmetric shape at lower temperatures, which is an experimental signature of the permanent moment[1], is clearly seen in the profile at 20 K. At 300 K the deflection profile is more symmetric, which has been interpreted as a loss of the intrinsic moment[1], but is actually the effect of additional thermal averaging.

Finally we return to the question of (a lack of) symmetry that we began with. Our calculations have traced the origin of large spontaneous electric dipoles to the structural asymmetry of Nb_n clusters that is enhanced by the directional bonding favored by d electrons. These correlations can be sharpened. First, the large asymmetric inertial moments observed in systems with large electric dipole moment result from oblate, not prolate, cluster shapes. Second, although the magnitude and direction of the electric dipole correlates very strongly with an (asymmetric) imbalance of inertial moments, this cannot be the whole story, since breaking reflection symmetry—of which the inertial moment themselves provide no information—is required for dipole formation.

That the apparent temperature dependence of the electric dipole can be explained classically implies a more rigorous treatment of rotational dynamics[18] may be required to distinguish induced versus permanent dipole effects in experiment accurately. However, because the structure of the deflection profile is richer at low temperatures, and depends directly on the inertial moments of the cluster, future low-temperature molecular beam experiments have the potential to measure structural parameters that are directly comparable to theoretical predictions.

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[20] The niobium pseudopotential was generated using FHI98PP[19] code and included 4s and 4p semicore states. A cutoff energy of 90 Ry was used to converge the planewave basis set. The cluster was placed within a simple cubic supercell of 15 Å. Only the Γ-point was used for Brillouin zone integrations.

[21] In FIG. 1 we include the value of the dipole moment given by Moro *et al.* [1] in the inset of their FIG. 2, although elsewhere they state Nb_{10} is one of the clusters for which "the ferroelectric component is essentially absent."

[22] The dipole moment of Nb_3 is similar to that of ozone O_3 (0.6 D).