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Static anisotropic and isotropic electric dipole polarizabilities of Na_nF_{n-1} clusters

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Abstract. Recently, electric susceptibilities of $\mathrm{Na}_n\mathrm{F}_{n-1}$ clusters have been measured by deflecting a molecular beam in an inhomogeneous electric field. The analysis of the deflection of a cluster by the electric field needs the calculation of the electric properties. We present the calculation of the static anisotropic and average dipolar polarizabilities within a model in which the $\mathrm{Na}_n\mathrm{F}_{n-1}$ clusters ($2 \leq n \leq 23$) are treated as one electron embedded in the field of n ions Na^+ and of $n-1$ ions F^-. The accuracy of the results is evaluated and discussed on small clusters ($n \leq 5$) in comparison with *ab initio* calculations. The relationship between the polarizabilities, the electronic localization and the geometric structure is discussed.

PACS. 31.15.Ar Ab initio calculations – 61.72.Ji Point defects (vacancies, interstitials, color centers, etc.) and defect clusters – 33.15.Kr Electric and magnetic moments (and derivatives), polarizability, and magnetic susceptibility

1 Introduction

The electronic response of clusters to various excitations has given rise to an intense activity in the last two decades. The optical spectra of various clusters have been widely studied. Other properties of interest are the responses to external fields (electric or magnetic). The static electric dipole polarizability has been investigated for several families of clusters, including metal or semiconductor clusters, fullerenes, and related clusters such as endo- or exofullerenes. An overview can be found in the book by Bonin and Kresin [1]. Dipole moments and electric dipolar polarizabilities may be difficult to compute for large systems.

Recent experiments have been able to investigate susceptibilities of clusters formed in a supersonic beam by measuring their deviations due to an electrostatic field gradient [2–6]. The most recent results involved nonstoechiometric $\mathrm{M}_n\mathrm{X}_{n-1}$ alkali-halide clusters with an electron in excess, namely $\mathrm{Na}_n\mathrm{F}_{n-1}$ and $\mathrm{Cs}_n\mathrm{Br}_{n-1}$. Theoretically, the structural, electronic and optical properties of those clusters have been essentially rationalized [7–16] in terms of cubic structures and localization of the excesss electron in the neighbourhood of the possible defects (sodium tail, F-center, defecting edges or faces). The electric dipole polarizabilities are closely related to the absorption spectra, *via* for example the well known sum rules involving the oscillator strengths (see Eq. (2.5) in the book of Bonin and Kresin [1]). The measured susceptibilities however were found to be essentially related with the magnitude of the permanent dipole moments and their fluctuations [17] rather than with the isotropic electric dipole polarizabilities. Moreover, in an analogous scheme to that used for paramagnetism and paraelectricity, the results showed a significant temperature dependance, as predicted by the associated Langevin formula. The magnitude of the permanent dipole was shown to depend mostly on the arrangement of the ionic structure (n = 18, 19), or possibly to its deformation through the coupling with electron localization (n = 14, 23). In a recent publication [18], the electric dipole moments of $\mathrm{M}_{18}\mathrm{X}_{17}$ (M = Na, K, Rb, Cs, X = F, Cl, Br, I) were systematically studied at the Hartree-Fock (HF) level, confirming the previous analysis.

In our previous paper [17], we investigated the permanent dipole moments and isotropic static electric dipole polarizabilities obtained within a single electron pseudopotential model. The single electron model, which also incorporates ionic core polarization, allows to reach sizes

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up to a few tens of atoms. Obviously, the accuracy is expected to be less than with *ab initio* calculations. In particular, the determination of dipole moments with very weak values may turn out to be difficult as resulting of a compensation between the nuclear and electronic contributions with opposite signs. In $\mathrm{Na_2F}$ for instance, the dipole moment in the symmetric linear geometry is obviously zero; its value is 1.2 D with the single electron model in the bent equilibrium geometry ($\theta = 104$ degrees), to be compared with *ab initio* values: 0.7 D (HF), 0.3 D (MP2), 0.4 D (DFT-BPW91), and 0.8 D (DFT-B3LYP). The final result is obviously very sensitive to the exact value of the bending angle. In the model, it is somewhat sensitive to the approximations and to the parameters used for the core-polarization potential which may be also a cause of error. Nevertheless the trends obtained with this model were found to be consistent with the experimental results on a wide size range [17], emphasizing the role of the permanent dipole moment. Comparing the one electron model values [17] and the recently determined HF values [18] for $\mathrm{Na_{18}F_{17}}$, we can estimate the error in the model for this property below 30%.

In this paper, we present and discuss a detailed report of the anisotropic polarizabilities which provide further insight in the electronic properties of $\mathrm{Na}_n\mathrm{F}_{n-1}$ clusters. For the smallest species ($n \le 5$) we examine the validity of the results obtained using the previous model as compared with *ab initio* Hartree-Fock and Density Functional Theory (DFT) calculations; the model is shown to yield reasonable results. For $\mathrm{Na}_n\mathrm{F}_{n-1}$ clusters in the size range $n = 2$–23, we then determine the anisotropic polarizabilities within the one-electron model and discuss the relationship with electron localization.

2 Theory

$\mathrm{Na}_n\mathrm{F}_{n-1}$ clusters are considered as systems with one electron in the field of n $\mathrm{Na^+}$ and $(n-1)$ $\mathrm{F^-}$ ions and the total Hamiltonian is written as the sum of a quantum term for the electron, H_{el}, and of a classical part for the ion-ion pairs contributions (see Eq. (4) in [17]). This classical part is the sum of two terms, the repulsion V_{rep} between the $\mathrm{Na^+}$ and $\mathrm{F^-}$ ions (represented by a sum of Born-Mayer terms), and V_{coul} (the sum of Coulombic interactions between the ions). The total Hamiltonian is simply $H = H_{\mathrm{el}} + V_{\mathrm{rep}} + V_{\mathrm{coul}}$. The quantum Hamiltonian of the electron in the field of the ions is the one-electron operator:

$$H_{\mathrm{el}} = -\frac{\Delta}{2} + \sum_m^{\mathrm{Na}} \left(W_m^{\mathrm{Na}} - \frac{1}{r_m} \right) + \sum_p^{\mathrm{F}} \frac{1}{r_p} + \sum_m^{\mathrm{Na}} W_m^{\mathrm{CPP,Na}} + \sum_p^{\mathrm{F}} W_p^{\mathrm{CPP,F}}.$$

The W_m^{Na} is the standard electron-$\mathrm{Na^+}$ valence pseudopotential. $W_m^{\mathrm{CPP,Na}}$ and $W_m^{\mathrm{CPP,F}}$ are effective core polarization pseudopotentials (CPP) which account for the static and dynamical core polarizabilities as in the formalism first derived by Müller and Meyer [19] which we preferred to the perturbative formulation used in our first paper [16]. If $\boldsymbol{E}_c$ is the total electric field at core c due to the other ions and to the electron, the CPP operators read

$$W^{\mathrm{CPP},c} = -\frac{1}{2}\alpha_c \boldsymbol{E}_c \boldsymbol{E}_c$$

where α_c is the polarizability of the ionic core c ($\alpha_{\mathrm{Na^+}} = 1.01 a_0^3$ and $\alpha_{\mathrm{F^-}} = 16.65 a_0^3$ [20]). The electronic contribution to the field is truncated in order to avoid integral divergence in the calculation using a step function only active beyond a given cut-off radius [21]. The cut-off radius for sodium and $\mathrm{F^-}$ were taken respectively as 1.45 and $3.25 a_0$. The dipole moment of a cluster in its electronic ground state ϕ_0 is calculated as

$$\boldsymbol{\mu} = \left\langle \phi_0 \right| -\boldsymbol{r} + \sum_c^{\mathrm{Na,F}} (\boldsymbol{R}_c + \alpha_c \boldsymbol{E}_c) \left| \phi_0 \right\rangle \cdot$$

The effect of an external field $\boldsymbol{F}$ can be readily incorporated by including the associated potential in the Hamiltonian, and also substituting the intracluster field $\boldsymbol{E}_c$ with the total field $\boldsymbol{F} + \boldsymbol{E}_c$ in the core-polarization operator. The present calculation is thus variational with the electron coupled to the field. The polarizabilities were calculated either by diagonalizing the tensor of the second derivatives with respect to the field, or by extracting the induced part of the dipole moments. Both methods were checked to provide identical results.

3 Results and discussion

Table 1 presents the anisotropic α_1, α_2, α_3 polarizabilities and the isotropic polarizabilities $\alpha_0 = (\alpha_1 + \alpha_2 + \alpha_3)/3$ for $\mathrm{Na_2F}$, $\mathrm{Na_3F_2}$, $\mathrm{Na_4F_3}$ and $\mathrm{Na_5F_4}$, calculated within the single-electron model, as compared with Hartree-Fock (HF), second order Moller Plesset perturbation theory (MP2) only in the case of $\mathrm{Na_2F}$, and Density Functional Theory (BPW91 and B3LYP) calculations involving standard valence pseudopotentials for $\mathrm{F^-}$ (8 electrons). For $\mathrm{Na_3F_2}$ and $\mathrm{Na_5F_4}$, the model polarizabilities fall within the dispersion of the *ab initio* calculations. The model provides slightly overestimated values in the case of $\mathrm{Na_2F}$ (isotropic polarizability of 69 Å^3 for the model *versus* 45–55 Å^3 in the *ab initio* calculations). A larger discrepancy is found in the case of $\mathrm{Na_4F_3}$ (83 Å^3 for the single electron model *versus* 46–48 Å^3 *ab-initio*). One may notice that the most accurate cases correspond to electron localization on a sodium atom.

The anisotropic and isotropic polarizabilities for clusters in the range $n = 2$–23 are listed in Table 2. Most α_0 values are of the magnitude of a few tens Å^3. One may state the following remarks. The α_0 polarizabilities in a given family have the same order of magnitude. For sodium-tail clusters (n = 3, 5, 7, 10, 11, 17, 19), α_0 increases regularly from 42 to 84 Å^3. For F-center clusters (n = 2, 4, 6, 8, 9, 18), the values lie in the range 69–90 Å^3.

Table 1. Anisotropic dipole polarizabilities (α_1, α_2 and α_3, Å^3) and mean polarizabilities (α_0, Å^3) calculated with the single electron model. Comparison with *ab initio* results (6-31^{++}G** basis sets) for Na_nF_{n-1} ($n \leq 5$) clusters; $^{(a)}$ Hartree-Fock, $^{(b)}$ MP2, $^{(c)}$ BPW91 and $^{(d)}$ B3LYP. Except for MP2, all results are obtained at their consistently optimized geometry.

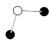
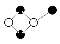
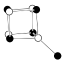
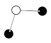
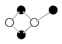
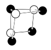
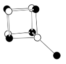
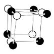
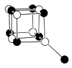
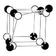
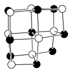
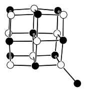
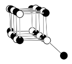
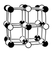
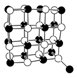
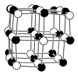
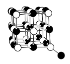
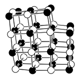
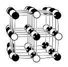
n	Cluster	α_1	α_2	α_3	α_0
2		139	40	29	69
	1×2×2−F (C_{2v})	$110^{(a)}$	$36^{(a)}$	$20^{(a)}$	$55^{(a)}$
		$113^{(b)}$	$37^{(b)}$	$24^{(b)}$	$58^{(b)}$
		$87^{(c)}$	$31^{(c)}$	$23^{(c)}$	$47^{(c)}$
		$83^{(d)}$	$28^{(d)}$	$22^{(d)}$	$45^{(d)}$
3		60	36	32	42
	1×2×2+Na (C_s)	$69^{(a)}$	$42^{(a)}$	$30^{(a)}$	$47^{(a)}$
		$57^{(c)}$	$33^{(c)}$	$32^{(c)}$	$41^{(c)}$
		$54^{(d)}$	$34^{(d)}$	$31^{(d)}$	$40^{(d)}$
4		99	99	49	83
	2×2×2−F (C_{3v})	$61^{(a)}$	$61^{(a)}$	$22^{(a)}$	$48^{(a)}$
		$55^{(c)}$	$55^{(c)}$	$28^{(c)}$	$46^{(c)}$
		$55^{(d)}$	$55^{(d)}$	$31^{(d)}$	$47^{(d)}$
5		50	50	46	48
	2×2×2+Na (C_{3v})	$56^{(a)}$	$56^{(a)}$	$36^{(a)}$	$49^{(a)}$
		$49^{(c)}$	$49^{(c)}$	$47^{(c)}$	$49^{(c)}$
		$44^{(d)}$	$44^{(d)}$	$44^{(d)}$	$44^{(d)}$

Table 2. Anisotropic dipole polarizabilities (α_1, α_2 and α_3, Å^3), mean polarizabilities (α_0, Å^3) calculated with the single electron model.

n	Cluster		α_1	α_2	α_3	α_0
2		1×2×2−F (C_{2v})	139	40	29	69
3		1×2×2+Na (C_s)	60	36	32	42
4		2×2×2−F (C_{3v})	99	99	49	83
5		2×2×2+Na (C_{3v})	50	50	46	48
6		2×2×3−F (C_s)	104	69	43	72
7		2×2×3+Na (C_s)	55	55	49	53
8		2×2×4−F (C_s)	152	89	56	99
9		2×3×3−F (C_s)	98	65	34	66
10		2×3×3+Na (C_s)	63	58	57	60
11		2×2×5+Na (C_s)	65	64	60	63
14		3×3×3 (C_{3v} apex)	173	173	122	156
		3×3×3 (O_h deloc.)	1009	1009	1009	1009
17		2×4×4+Na (C_s)	81	78	76	78
18		3×3×4−F (C_s)	88	83	72	81
19		3×3×4+Na (C_s)	88	82	81	84
23		3*×4×4−NaF$_2$ (C_{2v})	636	254	133	341
		3×3×5 (C_s apex)	190	188	138	172
		3×3×5 (D_{4h} deloc.)	5773	1587	1587	2983

There is no difference in the order of magnitude between those two families. The anisotropic dipole polarizabilities obviously reflect the cluster symmetry (through degeneracy) which is given in Table 2. The largest anisotropies for the above discussed clusters occur for $n = 2$ ($\alpha_1/\alpha_3 = 4.8$) and $n = 8$ ($\alpha_1/\alpha_3 = 2.7$). It is usually larger for F-centers clusters than for Na-tail clusters and this can be associated with the largest delocalization of the F-center electron in a plane containing the three surrounding sodium atoms (only two for Na_2F). In Na_4F_3 for instance, which has C_{3v} symmetry, the smallest polarizability α_3 is associated with a smaller flexibility along the C_3 axis, whereas the two degenerate polarizabilities are associated with a larger electron flexibility in a perpendicular plane including three equivalent sodium atoms. This can be contrasted with the situation in Na_5F_4 (C_{3v} sodium tail cluster) which presents an extremely weak anisotropy.

Two clusters in their lowest energy equilibrium structure $n = 14$ and 23, have averaged polarizabilities 156 and 341 Å^3, higher than the other clusters. In $Na_{14}F_{13}$, the electron is weakly localized at an apex, resulting from second-order C_{3v} Jahn-Teller deformation with respect to the O_h 3×3×3 cubic structure. The anisotropy ratio (1.41) is moderate, the weakest polarizability being associated with the on-axis electronic displacement. It is interesting to notice that the second isomer for $n = 23$ presents an analogous situation, corresponding to the deformation of a $3 \times 3 \times 5$ parallepiped. $Na_{23}F_{22}$ is characteristic of another weak localization type labelled edge-state [22] where the electron substitutes three atoms of a missing edge. The anisotropy is significantly large (4.78) and corresponds to an easy polarization direction along the edge.

Finally, we have reported in Table 2 the static polarizabilities of the most symmetric $3 \times 3 \times 3$ ($n = 14$, O_h)

and $3 \times 3 \times 5$ ($n = 23$, D_{4h}) structures, for which the electron is delocalized over the whole surface of the cluster. These polarizabilities are one order of magnitude larger ($\alpha_0 = 1009$ and 2983 Å^3 respectively) than those of the lowest energy non-symmetric structures.

4 Conclusion

We have determined and rationalized the static dipole polarizabilities of excess electron $\mathrm{Na}_n\mathrm{F}_{n-1}$ clusters with $n \leq 23$. For small sizes, the single electron model was shown to present an agreement for the isotropic polarizabilities in the range 10−30% with more sophisticated *ab initio* calculations. The anisotropy character obtained with the model was also found to be reasonable. Thus we think that the trends obtained for the larger cluster should be reliable. Obviously *ab initio* calculations are needed to establish a fully quantitative picture. The average values and anisotropy mainly reflect the electron localization and its coupling to the geometric structure of the cluster. As mentioned in the introduction, the static polarizability contribution to the electric susceptibility observed in experiments is small when compared to the fluctuation term associated with the permanent dipole in a Langevin expression. Nevertheless a case such as $\mathrm{Na}_{14}\mathrm{F}_{13}$ is especially interesting since, due to the indirect Jahn-Teller effect, small cluster displacements are likely (i) to strongly change the magnitude of the permanent dipole (ii) strongly affect the electron localization or delocalization. The symmetric O_h structure lies at an energy very close to that of the global C_{3v} minimum. In such a flexible system, the influence of the dynamics on the electron-ion coupling and on the polarizabilities would be very interesting. Moreover, it would be also important to include the quantum aspects and determine the ground state vibrational wave function.

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