Eur. Phys. J. D **9**, 243–248 (1999)

THE EUROPEAN
PHYSICAL JOURNAL D
EDP Sciences

Static electric dipole polarizabilities of alkali clusters

D. Rayane[1], A.R. Allouche[1], E. Benichou[1], R. Antoine[1], M. Aubert-Frecon[1], Ph. Dugourd[1], M. Broyer[1], C. Ristori[2], F. Chandezon[2], B.A. Huber[2], and C. Guet[2]

[1] Laboratoire de Spectrométrie Ionique et Moléculaire, UMR 5579, CNRS and Université Lyon 1, bât. 205, 43 Bd du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France
[2] Département de Recherche Fondamentale sur la Matière Condensée, Service des Ions, des Atomes et des Agrégats, CEA Grenoble, 17 rue des Martyrs, F-38054 Grenoble Cedex 9, France

Received: 1 September 1998 / Received in final form: 12 October 1998

Abstract. We have measured the static dipole polarizability of lithium and sodium clusters ($n = 1 - 22$). Values measured for sodium are in agreement with previous experiments. While the polarizability per atom for sodium clusters decreases slowly as a function of the cluster size, a sharp decrease between sizes 1 and 4 is observed for lithium clusters. Experimental values are compared to Density Functional Theory (DFT/PW91) calculations. The size evolutions for sodium and lithium cluster polarizabilities are well reproduced by our calculations. The sharp decrease observed for small lithium clusters is discussed in terms of electronic density.

PACS. 36.40.-c Atomic and molecular clusters – 32.10.Dk Electric and magnetic moments, polarizability – 31.15.Ew Density functional theory

1 Introduction

The static electric dipole polarizability is useful as a basic observable for understanding the electronic properties of small clusters [1]. It is expected to be very sensitive to the electronic density of the valence electrons and to their delocalization. Despite the large number of papers recently devoted to alkali metal clusters, polarizability measurements are rather scarce, and results are only available for sodium clusters up to 40 and for a few sizes of potassium clusters [2, 3]. However, the lithium cluster polarizability is in many respects the most interesting to be determined. The lithium atomic polarizability is abnormally large. It is close to the sodium atomic value. On the other hand, the classical values for the corresponding metallic spheres ($\alpha_{\mathrm{cl}} = r_{\mathrm{s}}^3 N$) are very different since the Wigner–Seitz radii are 1.75 Å and 2.12 Å for Li and Na, respectively. The size evolution of the lithium cluster polarizability is therefore a direct measurement of the metallic bonding evolution and of the average atomic distances. Moreover, the optical response of lithium clusters is significantly redshifted as compared to the classical prediction for a finite metallic sphere [4, 5]. This shift has been attributed to a nonlocal effect in electron–ion interactions [6–8]. It remains to be studied to which extent the static polarizability is sensitive to these effects. In a recent paper [9], we showed that the lithium cluster polarizability is close to the finite metallic sphere for sizes larger than 3 or 4 atoms. In [9], we discussed in detail the values obtained for clusters with closed electronic shells ($N = 8$ and $N = 20$), as well as the consistency of the dynamic and static responses. In the present paper, we focus on the evolution of the static polarizability as a function of the cluster size. Besides experimental results, we present an *ab initio* theoretical study of lithium and sodium cluster polarizability in the size range $N = 1 - 8$. We show that the strong decrease in lithium polarizability at $N = 3 - 4$ is related to the onset of the metallic bonding and to the evolution of the average electronic density.

2 Experiment

The polarizability measurements are made by deflection of a cluster beam through a static inhomogeneous transverse electric field. Lithium and sodium clusters are produced in a seeded supersonic beam. The beam is collimated by two slits and goes through the deflector. With the electric field magnitude along the z axis denoted by F and the average static polarizability by α, the force acting on the passing cluster is $f_z = \alpha F \frac{\partial F}{\partial z}$. ($F \frac{\partial F}{\partial z}$ is in the range of $5 \times 10^{10}\,\mathrm{V}^2/\mathrm{cm}^3$). The deflection is measured to be 1 m after the deflector. Clusters are ionized by a low flux laser ($\lambda = 308$ nm or $\lambda = 266$ nm) and are mass-selected in a time-of-flight (TOF) mass spectrometer. The set of voltages applied to the TOF is adjusted so that the arrival time at the detector is sensitive to the ionization position. The polarizability is proportional to the measured deflection in the z direction: $\Delta z = K \frac{f_z}{M \nu^2}$, where M is the mass of the cluster and ν its velocity. The constant K is a geometrical factor which does not need to be precisely known because it cancels when one takes the ratio of the polarizability of a given cluster and the well-known polarizability of the sodium atom. The velocity is determined with a coaxial TOF mass spectrometer. Velocity measurements are described in detail in a forthcoming publication [10]. The precision of the measured polarizabilities is estimated to be in the range of $\pm 2\,\text{Å}^3$, the main source of error being the velocity measurement. The relative precision between clusters with neighboring masses is better.

3 Theoretical approach

We have determined the lowest-energy structure and the static dipole polarizability of small ($n \leq 8$) Li_n and Na_n clusters with nonlocal density-functional theory (DFT) calculations. Calculations were performed using the GAUSSIAN94 package [11]. As in our previous work for $n \leq 6$ [12], we obtained ground-state equilibrium geometries using gradient techniques to minimize the total energy calculated with the Perdew–Wang 91 functional (DFT/PW91) and using a 6-31G basis set. Results of *ab initio* calculations of the literature were used as initial configurations for the optimization process. Geometries for $n \leq 6$ are described in detail in [12]. For Li_7 and Na_7, the lowest-energy structures are pentagonal bipyramids (PBP). For Li_8, we obtained a capped centered trigonal prism (CTP) and for Na_8, a dicapped octahedron (DCO).

The permanent dipole moment $\boldsymbol{\mu}$ and the dipolar static polarizability $\overset{\leftrightarrow}{\alpha}$ may be defined in terms of a Taylor expansion of the cluster energy E in a uniform electric field F:

$$E(\mathbf{F}) = E(\mathbf{0}) - \sum_i \mu_i F_i - \frac{1}{2}\sum_{i,j} \alpha_{ij} F_i F_j + \ldots , \tag{1}$$

where $i, j \in \{x, y, z\}$. The components of the polarizability tensor are obtained as the second-order derivatives of the energy with respect to the Cartesian components of the electric field:

$$\alpha_{ij} = -\left[\frac{\partial^2 E}{\partial F_i \partial F_j}\right]_{\mathbf{F}=\mathbf{0}} . \tag{2}$$

In our calculations, these derivatives are computed analytically [13].

The static dipole polarizabilities are calculated for the lowest-energy structures of each species using two different basis sets: the 6-31G basis that we used for the geometry optimization and the Sadlej and Urban [14] (SU) basis, which has been specifically developed for the determination of the polarizability of alkali atoms.

4 Results and discussion

Figure 1 shows the absolute static polarizability (per atom) for lithium and sodium clusters. For lithium, the values measured for the atom and for the dimer ($24.3\,\text{Å}^3$ and $32.8\,\text{Å}^3$ respectively) are in agreement with published data ($24.3\,\text{Å}^3$ [15] and $34.0\,\text{Å}^3$ [16,17], respectively). A sharp decrease in the polarizability per atom by about a factor of 2 from the monomer to the trimer is observed. For larger sizes, $n > 3$, the polarizability per atom is slowly decreasing. Small oscillations are superimposed on the average trend, especially for $n > 14$, where one observes a marked odd–even alternation. The dashed line in Fig. 1 corresponds to the polarizability calculated for a finite metallic sphere,

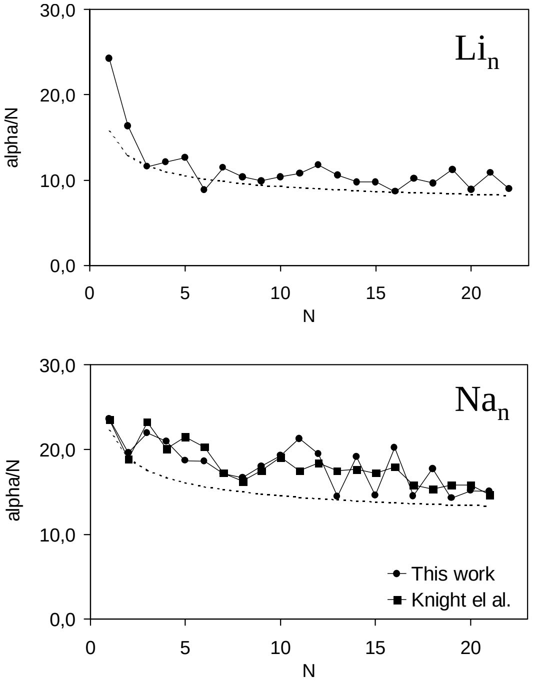

Fig. 1. Static dipole polarizabilities per atom (Å^3) of lithium and sodium clusters plotted as a function of the number of atoms in the cluster. The dashed lines represent the prediction from the classical metallic sphere (3) with a radius of 1.75 Å (2.12 Å) assumed, and an electron spill-out of 0.75 Å (0.69 Å) for lithium (sodium). For sodium, experimental data of [3] are plotted in the figure.

$$\alpha = \left(N^{1/3} r_{\mathrm{s}} + \delta\right)^3 , \tag{3}$$

where r_{s} is the Wigner–Seitz radius (1.75 Å) and δ is the electronic spill-out (0.75 Å) [4]. For sizes larger than 3, the experimental values, although globally higher, are relatively close to the calculated ones.

For sodium, we compare our values to those obtained by Knight *et al.* [3]. The average evolution is the same in both experiments. A very good agreement is observed for small sizes ($n < 10$). For larger sizes, the small odd–even alternation that was observed by Knight *et al.* is strongly enhanced in our data. Oscillations for sodium clusters are stronger than for lithium clusters. In the size range 15–21, the oscillation in sodium clusters is the reverse of the oscillation in lithium clusters. There is no clear explanation for this behavior. The most striking difference between sodium and lithium is that no sharp decrease is

Table 1. Present values for static dipole polarizabilities per atom (in Å^3) of Na_n and Li_n clusters ($n = 1-8$) calculated with the 6-31G and SU basis sets. Calculated polarizabilities are compared to experimental values.

Clusters	Symmetry	Basis	α_{xx}	α_{yy}	α_{zz}	α_{moy}
Li	O3	SU	22.4	22.4	22.4	22.4
		6-31G	20.3	20.3	20.3	20.3
		exp.				24.28
Li_2	D2h	SU	13.3	13.3	22.7	16.4
		6-31G	11.8	11.8	21.3	15.0
		exp.				16.38
Li_3 (obtuse)	C2v	SU	10.4	25.5	14.4	16.8
		6-31G	9.1	23.2	13.4	15.2
		exp.				11.54
Li_4 (rhombus)	C2v	SU	9.0	23.7	11.2	14.6
		6-31G	8.1	23.1	10.4	13.9
		exp.				12.12
Li_5 (trigonal bipyramid)	C3v	SU	18.2	14.0	9.1	13.8
		6-31G	17.5	13.0	8.4	13.0
		exp.				12.67
Li_6 (square bipyramid)	C4v	SU	14.6	14.6	8.0	12.4
		6-31G	14.0	14.0	7.4	11.8
		exp.				8.87
Li_7 (PBP)	C5v	SU	12.9	12.9	9.8	11.9
		6-31G	12.6	12.6	9.2	11.5
		exp.				11.41
Li_8 (CTP)	C2v	SU	11.2	11.2	10.9	11.1
		6-31G	10.8	10.8	10.2	10.6
		exp.				10.36
Na	O3	SU	24.3	24.3	24.3	24.3
		6-31G	24.1	24.1	24.1	24.1
		exp.				23.62
Na_2	D2h	SU	15.2	15.2	27.0	19.1
		6-31G	15.3	15.3	26.4	19.0
		exp.				19.65
Na_3 (obtuse)	C2v	SU	13.6	32.8	18.4	21.6
		6-31G	13.8	23.0	17.8	21.2
		exp.				21.97
Na_4 (rhombus)	C2v	SU	11.5	32.4	14.8	19.6
		6-31G	11.9	31.6	14.5	19.3
		exp.				20.95
Na_5 (planar)	C2v	SU	28.0	19.3	10.6	19.3
		6-31G	27.6	18.8	10.8	19.1
		exp.				18.67
Na_6 (pentagonal bipyramid)	C5v	SU	21.0	21.0	10.2	17.4
		6-31G	20.8	20.8	10.2	17.3
		exp.				18.63
Na_7 (PBP)	C5v	SU	17.4	17.4	12.9	15.9
		6-31G	16.9	16.9	12.5	15.4
		exp.				17.11
Na_8 (DCO)	C2v	SU	14.1	14.1	16.4	14.9
		6-31G	13.8	13.8	16.1	14.6
		exp.				16.69

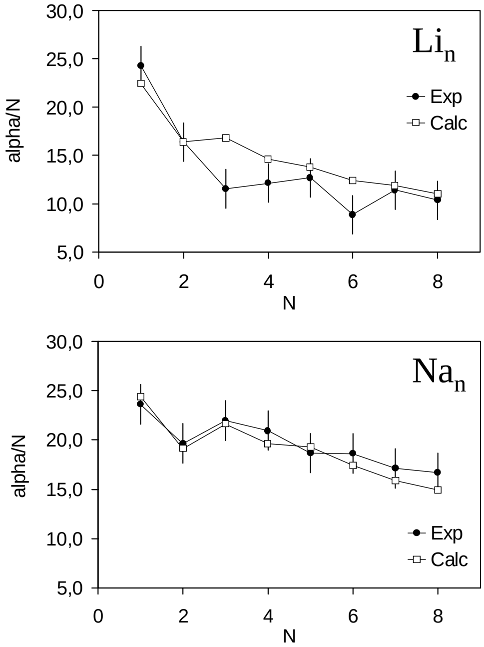

Fig. 2. Experimental and calculated polarizabilities per atom (this work, SU basis set) for lithium and sodium clusters plotted as a function of the cluster size ($n = 1 - 8$). Polarizabilities are in Å^3.

observed for small sizes in sodium. The polarizability per atom decreases slowly with the cluster size. Even for very small sizes, the evolution of experimental values is similar to the calculated evolution for a finite metallic sphere (dashed line).

DFT/PW91 polarizabilities have been obtained for sizes 1 to 8 both for lithium and sodium clusters using two basis sets: 6-31G and SU. Calculated values are given in Table 1. The values obtained with the 6-31G basis are systematically smaller than values deduced from the SU basis. This is because the SU basis contains more polarization (d orbital), and diffuse functions, which are expected to be important for polarizability calculations. Relative differences between the two sets of results are larger for Li$_n$ than for Na$_n$. Differences are around 9% for Li to Li$_3$ and 5% for Li$_4$, while for Na$_n$, the largest relative difference is less than 3%. The contribution of diffuse orbitals in polarizability calculations is more important for lithium than for sodium. For lithium clusters, the importance of these diffuse orbitals decreases as the cluster size increases.

Calculated values are plotted in Fig. 2 with the experimental values. The overall agreement is good. Calculations are able to reproduce both the smooth size evolution in sodium cluster polarizabilities and the sharp decrease in lithium clusters polarizabilities. For sodium, there is a perfect match between experimental and theoretical values. For lithium, the values calculated for Li$_3$ and Li$_6$ are larger than experimental results. Results of DFT calculations for the polarizabilities of small Na$_n$ clusters have been reported a few years ago [18, 19]. Moullet *et al.* [18] performed calculations for $n = 1 - 9$ in the local spin density approximation with a pseudopotential. Guan *et al.* [19] performed all-electron local and gradient-corrected density-functional calculations for $n = 1 - 6$. Our results are systematically higher than the previous ones (about 6% as compared to Moullet *et al.* (LDA–Bardley pseudopotential) and about 9% as compared to Guan *et al.* (B88x+P86c)). They are in better agreement with experimental data. For Li$_8$ and Na$_8$, which have closed electronic shells, numerous theoretical values are available in the literature. Several values [4, 8, 9, 18, 20, 21] are compared to our experimental data in Table 2. *Ab initio* calculations of [4] and DFT calculations of [21] have been able to predict accurately the optical absorption spectra but overestimate the Li$_8$ static dipole polarizability. A very good agreement with the experimental values is obtained with the *ab initio* DFT time-dependent local density approximation (TDLDA) of Pacheco and Martins [8]. For Na$_8$, present results, which underestimate the experimental value, are in good agreement with the TDLDA results.

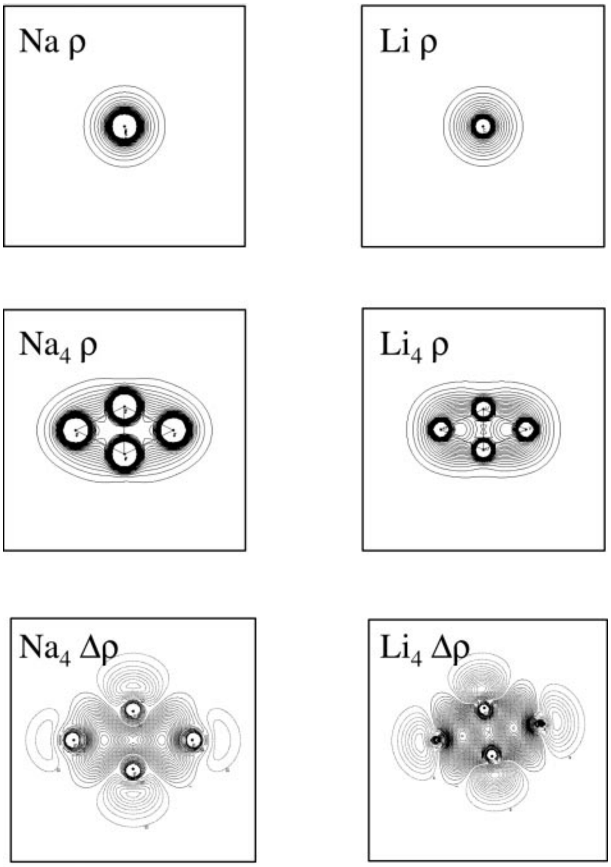

Fig. 3. Total electron density maps for lithium and sodium atoms and for tetramers calculated with the 6-31G basis set. Differential electron density maps for Li$_4$ and Na$_4$ calculated with the 6-31G basis set. The difference in density between 2 lines is 5×10^{-4} for the total density and 2×10^{-4} for the differential density. For differential densities, dashed lines correspond to negative contours and full lines to positive contours.

In clusters, the Li−Li bond is shorter and stronger than the Na−Na bond. As a consequence, the electronic dens-

Table 2. Comparison between theoretical polarizabilities per atom calculated for Na_8 and Li_8 and experimental values. Values are in Å^3.

	This work		CI	DFT[1]	DFT	S.O.S.[2]	TDLDA	Exp.
	DFT 6-31G	DFT SU	[4]	[18]	[21]	[9, 20]	[8]	(this work)
Li_8	10.6	11.1	12.4		12.1	10.6	10.34	10.3
Na_8	14.6	14.9		14.0 15.0		16.5	13.72[3] 14.77[3]	16.8

[1] LSD approximation and empirical Bardsley pseudopotential. The two values correspond to the D_{2d} isomer and the T_d isomer respectively.

[2] Sum over states. States are computed with a nonlocal pseudopotential.

[3] These two values correspond to two different pseudopotentials.

ity is higher in lithium, which appears in the different Wigner–Seitz radii ($r_s = 1.75$ Å and $r_s = 2.12$ Å for lithium and sodium, respectively). In the finite sphere model (1), this leads to different bulk limits for the polarizability per atom for lithium and sodium, in agreement with experimental results for large sizes (Fig. 1). However, the simple metallic sphere model cannot be used for very small sizes and cannot explain the different behaviors observed for sodium and lithium. To go further in the interpretation, we have plotted the total density ϱ_M for Li and Na atoms and tetramers as well as the differential electronic density $\varrho_M - \sum_{i=1}^{4} \varrho_{M_i}$ where ϱ_{M_i} is the electronic density of atom i (Fig. 3). If we consider the atoms, the volume occupied by the nonnegligible electronic density is almost the same for Li and Na. This explains the similarity of atomic polarizabilities. Moreover, the more diffuse character of the Li atom explains why a better value of the polarizability is obtained with the SU basis, while this is less important for sodium.

In tetramers, the contraction of the valence electron cloud is much more important in lithium than in sodium. In other words, the electron cloud of the Li atom is "pumped" by the metallic bonding, which is located between the atoms. The interatomic distance in Li_4 is close to the bulk value, and the polarizability per atom is already close to the bulk limit (spill-out included). The contraction of the electron cloud explains the sharp decrease in the polarizability observed from Li to Li_3 or Li_4. In the same way, the importance of the diffuse orbitals (and of the SU basis) decreases when the cluster size increases. Figure 3 and our polarizability measurements illustrate in a striking manner the occurrence of the metallic bonding for clusters as small as Li_3 and Li_4. In sodium, the metallic bonding appears also for very small sizes, but the influence on the polarizability is less important, and the size evolution is smoother. Finally, the strong metallic bonding and the short bond length in lithium clusters can be related to the electronic properties of the Li atom. The size of the ionic core in lithium is very small, and the valence electron is very diffuse. These two factors favor the creation of a strong metallic bond with valence electrons delocalized in between the atoms.

5 Conclusion

We have measured the static dipole polarizabilities of lithium and sodium clusters. Values obtained for sodium clusters are in agreement with previous experiments. Polarizabilities of sodium and lithium atoms are almost equal. For sizes larger than 4, the polarizability of lithium clusters is smaller than the polarizability of sodium clusters by a factor of about 1.5. This is in agreement with the ratio of Li$-$Li and Na$-$Na bond lengths in the bulk. The sharp decrease in polarizability observed from lithium atom to cluster sizes 3–4 is explained by the evolution of the electronic density and the occurrence of metallic bonding at very small sizes. The very diffuse character of the electron cloud in Li atom explains the large atomic polarizability. In clusters, the diffuse orbitals are less important, at least for the static response in the ground state. However, for excited states (dynamic response), the particular character of the atomic eigenfunctions of the lithium atom is responsible for the nonlocal interactions; this explains the optical absorption spectra.

The authors wish to thank F.W. Dalby and W.A. de Heer for stimulating discussions, and B. Vezin and J.C. Rocco for experimental help at the beginning of this work. We also acknowledge S.A. Blundell for the calculation of the nonlocal pseudopotential value for the polarizability of Na_8.

References

1. K.D. Bonin, V.V. Kresin: *Electric-dipole polarizabilities of atoms, molecules and clusters* (World Scientific, Singapore 1997)
2. W.A. de Heer: Rev. Mod. Phys. **65**, 611 (1993)
3. W.D. Knight, K. Clemenger, W.A. de Heer, W. A Saunders: Phys. Rev. B **31**, 2539 (1985)
4. J. Blanc, V. Bonačić-Koutecký, M. Broyer, J. Chevaleyre, Ph. Dugourd, J. Koutecký, C. Scheuch, J.P. Wolf, L. Wöste: J. Chem. Phys. **96**, 1793 (1992)
5. C. Bréchignac, Ph. Cahuzac, F. Carlier, J. Leygnier: Phys. Rev. Lett. **70**, 2036 (1993)

6. Ll. Serra, G.B. Bachelet, Nguyen Van Giai, E. Lipparini: Phys. Rev. B **48**, 14 708 (1993)
7. S.A. Blundell, C. Guet: Z. Phys. D **33**, 153 (1995)
8. J.M. Pacheco, J.L. Martins: J. Chem. Phys. **106**, 6039 (1997)
9. E. Benichou, R. Antoine, D. Rayane, B. Vezin, F.W. Dalby, Ph. Dugourd, M. Broyer, C. Ristori, F. Chandezon, B.A. Huber, J.C. Rocco, S.A. Blundell, C. Guet: Phys. Rev. A **59**, R1 (1999)
10. R. Antoine, D. Rayane, A.-R. Allouche, M. Aubert-Frecon, E. Benichou, F.W. Dalby, Ph. Dugourd, M. Broyer, C. Guet: J. Chem. Phys. **110**, 5568 (1999)
11. Gaussian 94, Revision B.3, M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople: Gaussian, Inc., Pittsburgh, PA 1995
12. E. Benichou, A.R. Allouche, M. Aubert-Frecon, R. Antoine, M. Broyer, Ph. Dugourd, D. Rayane: Chem. Phys. Lett. **290**, 171 (1998)
13. B.G. Johnson, M.J. Fisch: J. Chem. Phys. **100**, 7429 (1994)
14. A.J. Sadlej, M. Urban: J. Mol. Struct. (THEOCHEM) **80**, 234 (1991)
15. R.W. Molof, H.L. Schwartz, T.M. Miller, B. Bederson: Phys. Rev. A **10**, 1131 (1974)
16. R.W. Molof, T.M. Miller, H.L. Schwartz, B. Bederson, J.T. Park: J. Chem. Phys. **61**, 1816 (1974)
17. V. Tarnovsky, M. Bunimovicz, L. Vuskovi, B. Stumpf, B. Bederson: J. Chem. Phys. **98**, 3894 (1993)
18. I. Moullet, J.L. Martins, F. Reuse, J. Buttet: Phys. Rev. Lett. **65**, 476 (1990)
19. J. Guan, M.E. Casida, A.M. Köster, D.R. Salahub: Phys. Rev. B **52**, 2184 (1995)
20. For Na_8, the static dipole polarizability has been obtained from the dipole transitions calculations decribed in [7]
21. A. Rubio, J.A. Alonso, X. Blase, L.C. Balbas, S.G. Louie: Phys. Rev. Lett. **77**, 247 (1996), published value should be corrected by a factor 3, A. Rubio, X. Blase: private communication