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Electric dipole polarizabilities and C_6 dipole-dipole dispersion coefficients for alkali metal clusters and C_{60}

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Abstract

The frequency dependent polarizabilities of closed-shell alkali metal clusters containing up to ten lithium, potassium, and rubidium atoms have been calculated using the linear complex polarization propagator approach in conjunction with Hartree–Fock and Kohn–Sham density functional theory. In combination with polarizabilities for C_{60} from a previous work [J. Chem. Phys. **123**, 124312 (2005)], the C_6 dipole-dipole dispersion coefficients for the metal cluster-to-cluster and cluster-to-buckminster fullerene interactions are obtained via the Casimir–Polder relation. The B3PW91 results for the polarizabilities and dispersion interactions of the alkali metal dimers and tetramers are benchmarked against couple cluster calculations, and the whole series of calculations are compared against the corresponding work on sodium clusters [J. Chem. Phys. **125**, 124306 (2006)]. The error bars of the reported theoretical results for the C_6 coefficients are estimated to be 8%.

I. INTRODUCTION

The electric-dipole polarizability is the key microscopic property in several spectroscopies. Much theoretical and experimental work has been devoted to determine the polarization properties of atoms, molecules, and clusters,¹ and, in recent years, this research has included the study of metal clusters.² In particular sodium has played the role of model system for metal cluster research. The original measurements by Knight *et al.*³ of the polarizability of sodium clusters containing up to 40 atoms have spurred a large number of theoretical calculations^{4–11} and experiments^{12–14} devoted to the ground state electronic structure and optical properties of these systems. The polarization properties of lithium clusters have also attracted quite some attention in the literature both in the theoretical^{4,15–17} and experimental^{12,18} communities, whereas, for potassium and rubidium, earlier reports on cluster polarizabilities are restricted to the potassium dimer^{3,4,19} and the rubidium dimer.^{4,19}

The leading long-range dispersion interaction is the van der Waals dipole-dipole interaction which relates to the electric dipole polarizability via the Casimir–Polder relation.²⁰ It is a common procedure to express the strength of this interaction in terms of the C_6 dispersion coefficient. In an experiment by Kresin *et al.*²¹ sodium clusters were injected into a cavity containing a low concentration of C_{60} fullerenes and, from the measured scattering, the cluster-fullerene long-range interaction potential could be determined. In addressing this experiment, we recently reported first-principles calculations of the dispersion interaction between C_{60} and sodium clusters.²² To the best of our knowledge and prior to the present work, the potentials for long-range interactions have not been determined for alkali metal clusters containing lithium, potassium, or rubidium.

The evaluation of the C_6 coefficient for a pair of microscopic systems involves the determination of the dynamic polarizability at imaginary frequencies, i.e., $\alpha(i\omega)$, for each of the two individual systems. Different computational approaches have been designed for this purpose; it is, for instance, possible to determine $\alpha(i\omega)$ by turning to an expansion of the polarizability in the Cauchy moments as described in several papers.^{23–26} More recently it was argued that a more efficient strategy is to adopt a straightforward approach to the evaluation of $\alpha(i\omega)$ at the cost of introducing complex algebra into the time-dependent electronic structure code.^{27–29} A number of applications have demonstrated that accurate results for $\alpha(i\omega)$ can be determined in this way and that the scope of applications is significantly widened to include large-scale systems^{22,30} and excited states.³¹ In fact the computational scaling parallels that of traditional polarization propagator approaches developed for the calculation of the regular polarizability depending on a real frequency argument.

In the present work we will present a systematic study of the dispersion interactions for small alkali metal (lithium, sodium, potassium, and rubidium) clusters including up to ten atoms as well as the interactions between these clusters and the C_{60} fullerene. We will base our work on the aforementioned complex polarization propagator approach.^{27,29} The properties of the metal clusters are obtained at the Hartree–Fock (HF) and density functional theory (DFT) levels and it will be argued that the quality of the DFT results as obtained with the hybrid B3PW91 exchange-correlation functional will correspond to the second-order Møller–Plesset (MP2) wave function model. Our work is complementary to the previous investigation on sodium clusters,²² and, for the convenience of the reader and sake of completeness, parts of the results presented in Ref. 22 will be repeated here.

II. METHODOLOGY

Our approach is focused at a direct evaluation of the electric dipole polarizability $\alpha(i\omega)$ by turning to complex algebra in the time-dependent electronic structure method of choice.^{27,29} The polarizability corresponds to the first-order response in the molecular dipole moment as due to an external electric field; in the case of dispersion interactions between systems A and B, the external field exposed on system A is that due to the induced dipole moment in system B (and vice versa). If expressed in the basis of eigenstates to the molecular Hamiltonian, the polarizability of the molecular system evaluated for a frequency on the imaginary axis can be written in terms of a sum-over-states formula according to

$$\alpha_{\alpha\beta}(i\omega) = \hbar^{-1} \sum_{n}^{\prime} \left\{ \frac{\langle 0|\hat{\mu}_{\alpha}|n\rangle \langle n|\hat{\mu}_{\beta}|0\rangle}{\omega_{n} - i\omega} + \frac{\langle 0|\hat{\mu}_{\beta}|n\rangle \langle n|\hat{\mu}_{\alpha}|0\rangle}{\omega_{n} + i\omega} \right\},\tag{1}$$

where $\hat{\mu}_{\alpha}$ is the electric dipole operator along the molecular axis α , ω_n is the transition frequency of the excited state $|n\rangle$, and the prime indicates omission of the ground state in the summation. Once the polarizability has been determined, the C_6 dispersion coefficient of the orientationally averaged long-range dipole–dipole interaction between systems A and B is given by²⁰

$$C_6 = \frac{3\hbar}{\pi} \int_0^\infty \overline{\alpha}_A(i\omega) \overline{\alpha}_B(i\omega) d\omega, \qquad (2)$$

where $\overline{\alpha}$ denotes the trace of the polarizability tensor. It is clear that in order to carry out the integration in Eq. (2) we must, at least in principle, determine the polarizabilities of systems A and B on the entire imaginary axis. In practice, however, we can calculate $\alpha(i\omega)$ for a set of discrete frequencies and use a quadrature scheme for the integration, see Section III for details on how the integration in Eq. (2) is carried out in the present work.

Apart from the case of calculations based on the configuration interaction method in quantum chemistry, the eigenstates of the quantized Hamiltonian are not included in the excitation manifold and the sum-over-states property expressions that we meet in an exact formulation are instead represented by matrix equations. In the single determinant Hartree– Fock or Kohn–Sham approximations, the polarizability in Eq. (1) corresponds to the well known random phase approximation equation^{27,29}

$$\langle \langle A; B \rangle \rangle_{i\omega} = -A^{[1]^{\dagger}} \left\{ E^{[2]} - i\omega S^{[2]} \right\}^{-1} B^{[1]},$$
 (3)

where $E^{[2]}$ and $S^{[2]}$ are the so-called Hessian and overlap matrices, and $A^{[1]}$ and $B^{[1]}$ are the property gradients composed from the ground-to-excited state transition moments of dipole moment operators $\hat{\mu}_{\alpha}$ and $\hat{\mu}_{\beta}$, respectively.

Equation (3) is complex, and corresponds to a set of two coupled real matrix equations. In Ref. 28 we gave explicit account of how these coupled equations could be efficiently solved, and the resulting polarizability is a well-behaved monotonic function that has its maximum in the static limit $\alpha(0)$ and then tends to zero as $\omega \to \infty$. The rate at which $\alpha(i\omega)$ tends to zero is sometimes expressed in terms of a so-called effective frequency ω_1 that is defined in the London approximation

$$\overline{\alpha}(i\omega) = \frac{\overline{\alpha}(0)}{1 + (\omega/\omega_1)^2},\tag{4}$$

Having introduced this approximation, the evaluation of the integral for the dispersion coefficient [Eq. (2)] can be made analytically and, for like molecules, one obtains the relation

$$C_6 = \frac{3\hbar\omega_1}{4} \left[\overline{\alpha}(0)\right]^2.$$
(5)

It was shown in Ref. 32 that the effective frequency can be regarded as more or less constant for an entire class of systems, and, for that reason, property predictions based on extrapolation of results can sometimes be accurately made. Therefore, resulting values for the effective frequencies of the alkali metal clusters have been included in the present work.

III. COMPUTATIONAL DETAILS

The polarizabilities at imaginary frequencies were determined from Eq. (3) at the timedependent HF and DFT levels of theory with use of the DALTON program.³³ The DFT calculations were performed with use of the hybrid B3PW91 exchange-correlation functional.^{34,35} Unless specified, the polarization basis sets of Sadlej³⁶ were employed in the property calculations for all alkali metal clusters; however, for the dimer and tetramer compounds, larger basis sets³⁷ [19s15p12d6f] were also used (but then marked with a footnote in the tables). For lithium and sodium, all calculations refer to all-electron parametrization of the density, but, for potassium and rubidium, we used the Stuttgart effective core potentials (ECPs).³⁸ The property calculations made with ECPs employ the all-electron polarization basis sets of Sadlej^{36,37} for the description of the valence orbitals, i.e., the core atomic orbitals are left to be projected out by the projectors in the ECPs.

In order to evaluate the Casimir–Polder integral [Eq. (2)] for the C_6 dispersion coefficients, the polarizabilities were calculated at the imaginary frequencies taken from a Gauss– Legendre integration scheme with the transformation of variables according to

$$i\omega = i\omega_0(1-t)/(1+t).$$
 (6)

Here we used a transformation factor of $\omega_0 = 0.3E_h$ as suggested in Ref. 39, followed by a Gauss-Legendre quadrature in the interval $-1 \leq t \leq 1$. For the interactions between the alkali clusters and C_{60} , results for the polarization of the fullerene were taken from our previous work.³⁰ We use the six-point Gauss-Legendre integration in the present work.

The coupled cluster model with single and double excitations $(\text{CCSD})^{26,40}$ was used to obtain the Cauchy moments and the C_6 coefficients of the alkali metal dimers and tetramers. The frequency-dependent polarizabilities can be obtained from the Cauchy moments by the Cauchy moments expansion, and the C_6 dispersion coefficients can be directly evaluated from the Cauchy moments with use of the lower $[n, n-1]_{\alpha}$ and upper $[n, n-1]_{\beta}$ Padé approximants recommended by Langhoff and Karplus.⁴¹ With n = 4, the value of the C_6 coefficients for the dimers and tetramers are converged to within 1%.

For the dimers Li₂, Na₂, K₂, and Rb₂, we used the experimental bond lengths of 2.6725,⁴² 3.0788,⁴² 3.923,⁴² and 4.18 Å,⁴³ respectively; for the lithium clusters, we used the B3LYP/6-311+G(d) optimized structures from Ref. 15 (these structures were optimized without enforc-

ing point group symmetry); for the sodium clusters, we used the B3LYP/6-311+G(d) optimized structure from Ref. 10 for the tetramer and the B3LYP/6-31G(d) optimized structures from Ref. 9 for others. For the potassium and rubidium clusters, structure optimizations were carried out in the present work by use of the GAUSSIAN03 program;⁴⁴ the geometries were optimized at the DFT/B3LYP level³⁴ using the Stuttgart ECPs and valence basis sets as included in the basis set library.

IV. RESULTS AND DISCUSSION

We begin our discussion by estimating the accuracy of the theoretical results for the polarizabilities and the C_6 dipole-dipole dispersion coefficients. We then turn to a presentation of the long-range interactions between closed-shell alkali metal clusters containing up to ten lithium, sodium, potassium, and rubidium atoms and the fullerene C_{60} .

A. Estimating the quality of results

Apart from the diatomic systems, experimental results for the cluster structures are unavailable, and, in addition, for the potassium and rubidium clusters there are neither experimental nor theoretical geometries available. For that reason we conducted geometry optimizations for the K_n and Rb_n (n = 4, 6, 8, and 10) systems. For the larger clusters there are clearly a large number of possible configurations, and we have made no attempt to find the global minima of the potassium and rubidium clusters. Instead we argue that it is plausible that the optimal configuration of the potassium and rubidium clusters should possess the symmetry elements of the corresponding sodium clusters for which the structure minima are reported in Refs. 9 and 10, and we therefore use the optimized sodium structures 9,10 as initial configurations in the optimizations of potassium and rubidium clusters. The B3LYP optimized bond lengths of the Na_n , K_n and Rb_n clusters are given in Table I (the bond labels are illustrated in Fig. I). The corresponding bond parameters for the Li_n clusters are not included in the table because point group symmetries were not enforced in the original molecular structure optimizations which lead to slightly asymmetric clusters.¹⁵ This aspect of asymmetry is also reflected by the tensor components of the polarizability that are reported in the present work (compare for instance the three α -components of Li₈ in

Table II).

The quality of our results for the fullerene and the sodium clusters was established in our previous work by a comparison to experimental results as well as, for the smaller clusters, theoretical results obtained with more sophisticated *ab initio* approaches, and it was concluded that the DFT results for $\overline{\alpha}(0)$ and the C_6 coefficient had error bars of 2% and 5%, respectively.^{22,30} In the present work, we will address the quality of the property calculations for the other alkali metal clusters. It is clear from the DFT calculations by Chandrakumar *et al.*¹⁰ that the accuracy of polarizabilities for sodium clusters is significantly improved by the use of hybrid exchange-correlation functionals, and we therefore adopt the hybrid B3PW91 functional^{34,35} for the calculations of polarizabilities of alkali metal clusters.

Experimental results have not been found for the dispersion coefficients involving lithium, potassium, or rubidium clusters, but, for the static polarizability $\overline{\alpha}(0)$ there exists experimental data for the set of lithium clusters^{12,18} as well as the potassium^{3,19} and rubidium¹⁹ dimers. In establishing the quality of the DFT results for the polarization and dispersion properties of Li_n, K_n, and Rb_n, we also compare our results to theoretical results that are obtained with wave function correlated methods. With respect to results found in the literature attention is paid to the employed cluster geometries and basis sets. We address these issues by carrying out a set of coupled cluster calculations on the dimers and tetramers, so that we are in control of the computational parameters. Our wave function correlated calculations are of course carried out with use of identical parameter sets (geometry and basis set) as those used in our DFT calculations. We can also determine the dispersion coefficient at the coupled cluster level so that we can get an estimate of the quality of the dispersion of the polarizability $\overline{\alpha}(i\omega)$ (and not only the static value) at the DFT level of theory.

In Table II, we present the results for the polarizability of the lithium dimer and tetramer and comparison is made against the results from the literature that are obtained with highly correlated wave function methods.^{4,15–17} For Li₂, the MP2 result for $\overline{\alpha}(0)$ from Ref. 15 is 202.8 a.u. at the optimized bond length of 2.709 Å, which is to be compared with our CCSD result of 205.0 a.u. at the experimental bond length of 2.6725 Å. Our coupled cluster calculation employ a large uncontracted basis set of size [19s15p12d6f] that should be flexible enough to provide a quite accurate CCSD result for the polarizability. The bond distances in the two compared calculations differ, however, and we have therefore also determined $\overline{\alpha}(0)$ at a bond length of 2.709 Å using CCSD and the same large uncontracted basis set. The result of this calculation is 204.4 a.u., so we conclude that the MP2 and CCSD results are in close agreement. The CCSD and CCSD(T) results of Urban and Sadlej⁴ are 215.7 and 216.0 a.u., respectively, which is significantly larger than our best CCSD result. This discrepancy is due the use of a smaller basis, as is seen in Table II where we have reproduced the CCSD result with use of Sadlej's polarization basis set.³⁶ More specifically, it is mainly the reduced basis set flexibility due the contractions that are the main cause for the discrepancy; with a decontracted Sadlej basis set of size [10s6p4d], Pecul *et al.*¹⁶ reported the value of $\overline{\alpha}(0)$ to be 208.7 a.u. (at the same bond distance), which is in much closer agreement with our best CCSD result. The MP2 result from Ref. 15 for the tetramer is 343.7 a.u. which is in close agreement with our CCSD result of 342.4 a.u. For the tetramer we are unable to employ the larger basis set in the CCSD, but, based on the above discussion of the results for the dimer, it is reasonable to expect that this value is somewhat too large compared to the basis set limiting value. We conclude, however, that the quality of referenced MP2 results¹⁵ for polarizability of the lithium dimer and tetramer is at the level of the corresponding CCSD results with an appropriate basis set, and we consider the MP2 results for the larger lithium clusters as the best available reference for our calculations of $\overline{\alpha}(0)$. Indeed there is a CCSD value of 540.9 a.u. reported for the polarizability of Li_{8} ¹⁶ but the predominant reason for the large discrepancy between this result and the MP2 value¹⁵ of 609.2 a.u. is the difference in the molecular configurations rather than the difference in the treatment of electron correlation. Since we have adopted the lithium cluster structures of Ref. 15 we choose to use the MP2 results as our reference values.

The reason for us to establish the quality of the referenced MP2 results for the polarizability of the lithium clusters is that these results are in close agreement with our results obtained at the Kohn–Sham DFT level of theory using the B3PW91 functional. Comparing our DFT results with the MP2 reference values, we see that the discrepancies in $\overline{\alpha}(0)$ amount to 4% for the lithium tetramer and to less than 2% for others. This finding is in line with the conclusion made in Ref. 22 about the DFT/B3PW91 results for the polarizability of the sodium clusters namely that the quality of the DFT results parallels that of the corresponding MP2 results. In Table III we present parts of the sodium cluster results from our previous work²² with the addition made here of providing the results for the individual tensor components of the polarizability. But we refer to the original work for the discussion that lead us to the conclusion that the error bar of our DFT/B3PW91 results for the polarizability of the sodium clusters is 2%.

When it comes to the polarizability of the potassium and rubidium clusters results in the literature are scarce, but for the two dimers there is the work of Urban and Sadlej.⁴ For the potassium dimer our CCSD result for the polarizability is in close agreement with their CCSD(T) result (see Table IV), but for the rubidium dimer the discrepancy is much larger (see Table V). For the rubidium dimer, Urban and Sadlej⁴ employed an optimized bond length that is some 12 pm longer than the experimental bond length used in the present work, and the authors also mention that their disregard of relativistic effects may be associated with an overestimation of the bond length.⁴ As a consequence of an overestimated bond length, it is to be expected that the polarization along the bond axis becomes too large (i.e., an overestimated value for α_{zz} with our choice of coordinate system). So the fact that their CCSD(T) result⁴ for α_{zz} is some 6% larger than our CCSD value for the same tensor component is to some extent explained by the differences in bond lengths. We note, however, that there exist also a large discrepancy in the perpendicular component of the polarizability which is not explained by differences in geometry. We have determined the uncorrelated Hartree–Fock value of $\overline{\alpha}(0)$ at the optimized bond length of 4.298 Å and the result is 665.1 a.u. which is some 15 a.u. larger than the value at the experimental bond length of 4.18 Å but still significantly lower than the Hartree–Fock value of 698.9 a.u. that is reported in Ref. 4. This clearly indicates that there is a relativistic contraction of the electron density that we account for by using relativistic ECPs in the present work. The DFT/B3PW91 method overestimates the effects of electron correlation for $\overline{\alpha}(0)$ of the potassium and rubidium dimers but is in excellent agreement with the CCSD method when it comes to the polarizability of the two tetramers.

For the series of alkali metal dimers, a relative measure of the effects of electron correlation on the polarizability is given in Fig. 2; we compare the uncorrelated Hartree–Fock results to the corresponding CCSD results in this figure. The effects of electron correlation on the parallel components are 22%, 9%, 7%, and 1% for Li₂, Na₂, K₂, and Rb₂, respectively, whereas, reported in the same order, the effects on the perpendicular components are -6%, -8%, -18%, and -19%. The correlation effects on the individual tensor components are thus large, and, for the alkali metal dimers, it is clear that the DFT/B3PW91 approach performs better for the perpendicular component than for the parallel component. The accuracy of the DFT results for the averaged value $\overline{\alpha}(0)$ relies on a cancellation of errors between the components, and the accuracy of the DFT results for the anisotropy of the polarizability is not as high.

Since there is a square dependence between the polarizability and the dispersion coefficient, one can expect the magnitude of the errors for the C_6 coefficients to be twice the errors for $\overline{\alpha}(0)$. We estimate that the error bar of our best DFT results for the C_6 coefficients of the alkali metal clusters is 8%.

B. Dispersion interactions of alkali metal clusters and the fullerene

The dispersion coefficients for the interactions between the alkali clusters and the fullerene C_{60} are given in Tables II–V. The HF and DFT/B3LYP polarizabilities of C_{60} as given in Ref. 30 were utilized for evaluation of the C_6 coefficients in the present work. The difference in the resulting dispersion coefficients depending on which data set is used for the polarizability of the fullerene is not significant, but we note that it was argued in Ref. 30 that the uncorrelated Hartree–Fock results for the polarizability $\overline{\alpha}(i\omega)$ showed a somewhat better dispersion (i.e., frequency dependence).

In Fig. 3, we compare our best DFT results for the dispersion coefficients of the metal cluster-to-fullerene interactions against the experimental data of Kresin $et \ al.^{21}$ The error bars of the experiment are about 30% and included in the figure. As mentioned in our previous work,²² the theoretical results for the smaller sodium clusters (including up to ten atoms) are in close agreement with experiment. In the case of larger clusters (not included in Fig. 3 but reported in the original work²²), the agreement, although still within the error bars, is less convincing; there is a trend of theoretical results being smaller than the experimental counterparts. We believe that this reflects an experimental situation where there is a distribution of different metal cluster configurations with varying volume, some of which have a larger volume than the theoretically optimized volume used in the calculations. We have not pursued an investigation of the configuration dependence of the dispersion coefficients, but, if called for, it could easily be done in order to for instance correlate an accurate experimental value for the dispersion interaction with the molecular structure. We emphasize that the error bar in the theoretical results should be the same regardless of the size of the cluster, so our approach should be accurate enough to distinguish between different cluster configurations from the differences in dispersion coefficients. In addition we

have argued in the present work that the accuracy reached in the density functional based calculations is the same for clusters involving different alkali metals, and our results should serve as appropriate reference values for future experimental work on lithium, potassium, and rubidium clusters, if such are carried out. It is apparent that the interactions between the fullerene and the clusters vary quite strongly with the species that make up the cluster; the heavier the atom the stronger the interactions, see Fig. 3.

We have also included the results for the characteristic frequency ω_1 [Eq. (5)] in Tables II– V. For a given electronic structure method, a small spread of 0.01 a.u. in ω_1 is found for clusters composed of the same atom, and the mean values of ω_1 are 0.090, 0.089, 0.065, and 0.064 a.u. for the lithium, sodium, potassium, and rubidium clusters, respectively. The existence of universal characteristic frequencies for the metal clusters suggests that it is possible to construct simple structure-to-property relations for the dispersion coefficients of alkali metal clusters. We note that such a relation has also been presented for the *n*alkanes in our previous work.^{28,32} For sodium clusters, Chandrakumar *et al.*¹⁰ showed a linear dependence between the static mean polarizability and the cluster volume. Combined with our finding of universal characteristic frequencies, one can directly find relations between the cluster volumes and the C_6 coefficients with help of Eq. (5).

V. CONCLUSIONS

The complex polarization propagator approach has been shown to be an effective and direct way to determine the polarizability on the imaginary frequency axis for the metal alkali clusters. We present first-principles calculations of the electric dipole polarizabilities and the dipole-dipole dispersion coefficients of the closed-shell alkali clusters involving up to ten lithium, sodium, potassium, and rubidium atoms and the C_{60} fullerene. The method allows for the employment of large and diffuse basis sets that are optimized for the calculations of the polarizabilities, and it therefore has the potential to be accurate for the determination of C_6 dispersion coefficients. When benchmarked against results from wave function correlated methods, the density functional theory results with use of the B3PW91 exchange-correlation functional are shown to be quite accurate for the isotropic polarizabilities but much less accurate for the anisotropic polarizabilities. The performance of the density functional based approach is consistent for the series of alkali metals, and the treatment of electron correlation in the metal clusters parallels that of the second-order Møller–Plesset method. The estimated error bars for the B3PW91 results for $\overline{\alpha}(0)$ and the C_6 coefficients are 4% and 8%, respectively. The theoretical results for dispersion interactions of the sodium clusters and the fullerene are well within the error bars of the experiment, and our set of results for the series of alkali metal cluster-to-cluster and cluster-to-fullerene dispersion interactions provides a set of theoretical reference values of consistent accuracy.

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FIG. 1: Molecular structures for the alkali metal clusters. The bond labels refer to the optimized bond distances given in Table I.

FIG. 2: Effects of electron correlation on the static polarizabilities of the alkali metal dimers.

FIG. 3: C_6 dispersion coefficients for alkali clusters containing up to 10 atoms and the fullerene C_{60} . Experimental data with error bars for the sodium clusters and C_{60} are taken from Ref. 21.

n	Point group	Bond^a	Na_n^b	K_n	Rb_n
4	D_{2h}	а	3.503	4.492	4.839
		b	3.064	4.016	4.345
6	C_{5v}	а	3.610	4.573	4.878
		b	3.437	4.346	4.712
8	T_d	а	3.476	4.486	4.810
		b	3.573	4.601	5.062
10	D_{4d}	а	3.516	4.523	4.868
		b	3.366	4.367	4.738
		с	3.761	4.767	5.146

TABLE I: B3LYP optimized geometries for the sodium, potassium and rubidium clusters. All bond lengths are given in units of Ångström.

 $^a\mathrm{The}$ bond labels refer to the labeling made in Fig. 1.

 $^b\mathrm{The}\ \mathrm{B3LYP}/\mathrm{6\text{-}311+G(d)}$ optimized structure for the tetramer was taken from Ref. 10 and the

B3LYP/6-31G(d) optimized structures for the larger clusters were taken from Ref. 9.

							Li_n	$-\operatorname{Li}_n$	Li_n -	– C ₆₀
Cluster	$Method^a$	Ref.	α_{xx}	$lpha_{yy}$	α_{zz}	$\overline{\alpha}$	C_6	ω_1^b	C_6^c	C_6^d
Li_2^e	HF		180.6	180.6	253.6	204.9	2.736	0.0869	12.01	12.23
	DFT		174.1	174.1	276.5	208.2	2.747	0.0845	11.98	12.20
	DFT^f		169.3	169.3	266.4	201.7	2.626	0.0861	11.85	12.06
	MP2	15				202.8				
	CCSD^g		169.2	169.2	308.7	215.7	2.862	0.0820		
	$\mathrm{CCSD}^{f,g}$		151.6	151.6	312.0	205.0	2.661	0.0844		
	$\operatorname{CCSD}(T)$	4	169.2	169.2	309.7	216.0				
	Expt.	18				221.3				
		12				221.1				
Li_4	$_{ m HF}$		290.8	523.1	239.5	351.1	8.198	0.0887	21.31	21.67
	DFT		286.5	579.4	233.7	366.5	8.527	0.0846	21.54	21.92
	DFT^f		280.8	566.1	231.1	359.3	8.306	0.0858	21.45	21.82
	MP2	15				343.7				
	MP2	17	301.3	596.2	247.1	381.5				
	CCSD	16	284.6	485.7	228.9	333.1				
	CCSD^g		294.0	498.6	234.7	342.4	8.062	0.0917		
	$\operatorname{CCSD}(T)$	17	296.4	621.4	243.2	387.0				
	Expt.	18				326.6				
		12				327.2				

TABLE II: Static mean polarizabilities (a.u.), dipole-dipole dispersion coefficients (10^3 a.u.), and effective frequencies (a.u.) for the Li_n clusters and C₆₀.

 $^a \mathrm{Unless}$ specified, Sadlej's polarization basis set is used. 36

^bEffective frequency is determined as $\omega_1 = 4C_6/3 [\overline{\alpha}(0)]^2$.

 c Results for C₆₀ are taken from Ref. 30 and obtained at the Hartree–Fock level with Sadlej's basis set.

 d Results for C₆₀ are taken from Ref. 30 and obtained at the DFT/B3LYP level with Sadlej's basis set.

 e The experimental bond length of 2.6725 Å is used in the present work. At the optimized bond length of

2.709 Å used in the MP2 calculation, our DFT/B3PW91 result for $\overline{\alpha}$ in the large basis set is 204.4 a.u.

 f Calculated with a large [19s15p12d6f] basis set.

 ${}^{g}C_{6}$ result is obtained from the mean value of the lower $[n,n-1]_{\alpha}$ and upper $[n,n-1]_{\beta}$ Padé approximants.^{26,41}

							Li_n	$-\operatorname{Li}_n$	Li_n -	– C ₆₀
Cluster	$Method^a$	Ref.	α_{xx}	α_{yy}	α_{zz}	$\overline{\alpha}$	C_6	ω_1^b	C_6^c	C_6^d
Li ₆	HF		603.6	313.9	609.6	509.0	17.74	0.0913	31.36	31.90
	DFT		610.2	302.9	616.9	510.0	17.58	0.0901	31.31	31.85
	MP2	15				507.1				
	Expt.	18				360.4				
		12				359.1				
Li ₈	$_{ m HF}$		608.1	608.3	608.4	608.3	25.95	0.0935	38.77	39.42
	DFT		617.7	619.3	618.8	618.6	26.47	0.0922	39.06	39.71
	MP2	15				609.2				
	CCSD	16	526.4	544.3	552.0	540.9				
	Expt.	18				561.5				
		12				559.3				
Li_{10}	$_{ m HF}$		612.8	613.0	949.5	725.1	37.68	0.0956	47.08	47.85
	DFT		605.5	605.9	995.4	735.6	38.10	0.0939	47.24	48.02
	MP2	15				744.6				
	Expt.	18				701.8				

TABLE II: Continued.

							Na_n	$-Na_n$	Na _n	$- C_{60}$
Cluster	$Method^a$	Ref.	α_{xx}	$lpha_{yy}$	α_{zz}	$\overline{\alpha}$	C_6	ω_1^b	C_6^c	C_6^d
Na ₂	HF		229.9	229.9	358.2	272.6	4.681	0.0840	15.77	16.02
	DFT		204.9	204.9	352.3	254.0	4.187	0.0865	15.10	15.36
	DFT^e		204.4	204.4	350.1	252.9	4.174	0.0870	15.14	15.41
	MP2	11				252.5				
	CCSD^f		210.6	210.6	391.4	270.9	4.659	0.0846		
	$\mathrm{CCSD}^{e,f}$		189.1	189.1	400.4	259.5	4.362	0.0864		
	$\operatorname{CCSD}(T)$	11				263.3				
	Expt.	3				255.8				
		12				265.2				
		21							17.62	
Na ₄	$_{ m HF}$		416.9	839.2	334.2	530.1	17.06	0.0810	30.19	30.72
	DFT		388.8	833.8	304.9	509.2	15.98	0.0822	29.43	29.94
	DFT^{e}		385.4	830.9	308.1	508.2	15.99	0.0826	29.55	30.06
	MP2	10				508.6				
	CCSD^f		407.5	809.5	317.5	511.5	16.80	0.0856		
	$\operatorname{CCSD}(T)$	10				509.6				
	Expt.	3				545.9				
		12				565.5				
		21							26.56	

TABLE III: Static mean polarizabilities (a.u.), dipole-dipole dispersion coefficients (10^3 a.u.), and effective frequencies (a.u.) for the Na_n clusters and C₆₀.

 $^a\mathrm{Unless}$ specified, Sadlej's polarization basis set is used. 36

^bEffective frequency is determined as $\omega_1 = 4C_6/3 [\overline{\alpha}(0)]^2$.

 c Results for C₆₀ are taken from Ref. 30 and obtained at the Hartree–Fock level with Sadlej's basis set.

 d Results for C₆₀ are taken from Ref. 30 and obtained at the DFT/B3LYP level with Sadlej's basis set.

 $^e\mathrm{Calculated}$ with a large [19s15p12d6f] basis set. 37

approximants.^{26,41} For the dimer, the CCSD values reported by Urban and Sadlej⁴ and Maroulis¹¹ are 269.7 and 263.7 a.u., respectively.

 $^{{}^{}f}C_{6}$ result is obtained from the mean value of the lower $[n,n-1]_{\alpha}$ and upper $[n,n-1]_{\beta}$ Padé

							Na_n	$-Na_n$	Na_n	$- C_{60}$
Cluster	$Method^a$	Ref.	α_{xx}	$lpha_{yy}$	α_{zz}	$\overline{\alpha}$	C_6	ω_1^b	C_6^c	C_6^d
Na ₆	HF		885.8	457.2	888.8	743.9	35.55	0.0856	44.09	44.85
	DFT		838.9	418.2	841.9	699.7	32.47	0.0884	42.60	43.33
	Expt.	3				823.7				
		12				754.3				
		21							38.91	
Na ₈	$_{ m HF}$		883.9	883.9	883.9	883.9	52.68	0.0899	54.71	55.63
	DFT		845.9	845.9	845.9	845.9	49.47	0.0922	53.44	54.33
	Expt.	3				880.4				
		12				901.0				
		14				955.6				
		21							55.01	
Na ₁₀	HF		867.3	867.3	1425	1053	76.60	0.0921	66.53	67.63
	DFT		800.7	800.7	1397	999.4	70.88	0.0946	64.62	65.67
	Expt.	3				1296				
		21							63.71	

TABLE III: Continued.

							\mathbf{K}_n	$-K_n$	\mathbf{K}_n -	- C ₆₀
Cluster	$Method^{a}$	Ref.	α_{xx}	α_{yy}	α_{zz}	$\overline{\alpha}$	C_6	ω_1^b	C_6^c	C_6^d
K_2	HF		465.4	465.4	736.7	555.8	14.17	0.0612	25.79	26.28
	DFT		389.9	389.9	694.5	491.4	11.81	0.0652	24.20	24.64
	DFT^e		396.1	396.1	700.2	497.5	12.00	0.0646	24.32	24.76
	CCSD^f		380.5	380.5	789.6	516.9	13.15	0.0656		
	$\operatorname{CCSD}(T)$	4	381.8	381.8	758.8	507.5				
	Expt.	3				485.9				
		19				$519.6 {\pm} 40.5$				
K_4	HF		858.6	1705	688.8	1084	52.02	0.0590	49.48	50.41
	DFT		776.1	1659	599.5	1012	46.77	0.0610	47.69	48.57
	DFT^e		769.3	1662	606.5	1013	46.77	0.0608	47.68	48.55
	CCSD^f		806.8	1629	608.0	1015	50.20	0.0650		
K_6	HF		1788	914.6	1788	1497	105.4	0.0627	71.75	73.07
	DFT		1636	805.5	1637	1359	91.91	0.0663	68.49	69.72
K_8	HF		1838	1838	1838	1838	164.0	0.0647	90.96	92.59
	DFT		1710	1710	1710	1710	148.3	0.0676	87.96	89.51
K_{10}	HF		1791	1791	2851	2145	232.7	0.0674	109.9	111.9
	DFT		1598	1598	2751	1983	208.0	0.0706	105.9	107.7

TABLE IV: Static mean polarizabilities (a.u.), dipole-dipole dispersion coefficients (10^3 a.u.), and effective frequencies (a.u.) for the K_n clusters and C₆₀.

 $^a\mathrm{Unless}$ specified, Sadlej's polarization basis set is used. 36

^bEffective frequency is determined as $\omega_1 = 4C_6/3 \left[\overline{\alpha}(0)\right]^2$.

 c Results for C₆₀ are taken from Ref. 30 and obtained at the Hartree–Fock level with Sadlej's basis set.

 d Results for C₆₀ are taken from Ref. 30 and obtained at the DFT/B3LYP level with Sadlej's basis set.

 $^e\mathrm{Calculated}$ with a large [19s15p12d6f] basis set.

 ${}^{f}C_{6}$ result is obtained from the mean value of the lower $[{\rm n,n-1}]_{\alpha}$ and upper $[{\rm n,n-1}]_{\beta}$ Padé approximants.^{26,41}

							Rb_n	$-\operatorname{Rb}_n$	Rb_n	$- C_{60}$
Cluster	$Method^{a}$	Ref.	α_{xx}	α_{yy}	α_{zz}	$\overline{\alpha}$	C_6	ω_1^b	C_6^c	C_6^d
Rb_2	HF		533.0	533.0	883.8	649.9	18.74	0.0591	29.87	30.43
	DFT		434.6	434.6	793.8	554.3	14.93	0.0648	27.66	28.15
	DFT^{e}		447.7	447.7	801.5	565.6	15.32	0.0639	27.87	28.37
	CCSD^f		429.4	429.4	888.5	582.4	16.70	0.0656		
	$\operatorname{CCSD}(T)$	4	471.2	471.2	941.7	628.0				
	Expt.	19				$533.1 {\pm} 40.5$				
Rb_4	HF		1033	2136	820.0	1330	73.64	0.0555	58.65	59.74
	DFT		909.8	2007	699.7	1206	63.85	0.0586	55.96	56.97
	DFT^{e}		907.5	1998	711.0	1205	63.80	0.0585	55.90	56.91
	CCSD^f		958.0	2036	716.2	1237	70.78	0.0617		
Rb_6	HF		2136	1099	2136	1790	144.3	0.0600	84.22	85.74
	DFT		1912	945.5	1912	1590	122.3	0.0645	79.79	81.18
Rb_8	HF		2227	2227	2227	2227	228.8	0.0615	107.5	109.5
	DFT		2009	2009	2009	2009	198.8	0.0656	102.7	104.5
Rb_{10}	HF		2125	2125	3537	2596	326.5	0.0646	130.7	133.0
	DFT		1891	1891	3334	2372	287.6	0.0682	125.4	127.5

TABLE V: Static mean polarizabilities (a.u.), dipole-dipole dispersion coefficients (10^3 a.u.), and effective frequencies (a.u.) for the Rb_n clusters and C₆₀.

^aUnless specified, Sadlej's polarization basis set is used.³⁶

^{*b*}Effective frequency is determined as $\omega_1 = 4C_6/3 \left[\overline{\alpha}(0)\right]^2$.

 c Results for C₆₀ are taken from Ref. 30 and obtained at the Hartree–Fock level with Sadlej's basis set.

 d Results for C₆₀ are taken from Ref. 30 and obtained at the DFT/B3LYP level with Sadlej's basis set.

 e Calculated with a large [19s15p12d6f] basis set.

 ${}^{f}C_{6}$ result is obtained from the mean value of the lower $[n,n-1]_{\alpha}$ and upper $[n,n-1]_{\beta}$ Padé approximants.^{26,41}









Fig. 3; Jiemchooroj, Sernelius, and Norman

