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

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The frequency-dependent polarizabilities of closed-shell sodium clusters containing up to 20 atoms have been calculated using the linear complex polarization propagator approach in conjunction with Hartree-Fock and Kohn-Sham density functional theories. 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 [Phys. Rev. **73**, 360 (1948)]. The B3PW91 results for the polarizability of the sodium dimer and tetramer are benchmarked against coupled cluster calculations. The error bars of the reported theoretical results for the C_6 coefficients are estimated to be 5%, and the results are well within the error bars of the experiment. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2348882]

I. INTRODUCTION

The long-range dispersion interaction, or van der Waals interaction, has earned much attention from both theoretical and experimental fields of physics, chemistry, and biology. Its important role is due to the fact that it accounts for the attractive interactions between pairs of neutral systems, such as colloidal particles in chemistry and biology.[1] At large separations, i.e., in the van der Waals region, the interaction energy between neutral polarizable species has an R^{-6} dependence (once the orientational averaging has been considered), whereas at even larger separation, retardation effects become noticeable and the interaction energy drops off faster. At the microscopic level, the interaction energy and the C_6 dispersion coefficients are directly related to the electric dipole polarizability according to the Casimir-Polder relation.[2]

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[4–9] and experiments[10–12] devoted to the ground state electronic structure and optical properties of these systems. Sodium clusters attract interest not only because they are fundamental metal clusters with available experimental data but also due to their physical and chemical properties. Due to computational issues, high precision calculations have been performed only on the smaller clusters,[8,9] whereas for the larger clusters, one has been forced to employ more approximative methods at the cost of a reduced accuracy. It is our intention in this work to perform state-of-the-art density based calculations for the larger clusters by use of the complex polarization propagator approach[13,14] which, in this context, has proven successful in a series of applications.[15–17]

The computational technique adopted in this work allows for the employment of large basis sets, with polariza-tion and diffuse functions, which is essential in calculations of the molecular property of interest. The results are expected to be close to the corresponding basis set limiting values. The effect of electron correlation has been investigated with the use of Kohn-Sham density functional theory together with the hybrid B3PW91 exchange-correlation functional.[18,19] The results are also compared to those obtained with the second-order Møller-Plesset (MP2) perturbation theory[8,9] and the coupled cluster model with single and double excitations (CCSD) and perturbative triple excitations [CCSD(T)].[8,9]

In the past decade, the C_{60} fullerene has become one of the most studied materials in both the theoretical and experimental communities.[17,20–23] Recent work has been devoted to systematic calculations of static polarizabilities for the C_{60} fullerene[17,20–23] as well as for sodium clusters.[5–9] Despite the fact that the C_{60} to metal-cluster interactions are of fundamental interest in, e.g., the use of scanning microscope tips, there is, to the best of our knowledge, a lack of theoretical work devoted to the C_6 dispersion coefficients of the larger clusters themselves as well as in combination with the fullerene. In addition, the experimental work of Kresin *et al.*[24] shows a remarkably strong attractive interaction between sodium clusters and C_{60}, and the determination of accurate theoretical reference values of the C_6 dispersion coefficients for these systems is therefore well motivated.

II. METHODOLOGY AND COMPUTATIONAL DETAILS

The C_6 long-range orientation averaged dipole-dipole dispersion coefficient between two atoms or molecules A and B is related to the electric dipole polarizability by the Casimir-Polder relation[2]

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$$C_6 = \frac{3\hbar}{\pi} \int_0^\infty \bar{\alpha}_A(i\omega^I)\bar{\alpha}_B(i\omega^I)d\omega^I, \qquad (1)$$

where $\bar{\alpha}_A(i\omega^I)$ is the isotropic average of the dipole polarizability of molecule A at the imaginary frequency $i\omega^I$ and is defined as

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \qquad (2)$$

For a general complex frequency, $\omega = \omega^R + i\omega^I$, the dipole polarizability may be expressed in terms of a sum-over-states (SOS) formula according to

$$\alpha_{\alpha\beta}(\omega) = \frac{1}{\hbar}\sum_n{}' \left[\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{\omega_{0n} - \omega} + \frac{\langle 0|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{\omega_{0n} + \omega} \right], \qquad (3)$$

where $\hat{\mu}_\alpha$ is the electric dipole moment operator along the molecular axis α and $\hbar\omega_{0n}$ are the transition energies between the ground state $|0\rangle$ and the excited states $|n\rangle$. The prime on the summation denotes the exclusion of the ground state. A direct evaluation of Eq. (3) can be performed using the complex linear polarization propagator approach for which a detailed description is given in the original work;[13] for approximate state methods an explicit resolution of the excited states is avoided and Eq. (3) does in this case correspond to a matrix equation. The method has been successfully applied to determine the dispersion energy of the electronic ground state for the noble gases and n-alkanes,[15] for the polyacenes and fullerene C_{60},[17] and for the first $\pi \rightarrow \pi^*$ excited state of azabenzenes.[16]

The polarizabilities at imaginary frequencies were calculated by means of the linear response functions at the time-dependent Hartree-Fock level and the time-dependent density functional theory level with the hybrid B3PW91 exchange-correlation functional.[18,19] Unless specified, the polarization basis set of Sadlej[25] was used in all calculations; a larger basis set[26] $[19s15p12d6f]$ was employed only in calculations on the sodium dimer and tetramer.

In order to evaluate the Casimir-Polder integral for the C_6 dispersion coefficients in Eq. (1), the polarizabilities were calculated at the imaginary frequencies taken from a Gauss-Legendre integration scheme with the transformation of variables according to

$$i\omega^I = i\omega_0(1 - t)/(1 + t). \qquad (4)$$

Here we used a transformation factor of $\omega_0 = 0.3E_h$ as suggested in Ref. 27, followed by a Gauss-Legendre quadrature in the interval $-1 \leq t \leq 1$. For the interactions between the sodium clusters and the fullerene C_{60}, the accurate results of the C_{60} fullerene were taken from our previous work.[17] We use the six-point Gauss-Legendre integration in the present work, which has been shown to be accurate for the integration in Eq. (1).

The CCSD model[28,29] was used to obtain the Cauchy moments and the C_6 coefficients of Na_2 and Na_4. The frequency-dependent polarizabilities can be obtained from the Cauchy moments by the Cauchy moment expansion. The C_6 dispersion coefficients can be directly evaluated from the Cauchy moments with the use of the lower $[n, n-1]_\alpha$ and upper $[n, n-1]_\beta$ Padé approximants recommended by Lang-

hoff and Karplus.[30] With $n = 4$, the values of the C_6 coefficients for the dimer and the tetramer are converged to within 1%.

The experimental bond length[31] of 3.0788 Å was used for the dimer, and the B3LYP/6-311+G(d) optimized structure[8] was employed for the tetramer. For the case of larger clusters, the B3LYP/6-31G(d) optimized structures were taken from Ref. 7.

All property calculations were performed with the DALTON program.[32]

III. RESULTS AND DISCUSSION

In this work we present calculations of electric dipole polarizabilities and dipole-dipole dispersion coefficients for a series of sodium clusters ranging from the dimer to a cluster with 20 atoms. Our results are combined with a set of data from our previous work on the C_{60} fullerene[17] and we can thereby determine the metal-cluster-to-fullerene interactions as well.

A. Estimating the quality of results

The quality of the fullerene results are discussed in detail in the original work[17] and we therefore focus here at establishing the level of quality for the calculations on the metal clusters. The orientationally averaged static polarizabilities $\bar{\alpha}$ and C_6 dispersion coefficients for the sodium clusters are collected in Table I. For the smaller clusters, Na_2 and Na_4, there exist several theoretical and experimental reference values in the literature, against which we can evaluate our calculations. However, due to the wide spread in the experimental values for $\bar{\alpha}$ of the dimer and tetramer (as well as larger clusters), we are inclined to use the theoretical references for an evaluation of the quality of our results.

Highly correlated results for the dimer and tetramer polarizabilities have recently been presented in the literature[8,9] and are included in Table I for reference. For the dimer the MP2 result for $\bar{\alpha}$ from Ref. 9 is 252.5 a.u., a result which is obtained in a large basis set. The CCSD and CCSD(T) results in the same work[9] are 263.7 and 263.3 a.u., respectively, but these results are obtained with a smaller basis set of size $[12s9p7d1f]$. We have determined a CCSD value for $\bar{\alpha}$ using our large basis set of size $[19s15p12d6f]$ and obtained a value of 259.5 a.u., which we believe is quite close to the basis set limit. We thus conclude that the MP2 result is some 2% below an *estimated* CCSD(T) result as obtained with a large basis set. The reason we are focusing on the MP2 reference values is that these are in close agreement with our results obtained at the Kohn-Sham density functional theory (DFT) level of theory with the B3PW91 functional, see Table I; this agreement is observed for the dimer as well as the tetramer. For the tetramer, however, the quality of the basis set in the wave function correlated calculation does not match that in the dimer calculation and the observed close agreement between MP2, CCSD, and CCSD(T) results for $\bar{\alpha}$ may therefore be somewhat fortuitous.

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

TABLE I. Static mean polarizabilities, dipole-dipole dispersion coefficients ($\times 10^{-3}$), and effective frequencies for the Na clusters and C_{60}. All quantities are in a.u.

Cluster	Method[a]	Reference	$\bar{\alpha}$	$Na_n - Na_n$ C_6	ω_1[b]	$Na_n - C_{60}$ C_6[c]	C_6[d]
Na_2	HF	This work	272.6	4.681	0.0840	15.77	16.02
	DFT/B3PW91	This work	254.0	4.187	0.0865	15.10	15.36
	DFT/B3PW91[e]	This work	252.9	4.174	0.0870	15.14	15.41
	MP2	9	252.5				
	CCSD[f]	This work	270.9	4.659	0.0846		
	CCSD[e,f]	This work	259.5	4.362	0.0864		
	CCSD(T)	9	263.3				
	Expt.	3	255.8				
		10	265.2				
		24				17.62	
Na_4	HF	This work	530.1	17.06	0.0810	30.19	30.72
	DFT/B3PW91	This work	509.2	15.98	0.0822	29.43	29.94
	DFT/B3PW91[e]	This work	508.2	15.99	0.0826	29.55	30.06
	MP2	8	508.6				
	CCSD[f]	This work	511.5	16.80	0.0856		
	CCSD(T)	8	509.6				
	Expt.	3	545.9				
		10	565.5				
		24				26.56	
Na_6	HF	This work	743.9	35.55	0.0856	44.09	44.85
	DFT/B3PW91	This work	699.7	32.47	0.0884	42.60	43.33
	Expt.	3	823.7				
		10	754.3				
		24				38.91	
Na_8	HF	This work	883.9	52.68	0.0899	54.71	55.63
	DFT/B3PW91	This work	845.9	49.47	0.0922	53.44	54.33
	Expt.	3	880.4				
		10	901.0				
		12	955.6				
		24				55.01	
Na_{10}	HF	This work	1053	76.60	0.0921	66.53	67.63
	DFT/B3PW91	This work	999.4	70.88	0.0946	64.62	65.67
	Expt.	3	1296				
		24				63.71	
Na_{12}	HF	This work	1342	119.6	0.0885	82.31	83.70
	DFT/B3PW91	This work	1290	112.7	0.0902	80.47	81.81
	Expt.	3	1495				
		12	1506				
		24				92.52	
Na_{14}	HF	This work	1652	174.9	0.0854	98.57	100.3
	DFT/B3PW91	This work	1596	165.8	0.0868	96.61	98.25
	Expt.	3	1668				
		12	1748				
		24				108.3	
Na_{18}	HF	This work	1725	214.9	0.0963	113.0	114.8
	DFT/B3PW91	This work	1622	198.4	0.1006	109.9	111.7
	Expt.	3	1875				
		12	1980				
		24				139.0	
Na_{20}	HF	This work	1988	272.3	0.0919	126.8	128.8
	DFT/B3PW91	This work	1818	244.8	0.0988	122.1	124.0
	Expt.	3	2077				

TABLE I.   (*Continued.*)

Cluster	Method[a]	Reference	$\bar{\alpha}$	Na$_n$–Na$_n$		Na$_n$–C$_{60}$	
				C_6	ω_1[b]	C_6[c]	C_6[d]
		12	2267				
		24				169.2	

[a]Unless specified, Sadlej's polarization basis set is used (see Ref. 25).
[b]Effective frequency is determined by $\omega_1 = 4C_{6,ii}/3\bar{\alpha}_i(0)^2$.
[c]Results for C$_{60}$ are taken from Ref. 17 and obtained at the Hartree-Fock level with Sadlej's basis set.
[d]Results for C$_{60}$ are taken from Ref. 17 and obtained at the DFT/B3LYP level with Sadlej's basis set.
[e]Calculated with a large $[19s15p12d6f]$ basis set (see Ref. 26).
[f]Mean value is obtained from the lower $[n,n-1]_\alpha$ and upper $[n,n-1]_\beta$ Padé approximants (see Refs. 28 and 30). For the dimer, the CCSD values reported by Urban and Sadlej (Ref. 4) and Maroulis (Ref. 9) are 269.7 and 263.7 a.u., respectively.

that of $\bar{\alpha}$. If we compare the DFT/B3PW91 and CCSD results for the C_6 coefficient of the dimer we see that the discrepancy is some 4% (the DFT result is 4.174×10^3 a.u.), and which thus amounts to a doubling of the error for the polarizability.

Our large basis set can be employed in the DFT calculations of the dimer and tetramer but, due to computational issues, not for the larger clusters. Fortunately, however, the basis set dependence in the DFT approach is less pronounced than in wave function correlated approaches. From our results in Table I it is clear that there is a perfect agreement between DFT results obtained with our large basis set and those obtained with the smaller polarization basis set of Sadlej.

In conclusion regarding the accuracy of the results presented for the C_6 coefficients of the metal clusters, we estimate the DFT/B3PW91 results to be within 5% of highly correlated wave function values, if such could be determined for the whole series of systems.

B. Metal-cluster-to-fullerene interaction

The van der Waals interaction between sodium clusters and the buckminster fullerene has been studied in collision scattering experiments by Kresin *et al.*[24] In their work, the C_6 coefficients were determined from a fit to integral scattering cross sections measured from collisions between sodium cluster beams and a fullerene vapor, and the error bars in this procedure are estimated to be about 30%.[24] The molecular structure of the metal clusters is not possible to determine in the experiment, and for the larger clusters the experiment may well refer to a statistical mixture of the possible conformations. Our calculations, on the other hand, refer to, for each cluster size, a single structure obtained from theoretical structure optimizations.[7,8] We have not studied the conformational dependence of the van der Waals interaction in the present work.

In Table I we report the C_6 dispersion coefficients for the interaction between the sodium clusters and C$_{60}$. The Hartree-Fock (HF) and DFT/B3LYP polarizabilities of C$_{60}$ as given in Ref. 17 were utilized for evaluation of the C_6 coefficients. The difference in the resulting dispersion coefficients depending on which data set is used for the polariz-

ability of the fullerene is insignificant, but it was argued in Ref. 17 that the set of HF polarizabilities is the better of the two.

In Fig. 1 we compare the theoretical results for the dispersion coefficients of the metal-cluster-to-fullerene interaction against the experimental results reported Kresin *et al.*[24] As mentioned above, the estimated error bar in the experiment amounts to about 30%,[24] and our theoretical data are in all cases well within the experimental error bars. It is apparent, however, that the discrepancy between theory and experiment increases with the size of the metal cluster. Since the quality of the calculations remains constant for different cluster sizes, we are inclined to believe that the explanation for the increasing discrepancy lies in the issue of metal cluster conformations. Our choice of optimized structures may not refer to the experimental situation, e.g., more spatially extended conformations will lead to enhanced values for the polarizabilities.

The frequency-dependent polarizability is often represented by a simple model with an effective, or characteristic, frequency ω_1 according to

$$\bar{\alpha}(i\omega^I) = \frac{\bar{\alpha}(0)}{1 + (\omega^I/\omega_1)^2}. \tag{5}$$

This is the so-called London approximation and it has been suggested since the polarizability on the imaginary frequency axis decreases monotonically from the static value to zero as
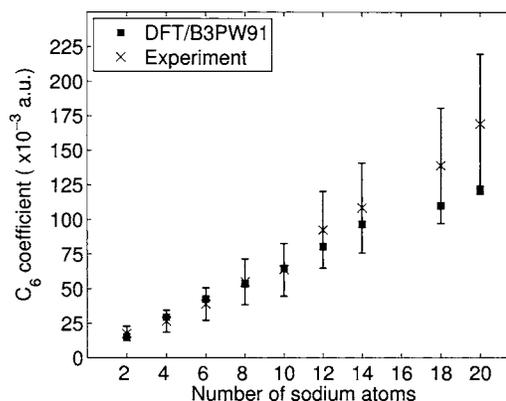

FIG. 1. The C_6 dispersion coefficients for interactions between sodium clusters containing up to 20 atoms and fullerene C$_{60}$. The experimental data with error bars are taken from Ref. 24.

the frequency tends to infinity, and its validity is based on the assumption that there is one dominant state in the linear absorption spectrum, so that the corresponding oscillator strength is larger than the sum of others. It was shown in our previous work[17] that the errors involved with an estimation of the frequency-dependent polarizability from Eq. (5) are substantial. Nevertheless, the model may be useful not so much for a determination of $\alpha(i\omega^I)$ as such but for expressing the correlation between the static polarizability and the corresponding dispersion coefficient. With the approximation in Eq. (5) made, the integral to obtain the C_6 coefficient [Eq. (1)] for like molecules can be evaluated analytically, and the expression for the dispersion coefficient becomes

$$C_6 = \frac{3\omega_1}{4} \bar{\alpha}(0)^2. \qquad (6)$$

In this respect the characteristic frequency ω_1 becomes a fit parameter.

The values of the characteristic frequencies of the sodium clusters are included in Table I. A small spread in ω_1 ranging from 0.08 to 0.10 a.u. is found and the mean value of ω_1 is 0.091 a.u. This observation suggests that it may be possible to construct simple structure-to-property relations for the dispersion coefficients, in a similar way that was done in our earlier work for the n-alkanes.[15,33] In a recent theoretical study of Chadrakumar et al.[8] it was shown that the static polarizability displays a linear dependence on the sodium cluster volume. So, since we have found that the characteristic frequency is almost independent of cluster size, one can directly relate the cluster volume to the C_6 coefficients with the help of Eq. (6). It is noted that, for other classes of compounds, such as π-conjugated polyacenes, structure-to-property relations are not found in this way due to an effective frequency that varies strongly with system size.[17]

IV. 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 sodium clusters. We present first-principles calculations of the electric dipole polarizabilities and the dipole-dipole dispersion coefficients of the closed-shell sodium clusters up to 20 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 therefore accurate for the determination of the C_6 dispersion coefficients. In cases where comparison to experimental data can be made—referring to polarizabilities as well as dispersion coefficients—our theoretical values are well within the error bars of the experiment.[24] We conclude that our results, obtained at the time-dependent density functional theory with the B3PW91 functional, for the metal-cluster-to-cluster and cluster-to-fullerene dispersion interactions do provide a set of accurate theoretical reference values. Our results are close to the basis set limiting values, and the treatment of electron correlation in the metal clusters parallels that of the second-order Møller-Plesset method.

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