

**Dispersion coefficients for H and He interactions with alkali-metal and alkaline-earth-metal atoms**

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The van der Waals coefficients  $C_6$ ,  $C_8$ , and  $C_{10}$  for H and He interactions with the alkali-metal (Li, Na, K, and Rb) and alkaline-earth-metal (Be, Mg, Ca, and Sr) atoms are determined from oscillator strength sum rules. The oscillator strengths were computed using a combination of *ab initio* and semiempirical methods. The dispersion parameters generally agree with close to exact variational calculations for Li-H and Li-He at the 0.1% level of accuracy. For larger systems, there is agreement with relativistic many-body perturbation theory estimates of  $C_6$  at the 1% level. These validations for selected systems attest to the reliability of the present dispersion parameters. About half the present parameters lie within the recommended bounds of the Standard and Certain compilation [J. Chem. Phys. **83**, 3002 (1985)].

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**I. INTRODUCTION**

The long-range van der Waals interaction plays an important part in determining the dynamics of two interacting atoms when they are a long distance apart. The interaction potential is written

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots, \quad (1)$$

where the  $C_n$  parameters are the dispersion coefficients.

In this paper, dispersion coefficients for hydrogen and helium atoms interacting with alkali-metal and alkaline-earth-metal atoms are presented. The motivation for this comes from a variety of reasons. First and foremost, there is the interest in cold-collision physics stimulated by the recent creation of Bose-Einstein condensates (BEC) for the alkali-metal atoms Li, Na, Rb, and atomic hydrogen [1,2]. The stability, size, and excitation modes of BECs depend on the sign (and magnitude) of the scattering length, and the scattering length depends on the precise values of the dispersion constants [3,4]. There has also been recent activity in studying the spectroscopic properties of atoms solvated in, or attached to, nanoscale helium droplets [5–7]. One interesting phenomenon is the property that some metal atoms (Al, Ag) dissolve in He nanodroplets while others (Li, K) stay on the droplets' surface. In addition, there is interest in the metal hydrides due to astrophysical considerations [8,9]. The spectra of metal hydrides appear in such places as sunspots, dense molecular clouds in the interstellar medium, and cool stellar atmospheres of  $M$  and later type stars.

Conventional quantum chemical calculations can accurately describe the potential energy surface for any number of diatomic molecules with an impressive degree of accuracy in the bonding region. However, at large nuclear distances

where the interatomic potentials are rather weak, it is better to rely on alternate methods that use dispersion integrals or oscillator strength sum rules.

In this paper, the  $C_6$ ,  $C_8$ , and  $C_{10}$  dispersion parameters are computed by directly utilizing the oscillator strength sum rules. The underlying oscillator strength distributions were computed from semiempirical calculations that treated the valence particles in an *ab initio* manner while using a semiempirical model potential to describe the core-valence interaction [10–14]. The model potential is quite realistic since the direct and exchange interactions with the core were computed exactly from a Hartree-Fock wave function; only the core polarization potential was described with a model potential. The resulting polarizabilities and dispersion parameters for homonuclear pairs of atoms were generally within 0.1% of the best variational calculations for Li or Be, and for heavier atoms they were generally within 1–2% of results coming from large-scale fully relativistic calculations combining configuration interaction and many-body perturbation theory techniques [10]. With such high levels of accuracy being achieved, it was natural to utilize the oscillator strength distributions generated for the alkali-metal and alkaline-earth-metal atoms and combine them with  $f$ -value distributions for H and He to determine a set of dispersion parameters of improved accuracy and reliability.

A set of recommended dispersion parameters for a large number of atom-atom combinations including those of interest to this paper was compiled by Standard and Certain (SC) in 1985 [15]. However, the primary data (this includes theoretical calculations as well as experimental data) used by SC to establish the upper and lower bounds on the dispersion parameters are now rather dated and the present values are more accurate.

**II. CALCULATIONS USING OSCILLATOR STRENGTH SUM RULES**

All of the dispersion parameters are computed from their respective oscillator strength sum rules with the multipole oscillator strengths  $f_{0i}^{(\ell)}$  from the ground to the  $i$ th excited state defined as

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$$f_{0i}^{(\ell)} = \frac{2|\langle \psi_0 \| r^\ell \mathbf{C}^\ell(\hat{\mathbf{r}}) \| \psi_i \rangle|^2 \epsilon_{0i}}{(2\ell+1)}. \quad (2)$$

In this expression,  $\mathbf{C}^\ell$  is the spherical tensor of rank  $\ell$  while  $\epsilon_{0i}$  is the excitation energy of the transition.

The sum rule for the adiabatic multipole polarizability,  $\alpha^{(\ell)}$ , is

$$\alpha^{(\ell)} = \sum_i \frac{f_{0i}^{(\ell)}}{\epsilon_{0i}^2} = S^{(\ell)}(-2). \quad (3)$$

Expressions for dispersion parameters have been published in a number of works [10,15–17]. The dipole-dipole dispersion parameter  $C_6$  between two atoms  $a$  and  $b$  is

$$C_6 = \frac{3}{2} \sum_{\substack{i \in a \\ j \in b}} \frac{f_{0i}^{(1)} f_{0j}^{(1)}}{\epsilon_{0i} \epsilon_{0j} (\epsilon_{0j} + \epsilon_{0i})}, \quad (4)$$

the dipole-quadrupole dispersion parameter  $C_8$  is

$$C_8 = \frac{15}{2} \sum_{\substack{i \in a \\ j \in b}} \frac{f_{0i}^{(1)} f_{0j}^{(2)}}{\epsilon_{0i} \epsilon_{0j} (\epsilon_{0j} + \epsilon_{0i})} + \frac{15}{2} \sum_{\substack{i \in a \\ j \in b}} \frac{f_{0i}^{(2)} f_{0j}^{(1)}}{\epsilon_{0i} \epsilon_{0j} (\epsilon_{0j} + \epsilon_{0i})}, \quad (5)$$

and the  $C_{10}$  dispersion parameter is

$$C_{10} = 7 \sum_{\substack{i \in a \\ j \in b}} \frac{f_{0i}^{(1)} f_{0j}^{(3)}}{\epsilon_{0i} \epsilon_{0j} (\epsilon_{0j} + \epsilon_{0i})} + 7 \sum_{\substack{i \in a \\ j \in b}} \frac{f_{0i}^{(3)} f_{0j}^{(1)}}{\epsilon_{0i} \epsilon_{0j} (\epsilon_{0j} + \epsilon_{0i})} + \frac{35}{2} \sum_{\substack{i \in a \\ j \in b}} \frac{f_{0i}^{(2)} f_{0j}^{(2)}}{\epsilon_{0i} \epsilon_{0j} (\epsilon_{0j} + \epsilon_{0i})}. \quad (6)$$

The sum rules implicitly include a sum over excitations to bound states and an integration taking into account excitations to continuum states. It is known that  $C_6$  parameters derived from pseudostate calculations generally converge very quickly as the dimension of the pseudostate basis is increased [18,19].

It should be noted that all of the sum-rule evaluations involved contributions from both core and valence excitations. It has often been the case that model potential calculations of dispersion parameters have simply omitted contributions from the core [16,20–23] to the  $f$ -value sums or the frequency-dependent polarizabilities. The valence contributions were evaluated by simply diagonalizing the model Hamiltonian in a very large basis. This is essentially a brute-force evaluation of the sum rules. We used  $f$ -value sum rules that can be equated to ground-state expectation values to determine the  $f^{(\ell)}$ -value distribution for the core electrons [10,11].

### III. RESULTS OF THE CALCULATIONS

The dispersion coefficients of hydrogen with the alkali-metal and alkaline-earth-metal atoms are listed in Table I. Table II lists the dispersion coefficients of helium with these atoms. All quantities are given in atomic units (a.u.). The

TABLE I. The dispersion coefficients  $C_6$ ,  $C_8$ , and  $C_{10}$  for all the possible HX dimers, where X is an alkali-metal or alkaline-earth-metal atom. The number in brackets for the MBPT entries is an estimate of the uncertainty in the last digit. All values are in atomic units.

Method/source	$C_6$	$10^{-3} C_8$	$10^{-5} C_{10}$
Li			
Present	66.544	3.2821	2.2318
Variational [24]	66.536	3.27999	2.23017
CI [25]	65.91	3.266	2.208
PT [23]	65.82	3.211	2.176
MK: pseudo [22]	65.93		
SC [15]	65.8–66.8	3.06–3.27	1.89–2.17
Na			
Present	74.18	4.016	2.988
MBPT [26]	73.83(9)	4.059	
CC [27]	73.97	5.311	3.944
CI [25]	71.64	3.973	2.883
PT [23]	71.26	3.828	2.775
MK: pseudo [22]	72.05		
SC [15]	70.2–175	3.68–4.90	2.46–2.96
K			
Present	112.0	7.984	7.428
MBPT [26]	111.2(2)		
CI [25]	100.4	7.777	7.739
PT [23]	102.4	7.296	6.654
MK: pseudo [22]	104.6		
SC [15]	111–116	7.14–7.67	5.82–6.60
Rb			
Present	124.6	9.540	9.304
MBPT [26]	124.3(3)		
PT [23]	110.6	8.485	8.138
SC [15]	118–126	8.38–9.14	7.71–8.54
Be			
Present	34.752	1.2143	0.46653
MK: pseudo+CI [22]	34.39		
MP4 [28]	34.2		
SC [15]	35.5–35.8	1.21–1.27	0.445–0.494
Mg			
Present	57.59	2.560	1.221
MBPT [29]	57.8(6)		
MK: pseudo+CI [22]	57.75		
SC [15]	57.4–58.5	2.49–2.66	1.15–1.29
Ca			
Present	100.1	6.292	4.021
MK: pseudo+CI [22]	93.04		
SC [15]	119–123	4.77–6.51	3.35–3.96
Sr			
Present	120.9	8.384	5.942

upper and lower bounds from the SC [15] tabulations are also listed.

The programs used to compute  $C_6$ ,  $C_8$ , and  $C_{10}$  were tested by evaluating these coefficients for the H-H homonuclear pair. The numbers obtained—6.499 026 7 a.u.,

TABLE II. The dispersion coefficients  $C_6$ ,  $C_8$ , and  $C_{10}$  for all the possible HeX dimers, where X is an alkali-metal or alkaline-earth-metal atom. All values are in atomic units.

Method/source	$C_6$	$10^{-3} C_8$	$10^{-4} C_{10}$
Li			
Present	22.512	1.0841	7.2664
Variational [24]	22.507	1.08316	7.26021
CI [25]	22.18	1.081	7.204
MK: pseudo [22]	22.04		
SC [15]	22.18–22.8	0.991–1.08	5.92–7.06
Na			
Present	25.76	1.329	9.774
CI [25]	24.25	1.317	9.435
MK: pseudo [22]	24.20		
SC [15]	23.7–68.7	1.20–1.50	7.73–9.28
K			
Present	39.46	2.627	24.26
CI [25]	33.32	2.551	25.49
MK: pseudo [22]	34.42		
SC [15]	37.8–41.8	2.30–2.50	18.4–21.4
Rb			
Present	44.69	3.145	30.38
SC [15]	40.1–46.3	2.69–2.98	24.6–27.7
Be			
Present	13.22	0.42534	1.4585
VS: model+CI [36]	13.29		
MK: pseudo+CI [22]	12.98		
MP4 [28]	12.9		
SC [15]	13.6–13.9	0.417–0.447	1.32–1.56
Mg			
Present	21.45	0.8864	3.936
CC [6]	20.0	1.1	
VS: model+CI [36]	20.87		
MK: pseudo+CI [22]	21.11		
SC [15]	21.1–22.1	0.843–0.924	3.55–4.19
Ca			
Present	36.59	2.138	13.19
CC [6]	35.0	3.1	
MK: pseudo+CI [22]	32.49		
SC [15]	45.1–48.5	1.48–2.19	10.8–12.9
Sr			
Present	44.41	2.835	19.52
PS [37]	50.5	3.31	

124.399 08 a.u., and 3285.8284 a.u., respectively—agree perfectly with the best variational estimates [24].

#### A. The H–alkali-metal combinations

Also shown in Table I are the results of a relativistic many-body perturbation theory (MBPT) calculation [26], some close to exact dispersion parameters for Li taken from very large-scale variational calculations [24], some all-electron configuration interaction (CI) calculations [25], the pseudopotential calculation of Maeder and Kutzelnigg [22], and some coarse estimates by Patil and Tang (PT) using pa-

rametrized wave functions tuned to the experimental binding energies [23]. The relativistic MBPT calculations are expected to be quite accurate since the method has been extensively validated [30–32] and furthermore they made empirical corrections to their *ab initio* dynamic dipole polarizabilities by incorporating the most accurate experimental transition rate data. The analysis of Proctor and Stwalley [16] used single-electron calculations in conjunction with combination rules involving single-atom *f*-value sums to estimate the dispersion parameters. The use of the combination rules added an extra degree of uncertainty and so for reasons of brevity the Proctor and Stwalley data are not reproduced in the table.

The lithium atom has relatively small core polarizabilities with  $\alpha^{(1)} = 0.1925$  a.u. and the error associated with using a model core would be small. The comparison with close to exact variational calculations [24] in Table I shows that the present model gives dispersion parameters that are accurate to within 0.1%.

A notable feature of Table I is the almost perfect agreement with the  $C_6$  parameters computed using relativistic many-body perturbation theory. The level of agreement is better than 1% for Na, K, and Rb. The relativistic calculations are semiempirical in nature; the transition energies and dipole matrix elements for the resonant transitions were taken directly from experiment when the polarizability integral over imaginary frequencies was performed. Error limits largely determined by the uncertainties in the experimental transition moments are also associated with the MBPT values of  $C_6$ . We suspect the very small errors ascribed to  $C_6$  may be a bit optimistic, but even if one takes the small uncertainty at face value, an overall level of agreement between the two sets of  $C_6$  values of better than 1% certainly increases confidence in the reliability of these two completely different calculations. One qualification about the present calculation must be made, namely the manner in which the contribution from the core excitations to the sum rule is included does lead to dispersion parameters which are slightly too large. For the Na-H, K-H, and Rb-H dimers, the effect is expected to range from 0.1% to 2%. This is not a large amount, but the present  $C_6$  parameters are all slightly larger than the MBPT parameters by amounts of roughly the same size.

In the context of the good agreement between the present and MBPT  $C_6$  parameters, the difference between the present (4016 a.u.) and MBPT (4059 a.u.)  $C_8$  parameters for Na is uncomfortably large (note, the calculation in [26] is described as a relativistic coupled-cluster calculation). However, it is evident from the description in [26] that this calculation represented a preliminary application of MBPT to the calculation of the dynamic quadrupole polarizability. For example, it gave a quadrupole polarizability of 1922 a.u. A later MBPT calculation of the quadrupole polarizability involving the same author, Derevianko [33], gave a polarizability of 1885 a.u. The oscillator strength distribution used for the present work gives a quadrupole polarizability of 1881 a.u. and the present  $C_8$  is likely to be more reliable than that of [26]. However, it is highly likely the 1% difference between the present and MBPT values would be significantly

reduced if the new MBPT frequency-dependent quadrupole polarizability of Na was used to compute  $C_8$ . For example, the present model predicts a value of  $C_8 = 11.60 \times 10^4$  for the  $\text{Na}_2$  dimer [10] while the MBPT calculation [33] also gave  $11.60 \times 10^4$  a.u.

The difficulties in extracting dispersion coefficients from a conventional calculation of the interatomic potential are evident in the comparison with the coupled-cluster (CC) calculation of Taylor and Newman [27]. This calculation included single, double, and triple excitations and a good deal of effort was made to ensure that the potential curve was accurate. While the CC  $C_6$  of 73.97 a.u. is compatible with the present calculation, the values of  $C_8$  and  $C_{10}$  are about 30% larger than the present value. The long-range interaction energies are small and obtained by subtracting two large energies from each other. Under such circumstances, it is not surprising that the higher-polarity parameters such as  $C_8$  and  $C_{10}$  cannot be obtained precisely. This reinforces the point that it is really very difficult to extract precise dispersion parameters from conventional quantum chemistry calculations [26].

The CI calculations of Spelsberg *et al.* [25] give dispersion parameters in reasonable agreement with the present values for Li and Na, but exhibit discrepancies up to 10% for K. Comparison of the Spelsberg *et al.* polarizabilities for K reveal differences with polarizabilities computed by the present method [10] and MBPT [33]. It is probable that the CI calculations of the dynamic polarizability were harder to converge for K than for Na and Li.

The comparison with the results of PT [23] reveals that their calculations consistently underestimate the dispersion parameters by amounts ranging from 2 to 10%. However, there is no reason to expect that  $f^{(\ell)}$ -value sum rules evaluated with simple parametrized wave functions should give dispersion parameters accurate to better than 10%.

One relatively common aspect of the comparisons is that the other calculations give consistently smaller  $C_6$  dispersion coefficients than the present and MBPT calculations for Na-H and K-H. The underlying reason for this is that these other calculations simply omit the core in their calculations of  $C_6$ . This can be tested by recomputing  $C_6$  for K-H with the core contribution simply omitted. The value of  $C_6$  is reduced by 10% and the without-core dispersion coefficient is 100.3 a.u.

The SC tabulations are not particularly reliable for the alkali metals. The present and MBPT dispersion parameters lie outside the SC bounds for seven out of the twelve combinations listed in Table I. This is not surprising since one of the primary inputs into their bounds for  $C_8$  and  $C_{10}$  was the pseudopotential calculations of Maeder and Kutzelnigg (MK) [22]. The MK calculation omitted the core from the dispersion parameter computations and they diagonalized the Hamiltonian for  $\ell = 2$  and  $\ell = 3$  excitations in a basis limited to five  $d$  orbitals and five  $f$  orbitals. The MK basis is not large enough to recover all of the quadrupole and octupole polarizabilities [10,33]. In not one single instance do the SC bounds encompass the current values of  $C_{10}$ .

## B. The He-alkali-metal combinations

There have been relatively few calculations of the dispersion coefficients for helium interacting with alkali-metal atoms. However, an exacting test of the present methodology is possible for the Li-He pair since close to exact dispersion parameters have been derived from large-scale variational calculations [24]. Once again, the present method agrees with the variational results to within 0.1%.

The quality of agreement between the present parameters and the CI calculations of Spelsberg *et al.* [25] is reminiscent of the situation for the H-alkali-metal dimers. There is reasonable agreement for the Li-He and Na-He combinations, but the quality of the agreement deteriorates for the K-He pair.

The dispersion coefficients of the MK calculation tend to be slightly smaller than the present values of  $C_6$ . As mentioned earlier, one of the factors that leads to the underestimations was the omission of the core from the MK computations. The K-He  $C_6$  parameter was 33.22 a.u. when it was recomputed with the core contributions to the oscillator strength distribution function simply omitted. The fact that the present  $f^{(1)}$  distribution function without core can largely agree with MK confirms that the absence of the core from the MK calculation results in estimates that are too small. As will be seen later, the absence of a core in the MK model also resulted in their  $C_6$  dispersion coefficients for Ca-H and Ca-He being underestimated by a noticeable amount.

The bounds of the SC tabulation are also not terribly reliable; once again the present values lies outside the SC bounds on seven out of twelve occasions. In not one single instance do the SC bounds encompass the current values of  $C_{10}$ .

## C. The H-alkaline-earth-metal combinations

The results of the present calculations for the alkaline-earth-metal atoms are compared with some other calculations in Table I.

The  $C_6$  parameter of the fourth-order Moller-Plesset (MP4) calculation [28] for Be agrees with the present calculation to within 2%. It should be noted that the MP4 value of 34.2 a.u. was actually calculated with a combination rule and so cannot be expected to have an accuracy better than a couple of percent.

One exacting test of the present approach occurs for the Mg-H dimer. A large-scale relativistic MBPT calculation gave  $C_6 = 57.8 \pm 0.6$  a.u. This is less than 0.5% larger than the present value of 57.59 a.u.

Apart from the SC tabulation, there are relatively few data sets in the literature for the heavier alkaline-earth-metal atoms. The CI+pseudopotential calculations of MK [22] used a moderately sized CI expansion by today's standards and their polarizabilities and dispersion parameters were probably 10–20% from the variational limit. The absence of core terms also contributes to their value of  $C_6$  for Ca-H being 7% smaller than the present value of 100.1 a.u.

The present data lie outside the SC bounds for three out of nine combinations. It is somewhat surprising that one of the occurrences is for the Be-H combination where the present

$C_6$  of 34.79 a.u. is about 2% smaller than the SC lower bound of 35.5 a.u. It is known that the SC bounds constraining  $C_6$  for systems containing calcium are of questionable reliability [10,34] since the accuracy of the underlying source of theoretical data [35] has been criticized.

#### D. The He–alkaline-earth-metal combinations

The dispersion parameters for the He-Be system are expected to be accurate to better than 0.5%. The 2% discrepancy with the fourth-order MP4 calculation of Maroulis and Thakkar [28] is not a concern since the Maroulis and Thakkar value was obtained from a combination rule.

The calculation by Victor and Slavsky (VS) [36] was a CI calculation with the core being represented by a model potential. Their estimates of  $C_6$  for the Be-He and Mg-He combinations are within a few percent of the present estimates.

The coupled-cluster (CC) calculation of Hinde [6] included single, double, and triple excitations and was quite an exacting calculation. Accuracies of  $\pm 3\%$  were claimed for  $C_6$  and  $\pm 8\%$  for  $C_8$ . None of the dispersion parameters computed by Hinde agree with the present values to within the error bounds. The  $C_6$  parameters of Hinde are between 5% and 8% smaller than the present estimates while their estimates of  $C_8$  are more than 20% larger than the present values. Once again the difficulties in extracting precise dispersion parameters from conventional quantum chemistry calculations manifest themselves [26].

The only previous estimate of the dispersion parameters for the Sr-He combination came from a model wave function tuned to have the correct ionization energies [37]. The  $C_6$  and  $C_8$  dispersion parameters that were derived by Patil and Setlur (PS) are some 10–15% larger than the present values.

The reliability of the SC bounds are best for the He–alkaline-earth-metal systems. The present results lie outside the SC bounds on three out of nine occasions. One interesting aspect is that one of these discrepancies is for the Be-He combination. The Be-He system should in principle be the easiest of the alkaline-earth-metal–helium systems to model correctly.

#### IV. CONCLUSIONS

The results of the nonrelativistic model potential analysis for the alkali-metal atoms give dispersion coefficients and polarizabilities that are in excellent agreement with relativistic MBPT calculations. Taking the present results in conjunction with the MBPT data leads one to the conclusion that the leading dispersion parameter  $C_6$  for the alkali-metal hydrides is known with a precision of about 1%. The present data for

the higher-order dispersion parameters of the alkali-metal hydrides should be similarly accurate.

The precision in the dispersion coefficients for the alkali-metal–He combinations will not be as great. Although the oscillator strength distributions for He and the valence part of the alkali-metal-atom distribution are accurate, the smaller dipole polarizability of He means that the contribution to the  $C_n$  parameters from the alkali-metal-atom cores is proportionally greater. Previous work [10] suggests that this could lead to dispersion parameters that are slightly too large. Some numerical experiments with the core  $f^{(1)}$  distribution suggest that the K-He  $C_6$  parameter could be too large by about 2%. One would expect the possible overestimation of  $C_6$  for Rb-He to be larger, and the possible overestimation for Na-He to be smaller.

The dispersion parameters involving the alkaline-earth atoms have larger uncertainties since the ground- and excited-state oscillator strengths come from CI calculations. For Be and Mg, the uncertainties are minor since the two-electron basis was effectively saturated. All the evidence available from calculations of the Be<sub>2</sub> dimer [10] suggests that the present dispersion parameters for this atom have an accuracy that is better than 0.5%. Comparisons of polarizabilities and  $C_6$  parameters of the Mg<sub>2</sub> dimer [10] using the present  $f^{(\ell)}$  values with MBPT calculations [38,39] suggest an overall level of accuracy at the 1% level for the Mg-H and Mg-He dispersion parameters. There are much larger uncertainties for calcium and strontium. The 3*d* orbital for Ca and the 4*d* orbital for Sr do penetrate into the core and tend to change the charge density of the core electrons [40,41]. This means that there are additional uncertainties in the definition of the underlying semiempirical core potential that do not occur for Be and Mg. An overall level of consistency achieved with MBPT calculations [38,39] in calculations of polarizabilities and oscillator strengths for Ca and Sr [10] suggests that the  $C_6$  for dimers containing either Ca or Sr should be accurate to about 1–2%. The  $C_8$  and  $C_{10}$  parameters more directly involve transitions to states with occupied 3*d* and 4*d* orbitals and might therefore be more susceptible to error. However, CI calculations of the transition arrays for Ca have not revealed any glaring anomalies in the transitions involving the <sup>1</sup>*D*<sup>e</sup> and <sup>1</sup>*F*<sup>o</sup> manifolds of states [40,41]. So an initial guess of the uncertainty in the higher-order dispersion parameters would be between 5 and 10%.

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