TDMP2 calculation of dynamic multipole polarizabilities and dispersion coefficients for the halogen anions F^-, Cl^-, Br^- and I^-

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A systematic *ab initio* study of the dynamic multipole polarizabilities of the halogen anions F^-, Cl^-, Br^- and I^- is presented. The effects of electron correlation are included for the static as well as for the frequency-dependent polarizabilities using time-dependent second-order Møller-Plesset perturbation theory. Large one-particle basis sets, optimized for polarizabilities, are used to obtain results near the MP2 basis set limit. For the anions Br^- and I^- also scalar relativistic effects are accounted for by means of the spin-free no-pair Hamiltonian $\hat{H}_+^{sf1}$. For the static dipole polarizabilities of the anions F^- and Cl^- we find good agreement with recent correlated *ab initio* calculations, but for the higher multipole polarizabilities and for the anions Br^- and I^- the discrepancies relative to previous calculations and empirical estimates are large. The effects of electron correlation on the polarizabilities of these anions are in general extremely large, while relativistic effects are in all four investigated halogen anions only of minor importance. The dynamic polarizabilities of the halogen anions are combined with previously calculated dynamic polarizabilities for rare gas atoms and the molecules CO and N_2 to obtain isotropic and anisotropic dispersion coefficients for the corresponding van der Waals complexes. © *1998 American Institute of Physics.* [S0021-9606(98)02610-5]

I. INTRODUCTION

The static and frequency-dependent multipole polarizabilities of the halogen anions F^-, Cl^-, Br^- and I^- are important properties needed for the modeling of solvent effects on S_N2 reactions and for the modeling of ion-ether interactions.[1] Van der Waals interactions of anions with other atoms or molecules are also important for an understanding of the transport properties of anions.[2] The interaction of halogen anions with rare gas atoms has been studied experimentally for example by inversion of measured ion mobilities[3,4] and diffusion coefficients and by molecular beam scattering experiments.[5,6] Despite the importance of the dynamic polarizabilities of the halogen anions, no reliable *ab initio* calculation exists for these properties. Even for the static polarizabilities only few *ab initio* studies have been published, some of these using insufficient basis sets.

The purpose of the present paper is to present for the first time a systematic *ab initio* study of the frequency-dependent multipole polarizabilities of all four halogen anions F^-, Cl^-, Br^- and I^-. Of great importance for the calculation of these properties is the inclusion of dynamical electron correlation which accounts for a large fraction of the polarizability of anions. For example, for the fluorine anion, the correlation contribution to the static dipole polarizability is more than 35% of the total dipole polarizability. We include electron correlation for the static and the frequency-dependent polarizabilities on equal footing by employing the recently developed time-dependent second-order Møller-Plesset perturbation theory (TDMP2).[7] Within the TDMP2 method the frequency-dependent polarizability is calculated as the second derivative of the real part of the MP2 quasienergy with respect to the strength of two external fields, oscillating with the same frequency. In the static limit this approach becomes equivalent to MP2 finite field calculations. The TDMP2 method has been shown in previous applications to be a valuable tool for the calculation of frequency-dependent polarizabilities.[8–10] For systems, where second-order Møller-Plesset perturbation theory is adequate, we obtained for dynamical polarizabilities and dispersion coefficients accurate results close to or within the experimental uncertainities.

A critical point in the calculation of polarizabilities for anions is the choice of the basis set. Already for the unperturbed anions a sufficient number of diffuse functions has to be included in the basis to obtain an accurate description of its electronic structure. To calculate the polarizability tensors for anions the basis sets must be augmented further with additional diffuse polarization functions with higher angular momenta. To obtain reliable results for the dipole, quadrupole and octupole polarizabilities we use large one-particle basis sets which we have calibrated for polarizability calculations for the anions on the time-dependent Hartree-Fock (TDHF) level. For the Br^- and the I^- anions we include in the calculations scalar relativistic effects variationally through the spin-free no-pair Hamiltonian $\hat{H}_+^{sf1}$, which is obtained by a Douglas-Kroll transformation of the no-pair Hamiltonian correct to second-order in the potential gener-

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ated by the nuclei.[11–15] The important approximations made in this ansatz for the relativistic Hamiltonian are the use of the unmodified nonrelativistic potentials for the electron–electron interaction and the interaction with the external fields. $\hat{H}_+^{sf1}$ averages over the fine-structure components, thus a one-component formalism is retained.

II. THEORY

In response theory, the frequency-dependent polarizability $\alpha_{AB}(-\omega;\omega)$ is usually defined as the linear response of the expectation value $\langle A\rangle$ to a field described by the operator $\hat{B}$, which oscillates with frequency ω.[16] Langhoff, Karplus and Epstein[17] have shown that alternatively frequency-dependent polarizabilities can be calculated as second derivatives of the time-averaged level shift, also known as quasienergy,[18] with respect to the strength of two external fields oscillating with frequencies of the same absolute value but opposite signs. We assume a system described by the Hamiltonian

$$\hat{H}(t)=\hat{H}^{(0)}+\hat{h}^A(\omega,t)+\hat{h}^B(\omega,t), \tag{1}$$

where $\hat{h}^A(\omega,t)$ is defined as

$$\hat{h}^A(\omega,t)=[f_A(\omega)e^{-i\omega t}+f_A(-\omega)e^{+i\omega t}]\hat{A}, \tag{2}$$

and a similar definition holds for $\hat{h}^B(\omega,t)$. The frequency-dependent polarizability can then be calculated as

$$\begin{aligned}\alpha_{AB}(-\omega;\omega)&=-\left.\frac{d^2\{\mathscr{W}\}_T}{df_A(-\omega)df_B(\omega)}\right|_0\\&=-\left.\frac{d^2\bar{\mathscr{W}}}{df_A(-\omega)df_B(\omega)}\right|_0,\end{aligned} \tag{3}$$

where the quasienergy $\{\mathscr{W}\}_T$ is defined as the time-average of the level shift $\bar{\mathscr{W}}(t)$, i.e., the expectation value of the Schrödinger operator $(\hat{H}(t)-i\,d/dt)$ over the phase-isolated wavefunction[18]

$$\{\mathscr{W}\}_T=\lim_{t\to\infty}\int_{-t}^{+t}\bar{\mathscr{W}}(t')dt', \tag{4}$$

$$\bar{\mathscr{W}}(t)=\langle\tilde{\Psi}(t)|\hat{H}(t)-i\,\frac{d}{dt}\,|\tilde{\Psi}(t)\rangle. \tag{5}$$

The phase-isolated wavefunction $\tilde{\Psi}(t)$ is related to the complete time-dependent wavefunction by the transformation

$$\Psi(t)=\exp\left(-i\int_{-\infty}^{t}\bar{\mathscr{W}}(t')dt'\right)\tilde{\Psi}(t), \tag{6}$$

and is required to have always postive real overlap with the time-independent wavefunction of the unperturbed system, described by $\hat{H}^{(0)}$.[17]

The advantage of defining dynamic polarizabilities as second derivatives of the quasienergy (instead as first derivatives of expectation values), is that this definition can straightforwardly be applied to nonvariational approximate wavefunctions for which the Hellman-Feynman theorem does not hold. For such wavefunctions the definition of second-order properties as first derivatives of expectation values would result in an inequivalent treatment of the two involved operators and would consequently break the symmetry

$$\alpha_{AB}(-\omega;\omega)=\alpha_{BA}(\omega;-\omega). \tag{7}$$

In the TDMP2 method a correlation correction to the TDHF frequency-dependent polarizability, correct through second-order in the electron fluctuation potential, is calculated as second derivative of the time-dependent MP2 quasienergy

$$\alpha_{AB}^{\mathrm{TDMP2}}(-\omega;\omega)=\alpha_{AB}^{\mathrm{TDHF}}(-\omega;\omega)+\Delta\alpha_{AB}^{\mathrm{TDMP2}}(-\omega;\omega), \tag{8}$$

$$\Delta\alpha_{AB}^{\mathrm{TDMP2}}(-\omega;\omega)=-\left.\frac{d\Delta\bar{\mathscr{W}}^{\mathrm{MP2}}}{df_A(-\omega)df_B(\omega)}\right|_0, \tag{9}$$

with

$$\Delta\bar{\mathscr{W}}^{\mathrm{MP2}}=Re\langle\tilde{0}|\hat{V}|\tilde{\Psi}_0^{(1)}\rangle. \tag{10}$$

In Eq. (10), $\tilde{0}$ is the TDHF wavefunction which is used as reference state in time-dependent Møller-Plesset perturbation theory and $\tilde{\Psi}_0^{(1)}$ is the first-order perturbation correction for the wavefunction. $\hat{V}$ is the electron fluctuation potential.

To obtain for the second-derivative of the MP2 quasienergy efficient and numerical stable expressions, we used the Lagrangian technique,[19,20] originally developed in the context of geometrical derivatives. The central idea of the Lagrangian technique is to combine the (quasi)energy functional with the equations that determine the wavefunction parameters to a Lagrangian functional which can be required to be stationary in all its variables. This allows to formulate derivatives for nonvariational methods very similar to derivatives for variational methods. The Lagrangian technique leads in particular straightforwardly to numerical stable expressions which do not reference redundant orbital rotation parameters, and it can be shown that a $2n+1$ rule holds for the wavefunction parameters.[19,20] For the Lagrangian multipliers even a $2n+2$ rule holds.[19,20] The resulting expressions for TDMP2 frequency-dependent polarizabilities are detailed in Ref. 7.

If A and B are real electric multipole operators, the polarizability is a real function for pure imaginary or real frequencies with the exception of the poles occuring if the frequency matches an excitation energy. In the normal dispersion region below the first transition frequency, $\alpha_{AB}(-\omega;\omega)$ can be expanded in a Cauchy moment series:

$$\alpha_{AB}(-\omega;\omega)=\sum_{k=0}^{\infty}\omega^{2k}S_{AB}(-2k-2). \tag{11}$$

Eq. (11) is a Taylor expansion of the dynamic polarizability in ω, i.e., the Cauchy moments $S_{AB}(-2k-2)$ with $k \geq 0$ can be calculated as derivatives of $\alpha_{AB}(-\omega;\omega)$. For exact states the Cauchy moments can alternatively be expressed as a sum over states of oscillator strengths multiplied by powers of the transition energies

$$S_{AB}(k) = \sum_{n \neq 0} 2(E_n - E_0)^{k+1} \langle 0|\hat{A}|n\rangle\langle n|\hat{B}|0\rangle$$

$$= \sum_{n \neq 0} (\Delta E_{n0})^k f_{n0}. \qquad (12)$$

In the case of methods for which Cauchy moments are not available analytically, they could in principle be calculated as numerical derivatives of the frequency-dependent polarizabilities. But, as has been pointed out in the literature,[21,22] such a procedure becomes easily numerically unstable due to the singularities of $\alpha_{AB}(-\omega;\omega)$ at the transition frequencies. An alternative possibility is to fit an effective spectrum to the dynamic polarizabilities

$$\alpha_{AB}(-\omega;\omega) = \sum_m \tilde{f}_{AB,m}/(\widetilde{\Delta E}_{AB,m} - \omega^2) \qquad (13)$$

and to calculate the Cauchy moments from the effective oscillator strength distributions via eq. (12). In Ref. 8 it was shown that this procedure gives accurate Cauchy moments $S(k)$ for odd as well as for even $k \leq 0$.

III. TECHNICAL DETAILS

As has been pointed out in the introduction, one of the most critical points in the calculation of polarizabilities for anions is the construction of the one-particle basis sets. Especially if higher-rank polarizabilities are to be computed, standard basis sets, taken from the literature, cannot be used as they stand, but must be augmented carefully with polarization functions with appropriate angular momenta and exponents. For the halogen anions, the main contribution to the polarizability comes from the electrons in the valence s and p shells. Hence, according to group theoretical arguments[8] one needs at least d polarization functions for the dipole polarizability and f functions for the quadrupole polarizability. For the calculation of octupole polarizabilities also g functions must be included in the basis set.

A. Fluorine

For the F^- anion we started with the construction of the basis set from the correlation-consistent aug-cc-pV5Z basis of Woon and Dunning.[23,24] From this basis we took the $(15s9p)/[7s6p]$ subset, which we augmented with three additional diffuse s and p functions with exponents determined by extrapolating the most diffuse exponents of the aug-cc-pV5Z set as even tempered series ($\zeta_s = 0.0278$, 0.0096, 0.0033 and $\zeta_p = 0.0192$, 0.0067, 0.0023). To this set we added eight primitive d functions with the exponents taken from the p orbitals ($\zeta_{d1-d8} = \zeta_{p4-p11}$). The innermost two d functions were contracted with the contraction coefficients determined from those of the first p orbital according to the scheme devised by Sadlej.[25] Furthermore, we added six f functions ($\zeta_{f1-f6} = \zeta_{p6-p11}$) and five g functions ($\zeta_{g1-g5} = \zeta_{p6-p10}$), which were left uncontracted. For the resulting $(18s12p8d6f5g)/[10s9p7d6f5g]$ basis set the CHF dipole and quadrupole polarizabilities differ less than 0.1% from the numerical CHF value, while for the octupole polarizability the remaining basis set error on the CHF level is about 0.25%.

B. Chlorine

The chlorine basis set was constructed in a similar way as the argon basis in Ref. 8. We started again from the correlation-consistent aug-cc-pV5Z basis of Woon and Dunning,[23] from which we took the $(21s13p)/[8s7p]$ subset and augmented it with four diffuse s and p functions ($\zeta_s = 0.0183$, 0.0070, 0.0027, 0.0010 and $\zeta_p = 0.0130$, 0.0049, 0.0018, 0.0007). Furthermore, we included ten d functions ($\zeta_{d1-d10} = \zeta_{p6-p15}$), seven f functions ($\zeta_{f1-f7} = \zeta_{p9-p15}$) and six g functions ($\zeta_{g1-g6} = \zeta_{p9-p14}$), which were left uncontracted. We obtained a $(25s17p10d7f6g)/[14s13p10d7f6g]$ basis which on the CHF level gives dipole, quadrupole and octupole polarizabilities within 0.1% of the numerical Hatree-Fock values (cmp. Table II).

C. Bromine

For the bromine atom we started from the $(26s20p14d)$ primitive Gaussian Well-Tempered Formula (WTF) basis from Huzinaga and Klobukowski.[26] In the WTF basis sets the same exponents are used for all angular momenta. This basis set was first contracted, using a generalized contraction scheme with SCF orbital coefficients, to a $[4s3p1d] + (9s8p6d)$ set, where $(9s8p6d)$ denotes the outermost primitive functions which have been left uncontracted. We augmented this basis by four diffuse s functions with exponents determined by extrapolating the outermost s functions as even-tempered series. Futhermore, we added four diffuse p and six diffuse d functions. Finally, we included six f functions ($\zeta_{f1-f6} = \zeta_{s23-s28}$) and five g functions ($\zeta_{g1-g5} = \zeta_{s23-s27}$) which were left uncontracted. For the relativistic calculations we constructed a completely analogous second basis set, using the same exponents but contraction coefficients determined from a relativistic SCF calculation. Within the WTF scheme for the determination of the exponents, these basis sets give CHF dipole, quadrupole and octupole polarizabilities converged within 0.05%. Numerical Hartree-Fock values for the polarizabilities of the bromide anion have not been published in the literature, but from our experience with the WTF basis sets for the rare gas atoms Kr and Xe[8] we expect the remaining basis set errors for α_1, α_2 and α_3 to be less than 0.1%.

D. Iodine

For the iodine atom we use again the WTF basis set, which in this case consists of a $(28s23p17d)$ set of primitive Gaussians. This basis set was first contracted, using again a generalized contraction scheme and SCF orbital coefficients, to a $[5s4p2d] + (10s8p6d)$ set. To this basis we added four

TABLE I. Static dipole, quadrupole and octupole polarizabilities and Cauchy moments for the flourine anion (in a.u.).

	TDHF	TDMP2	Literature
α_1	10.660	16.65	18.84,[b] 18.99[c]
	10.66[a]		17.96,[d] 17.15[e]
α_2	76.63	142.53	108.15[b]
	76.68[a]		
α_3	1176	2874	
	1179[a]		
$S_1(0)$	9.667	9.667	10.00[f]
$S_1(-1)$	6.628	7.738	
$S_1(-3)$	27.22	56.54	
$S_1(-4)$	89.87	235.8	
$S_2(0)$	31.62	35.16	
$S_2(-1)$	37.37	53.09	
$S_2(-3)$	217.6	510.7	
$S_2(-4)$	737.4	2111	
$S_3(0)$	313.2	477.8	
$S_3(-1)$	511.2	974.5	
$S_3(-3)$	3311	10027	
$S_3(-4)$	10607	38616	

[a]Numerical coupled Hartree-Fock, Ref. 40.
[b]CCSDT-1, $[6s5p3d1f]$ basis, the SCF results in the same basis set are: $\alpha_1=10.40$ a.u., $\alpha_2=50.46$ a.u., Ref. 32.
[c]CCSD+T(4), Ref. 44.
[d]QCISD(T), uncontracted $(14s9p6d2f)$ basis, SCF: $\alpha_1=10.91$ a.u., MP2: $\alpha_1=17.19$ a.u., MP3: $\alpha_1=12.86$ a.u., MP4: $\alpha_1=21.05$ a.u., Ref. 36.
[e]CCSD(T), SCF: $\alpha_1=10.67$ a.u., MP2: $\alpha_1=16.73$ a.u., Ref. 23.
[f]Exact value corresponding to the Thomas-Reiche-Kuhn sum rule.

diffuse s and p functions with exponents chosen as even-tempered extrapolation of the outermost WTF exponents. Furthermore we added six d functions ($\zeta_{d18-d23}=\zeta_{s26-s31}$), nine f functions ($\zeta_{f1-f9}=\zeta_{s22-s30}$) and five g functions ($\zeta_{g1-g5}=\zeta_{s24-s28}$), which were left uncontracted.

TABLE II. Static dipole, quadrupole and octupole polarizabilities and Cauchy moments for the chlorine anion (in a.u.).

	TDHF	TDMP2	Literature
α_1	31.552	36.997	37.43,[b] 38.01[c]
	31.55[a]		
α_2	317.9	399.7	423[c]
	317.9[a]		
α_3	7380	10326	
	7384[a]		
$S_1(0)$	17.90	17.90	18.00[d]
$S_1(-1)$	13.59	14.33	
$S_1(-3)$	100.6	135.0	
$S_1(-4)$	394.0	605.7	
$S_2(0)$	75.58	77.78	
$S_2(-1)$	126.3	141.2	
$S_2(-3)$	1058	1504	
$S_2(-4)$	18644	6712	
$S_3(0)$	1156	1509	
$S_3(-1)$	2521	3209	
$S_3(-3)$	25842	40590	
$S_3(-4)$	428000	178317	

[a]Numerical coupled Hartree-Fock, Ref. 40.
[b]CCSD(T), SCF: $\alpha_1=31.48$ a.u., MP2: $\alpha_1=37.09$ a.u., Ref. 23.
[c]MBPT(4), SCF: $\alpha_1=31.49$ a.u., $\alpha_2=317.8$ a.u., Ref. 33.
[d]Exact value corresponding to the Thomas-Reiche-Kuhn sum rule.

TABLE III. Static dipole, quadrupole and octupole polarizabilities and Cauchy moments for the bromine anion (in a.u.). Listed are the results of calculations including scalar relativistic effects, the percentage relativistic effect on the results $(X_{\text{rel}}-X_{\text{non-rel}})/X_{\text{rel}}\times 100\%$ is given in parentheses.

	TDHF	TDMP2	Literature
α_1	43.305 (1.0)	49.05 (1.3)	8.71[a]
α_2	496.1 (0.7)	588.2 (1.1)	378.1[a]
α_3	13363 (1.4)	16874 (2.0)	
$S_1(0)$	22.45 (−0.8)	22.45 (−0.8)	36.00[b]
$S_1(-1)$	16.77 (0.2)	17.53 (0.3)	
$S_1(-3)$	153.1 (2.4)	192.8 (2.9)	
$S_1(-4)$	663.5 (4.1)	929.6 (4.6)	
$S_2(0)$	94.88 (−0.9)	97.71 (−0.8)	
$S_2(-1)$	178.7 (−0.4)	194.3 (−0.2)	
$S_2(-3)$	1803 (2.1)	2344 (2.5)	
$S_2(-4)$	7796 (3.4)	11074 (3.9)	
$S_3(0)$	1689 (−0.7)	1972 (−0.2)	
$S_3(-1)$	4113 (0.3)	4790 (0.8)	
$S_3(-3)$	51654 (2.5)	71443 (3.2)	
$S_3(-4)$	222370 (3.6)	336709 (4.4)	

[a]SCF, Ref. 37.
[b]Exact value corresponding to the Thomas-Reiche-Kuhn sum rule.

For the resulting $(32s27p23d9f5g)/[19s16p14d9f5g]$ basis set, the dipole, quadrupole and octupole polarizabilities were on the CHF level converged within 0.1% with respect to augmentation with further diffuse or steep primitive functions.

In the TDMP2 calculations we correlated all electrons, no frozen-core approximation was used. For all four halogen anions we calculated frequency-dependent dipole, quadrupole and octupole polarizabilities, which we combined with

TABLE IV. Static dipole, quadrupole and octupole polarizabilities and Cauchy moments for the iodine anion (in a.u.). Listed are the results of calculations including scalare relativistic effects, the percentage relativistic effect on the results $(X_{\text{rel}}-X_{\text{non-rel}})/X_{\text{rel}}\times 100\%$ is given in parentheses.

	TDHF	TDMP2	Literature
α_1	63.276 (1.2)	69.34 (1.9)	55.75,[a] 70.2[b]
α_2	875.0 (−0.4)	990.0 (0.5)	797.9[a]
α_3	27957 (0.6)	32587 (2.1)	
$S_1(0)$	34.51 (−0.1)	34.51 (−0.1)	54.00[d]
$S_1(-1)$	23.53 (0.3)	24.26 (0.5)	
$S_1(-3)$	248.1 (3.6)	296.0 (4.7)	
$S_1(-4)$	1179 (6.7)	1538 (8.0)	
$S_2(0)$	135.4 (−2.6)	141.6 (−2.3)	
$S_2(-1)$	282.9 (−2.3)	299.9 (−1.6)	
$S_2(-3)$	3471 (2.1)	4230 (3.2)	
$S_2(-4)$	16284 (4.7)	21339 (5.8)	
$S_3(0)$	2658 (−2.7)	4396 (−1.4)	
$S_3(-1)$	7613 (−1.2)	8750 (−0.2)	
$S_3(-3)$	120490 (2.5)	149322 (4.2)	
$S_3(-4)$	575030 (4.4)	764582 (6.3)	

[a]SCF, Ref. 37.
[b]MP2, ECP with a $[4sp3d]$ basis, Ref. 1.
[c]Empirical estimate, Ref. 39.
[d]Exact value corresponding to the Thomas-Reiche-Kuhn sum rule.

TABLE V. Dispersion coefficients for halogen anion-rare-gas interactions. If available, the percentage relativistic corrections $\Delta_{rel}=(X_{rel}-X_{non\text{-}rel})/X_{rel}\times 100\%$ are given in parentheses.

	C_6			C_8			C_{10}		
	TDHF	TDMP2	Lit.	TDHF	TDMP2	Lit.	TDHF	TDMP2	Lit.
F^-–He	7.1693	9.3651	7.83,[a]7.18[b]	147.69	225.1	165[a]	4411.4	8556.9	4450[a]
F^-–Ne	13.858	19.421	16.3[a]	310.76	509.64	358[a]	9607.1	19954	9810[a]
F^-–Ar	49.685	66.396	55.2[a]	1423.9	2137.9	1530[a]	52585	94166	52100[a]
F^-–Kr	71.277	95.157		2244	3324.7		90277	155580	
F^-–Xe	107.01(−1.0)	143.2(−0.7)		3883.5(−3.3)	5661.9(−2.7)				
F^-–Rn	127.1(−3.2)	170.33(−2.2)							
Cl^-–He	17.341	19.136	19.8,[a]17.4[c]	500.79	584.95	530[a]	20977	27105	16760[a]
Cl^-–Ne	32.87	39.374	40.7[a]	1016.8	1296.3	1120[a]	43526	61590	36050[a]
Cl^-–Ar	123.76	137.71	142,[a] 251[d]	4533.3	5299.4	4780[a]	218950	276990	18700[a]
Cl^-–Kr	179.19	198.16		7059.4	8158.8		361880	447700	
Cl^-–Xe	271.81(−1.0)	299.49(−0.7)		12009(−2.9)	13699(−2.4)				
Cl^-–Rn	323.58(−3.4)	356.53(−2.3)							
Br^-–He	22.153(0.3)	24.047(0.5)		716.23(−0.2)	809.5(0.1)		34120(0.5)	40856(0.9)	
Br^-–Ne	41.845(0.3)	49.397(0.5)		1438.9(−0.2)	1779.3(0.1)		69725(0.4)	91837(0.8)	
Br^-–Ar	159.18(0.4)	173.94(0.5)		6379.5(0.0)	7230.2(0.3)		342890(0.4)	407790(0.8)	
Br^-–Kr	231.04(0.4)	250.74(0.5)		9899.1(0.0)	11096(0.3)		560150(0.4)	654320(0.8)	
Br^-–Xe	351.56(−0.7)	379.78(−0.2)		16745(−2.7)	18540(−2.0)				
Br^-–Rn	418.92(−3.1)	452.4(−1.8)							
I^-–He	30.095(0.2)	32.066(0.5)		1145.1(−1.8)	1255.3(−1.1)		63354(−0.9)	72762(0.1)	
I^-–Ne	56.835(0.2)	65.916(0.5)		2271(−1.7)	2728.3(−1.0)		127390(−1.0)	161320(0.0)	
I^-–Ar	217.27(0.2)	232.73(0.6)		9975.2(−1.4)	10979(−0.7)		612170(−0.9)	699570(0.0)	
I^-–Kr	316.1(0.2)	336.05(0.6)		15392(−1.3)	16761(−0.6)		987120(−0.9)	1109600(0.0)	
I^-–Xe	482.51(−0.8)	510.2(−0.1)	1540[d]	25804(−3.7)	27776(−2.6)				
I^-–Rn	575.6(−3.3)	608.27(−1.7)							

[a]Slater-Kirkwood formula and numerical CHF polarizabilities, Ref. 2.
[b]Ref. 42.
[c]Ref. 43.
[d]Ref. 1.

polarizabilities for rare gas atoms from Refs. 7, 8 and with the polarizabilities for CO and N_2 from Ref. 9 to obtain dispersion coefficients for the corresponding van der Waals pair interactions. For the atom-atom and atom-diatom complexes we give the dispersion coefficients in the LLM convention,[27,28] which is defined by an expansion of the dispersion energy in Legendre polynomials[29]

$$E^{(\mathrm{disp})}=-\sum_{n=0}^{\infty} R^{-n}\sum_{L=0}^{n-4} C_n^{(L)} P_L(\cos\Theta). \tag{14}$$

To evaluate the Casimir-Polder integrals which occur in the calculation of the dispersion coefficients, we used the numerical N-point Gauss-Chebyshev quadrature described in Ref. 30

$$\frac{1}{2\pi}\int_0^{\infty}\alpha^A(i\omega)\alpha^B(i\omega)d\omega \approx \frac{1}{4N}\sum_{j=1}^{N}\frac{\alpha^A(i\cot\phi_j)\alpha^B(i\cot\phi_j)}{\sin^2\phi_j}, \tag{15}$$

with grid points $\phi_j=\pi(2j-1)/4N$. As in our previous work on the rare gas atoms and the molecules CO and N_2, we calculated the polarizabilities for the halogen anions at the frequencies $\cot\phi_j$ for grids with $N=10$, 15 and 20. Comparison of the dispersion coefficients obtained with 15 and 20 grid points indicate that the numerical integration was converged within the number of digits given in Tables I–XI. To the TDMP2 results for the static polarizabilities and the dynamic polarizabilities at these totally 45 grid points we fitted effective spectra that reproduce the calculated polarizabilities with relative errors less than 10^{-5}. The effective oscillator strength distributions are given in Tables VIII–XI. From the effective spectra we calculated TDMP2 Cauchy moments for $k=0$, -1, -3 and -4. The TDHF Cauchy moments were calculated analytically.[31]

IV. RESULTS AND DISCUSSION

In Tables I–IV we have compiled the Hartree-Fock and MP2 results for the polarizabilities and the Cauchy moments $S(0)$ through $S(-4)$. As mentioned in the introduction, only very few accurate *ab initio* studies on the polarizabilities of the halogen anions are available in the literature. For the

TABLE VI. Dispersion coefficients for halogenid anion complexes of N_2 (LLM convention, a.u.). If available, the relativistic correction $(X_{rel} - X_{non\text{-}rel})/X_{rel} \times 100\%$ is given in parentheses.

n	L	TDHF	TDMP2
	$F^- \cdot N_2$		
	0	53.75	69.50
6	2	6.54	7.40
8	0	1765	2604
8	2	1024	1566
8	4	−40	−62
10	0	68311	119400
10	2	51143	88279
10	4	5021	7295
10	6	−423	−620
	$Cl^- \cdot N_2$		
6	0	133.52	143.84
6	2	16.93	15.58
8	0	5466	6310
8	2	2638	3324
8	4	−111	−136
10	0	273560	341960
10	2	164420	219810
10	4	11082	14071
10	6	−1156	−1347
	$Br^- \cdot N_2$		
6	0	171.67 (0.3)	181.58 (0.5)
6	2	21.98 (0.4)	19.77 (0.6)
8	0	7623 (0.0)	8531 (0.3)
8	2	3451 (0.3)	4248 (0.6)
8	4	−147 (0.7)	−175 (0.7)
10	0	422700 (0.3)	497990 (0.3)
10	2	233240 (0.1)	301020 (0.3)
10	4	13429 (0.4)	17015 (0.5)
10	6	−1524 (0.5)	−1738 (0.7)
	$I^- \cdot N_2$		
6	0	234.31 (0.3)	242.91 (0.6)
6	2	30.20 (0.2)	26.51 (0.6)
8	0	11771 (−1.2)	12774 (−0.6)
8	2	4851 (−0.1)	5807 (0.4)
8	4	−206 (0.5)	−240 (0.8)
10	0	743400 (−1.0)	840770 (−0.1)
10	2	368970 (−1.2)	460430 (−0.5)
10	4	16526 (1.0)	20902 (1.1)
10	6	−2126 (0.3)	−2373 (0.9)

TABLE VII. Dispersion coefficients for halogenid anion complexes of CO (LLM convention). If available, the relativistic correction $(X_{rel} - X_{non\text{-}rel})/X_{rel} \times 100\%$ is given in parentheses.

n	L	TDHF	TDMP2
	$F^- \cdot CO$		
	0	54.71	74.97
6	2	4.71	6.86
7	1	−154.3	−238.1
7	3	11.4	13.6
8	0	1987	3026
8	2	1503	2110
8	4	−79	−107
9	1	−9522	−15181
9	3	−3515	−4393
9	5	244	295
10	0	81757	145960
10	2	83284	129740
10	4	10137	12437
10	6	−785	−918
	$Cl^- \cdot CO$		
6	0	136.65	155.80
6	2	12.01	14.41
7	1	−406.4	−506.3
7	3	32.1	29.9
8	0	6087	7283
8	2	3876	4480
8	4	−222	−234
9	1	−28880	−36150
9	3	−8768	−9074
9	5	683	644
10	0	318620	411360
10	2	263500	319160
10	4	23336	24228
10	6	−2199	−2002
	$Br^- \cdot CO$		
6	0	175.98 (0.4)	197.04 (0.5)
6	2	15.51 (0.4)	18.26 (0.5)
7	1	−530.2 (0.4)	−645.9 (0.6)
7	3	42.7 (0.5)	38.9 (1.0)
8	0	8457 (0.1)	9827 (0.3)
8	2	5049 (0.3)	5724 (0.5)
8	4	−296 (0.7)	−302 (0.7)
9	1	−40024 (0.2)	−48697 (0.4)
9	3	−11194 (0.4)	−11399 (0.6)
9	5	909 (0.6)	836 (0.8)
10	0	487890 (0.3)	596020 (0.7)
10	2	370960 (0.4)	435290 (0.4)
10	4	28674 (0.4)	29413 (0.5)
10	6	−2926 (0.6)	−2595 (0.8)
	$I^- \cdot CO$		
	0	240.58 (0.2)	264.03 (0.6)
6	2	21.19 (0.2)	24.45 (0.6)
7	1	−732.0 (0.2)	−871.3 (0.7)
7	3	60.4 (0.5)	53.6 (1.1)
8	0	12975 (−1.1)	14658 (−0.5)
8	2	7019 (0.0)	7794 (0.5)
8	4	−417 (0.5)	−415 (1.0)
9	1	−61020 (−0.8)	−72327 (0.2)
9	3	−14972 (0.4)	−14986 (0.8)
9	5	1283 (0.4)	1149 (1.0)
10	0	849030 (−1.0)	997710 (0.1)
10	2	579610 (−1.1)	660680 (0.5)
10	4	35878 (1.0)	36252 (1.1)
10	6	−4127 (0.4)	−3565 (1.0)

dipole polarizabilities of F^- and Cl^- the most reliable correlated reference data are the results of a basis set investigation by Woon and Dunning.[23] This study was based on series of correlation consistent basis sets and several *ab initio* methods. For both anions F^- and Cl^- our MP2 results of 16.65 a.u. and 37.00 a.u. are in very good agreement with the respective MP2 results of Woon and Dunning (16.73 a.u. and 37.09 a.u.). For the quadrupole polarizability of F^- the only result of a correlated ab initio calculation is the CCSDT-1 value of Pluta *et al.*,[32] which was performed in a rather small basis set which on the SCF level gave only two-thirds of the numerical Hartree-Fock result. Nevertheless, the relative cor-

TABLE VIII. Effective spectra for the dynamic dipole, quadrupole and octupole polarizabilities of the fluorine anion. (Powers of 10 are indicated in parentheses.)

	α_1	α_2	α_3
f_1	9.186273(−2)	3.298575(−1)	1.599909(+1)
ϵ_1	1.784498(−1)	1.773982(−1)	1.945906(−1)
f_2	2.398361(−1)	2.935615	8.502411(+1)
ϵ_2	2.185985(−1)	2.131759(−1)	2.487039(−1)
f_3	7.504246(−1)	8.012698	1.810964(+2)
ϵ_3	3.805631(−1)	3.915981(−1)	4.332883(−1)
f_4	1.687140	1.090383(+1)	1.121556(+2)
ϵ_4	7.956409(−1)	9.150951(−1)	1.044901
f_5	2.641830	9.504449	2.151572(+1)
ϵ_5	1.841355	2.156569	1.953074
f_6	1.965837	3.116884	4.534428(+1)
ϵ_6	4.109096	4.866098	3.633246
f_7	7.293837(−1)	3.548376(−1)	1.670919(+1)
ϵ_7	9.842024	1.098564(+1)	1.008650(+1)
f_8	1.561090		
ϵ_8	3.331431(+1)		

TABLE X. Effective spectra for the dynamic dipole, quadrupole and octupole polarizabilities of the bromine anion. (Powers of 10 are indicated in parentheses.)

	α_1	α_2	α_3
f_1	2.261308(−1)	1.042253	3.648000(+1)
ϵ_1	1.466781(−1)	1.427353(−1)	1.503828(−1)
f_2	7.421557(−1)	6.034683	2.835163(+2)
ϵ_2	2.197321(−1)	1.811943(−1)	1.949057(−1)
f_3	1.954419	1.649217(+1)	4.998691(+2)
ϵ_3	3.701506(−1)	2.859505(−1)	2.998718(−1)
f_4	3.126125	2.564170(+1)	4.698164(+2)
ϵ_4	6.495011(−1)	4.898389(−1)	5.163191(−1)
f_5	1.734103	3.019773(+1)	3.505863(+2)
ϵ_5	1.143779	8.791300(−1)	9.307894(−1)
f_6	2.203026	1.301578(+1)	1.832128(+2)
ϵ_6	3.994408	1.548280	1.692023
f_7	3.095769	2.853920	1.070188(+2)
ϵ_7	1.056841(+1)	3.915097	3.927333
f_8	9.369272	2.429146	4.195897(+1)
ϵ_8	6.007640(+1)	1.102020(−1)	1.032263(+1)

relation effect of about 100% of the SCF value is in fair agreement with the result of our calculation. For the Cl^- anion the TDMP2 value for α_2 is slightly smaller than the MBPT(4) result of Ref. 33.

If one compares the MP2 results with the CCSD(T) values of Ref. 23, which can be expected to be close to the exact results, one observes that second-order Møller-Plesset perturbation theory underestimates the correlation contribution to the dipole polarizability of the halogen anions by a few percent. This is very similar to what was found for the rare gas atoms[8,23,34] and shows that MP2 gives a balanced description of the correlation effects on the halogen anion polarizabilities although the Møller-Plesset perturbation series is known to diverge, for example, for F^- in basis sets containing diffuse polarization functions.[35] The influence of this divergence can be seen from the large oscillations from the MP2 to the MP3 and MP4 results for the F^- dipole polarizability from Canuto:[36] MP3 results in a large underestimation of the correlation contribution and MP4 gives a much too large result. But despite of these divergences of higher-order MPn calculations, MP2 gives usually a very good approximation of the correlation energy as long as the ground state is single configuration dominated and static correlation effects are unimportant.[35]

Only very little data is available about the polarizabilities of the heavier halogen anions Br^- and I^-. Schmidt *et al.*[37] have performed CPHF calculations for the static dipole and quadrupole polarizabilities for these anions, but because they used insufficient basis sets their results are considerably smaller than the present TDHF results. Recently Smith *et al.*[1] have calculated the static dipole polarizability of I^- using an effective-core potential and second-order Møller-Plesset perturbation theory. Their result of 70.2 a.u. is in very good agreement with our relativistic TDMP2 result of 69.34 a.u. The scalar relativistic effects on the polarizabilities of Br^- and I^- are for all three investigated multipole

TABLE IX. Effective spectra for the dynamic dipole, quadrupole and octupole polarizabilities of the chlorine anion. (Powers of 10 are indicated in parentheses.)

	α_1	α_2	α_3
f_1	2.001187(−1)	1.413596(−1)	3.220807
ϵ_1	1.584287(−1)	1.388873(−1)	1.422493(−1)
f_2	5.588341(−1)	4.016603	1.513546(+2)
ϵ_2	2.312736(−1)	1.768064(−1)	1.899748(−1)
f_3	1.077637	1.435356(+1)	4.086372(+2)
ϵ_3	3.558200(−1)	2.914559(−1)	3.002385(−1)
f_4	2.547837	2.683830(+1)	1.627807(+2)
ϵ_4	5.754114(−1)	5.908663(−1)	4.920071(−1)
f_5	2.264499	2.016304(+1)	3.686016(+2)
ϵ_5	1.006611	1.145430	7.541917(−1)
f_6	9.811278(−1)	6.603153	2.943912(+2)
ϵ_6	3.509194	1.661539	1.622079
f_7	5.894057	3.347459	9.103282(+1)
ϵ_7	1.066701(+1)	2.353265	3.580909
f_8	4.377888	2.318280	2.917301(+1)
ϵ_8	4.071300(+1)	1.164236(+1)	1.625270(+1)

TABLE XI. Effective spectra for the dynamic dipole, quadrupole and octupole polarizabilities of the iodine anion. (Powers of 10 are indicated in parentheses.)

	α_1	α_2	α_3
f_1	2.639129(−1)	2.515097	82.89991(+1)
ϵ_1	1.354797(−1)	.1364907(−1)	.1413645(−1)
f_2	9.558996(−1)	10.06883(+1)	460.1086(+2)
ϵ_2	2.041515(−1)	.1818766(−1)	.1834872(−1)
f_3	2.523500	24.30429(+1)	769.4404(+2)
ϵ_3	3.444783(−1)	.2795619(−1)	.2751810(−1)
f_4	3.327651	35.17953(+1)	769.4446(+2)
ϵ_4	6.061091(−1)	.4576547(−1)	.4723180(−1)
f_5	1.242448	39.29400(+1)	800.4972(+2)
ϵ_5	1.248504	.7796686(−1)	.8670053(−1)
f_6	8.772360	11.91753(+1)	267.1129(+2)
ϵ_6	3.424812	1.366643	1.931458
f_7	7.242397	7.472341	622.3568(+2)
ϵ_7	6.794417	3.778580	5.508854
f_8	1.017983(+1)	10.86403(+1)	624.4969(+2)
ϵ_8	5.379941(+1)	8.757904	11.06851(+1)

components small and positive, i.e., the relativistic effects increase the polarizabilities. This is different from what was found in Refs. 8, 38 for the rare gas atoms, where the inclusion of scalar relativistic effects lead to a decrease of the polarizabilities. The relativistic increase of the polarizabilities for the Br^- and I^- anions can be explained by a decrease of the first excitation energies, when the scalar relativistic effects are included in the calculations.

No accurate experimental data is available in the literature for the polarizabilities of the halogen anions. Some empirical estimates from Coher[39] for the dipole polarizabilities (F^-: 9.31 a.u., Cl^-: 26.59 a.u., Br^-: 35.22 a.u., I^-: 52.7 a.u.) disagree significantly from the TDMP2 and other correlated results and we conclude that they are inaccurate.

For the dispersion coefficients of halogen anion–rare gas interactions some reference data is available from the work of Ahlrichs *et al.*,[2] who used the CHF polarizabilities of Ref. 40 and the Slater-Kirkwood formula[41] to estimate dispersion coefficients for the interaction of F^- and Cl^- with He, Ne and Ar. As can be seen from Table V, the results of these estimates are in most cases halfway between our TDHF and TDMP2 results. Only for the C_6 coefficients for the interaction of Cl^- with He, Ne, Ar are these estimates slightly larger than the TDMP2 results, while for the C_{10} coefficients for $Cl^-\cdot X$ (X=He,Ne,Ar) complexes these estimates are too small. The C_6 dispersion coefficients for $F^-\cdot He$ and $Cl^-\cdot He$ calculated by Fowler and Hutson[42] and Hutson and Fowler[43] are very similar to our TDHF results for the C_6 coefficients. Smith *et al.*[1] have determined C_6 coefficients for $Cl^-\cdot Ar$ and $I^-\cdot Xe$ by fits to the long-range part of a supermolecular MP2 calculation. These coefficients overshoot our results for the C_6 coefficients for $Cl^-\cdot Ar$ and $I^-\cdot Xe$ by a factor of 2 and 3, respectively, which is probably caused by the neglect of the higher (C_8,C_{10}) dispersion coefficients in the fit to the MP2 potential curve.

According to the accuracy we obtained for the polarizabilities, we expect the TDMP2 values for the dispersion coefficients for the halogen anion–rare gas dimers to be accurate within ca. 2%–5% depending on the interacting atoms and the rank of the coefficients. For the interactions involving the F^- anion, for which higher-order correlation effects are significant, and for the C_{10} coefficients the errors are probably close to 5%, while for the C_6 and C_8 coefficients of the complexes with heavier halogen anions the errors will be smaller.

A similar accuracy is expected for the isotropic dispersion coefficients for the van der Waals complexes of the halogen anions with N_2 and CO. The anisotropic coefficients will be slightly less accurate because of larger errors in the anisotropic polarizability components of N_2 and CO.

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[1] G. D. Smith, R. L. Jaffe, and H. Partridge, J. Phys. Chem. **101**, 1705 (1997).
[2] R. Ahlrichs, H. J. Böhm, S. Brode, K. T. Tang, and J. P. Toennies, J. Chem. Phys. **88**, 6290 (1988).
[3] L. A. Viehland, Chem. Phys. **78**, 279 (1983).
[4] L. A. Viehland, Chem. Phys. **85**, 295 (1984).
[5] E. Böttner, W. L. Dimpl, U. Ross, and J. P. Toennies, Chem. Phys. Lett. **32**, 197 (1975).
[6] F. E. Budenholzer, E. A. Gislason, and A. D. Jorgensen, J. Chem. Phys. **66**, 4832 (1977).
[7] C. Hättig and B. A. Heß, Chem. Phys. Lett. **233**, 359 (1995).
[8] C. Hättig and B. A. Heß, J. Phys. Chem. **100**, 6243 (1996).
[9] C. Hättig and B. A. Heß, J. Chem. Phys. **105**, 9948 (1996).
[10] C. Kunz, C. Hättig, and B. A. Heß, Mol. Phys. **89**, 139 (1996).
[11] B. A. Heß, C. M. Marian, and S. D. Peyerimhoff, in, *Modern Electronic Structure Theory*, edited by D. R. Yarkony (World Scientific, Singapore, 1995), Chapter, ''*Ab initio* Calculation of Spin-Orbit Effects in Molecules Including Electron Correlation.''
[12] J. Sucher, Phys. Rev. A **22**, 348 (1980).
[13] W. Buchmüller and K. Dietz, Z. Phys. C **5**, 45 (1980).
[14] B. A. Heß, Phys. Rev. A **33**, 3742 (1986).
[15] G. Jansen and B. A. Heß, Phys. Rev. A **39**, 6016 (1989).
[16] J. Olsen and P. Jørgensen, J. Chem. Phys. **82**, 3235 (1985).
[17] P. W. Langhoff, S. T. Epstein, and M. Karplus, Rev. Mod. Phys. **44**, 602 (1972).
[18] H. Sambe, Phys. Rev. A **7**, 2203 (1972).
[19] T. Helgaker and P. Jørgensen, Theor. Chim. Acta **75**, 111 (1989).
[20] P. Jørgensen and T. Helgaker, J. Chem. Phys. **89**, 1560 (1988).
[21] G. D. Zeiss and W. J. Meath, Mol. Phys. **30**, 161 (1975).
[22] U. Hohm, Mol. Phys. **78**, 929 (1993).
[23] D. E. Woon and T. H. Dunning, J. Chem. Phys. **100**, 2975 (1994).
[24] Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. PNL is a multiprogram laboratory operated by Batelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830.
[25] A. J. Sadlej, Theor. Chim. Acta **79**, 123 (1991).
[26] S. Huzinaga and M. Klobukowski, Chem. Phys. Lett. **212**, 260 (1993).
[27] A. J. Thakkar, H. Hettema, and P. E. S. Wormer, J. Chem. Phys. **97**, 3252 (1992).
[28] H. Hettema, P. E. S. Wormer, and A. J. Thakkar, Mol. Phys. **80**, 533 (1993).
[29] R. T Pack, J. Chem. Phys. **64**, 1659 (1976).
[30] W. Rijks and P. E. S. Wormer, J. Chem. Phys. **88**, 5704 (1988).
[31] B. Silvi and N. Fourati, Mol. Phys. **52**, 415 (1984).
[32] T. Pluta, J. Noga, and R. J. Bartlett, Int. J. Quantum Chem. **S28**, 379 (1994).
[33] V. Kellö, B. O. Roos, and A. J. Sadlej, Theor. Chim. Acta **74**, 185 (1988).
[34] J. Rice and N. C. Handy, Int. J. Quantum Chem. **43**, 91 (1992).
[35] J. Olsen, O. Christiansen, H. Koch, and P. Jørgensen, J. Chem. Phys. **105**, 5082 (1996).
[36] S. Canuto, Int. J. Quantum Chem. **S28**, 265 (1994).
[37] P. C. Schmidt, A. Weiss, and T. P. Das, Phys. Rev. B **19**, 5525 (1979).
[38] A. Nicklass, M. Dolg, and H. Preuss, J. Chem. Phys. **102**, 8942 (1995).
[39] Coher, J. Phys. Chem. **80**, 2078 (1976).
[40] R. P. McEachran, A. D. Stauffer, and S. Greita, J. Phys. B **12**, 3119 (1979).
[41] J. C. Slater and J. G. Kirkwood, Phys. Rev. **32**, 682 (1931).
[42] P. W. Fowler and J. M. Hutson, Phys. Rev. B **33**, 3724 (1986).
[43] J. M. Hutson and P. W. Fowler, Surf. Sci. **174**, 337 (1986).
[44] S. A. Kucharski, Y. S. Lee, G. D. Purvis III, and R. J. Bartlett, Phys. Rev. A **29**, 1619 (1984).