Relativistic effects on the electric polarizabilities and their geometric derivatives for hydrogen halides and dihalogens – a Dirac–Hartree–Fock study

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Abstract

The geometric derivatives of the static and dynamic electric dipole polarizability have been calculated at the all-electron Dirac–Hartree–Fock level for the dihalogen molecules F_2, Cl_2, Br_2, and I_2 and for the hydrogen halides HF, HCl, HBr, and HI. A comparison with the non-relativistic Hartree–Fock values shows that the relativistic corrections tend to be larger for the geometric derivatives of the polarizabilities than for the polarizabilities. The frequency dispersion of the corrections due to relativity is significant for the molecules containing bromine and iodine. As expected, for the same molecules relativistic effects are sizable, and they improve the agreement between theory and experiment for the electric dipole polarizabilities. In the case of the Raman scattering cross sections, only a few experimental data are available. In general the relativistic effects are in this case within the range of the experimental error.
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1. Introduction

There is much interest nowadays in developing computational methods capable of handling relativistic effects on the optical, electric and magnetic properties [1–9]. Fully relativistic four-component ab initio calculations have been performed for example for vibrational frequencies [5,6], molecular polarizabilities [1–4], electric field gradients [7], nuclear spin–spin coupling constants [8,9] and NMR shielding constants [9]. The relativistic effects are of special interest in particular for the optical properties, since much work is devoted to the development of inorganic materials with special optical performances, and many of these materials include heavy elements, where relativistic effects play a crucial role. Optical properties such as the electric dipole polarizability depend mainly on the outer shell electronic structure while the relativistic effects are more important for the core electrons. However, they influence indirectly the valence electron density, which in turn affects the optical properties [3].

There are several four-component studies on the relativistic effects on the electric dipole

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polarizabilities in the literature, see for instance [1–4]. However, to our knowledge, fully relativistic calculations have never been performed for the geometric derivatives of the polarizabilities, properties determining the vibrational Raman spectra. On the other hand, as a consequence of progress in experimental Raman spectroscopy stimulated by the advances in laser techniques, computational methods for calculating the Raman intensities are currently being intensively developed [10–14].

In our previous papers [13,14] we have studied the effects of optical dispersion and electronic correlation on the Raman scattering cross sections [13,14], and investigated the basis set requirements [13] for a few diatomic molecules. We extend here this investigation to another aspect of the ab initio calculations: relativistic effects. The main purpose of the present study is to check how the relativistic effects influence geometric derivatives of the polarizabilities, as compared to their importance for the polarizabilities. We focus also on the frequency dispersion of the relativistic corrections, a problem rarely considered to date [2]. Two groups of molecules, hydrogen halides and dihalogens, have been chosen for our study. Since the calculations are carried out at full four-component time-dependent Dirac–Hartree–Fock (DHF) level, the results can be used as benchmarks for verifying the performance of more approximated methods of including relativistic effects, such as those exploiting the use of effective core potentials [3,15].

2. Theory and computational details

The relativistic calculation of the frequency-dependent electric dipole polarizabilities has been carried out at the time-dependent self-consistent-field Dirac–Hartree–Fock level using the Dirac-Coulomb Hamiltonian, as implemented in the DIRAC program package [16]. The details of this implementation of the fully relativistic four-component Dirac–Hartree–Fock method for molecular polarizabilities are given elsewhere [2]. For the non-relativistic SCF-HF calculations the DALTON program [17] has been used.

For the hydrogen halides HX (X = F, Cl, Br and I) the dynamic polarizabilities have been evaluated for frequencies corresponding to wavelengths of 1064.0, 810.0, 514.5, 488.0, 435.8, and 351.1 nm. All these frequencies are comfortably lower than the first excitation energy, computed at Hartree–Fock (SCF-HF) level, vide infra. In the case of Cl_2 we present and discuss only results for the three longest wavelengths, whereas for F_2, Br_2 and I_2 only the results obtained for $\lambda = 1064.0$ and 810.0 nm are presented. This is due to the fact that for these dihalogens the three (four) shorter wavelengths in the set selected for the halides correspond to frequencies too close to (or higher than) the computed first SCF-HF excitation energy of the molecule, in all cases corresponding to an excitation to a triplet state. Static dipole polarizabilities have also been calculated for all molecules under study.

The choice of the basis set for relativistic calculations of electric dipole polarizability is in principle a difficult task. Firstly, only few basis sets designed for heavy elements are available in the literature. Secondly, flexible s and p sets are required for an accurate reproduction of the spin–orbit effects, while the basis set used for the calculations of electric properties should contain polarization and diffuse functions. A basis set fulfilling both these requirements may easily turn out to be too large to make four-component calculations affordable. A good compromise, and the main basis set used here, is that developed by Sadlej and coworkers [18–22] for calculations of electric properties, modified by decontracting all functions. It was previously used for the four-component calculations of static polarizabilities [3] and for studies of the electric field gradient (EFG) at the nuclei and the effect of external electric field on the EFG [23]. The calculations have also been carried out with the contracted Sadlej basis set. All the results presented, unless noted otherwise, have been obtained with the uncontracted Sadlej basis set for the large components. The small components have been determined using a kinetic balance condition.

The geometry derivatives of iso- and anisotropic polarizabilities have been calculated numerically using the three point formula, whose

numerical stability has been verified for selected cases against the five point formula. The bond distances for which the dipole polarizabilities and their geometry derivatives have been evaluated are the standard experimental ones [24].

Results for a laser frequency v_0 are given for the isotropic polarizability $\alpha_{iso}(v_0)$ and for the anisotropy $\alpha_{aniso}(v_0)$, which for diatomics are defined as

$$\alpha_{iso}(v_0) = \frac{1}{3}[2\alpha_\perp(v_0) + \alpha_\parallel(v_0)], \tag{1}$$

$$\alpha_{aniso}(v_0) = \alpha_\parallel(v_0) - \alpha_\perp(v_0), \tag{2}$$

where $\alpha_\perp(v_0)$ and $\alpha_\parallel(v_0)$ indicate the perpendicular and parallel component, respectively, of the electric dipole polarizability. By employing the computed bond-length derivatives of the isotropic electric dipole polarizability α_{iso} and polarizability anisotropy α_{aniso}, its is possible to evaluate the Raman scattering cross section $(d\sigma/d\Omega)$. According to Placzek's polarizability theory [25] for diatomics, in a harmonic approximation, the Q-branch $(\Delta J = 0)$ differential Raman cross section $(d\sigma/d\Omega)_Q(v_0)$ observed perpendicularly to the linearly polarized incoming beam is equal to

$$\begin{aligned}
\left(\frac{d\sigma}{d\Omega}\right)_Q(v_0) = {} & \frac{(2\pi)^4}{45} \frac{h}{8\pi^2 c_0 v_1 \mu} \\
& \times \left[\frac{(v_0 - v_1)^4}{1 - \exp(-hc_0 v_1/k_B T)}\right] \\
& \times \left\{ 45 \left[\frac{d\alpha_{iso}(v_0)}{dr}\right]^2 \right. \\
& \left. + \frac{7}{4}\left[\frac{d\alpha_{aniso}(v_0)}{dr}\right]^2 \right\},
\end{aligned} \tag{3}$$

where v_1 is the vibrational frequency (assumed to be given, as v_0, in cm^{-1}), μ the reduced mass (in kg), r the interatomic distance (in cm), and c_0 the velocity of light. Polarizabilities in Eqs. (1)–(3) are expressed in cm^3, and a Raman scattering cross-section in cm^2 sr^{-1}. The Boltzmann factor in Eq. (3) has been calculated for a temperature of 298 K. The reduced masses μ are those of the most abundant isotopes and the vibrational frequencies v_1 have been taken from experiment [26].

3. Results and discussion

3.1. Excitation energies

The linear response function corresponding to the electric dipole polarizability exhibits a well known pole structure, with poles corresponding to the excitation energies of the system. Recent developments, connected with the introduction of a complex theory formalism, allow in principle to bypass the problems arising with the unphysical divergences exhibited by usual propagator techniques at the poles [27]. As we are not yet able to employ these techniques, we have to establish the range of frequencies for the calculations of dynamic electric dipole polarizability and related geometrical derivatives so that all frequencies lie below the first excitation energy of the system. In usual SCF-HF calculations, as spin is conserved in interaction of the molecule with light, poles of the polarizability tensor appear, in our cases, for excited states of singlet spin symmetry. On the other hand, as spin symmetry is *not* conserved in our relativistic calculations, the SCF-DHF propagator exhibits poles *also* at the position corresponding to the SCF-HF triplet excited states.

The lowest vertical singlet and triplet excitation energies obtained at the SCF-HF level with uncontracted Sadlej's basis set [18–22] are given in Table 1. The selection of the frequencies employed in the dynamic electric dipole polarizability calculations, given in Section 2, was made according to these results. We will not discuss in detail the comparison of the calculated excitation energies with experiment, especially since only the vertical excitation energies have been calculated. As now well established, time dependent Hartree–Fock (or equivalently Random Phase Approximation, RPA) overestimates the excitation energies. For example, in the experimental spectrum of F_2 there is an absorption band at 481.8 nm [24] whereas according to our results the first singlet absorption should occur at 280 nm. Something similar occurs for Cl_2 (absorption continua starting from 479.6 nm [24]), Br_2 (absorption continua in bromine starting already from 510.6 nm [24]), and I_2, where the first triplet excitation actually falls at 847 nm [24], whereas RPA places it at 666 nm, see Table 1.

Table 1
Lowest singlet and triplet excitation energies for X_2 and HX, X = F, Cl, Br, I, RHF results with uncontrated Sadlej basis set

Molecule	Singlet			Triplet		
	Symmetry	ΔE (in a.u.)	λ (in nm)	Symmetry	ΔE (in a.u.)	λ (in nm)
HF	Π	0.4290	106	Π	0.4002	114
HCl	Π	0.3032	150	Π	0.2682	170
HBr	Π	0.2634	173	Π	0.2296	199
HI	Π	0.2188	208	Π	0.1792	254
F_2	Π_u	0.1625	280	Π_u	0.0863	528
Cl_2	Π_u	0.1531	298	Π_u	0.1022	446
				Σ_u^+	0.1923	237
				Π_g	0.2246	203
Br_2	Π_u	0.1215	375	Π_u	0.0785	581
	Σ_u^+	0.2169	210	Σ_u^+	0.1441	316
				Π_g	0.1766	258
I_2	Π_u	0.1074	424	Π_u	0.0684	666
	Π_g	0.1844	247			

The singlet excitation energies for hydrogen halides appear to be also overestimated [24].

3.2. Polarizabilities of hydrogen halides and dihalogens

3.2.1. Hydrogen halides

The isotropic polarizabilities and the anisotropies of the polarizabilities of the hydrogen halides HX calculated at the SCF-HF and SCF-DHF levels are presented in Table 2, which also includes the relative percentage differences between SCF-HF and SCF-DHF results. We will not discuss these results in detail, since the relativistic effects on the static polarizabilities of hydrogen halides have been the subject of a thorough study in the literature [3]. It is sufficient to say that, as expected, they are negligible (less than 1%) for all halides except HI. Even for HI the estimated relativistic effect is of some significance only for the anisotropy of the polarizability. The differences between SCF-HF and SCF-DHF results for each individual component of the polarizability tensor at non-zero frequencies are still very small but they have opposite sign for the parallel and perpendicular components, so they reinforce the effect for the anisotropy. The relative difference between SCF-HF and SCF-DHF results tends to be larger for α_{aniso} than for α_{iso}, albeit to a lesser extent, also

for the other halides. Our calculations confirm thus the conclusions of [3] that the relativistic corrections for electric dipole polarizabilities of hydrogen halides are much smaller than those originating from electron correlation [13,14] and nuclear motion [28,29].

The effects of the frequency dispersion on the calculated difference between SCF-DHF and SCF-HF results is practically negligible for HF and HCl. However, for the anisotropy of the polarizability of HBr and for isotropic polarizability of HI the relativistic correction in the UV region ($\lambda_0 = 351.1$ nm) differs significantly from the correction for higher wavelengths, even in its sign. Note that the first SCF-HF (triplet) excitation pole is comfortably far from this wavelength (198.5 nm for HBr and 254.2 nm for HI, see Table 1).

The relativistic effects on electric dipole polarizabilities of HX, as reproduced by the SCF-DHF calculations, tend to be smaller when contracted Sadlej basis sets are used. Large discrepancies between SCF-DHF results obtained with contracted and uncontracted Sadlej basis sets also occur for the polarizabilities of dihalogens and for the geometric derivatives of the polarizabilities. The contracted Sadlej basis set is probably too small to use even for qualitative estimations of the relativistic effects, and the results obtained with it will not be discussed any further here.

Table 2

Comparison of SCF-HF and SCF-DHF results for static and dynamic isotropic polarizabilities α_{iso} and polarizability anisotropies α_{aniso} (in a.u.) of the hydrogen halides HX, X = F, Cl, Br, I

λ (in nm)	α_{iso}			α_{aniso}		
	SCF-HF	SCF-DHF	Diff. (in %)	SCF-HF	SCF-DHF	Diff. (in %)
Hydrogen fluoride HF						
∞	4.90	4.92	−0.43	1.24	1.23	0.98
1064.0	4.91	4.94	−0.44	1.24	1.23	0.98
810.0	4.93	4.95	−0.44	1.25	1.23	0.98
514.5	4.97	4.99	−0.44	1.26	1.24	0.99
488.0	4.97	5.00	−0.44	1.26	1.24	1.00
435.8	4.99	5.02	−0.44	1.26	1.25	1.00
351.1	5.05	5.07	−0.45	1.27	1.26	1.02
Hydrogen chloride HCl						
∞	16.71	16.76	−0.25	1.76	1.75	0.47
1064.0	16.83	16.87	−0.26	1.76	1.75	0.50
810.0	16.91	16.95	−0.26	1.75	1.74	0.52
514.5	17.20	17.25	−0.27	1.73	1.71	0.60
488.0	17.26	17.31	−0.28	1.72	1.71	0.62
435.8	17.41	17.46	−0.28	1.70	1.69	0.67
351.1	17.82	17.88	−0.30	1.66	1.64	0.83
Hydrogen bromide HBr						
∞	23.22	23.25	−0.14	2.11	2.12	−0.73
1064.0	23.41	23.45	−0.16	2.09	2.10	−0.65
810.0	23.56	23.59	−0.17	2.07	2.08	−0.58
514.5	24.08	24.13	−0.21	2.01	2.01	−0.30
488.0	24.18	24.23	−0.22	1.99	2.00	−0.24
435.8	24.44	24.50	−0.24	1.95	1.96	−0.07
351.1	25.19	25.27	−0.32	1.83	1.82	0.57
Hydrogen iodide HI						
∞	35.32	35.19	0.35	2.42	2.53	−4.73
1064.0	35.71	35.60	0.32	2.37	2.48	−4.83
810.0	36.01	35.90	0.29	2.33	2.44	−4.91
514.5	37.10	37.04	0.18	2.16	2.28	−5.33
488.0	37.32	37.26	0.16	2.12	2.24	−5.43
435.8	37.88	37.84	0.09	2.02	2.14	−5.77
351.1	39.49	39.54	−0.14	1.69	1.82	−7.58

3.2.2. Dihalogens

Table 3 contains the relativistic SCF-DHF and non-relativistic SCF-HF results (and their relative differences) for the polarizabilities of the dihalogens X_2 (X = F, Cl, Br, I). Unlike for the hydrogen halides, we have found no trace in the literature of four-component calculations of the polarizability for any of these molecules. Our calculations show that the relativistic corrections on the static polarizabilities of dihalogens are small, as for the hydrogen halides, with the exception of iodine. In this case the relativistic correction for the anisot-

ropy of the polarizability is nearly 4 a.u. (8%). The difference between SCF-HF and SCF-DHF is larger for the anisotropy of the polarizability of I_2 than for the isotropic polarizability due to the different sign of the relativistic correction between parallel and perpendicular component, same as seen above for the hydrogen halides.

Concerning the variation of the relativistic corrections to the polarizabilities of dihalogens with the laser wavelength, for F_2 and Cl_2 the calculated relativistic corrections are negligible, similarly as for hydrogen halides, although dispersion

Table 3
Comparison of SCF-HF and SCF-DHF results for static and dynamic isotropic polarizabilities α_{iso} and polarizability anisotropies α_{aniso} (in a.u.) of the dihalogen molecules X_2, X = F, Cl, Br, I

λ (nm)	α_{iso}			α_{aniso}		
	SCF-HF	SCF-DHF	Diff. (in %)	SCF-HF	SCF-DHF	Diff. (in %)
Fluorine F_2						
∞	8.86	8.87	−0.13	9.75	9.77	−0.16
1024.0	8.90	8.91	−0.14	9.85	9.86	−0.17
810.0	8.93	8.94	−0.14	9.91	9.93	−0.18
Chlorine Cl_2						
∞	29.92	29.99	−0.24	18.32	18.37	−0.26
1024.0	30.14	30.21	−0.25	18.56	18.61	−0.28
810.0	30.30	30.37	−0.26	18.74	18.79	−0.30
514.5	30.88	30.97	−0.32	19.39	19.48	−0.47
Bromine Br_2						
∞	44.05	44.35	−0.68	28.52	29.15	−2.20
1024.0	44.49	44.88	−0.88	29.03	29.87	−2.87
810.0	44.82	45.33	−1.13	29.41	30.52	−3.76
Iodine I_2						
∞	70.00	71.25	−1.79	44.66	48.48	−8.54
1024.0	70.95	72.92	−2.79	45.79	51.41	−12.26
810.0	71.66	73.52	−2.59	46.64	56.72	−21.61

is more pronounced than for HF and HCl. For both Br_2 and I_2 the differences between SCF-HF and SCF-DHF are more substantial, and they vary significantly with the laser wavelength. All in all it seems that relativistic effects influence the electronic spectra of the heavier dihalogens more than they do for the corresponding hydrogen halides.

3.2.3. Comparison with experiment

The relativistic effects on the polarizabilities of light hydrogen halides and dihalogens are too small to be of relevance in the discussion of this section. We concentrate here on the effect of relativity in the comparison of computed and measured electric dipole polarizabilities of HI, Br_2 and I_2.

The static isotropic dipole polarizability of HI estimated from refractive measurements ranges from 34.25 to 35.30 a.u. [30], whereas the benchmark theoretical non-relativistic value (vibrationally averaged) is 36.52 a.u. [30]. Our relativistic correction of 0.13 a.u. goes then in the right direction but it is still too small to bridge the gap between experiment and theory. A four-component calculation including electron correlation

might perhaps achieve this. The only available experimental number for the anisotropy of the polarizability of HI, 11.4 a.u. [30], is in complete disagreement with the proposed non-relativistic theoretical estimate of 2.94 a.u. The inclusion of relativistic correction (0.11 a.u.) by no means reconciles the conflict. This indeed casts shadows on the experimental value, especially since its origin is uncertain [30].

Maroulis and Makris [31] have given a benchmark quality estimate of the static isotropic dipole polarizability of Br_2 for the ground vibrational state by means of non-relativistic ab initio calculations up to CCSD(T) level. Their value, 44.74 a.u., is to be compared with the experimental value of 45.0 a.u. [32] or 47.3 ± 1.2 a.u. [32]. The anisotropy is theoretically extrapolated at 25.39 a.u. [31] (no experimental result found in the literature). The theoretical value for α_{iso} with our relativistic correction of 0.49 a.u. is still closer to the experimental number of 45.0 a.u. than to 47.3 a.u., although the lack of the error bar on the former experimental data (extrapolated from the dynamic values to the static limit) leaves still some degree of indetermination in this comparison. After adding

the relativistic correction, the theoretical value for α_{aniso} of Br_2 increases to 26.7 a.u.

The experimental estimate of the static isotropic dipole polarizability of I_2 is 69.7 ± 1.8 a.u. [33] while the best non-relativistic theoretical value has been established at 70.9 ± 1.4 a.u. by extrapolation from correlated calculations up to CCSD(T) level and near Hartree–Fock limit estimates [33]. When taking into account the relativistic effects the ab initio result moves slightly away from the center of the error distribution of experiment. However, the corrections are small and leave the estimate within the error bars. The discrepancy between the best non-relativistic theoretical estimate for the anisotropy of the polarizability of I_2, 41.2 ± 0.8 a.u. [33], and the experimental value, 45.1 ± 2.3 a.u. [34], is larger. The error evaluation for both theory (estimate of the distance from the basis set limit) [33] and experiment (three times the standard deviation plus estimate of the systematic errors) [34] is rather conservative, so we can state that in this case the calculated relativistic correction, 3.8 a.u., goes in the right direction and apparently accounts perfectly for the discrepancy.

3.3. Geometric derivatives of the polarizabilities of hydrogen halides and dihalogens

3.3.1. Hydrogen halides

The SCF-HF and SCF-DHF results for the geometric derivatives of the isotropic polarizability at the experimental microwave bond distance – $(d\alpha_{iso}/dr)_{R_e}$ – and for the anisotropy of the polarizability – $(d\alpha_{aniso}/dr)_{R_e}$ – for the hydrogen halides HX are presented in Table 4. The relativistic effects on the derivatives, as estimated by the difference between SCF-DHF and SCF-HF values, are, as expected and similarly as for the polarizabilities, small for the lighter hydrogen halides HF and HCl. For HBr, however, whereas the relativistic corrections for the polarizability are negligible, they increase the SCF-HF value by 2–3% for the geometric derivatives of the isotropic polarizability, and by 1.5–2% for the geometric derivatives of the anisotropy. This tendency is even more evident for the geometric derivative of the isotropic polarizability of HI, for which the relativistic correction ranges from 5% to 11%, while

for the isotropic polarizability itself it is less than 0.5% for all wavelengths. The effect is also larger for $(d\alpha_{aniso}/dr)_{R_e}$ than for α_{aniso}, although the increase is less dramatic than seen for the isotropic polarizability.

The relative percentage difference between SCF-DHF and SCF-HF results is approximately independent on the laser wavelength for HF and HCl. For the two heavier hydrogen halides on the other hand the frequency dispersion of the relativistic effect is substantial. In this case the relativistic correction estimated only for the static case and transferred to the dynamic results would be significantly underrated.

3.3.2. Dihalogens

The geometric derivatives of the isotropic polarizability and of the anisotropy of the polarizability for the dihalogens, obtained at the SCF-DHF and SCF-HF levels, are tabulated in Table 5. It is immediately evident that there are rather large frequency dispersion effects on the relativistic corrections in the case of the geometric derivatives of the polarizabilities of the two heavier dihalogens, especially I_2. These are larger than those observed for the polarizabilities, were they were already non-negligible, compare the results for $\lambda = \infty$ and $\lambda = 1024.0$ nm from Tables 5 and 3. Also, the geometric derivatives of the polarizabilities are more sensitive than polarizabilities to the proximity of a resonance region, in agreement with what has been shown before [13]. This is evident in the case of I_2 at $\lambda = 810.0$ nm. No particular effect is observed for the electric dipole polarizability (see Table 5) whereas its geometric derivative computed at relativistic level and given in Table 3 shows a noticeable enhancement due to the proximity of the triplet character transition placed at 666 nm by our SCF-HF calculation, see Table 1.

Even for the static case, the relativistic corrections on the geometric derivatives of the polarizabilities of Br_2 and I_2 are far larger that those on the polarizabilities. This phenomenon has been already observed for HBr and HI (see Section 3.3.1). We conclude therefore that relativistic effects in general tend to be more significant for the geometric derivatives of the polarizabilities than for the polarizabilities themselves. The geometric

Table 4
Comparison of SCF-HF and SCF-DHF results for the geometry derivatives of static and dynamic isotropic polarizabilities $(d\alpha_{iso}/dr)_{R_e}$ and polarizability anisotropies $(d\alpha_{aniso}/dr)_{R_e}$ (in a.u.) of the hydrogen halides HX, X = F, Cl, Br, I

λ (nm)	$(d\alpha_{iso}/dr)_{R_e}$			$(d\alpha_{aniso}/dr)_{R_e}$		
	SCF-HF	SCF-DHF	Diff. (in %)	SCF-HF	SCF-DHF	Diff. (in %)
Hydrogen fluoride HF						
∞	2.56	2.57	−0.45	4.34	4.35	−0.20
1024.0	2.58	2.59	−0.47	4.37	4.38	−0.19
810.0	2.59	2.60	−0.46	4.40	4.40	−0.19
514.5	2.64	2.65	−0.47	4.48	4.49	−0.19
488.0	2.65	2.66	−0.46	4.50	4.51	−0.20
435.8	2.67	2.69	−0.47	4.54	4.55	−0.19
351.1	2.74	2.76	−0.48	4.65	4.66	−0.19
Hydrogen chloride HCl						
∞	4.07	4.09	−0.42	7.90	7.93	−0.37
1024.0	4.12	4.14	−0.43	8.00	8.03	−0.37
810.0	4.16	4.17	−0.43	8.08	8.11	−0.37
514.5	4.28	4.30	−0.45	8.35	8.38	−0.37
488.0	4.31	4.33	−0.46	8.40	8.43	−0.37
435.8	4.37	4.39	−0.47	8.54	8.57	−0.37
351.1	4.55	4.57	−0.51	8.91	8.94	−0.38
Hydrogen bromide HBr						
∞	4.73	4.83	−2.03	9.69	9.85	−1.64
1024.0	4.79	4.89	−2.11	9.85	10.01	−1.67
810.0	4.84	4.95	−2.16	9.96	10.13	−1.71
514.5	5.02	5.14	−2.40	10.38	10.57	−1.82
488.0	5.05	5.18	−2.45	10.46	10.65	−1.85
435.8	5.14	5.27	−2.59	10.66	10.87	−1.91
351.1	5.40	5.56	−3.08	11.24	11.48	−2.10
Hydrogen iodide HI						
∞	5.25	5.54	−5.40	11.72	12.33	−5.19
1024.0	5.33	5.64	−5.70	11.96	12.62	−5.46
810.0	5.39	5.71	−5.95	12.15	12.83	−5.67
514.5	5.61	6.00	−7.06	12.82	13.66	−6.59
488.0	5.65	6.06	−7.31	12.95	13.83	−6.80
435.8	5.76	6.22	−8.07	13.30	14.28	−7.41
351.1	6.06	6.74	−11.24	14.29	15.69	−9.85

derivatives of the polarizabilities have steeper computational requirements than the polarizabilities in all respects, since similar conclusions have been drawn also for electron correlation effects and basis set requirements [13,14].

3.3.3. Comparison with experiment

There are very few studies in the literature reporting actual measurements of the geometric derivatives of the polarizability, although such data can be extracted from the temperature dependence of the polarizability [35]. For Cl_2 the geometric

derivative of the static isotropic polarizability measured in this way is 7.21 ± 0.76 a.u. [35], while the best non-relativistic theoretical estimate is 7.03 a.u. [14]. The relativistic correction of 0.03 a.u. (Table 5) is very small and it leaves the excellent agreement between theory and experiment practically unaltered.

The calculated geometric derivatives can also be compared with experiment when converted to Raman scattering cross sections (see Eq. (3)). However, one should be aware that expression 3 is approximate, being valid only far from reso-

Table 5
Comparison of SCF-HF and SCF-DHF results for the geometry derivatives of static and dynamic isotropic polarizabilities $(d\alpha_{iso}/dr)_{R_e}$ and polarizability anisotropies $(d\alpha_{aniso}/dr)_{R_e}$ (in a.u.) of the dihalogen molecules X_2, $X = F$, Cl, Br, I

λ (nm)	$(d\alpha_{iso}/dr)_{R_e}$			$(d\alpha_{aniso}/dr)_{R_e}$		
	SCF-HF	SCF-DHF	Diff. (in %)	SCF-HF	SCF-DHF	Diff. (in %)
Fluorine F_2						
∞	6.21	6.21	−0.07	16.17	16.18	−0.03
1024.0	6.31	6.32	−0.12	16.48	16.49	−0.07
810.0	6.39	6.40	−0.19	16.70	16.73	−0.14
Chlorine Cl_2						
∞	8.88	8.91	−0.40	19.26	19.32	−0.32
1024.0	9.09	9.13	−0.49	19.79	19.87	−0.41
810.0	9.24	9.30	−0.59	20.19	20.29	−0.52
514.5	9.86	10.10	−2.39	21.64	22.23	−2.72
Bromine Br_2						
∞	11.86	12.35	−4.09	26.30	27.60	−4.94
1024.0	12.30	13.22	−7.50	27.30	29.74	−8.92
810.0	12.65	14.37	−13.57	28.04	32.52	−15.99
Iodine I_2						
∞	15.27	17.78	−16.41	33.42	40.63	−21.55
1024.0	16.02	21.52	−34.39	35.27	50.12	−42.08
810.0	16.61	262.46	−1480.11	36.68	−283.46	872.74

nance region and since it employs an harmonic approximation. Moreover, the experimental results are usually burdened with large error bars, on the average 10% for visible light and 15% for UV [26].

The Raman scattering cross sections without the explicit frequency factor (i.e., multiplied by $(v_0 - v_1)^{-4}$), calculated by means of the SCF-HF and SCF-DHF methods are compared with experimental results [26] in Table 6. The same laser wavelengths as used in experiment have been employed in the calculations. More experimental data are available in [26] for Cl_2, Br_2 and I_2 at laser wavelengths of 488 and 351.1 nm, shorter than corresponding to the lowest excitation energy in our relativistic calculations, see Table 1, and thus beyond our selected range of frequencies. Unfortunately, we have not been able to find in the literature the Raman scattering cross sections of Br_2 and I_2 measured far from the resonance frequencies.

The differences between SCF-HF and SCF-DHF for HBr and HI, although non-negligible, are within the range of the experimental error or only slightly larger. For HBr accounting for the relativistic effects brings the calculated Raman scattering cross section very close to experiment, which is most probably circumstantial, since electron correlation is not taken into account and the harmonic approximation is used. For HI the results obtained at the SCF-DHF level are farther from experiment than the SCF-HF ones, which probably means that electron correlation effects should be expected to be quite important.

For Cl_2 the relativistic correction brings the calculated Raman scattering cross sections closer to experiment. Note though that in these comparison one should keep in mind the limited

Table 6
Comparison of SCF-HF and SCF-DHF results for the frequencyless Q-branch Raman scattering cross sections, $(d\sigma/d\Omega)_Q (v_0)(v_0 - v_1)^{-4}$ (in cm^6 sr^{-1}), with experiment

	λ_0 (nm)	SCF-HF	SCF-DHF	Exp.[a]
HBr	488.0	2.41	2.59	2.58
HI	514.5	3.49	4.00	3.45
HI	488.0	3.55	4.08	3.57
Cl_2	514.5	2.64	2.77	3.35

[a] From the compilation of Schrötter and Klöckner [26].

validity of Placzek's approximation, influencing the results the more the closer to regions of optical absorption. Also, in all likelihood, the lack of electron correlation effects might influence anyway significantly the comparison with experiment, since electron correlation and relativistic effects are intertwined [5,6].

4. Summary and conclusions

In order to estimate the magnitude of relativistic effects, static and dynamic polarizabilities and their geometric derivatives have been computed at the SCF-HF and SCF-DHF levels for hydrogen halides and dihalogens.

The relativistic corrections on the polarizabilities are negligible for hydrogen halides, with an exception for HI, where the difference between SCF-HF and SCF-DHF result for the polarizability anisotropy ranges for different wavelengths from 4.5% to 7.5%. The frequency dispersion of the relativistic correction is negligible for HF and HCl but relatively significant for HBr and HI. Our results confirm the conclusion of [3] that relativistic effects on the electric dipole polarizabilities of hydrogen halides are much smaller than the electron correlation and ro-vibrational corrections. The relativistic calculation of the anisotropy of the polarizability of HI confirms Maroulis' conclusion [30] that the experimental estimate is most probably in error.

For light dihalogens the relativistic corrections on the polarizabilities are again small. For I_2 and for the anisotropy of the polarizability of Br_2 they amount to a few percent and depend noticeably on the laser frequency. The benchmark-quality non-relativistic theoretical polarizabilities of Br_2 and I_2 taken from the literature [31,33] are in agreement with the experiment after adding the calculated relativistic corrections. For the anisotropy of the polarizability of I_2 the relativistic correction is such that theoretical estimate gets substantially closer to the center of the error distribution of the experiment.

The relativistic corrections on the geometric derivatives of the static polarizabilities are still very small for the light hydrogen halides and

dihalogens but they cannot be neglected for HI, Br_2 and I_2. The effects of relativity follow the same trend as the basis set dependence and electron correlation effects [13,14]: they tend to be larger for the geometric derivatives of the polarizabilities than for the polarizabilities themselves. The frequency dispersion of the relativistic effect on the geometric derivatives of the polarizabilities is large, and our results show that estimating the relativistic corrections for the static case and transferring them to the derivatives of the dynamic polarizabilities should be classified as an incorrect procedure. The geometric derivatives of the polarizabilities of dihalogens calculated at the SCF-DHF level are also more sensitive than the polarizabilities to the proximity to the poles of the response function.

The comparison of the calculated Raman scattering cross sections with experiment is highly influenced by the fact that the experimental error on the one hand, and the approximations in the theoretical approach on the other do not allow to assess whether relativistic corrections improve the agreement with experiment or not. In some cases the apparent improvement of the agreement with experiment achieved by including the relativistic effects might be simply fortuitous.

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