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Triplet–singlet energy gaps in iodo-carbenes (I–C–X): Remarkable discrepancy between theory and experiment

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The triplet–singlet energy gaps in iodo-carbenes, I–C–X with X = H, F, Cl, Br and I, were computed using the MP2, CCSD(T), CASSCF/CASPT2, MR-SDCI, MR-ACPF and B3LYP methods, with basis sets up to 6-311++G(3df,2p) and aug-cc-pvTZ and effective core potentials. Corrections for relativistic effects were also incorporated. Our results indicate that diiodo-carbene (CI_2) is likely to possess a singlet ground state lying around 30 kJ mol^{-1} below the lowest triplet state, thus at variance with that of a recent negative ion photoelectron spectroscopic study (R. L. Schwartz, G. E. Davico, T. M. Ramont and W. C. Lineberger, *J. Phys. Chem.* A, 1999, **103**, 8213). In addition, the present study confirms the singlet character of other iodo-carbenes with substantial triplet–singlet gaps and also points out the remarkably large fluctuations and discrepancies in the absolute values of the energy splittings, not only between experiment and theory, but also between *ab initio* quantum chemical methods.

Carbenes (R_1–C–R_2) are neutral compounds featuring a divalent carbon atom and two non-bonded electrons. Owing to the presence of two near-degenerate 2p orbitals at the carbenoid centre (the in-plane 2p(σ) and out-of-plane 2p(π) orbitals), distribution of the two unpaired electrons generates three different electronic states, namely a triplet, an open-shell singlet and a closed-shell singlet state. This constitutes a classical example for the 2-electron-2-orbital problem. The ground electronic state of a carbene usually has either a triplet multiplicity or a closed-shell singlet. The carbene reactivity pattern is inherently dependent on their electronic structure: while closed-shell singlet carbenes usually undergo stereospecific insertion or addition reactions, their triplet counterparts often shown non-specific abstraction reactions.[1,2] Therefore, knowledge on the identity of ground state and triplet–singlet splittings is of fundamental importance in understanding the chemistry of these reactive intermediates. In this context, theoretical studies have proved to be more than complementary to experimental studies, as witnessed by the long history of the parent methylene.[3] It is well known that the substituents R_1 and R_2 play a crucial role in favouring one or other electronic state. While methylene (CH_2)[3] and methylcarbene (CH_3CH)[4] are triplet species, dimethylcarbene (CH_3CCH_3)[5,6] and probably higher dialkylcarbenes exhibit a singlet ground state. On the contrary, most diarylcarbenes have a persistent triplet multiplicity.[7] The singlet carbenes could usually be stabilised by strong π-donor groups such as F, Cl, NR_2, OR, PR_2, SR, *etc.* that reduce the π-electron deficiency.[8–12] In playing with the effect of these groups either with a cyclic or open framework, it has been possible to make stable, or even isolable, singlet carbenes under ordinary conditions.[13–15]

Regarding the halogenated carbenes, they are mainly transient species and could only be detected *in situ* by trapping agents or spectrometric methods. They have been the subject of several theoretical studies [*cf.* ref. 16–24 and references therein] that agree with each other, pointing toward a singlet ground state for either mono- or dihalogenated derivatives, even for chlorophenylcarbene in which a competition between two opposite effects ends up favouring the closed-shell singlet multiplicity.[25] Nevertheless these studies disagreed with each other as to the absolute values of the corresponding triplet–singlet energy gaps (ΔE_{T-S}). Two recent experimental studies[26,27] dealing with thermochemical parameters of halocarbenes have in particular attracted our attention. On the one hand, Lineberger and coworkers[26] evaluated the ΔE_{T-S} of four dihalocarbenes, namely CX_2 with X = F, Cl, Br and I, from negative ion photoelectron spectroscopy. On the other hand, Nibbering and coworkers[27] studied the standard heats of formation ($\Delta_f H$) and obtained the values of 226 ± 25 kJ mol^{-1}, for CCl_2, and around 267 and 324 kJ mol^{-1} for CClBr and CBr_2, respectively. The latter can be compared with the corresponding calculated G2 values of 227, 282 and 336 kJ mol derived by Schwartz and Marshall.[23] It appears that although the differences between theoretical and experimental $\Delta_f H$'s remain substantial, amounting to 15 kJ mol^{-1}, they lie rather within the expected error bars from both sides. In contrast, some remarkable discrepancies between theory and experiment on the ΔE_{T-S} values for dihalocarbenes have emerged.

Table 1 which lists the new experimental results along with the most recent theoretical estimates for the entire series of halocarbenes clearly points out these discrepancies. For CF_2, the newest experimental ΔE_{T-S} of 226 ± 12 kJ mol^{-1} can be compared with that of either 234 or 247 kJ mol^{-1} computed at the QCISD(T)/6-311+G(3df,2p) and G2 levels, respectively.[23] To avoid repeating the reported data, we would refer in particular to ref. 23 and 26 for a more detailed comparison of numerous earlier experimental and theoretical results on the triplet–singlet separations of various halocarbenes.

While an agreement on the energy gap seems to be reached for CF_2, the disagreement between available theoretical and experimental values on the splittings of other dihalocarbenes, CCl_2, CBr_2 and CI_2, is intriguing. In addition, Lineberger and coworkers[26] suggested a qualitative change for the di-

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Table 1 Summary of recent theoretical and experimental triplet–singlet energy gaps of halocarbenes (kJ mol^{-1})

Carbene	G2[a]	QCISD(T)[b]	Expt.[c]
CH$_2$	−28	−41	
CHF	73	60	
CHCl	38	24	
CHBr	35	20	
CHI	27	13	
CF$_2$	247	234	226 ± 12
CFCl	161	147	
CFBr	148	132	
CFI	123	110	
CCl$_2$	97	82	12 ± 12
CClBr	89	72	
CClI	70	56	
CBr$_2$	81	63	8 ± 12
CBrI	65	49	
CI$_2$	52	37	−4 ± 12

[a] At the G2 level taken from ref. 23. [b] At the QCISD(T)/6-311+G(3df, 2p) level taken from ref. 23. [c] From negative ion photoelectron spectroscopy from ref. 26.

iodinated derivative CI$_2$ which accordingly possesses rather a triplet ground state! Overall, it is obvious that energy differences amounting up to 70–80 kJ mol^{-1} are abnormally large with respect to the current standard in theoretical thermochemistry. In this context, it seems to us desirable to have another look at these perplexing discrepancies by using some alternative quantum chemical methods that have not been used systematically in earlier studies. Although the whole series of halocarbenes has been considered for the sake of systematic consideration, a particular attention has been paid to CI$_2$.

Ab initio calculations were carried out using the GAUSS-IAN 98,[28] Molcas-4[29] and Molpro[30] program packages. The geometries were fully optimized at different levels including second order perturbation theory (MP2), and coupled-cluster theory including all single and double and perturbative correction for triple excitations (CCSD(T)), as well as the hybride functional B3LYP method of density functional theory in conjunction with the 6-311++G(d,p) atomic basis set. For iodine, the effective core potential (ECP)[31,32] was used. The zero point energies (ZPE) were evaluated using B3LYP vibrational frequencies without scaling. To estimate further the influence of larger basis sets and higher excitations or multi-reference wavefunctions on the triplet–singlet splittings, single point electronic energies computations using the coupled-cluster theory CCSD(T), as well as second order perturbation theory based on complete active space wavefunctions (CASSCF/ CASPT2), were also carried out using CCSD(T)/6-311++G(d, p)-optimized geometries. Two additional atomic basis sets including 6-311++G(3df,2p) and aug-cc-pVTZ were also employed. The aug-cc-pVTZ basis set for bromine was taken from EMSL.[33] In the construction of CASSCF wavefunctions, the active spaces having the full valence electrons in smaller carbenes and going up to the 12-electrons-in-12-orbitals in larger carbenes have been selected. The corrections for relativistic effects were also included in the evaluation in two different ways. First we have used relativistic ECP's taken from Molcas basis set library (Barandiaran valence electron basis set with Cowan–Griffin-relativistic core potential).[29] As this basis set still seems small, we have therefore deleted some existing d-polarization and s-diffuse functions and added to basis sets of all atoms the 3df-polarization and sp-diffuse type of functions that were optimized for energy at level QCISD(T).[34] According to Glukhovtsev *et al.*,[34] in creating multiple sets of d-functions we have divided and multiplied the exponents of polarization d- functions by 2 for iodine and by 3 for bromine. The second way was the direct calculation of the mass–velocity term and Darwin one-electron contact term for the first order relativistic corrections, in conjunction with the all electron 6-311++G(3df,2p) basis sets, equally for iodine.

Finally, a set of multi-reference configuration interaction computations including all the single and double excitations (MR-SDCI) have also been carried out for the iodocarbenes (I–C–X) making use of the all electron 6-311++G(3df,3pd) basis functions. For this purpose, we have first constructed wavefunctions at the CASSCF(4,4) level including 4 electrons in four frontier orbitals. The resulting CASSCF wavefunctions were then used as references in a set of MR-SDCI calculations including all single and double excitations. The effects of higher-than-double excitations as well as the size-consistency were estimated in two ways, first by adding a Davidson correction to the MRCI energies (denoted as MR-SDCI +DC), and alternatively by an average-coupled-pair-functional method (denoted as MR-ACPF)[35] using the same MR-SDCI reference wavefunctions.

Table 2 records the optimized parameters of the halocarbenes in both electronic states using CCSD(T)/6-311++G(d,p) method. The singlet states have either $^1A_1$ or $^1A'$ symmetry for mono- or di-halogenated species, respectively, whereas the triplets have either $^3B_1$ or $^3A''$ symmetry. In general, these CCSD(T) values differ slightly from the QCISD/6-311G(d,p) ones reported in ref. 23. We note that in going from a singlet to its triplet counterpart, the C–X distance is markedly com-

Table 2 Bond distances and angles of halocarbenes CXY calculated at the CCSD(T)/6-311++G(d,p) level of theory[a]

Carbene CXY	Singlet[b]			Triplet[b]		
	r_s(CX)/Å	r_s(CY)/Å	α_s(XCY)/degrees	r_t(CX)/Å	r_t(CY)/Å	α_t(XCY)/degrees
CH$_2$	1.117	1.117	101.5	1.084	1.084	133.1
CHF	1.127	1.317	102.0	1.091	1.321	121.3
CHCl	1.116	1.707	102.3	1.087	1.678	125.8
CHBr	1.116	1.872	101.0	1.088	1.829	126.7
CHI	1.117	2.091	100.0	1.090	2.034	127.9
CF$_2$	1.307	1.307	104.7	1.321	1.321	119.1
CFCl	1.307	1.745	106.6	1.323	1.695	122.8
CFBr	1.301	1.936	106.8	1.328	1.874	123.4
CFI	1.296	2.193	107.4	1.318	2.087	124.3
CCl$_2$	1.730	1.730	110.0	1.690	1.690	127.5
CClBr	1.722	1.914	110.2	1.688	1.849	128.6
CClI	1.716	2.160	111.2	1.687	2.066	129.8
CBr$_2$	1.903	1.903	110.5	1.847	1.847	129.7
CBrI	1.893	2.145	111.4	1.843	2.061	130.7
CI$_2$	2.135	2.135	112.3	2.059	2.059	132.0

[a] The Stuttgart-ECP was used for iodine. [b] Index s stands for singlet and t for triplet.

pressed up to 0.08–0.09 Å, except for the C–F bonds that are somewhat stretched. The bond angles are consistently larger in the triplets in line with the Walsh diagrams.

Table 3 gives a summary of the results obtained in the present work on the triplet–singlet gaps of halocarbenes using 11 different computational methods ranging from B3LYP, MP2 to CCSD(T), CASPT2, MR-SDCI and MR-ACPF. For the latter levels, single point electronic energies have been computed using CCSD(T)/6-311++G(d,p) optimized geometries. From these results, a number of points are worth noting:

(i) The gaps tend to be increased upon extension of the atomic basis functions. For H and F, the 6-311++G(3df,2p) basis seems to be large enough whereas for heavier Cl, Br and I atoms, larger basis sets are apparently needed to reach a converged value. At the CCSD(T) level, the differences in the gaps computed with both 6-311++G(3df,2p) and cc-aug-pVTZ amount in fact to 1.1 kJ mol^{-1} for CH_2, 1.2 for CHF, 1.3 for CF_2, but to the larger value of 4.9 for CCl_2, 7.0 for CClBr and 3.2 for CBr_2 (levels 5 and 6 in Table 3). Unfortunately, calculations using larger basis sets are beyond our presently available computational resources.

(ii) Another point of concern is whether the use of ECP for iodine in conjunction with a full basis set for other atoms could lead to a consistent, balanced and thereby accurate description of the core electrons. It is interesting to note that for the CFI carbene, the CCSD(T) value is reduced from 119.5 to 118.0 kJ mol^{-1} in going from the 6-311++G(d,p) to 6-311++G(3df,2p) set, in opposition with the general trend noted above (levels 4 and 5 of Table 3). Comparison of the CASPT2 results obtained using two different basis functions (cf. Table 3: level 8 using ECPs and level 9 using full basis) indicates that there is an average and systematic difference of 5 kJ mol^{-1} on the energy gaps; use of ECPs apparently leads to smaller gaps.

(iii) The relativistic effects have also been computed in conjunction with the ECPs. As expected, the corrections on the ΔE_{T-S} are small for the lighter elements (less than 1 kJ mol^{-1}) but quite significant for the heavier ones (up to 8 kJ mol^{-1} in CI_2). (cf. Table 3, levels 7 and 8).

(iv) For a given basis set, the B3LYP method appears to provide results comparable to the CCSD(T) ones. However the deviations remain large for the purpose of prediction. The performance of DFT methods in computing singlet–triplet gaps has abundantly been commented upon in earlier papers.[20,22]

(v) Of particular interest are the results based on multi-reference wavefunctions. It is well known that the singlet state of a carbene is an inherently multi-configurational problem and could better be described by at least, two-configuration self-consistent-field wavefunctions. That is indeed the main cause for the difficulty encountered in treating its triplet–singlet energy difference by the methods based on single Hartree–Fock references. A small imbalance in the treatment of electron correlation in both states could induce a significant deviation on the quantity. Regarding the multi-reference methods, they are not panaceas for the problem either. In fact it is also known that the choice of either the active space, the zeroth-order Hamiltonian or the order of the perturbation theory induces a significant effect on the energy gaps. As a matter of fact, the CASPT2 method results in an over-estimation of the triplet energies. The consequence is that the CASPT2 enlarges the gap in CH_2 where the triplet is the lower state, and reduces it in other CXY species having lower-lying singlet states.[5] For methylene, the CCSD(T) values of −40.6 and −38.6 kJ mol^{-1} with two distinct basis sets (Table 3, levels 5 and 6) compare more favourably with the experimental value of −37.7 kJ mol^{-1}.[36] In contrast, the CASPT2 values of −58.9 and −53.4 kJ mol^{-1} are substantially over-estimated (Table 3, levels 8 and 9). Such overestimation of the triplet state energy is already noticed in recent studies on methylene and ethylidene using ANO type of atomic functions.[5] For CF_2, while the CCSD(T) gaps of 230–236 kJ mol^{-1} are similar to the QCISD(T) of 234 kJ mol^{-1} obtained using a comparable basis set[23] but larger than the most recent experimental value of 226 ± 12 kJ mol^{-1}[26] (see Table 1), the CASPT2 results of 215–220 kJ mol^{-1} seem to be systematically smaller (cf. Table 3, levels 8 and 9). The same remark can also be made for the trend between CCSD(T) and CASPT2 results. A similar CCSD(T) - CASPT2 behaviour difference was also noticed in a recent study[24] on CHCl and CFCl. For some systems such as CF_2 or CBr_2, both MP2 and CASPT2 values are comparable to each other in agreement with the fact that their singlet states are dominated by the Hartree–Fock references.

(vi) Due to a limitation of computational resources, the MR-CI wavefunctions were constructed only for the five iodo-carbenes (MR-CI calculations took about a week per carbene

Table 3 Calculated triplet–singlet gaps (ΔE_{T-S} in kJ mol^{-1}) of halocarbenes at 11 different levels of theory[a] including ZPE[b] and first order relativistic corrections[c]

CXY	1	2	3	4	5	6	7	8	9	10	11	ZPE[b]	rel corr[c]
CH_2	−48.7	−70.7	−61.2	−48.6	−40.4	−38.6	−45.0	−58.9	−53.4			1.9	0.3
CHF	48.6	38.0	44.5	55.6	59.9	61.1	56.5	38.9	45.4			0.3	0.5
CHCl	15.3	1.0	10.8	17.9	23.7	26.3	18.8	2.4	9.0			0.5	0.7
CHBr	14.0	−1.8	7.6	15.0	21.1	23.2	18.6	5.0	8.1			0.4	1.6
CHI	11.2	−3.9	4.7	13.5	18.9		9.7	−2.8	4.1	15.4	12.9	0.4	5.4
CF_2	216.7	213.0	224.8	227.4	235.1	236.3	229.7	215.2	220.4			−0.3	0.8
CFCl	139.0	131.5	139.0	144.2	147.6	150.5	140.7	126.1	131.2			0.3	1.0
CFBr	128.3	120.1	128.0	132.2	136.6	140.7	133.2	120.7	124.3			0.2	2.5
CFI	114.5	104.6	109.2	119.5	118.0		107.3	95.2	101.1	114.2	113.4	−0.1	5.9
CCl_2	76.7	67.8	76.7	79.6	82.8	87.8	74.5	59.2	72.2			1.0	1.3
CClBr	69.6	60.0	69.1	71.1	74.8	81.8	70.2	51.9	64.6			0.9	2.6
CClI	56.1	49.3	56.3	60.7	62.6		49.9	41.9	46.0	52.7	52.9	−0.8	6.1
CBr_2	63.1	53.0	61.4	63.6	67.5	70.7	65.6	55.2	58.3			0.8	3.7
CBrI	51.6	44.8	51.9	54.9	57.1		48.4	36.5	43.4	43.5	45.1	0.7	5.8
CI_2	44.2	38.8	44.6	48.2	49.2		34.5	25.9	31.0	30.5	33.1	0.7	8.4

[a] The levels of theory are defined as follows: CCSD(T)/6-311++G(d,p) geometry was used unless otherwise mentioned. 1, B3LYP/6-311++G(d,p)[d]//B3LYP/6-311++G(d,p)[d]; 2, MP2/6-311++G(d,p)[d]//MP2/6-311++G(d,p)[d]; 3, MP2/6-311++G(3df,2p)[d]//MP2/6-311++G(d,p)[d]; 4, CCSD(T)/6-311++G(d,p)[d]; 5, CCSD(T)/6-311++G(3df,2p)[d]; 6, CCSD(T)/aug-cc-pVTZ; 7, CCSD(T)/Modified Barandariaran ECP; 8, CASPT2/Modified Barandariaran ECP (CAS(12,12) reference); 9, CASPT2/AE (All electron 6-311++G(3df,3pd)); 10, MR-SDCI + Davidson Corr./AE (All electron 6-311++G(3df,3pd)); 11, MR-ACPF/AE (All electron 6-311++G(3df,3pd). [b] ZPE was calculated at the B3LYP/6-311++G(d,p)[d] level. [c] Relativistic correction was calculated with all electron 6-311++G(3df,3pd) basis set. [d] Stuttgart ECP was used for iodine.

on a fast workstation!). Of the set of values listed in Table 3 (levels 10 and 11), two distinct trends emerge: (a) for the lighter molecules CHI and CFI, the MR-SDCI results are closer to the CCSD(T) ones (Table 3, level 5), the difference amounts to around -5 kJ mol^{-1} relative to the CCSD(T) and (b) for the heavier molecules CClI, CBrI and CI$_2$, the MR-SDCI gaps approach rather the CASPT2 counterparts, especially for the latter. In ref. 24, results on CHCl and CFCl also showed a similar behaviour in that the MR-CI method gives results comparable to the CCSD(T). In all cases, the MR-CI values range between the CASPT2 (the smallest) and CCSD(T) (the largest).

After completing this manuscript, we became aware of three recent theoretical papers[37–39] dealing with the triplet–singlet gaps in CF$_2$, CCl$_2$, CBr$_2$ and CI$_2$; the reported results also emphasized the disagreement and fluctuations.

It can be concluded that there are large fluctuations in the computed values for the triplet–singlet energy gaps of halocarbenes even when using the most accurate theoretical methods to date; the deviations amount up to 20 kJ mol^{-1} between the values derived from both CCSD(T), CASPT2 and MR-CI methods. This difference is mainly due to the inherent shortcomings of these methods that are all truncated approximations of the full CI wavefunctions. While the basis set incompleteness plays a certain role, in particular for the iodo-systems, the other corrections such as the ZPEs or relativistic effects can be considered as small (but not neglible). In taking all the factors into account, it appears to us that the CCSD(T) values obtained with large basis sets (Table 3, levels 5 and 6) for the ΔE_{T-S} of halocarbenes could be used for the sake of a systematic comparison.

(vii) In spite of large fluctuations of computed values, they are internally consistent in revealing that there are actually large discrepancies with the most recent experimental values[26] for the gaps of CCl$_2$ and CBr$_2$. As seen in Tables 1 and 3, the experimental values of 12 ± 12 and 8 ± 12 kJ mol^{-1} for CCl$_2$ and CBr$_2$, respectively, are remarkably smaller than the corresponding ones of 88 and 71 kJ mol^{-1} by CCSD(T) or 72 and 58 kJ mol^{-1} by CASPT2. In addition, these computed values are in line, within the expected fluctuations, with those obtained previously by other methods such as GVB-CI, G2 and QCISD(T).[19–23]

In the most recent theoretical paper (ref. 37) dealing with CCl$_2$, the gap of 82 ± 8 kJ mol^{-1} derived using MO compu-

tations with large basis sets again differs from the values stated above (88 and 72 kJ mol^{-1}).

(viii) Regarding the iodinated carbenes CXI, the CHI seems to have the smallest energy gap of the whole series. Both MP2 and CASPT2 methods with small basis sets predict even a triplet ground state for it, but the singlet counterpart becomes favoured when using larger basis sets. The energy gap is found to be increased following replacement of the second H atom by another halogen, namely 19 kJ mol^{-1} in CHI, 49 in CI$_2$, 57 in CBrI, 65 in CClI and 118 in CFI (values from CCSD(T)/6-311++G(3df,2p), cf. Table 3, level 5; the same observation can also be made using MR-CI values given in Table 3, levels 10 and 11). This trend is thus coherent with that in the electronegativity of the halogens and that found in other series of CXY; that is, the more electronegative element induces a larger stabilisation of the singlet state. This is to point out that, for iodocarbenes, we have not found a species having a triplet ground state.

In view of such a quantitative and qualitative discrepancy between theory and experiment, we have carried out additional computations for the diiodocarbene CI$_2$. The results recorded in Table 4 again show a few intriguing fluctuations among the calculated values. The most obvious difference is that both CASSCF(6,6) and CASPT2(6,6) methods using a given ECP type of basis set, provide much smaller values than those derived from the CASSCF(12,12) and CASPT2(12,12) counterparts. This indicates once more the importance of the active space used. Overall, the MP2, B3LYP, CCSD(T), CASPT2 and MR-SDCI results agree qualitatively with each other pointing toward a closed-shell singlet character of the ground state of CI$_2$, irrespective of the atomic functions employed. Taking the CCSD(T), CASPT2 and MR-SDCI values with all electron basis sets into consideration, we would suggest an average value of ΔE_{T-S}(CI$_2$) = 30 kJ mol^{-1}, with an expected error of, at most, ± 12 kJ mol^{-1}. This estimate constitutes beyond any doubt the most remarkable discrepancy between theory and the most recent experiment of Lineberger et al.[26] using negative photoelectron techniques. The discrepancy arises presumably from an interpretation of the rather complicated experimental spectra on which we could not usefully comment (see ref. 39).

In summary, the present theoretical study on the triplet–singlet energy gaps of halocarbenes using coupled-cluster theory and multi-configurational second-order perturbation

Table 4 Calculated results for CI$_2$[a]

Level of theory	E(Singlet)	E(Triplet)	ΔE_{T-S}
B3LYP/6-311++G(d,p)[b]//B3LYP/6-311++G(d,p)[b]	$-60.829\,89$	$-60.816\,53$	35.1
MP2/6-311++G(d,p)[b]//MP2/6-311++G(d,p)[b]	$-60.447\,10$	$-60.435\,82$	29.6
MP2/6-311++G(3df,2p)[b]//MP2/6-311++G(d,p)[b]	$-60.556\,41$	$-60.542\,91$	35.4
CCSD(T)/6-311++G(d,p)[b]	$-60.491\,79$	$-60.476\,93$	39.0
CCSD(T)/6-311++G(3df,2p)[b]	$-60.616\,52$	$-60.601\,28$	40.0
CCSD(T)/Modified Barandariaran ECP	$-228.669\,02$	$-228.656\,15$	33.8
CAS(12,12)/Modified Barandariaran ECP	$-227.945\,01$	$-227.929\,68$	40.2
CASPT2[CAS(12,12)]/Modified Barandariaran ECP	$-228.652\,65$	$-228.643\,06$	25.2
CAS(12,12)/All Electron 6-311++G(3df,3pd)	$-13\,871.552\,91$	$-13\,871.537\,48$	40.5
CASPT2[CAS(12,12)]/All electron 6-311++G(3df,3pd)]	$-13\,873.131\,60$	$-13\,873.123\,28$	21.8
CAS(6,6)/Barandariaran ECP	$-227.839\,87$	$-227.852\,93$	-34.3
CASPT2[CAS(6,6)]/Barandariaran ECP	$-228.427\,66$	$-228.429\,52$	-4.9
CAS(6,6)/Modified[c] Barandariaran ECP	$-227.872\,79$	$-227.863\,97$	23.2
CASPT2[CAS(6,6)]/Modified[c] Barandariaran ECP	$-228.568\,66$	$-228.564\,83$	10.1
MR-SDCI[4,4]/All electron 6-311++G(3df,3pd)	$-13\,872.012\,95$	$-13\,872.008\,30$	12.2
MR-SDCI[4,4] + DC[d]/All electron 6-311++G(3df,3pd)	$-13\,872.100\,93$	$-13\,872.092\,77$	21.4
MR-ACPF[e]/All electron 6-311++G(3df,3pd)	$-13\,872.116\,18$	$-13\,872.107\,07$	23.9
ZPE [B3LYP/6-311++G(d,p) (in kJ mol^{-1})]	7.0	7.7	0.7
All electron 6-311++G(3df,3pd) Relativistic correction	$-372.435\,18$	$-372.431\,96$	8.4

[a] Total energies in hartree and triplet–singlet gaps (ΔE_{T-S} in kJ mol^{-1}) at different levels of theory Optimized geometries at CCSD(T)/6-311++G(d,p) unless otherwise mentioned. [b] Stuttgart ECP was used for iodine. [c] With added 3df-type polarization functions to the original Barandarian ECP in case of iodine. [d] Multi-reference configuration interaction including Davidson correction. [e] Multi-reference configuration interaction with average coupled pair function correction.

theory and multi-reference configuration interaction methods that were not employed systematically in earlier studies, confirms not only an interesting discrepancy between theory and experiment for CCl_2, CBr_2 and CI_2 but also the perplexing fluctuations among the theoretical results. While our best estimate suggests a triplet–singlet splitting of 30 ± 12 kJ mol^{-1} for CI_2, the most recent experimental measurement and interpretation provide a value of -4 ± 12 kJ mol^{-1}. It appears obvious that further efforts need to be made on both sides in order to resolve this challenging issue.

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