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Diatomic Halogen Anions and Related Three-Electron-Bonded Anion Radicals: Very Contrasted Performances of Møller−Plesset Methods in Symmetric vs Dissymmetric Cases

Benoît Braïda and Philippe C. Hiberty*

Laboratoire de Chimie-Physique, Groupe de Chimie Théorique, Université de Paris-Sud, 91405 Orsay Cedex, France

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The bonding distances, vibrational frequencies, and dissociation energies of a series of dihalogen radical anions, $X\therefore Y^-$ (X, Y = F, Cl, Br, I), held together by three-electron bonds, are calculated at the MP2 and MP4 levels and compared to the CCSD(T) level and to experimental values when available. In agreement with a qualitative model which is expressed in valence bond terms, it is found that Møller−Pesset calculations offer a good description of symmetrical homonuclear three-electron bonds by providing fairly accurate equilibrium bond lengths, stretching frequencies, and dissociation energies. By contrast, the Møller−Plesset method fails for some unsymmetrical systems, leading to largely erroneous equilibrium distances and stretching frequencies. The qualitative model predicts such errors to be related to an inaptitude of the UHF reference determinant to properly describe the sharing out of the charge between the two fragments. This inadequacy results in a set of optimized molecular orbitals that is poorly adapted to the subsequent perturbation calculation, and carries over to the MP2 and MP4 levels. In such a case, the three-electron bond is systematically found too short, while the corresponding stretching frequency is found too high. The MP2 error is shown to linearly correlate with a simple function of the calculated net charges, thus providing a simple way to check the validity of MP*n* calculations for dissymmetrical three-electron-bonded radical anions. The thumb rules that follow are further confirmed by applicatory test calculations on some three-electron-bonded anions of chemical interest: $HO\therefore SH^-$, $HO\therefore SCH_3^-$, $HO\therefore CF_3^-$, $HS\therefore SCH_3^-$, and $H_3CS\therefore CF_3^-$.

I. Introduction

The electron attachment to dihalogen molecules or other molecules of biological interest has attracted much attention in recent years. The resulting molecular anions are held together by a three-electron bond (noted $\therefore$), also called a σ* bond, in which one bonding σ molecular orbital (MO) is doubly occupied while the corresponding σ* antibonding MO is singly occupied, leading to a net bond order of 0.5 and to a bonding energy on the order of 1 eV or more.

A firm knowledge of the bonding characteristics of halogen molecule negative ions is of interest for interpreting phenomena related to self-trapped holes in ionic crystals,[1] in which two neighboring X^- anions are replaced by an X_2^- molecule. Accurate potential energy curves for the ground-state anions are also needed to interpret the absorption spectra of halogen molecule ions and the dynamics of their dissociation and recombination as well as the effects of solvation. Chen and Wentworth[2] have combined experimental data based on Raman spectroscopy in a rare gas matrix, electron spectroscopy in a crystal, and gas-phase dissociation attachment experiments for most of the diatomic halogen anions to create semiempirical potential energy curves for ground and excited states. Recently, these fits were improved by incorporating newer data.[3,4] It should be pointed out, however, that so far only the dissociation energies and vibrational frequencies have been measured directly. The equilibrium bond length, an essential parameter for the construction of the excited-state curves, was most of the time taken as the sum of covalent and ionic radii,[2,3] or indirectly obtained through simulations of the conventional photoelectron spectrum within the Franck−Condon approximation.[4] It is also unknown what effect matrixes or solutions have on the measurements to which the curves were fit. As a consequence, the considerable uncertainties in the potential parameters for halogen molecule anions, particularly the bond lengths, are in stark contrast to the precisely known neutral state curves.

In analogy to halogen molecule anions, three-electron bonds are also observed in molecular anions of biological interest, especially those involving an S−S linkage.[5−10] Thus, one-electron reduction of disulfides, leading to three-electron-bonded radical anions of the general type $RS\therefore SR'^-$, is one of the ways of cleaving the disulfide linkage present in numerous proteins, enzymes, and antibiotics. More generally, disulfide anions are involved in protection mechanisms for biological systems subject to ionizing radiations or other forms of free radical damage.[9] Other three-electron-bonded organic anions ($F_3C\therefore SH^-$, $F_3C\therefore SCH_3^-$, $RO\therefore OR^-$) have also been suggested to be absolute minima or critical points on the potential surface.[11,12] Now, while some of them have been subject to experimental observation,[5−10] the experimental probe of their spectroscopic parameters seems to be even more difficult than in the case of halogen molecule ions, hence the usefulness of theoretical studies[13−26] and the need to assess the adequacy of the various computational methods that are currently available.

As far as theoretical methods are concerned, it is well established that electron correlation is essential for the description of three-electron bonds, as the Hartree−Fock level yields bonding energies that are consistently much too small.[24] The Møller−Plesset many-body perturbation theory has often been used, at second order (MP2) for the determination of geometries

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and vibrational frequencies,[8,11,16,17] and sometimes at fourth order (MP4) for the dissociation energies.[8,25] The Gaussian-2 (G2) level, more accurate than MP2 for dissociation energies but using MP2 geometries and Hartree−Fock frequencies, has also been used for some halogen molecular ions.[18,19] The MCSCF approach, even in its complete-active-space version (CASSCF) including all valence orbitals, has proved disappointing,[20] showing that the electron correlation in this type of bond is essentially dynamical in nature. Thus, the multireference configuration interaction (MRCI) method, which has sometimes been used,[21,22] is not expected to be significantly better than single-reference methods, unless the starting MCSCF uses a very large active space. Last, the very popular density functional theory (DFT) has recently been shown to be definitely inappropriate for the description of three-electron bonds,[26,27] with the exception of the BHLYP functional that is better than the others in this respect,[23,26,27] but still not fully reliable. Thus, if one excludes very accurate methods such as those based on the couple-cluster or quadratic CI theories, the only candidate for the status of a standard economical method, which can serve as a routine tool for calculating physicochemical properties of molecule ions involving three-electron bonds, seems to be of the Møller−Plesset perturbation type. This latter level has been tested for its convergence from second to fourth order[25] and for its agreement with higher levels[26,28,29] in a number of three-electron-bonded radical cations, and is generally believed to be quite reliable. However, it should be noted that all the methodological comparisons that have been published to date have been performed on molecule ions displaying homonuclear three-electron bonds, with *left−right symmetry*, while the performances for unsymmetrical systems were taken for granted.

Now why should dissymmetric species cause problems? There is a clue that suggests that it might be so: the fact that F_2^- is subject to a symmetry-breaking artifact at the UHF level, in its equilibrium geometry, leading to nonsensical MP2 or MP4 wave functions if symmetry is not forced at the UHF step. Of course the remedy is obvious for a symmetrical species such as F_2^-, but what if one fluorine atom is replaced by one chlorine or bromine atom? Although symmetry is not formally present, some artifacts that are close in nature to symmetry breaking can be expected to spoil the MP*n* wave functions, and this remark holds for any dissymmetrical three-electron-bonded anion. It follows that such systems are potentially problematic and that their ability to be studied by standard economical computational methods must be verified. Our aim in this paper is therefore to compare the performances of the Møller−Plesset method in symmetrical vs dissymmetrical cases, using the family of dihalogen anions as model systems.

The paper is organized as follows. First, the spectroscopic parameters of a series of dihalogen anions, $X\therefore Y^-$ (X, Y = F, Cl, Br, I), will be computed at the MP2 and MP4 levels and compared to the results of the very accurate CCSD(T) level which will serve as a reference. Then the MP*n* performances in symmetrical vs dissymmetrical cases will be compared, and the findings will be interpreted by means of a qualitative valence bond model. From these results and their interpretation, some thumb rules will be derived to predict which conditions have to be met for Møller−Plesset calculations to be trusted. Last, the study will be extended to some molecule anions of chemical interest, to verify the generality of the aforementioned rules.

II. Theoretical Methods

One reason the performances of the MP2 method in 6-31G(d) basis set are of particular interest is that it is the standard method for geometry optimization in the G2 procedure.[30] A basis set of this type (BS1) has therefore been used throughout the present study, complemented with diffuse functions to account for the anionic character of the dihalogen species. A larger BS2 basis set has also been used for comparison. While BS1 is expected to be sufficient for geometry optimizations and vibrational frequencies, BS2 is required for calculations of bonding energies since it is the diffuse-augmented analogue of the standard 6-311G(3df) basis set that is routinely used for single-point energy calculations at the G2 level.[30] More specifically, for fluorine and chlorine, BS1 and BS2 consist of the standard 6-31+G(d) and 6-311+G(3df) basis sets, respectively. For bromine, BS1 consists of the SV4P basis set[31] augmented with d anf f polarization functions and s and p diffuse functions as recommended by Glukhovtsev et al.[19] for geometry optimizations, and BS2 is an all-electron basis set of the 6-311G type, also complemented with d,f polarization and s,p diffuse functions, devised by McGrath and Radom[32] and recommended by Glukhovtsev et al.[19] for single-point G2 energies. For iodine, both BS1 and BS2 valence basis sets use the orbital-adjusted effective core potential (ECP) of Hay and Wadt.[33] BS1 and BS2 consist, respectively, of the [21,21] and [111,111] contraction schemes of the Hay−Wadt basis set for iodine,[33] augmented by d and f polarization as well as by s and p diffuse functions as optimized by Glukhovtsev et al. for iodine-containing molecules.[19]

The Møller−Plesset many-body perturbation theory has been used at second (MP2) and fourth (MP4) order, as well as coupled-cluster theory[34] with inclusion of all single and double excitations and perturbative treatment of triple excitations (CCSD(T)). Unless otherwise specified, all theoretical methods have been used in their spin-unrestricted forms. The frozen core approximation has been used throughout. To estimate the effect of spin contamination at the MP2 level, the spectroscopic parameters have also been calculated at the PMP2 level, which annihilates spin contamination by projection. Throughout this work, the MP4 acronym stands for the MP4 level that includes single, double, triple, and quadruple interactions, usually referred to as MP4(SDTQ).

As first-order spin−orbit coupling effects are known to have a significant influence on the calculated dissociation energies of molecules involving heavy atoms, they have been included for species containing bromine or iodine. As in ref 19, first-order spin−orbit corrections were calculated for the atomic species from the experimental atomic levels in Moore's tables,[35] and amount to 3.51 kcal/mol for Br and 7.25 kcal/mol for I. These values have to be subtracted from the uncorrected dissociation energies each time the dissociation products involve either of these two atoms.

All calculations have been performed with the GAUSSIAN94 series of programs.[36]

III. Results for the Dihalogen Radical Anions

All the calculations of geometries, frequencies, and bonding energies have been performed with both BS1 and BS2 basis sets, to verify that the effect we are pointing out is independent of basis set improvements. Within each basis set, the notoriously accurate CCSD(T) level has been taken as the reference against which the other methods are evaluated.

A. Equilibrium Distances. The optimized bond lengths for the $X\therefore Y^-$ anions are displayed in Table 1. Let us first comment on the calculated bond lengths of the symmetrical molecules (F_2^-, Cl_2^-, Br_2^-, I_2^-). In both basis sets, the UMP2 bond lengths are in reasonable agreement with the CCSD(T) values, being

TABLE 1: Equilibrium Distances (Å) for the Dihalogen Anion Radicals

	BS1						BS2					
	UHF	MP2	PMP2	MP4	CCSD(T)	$\langle S^2\rangle$	UHF	MP2	PMP2	MP4	CCSD(T)	$\langle S^2\rangle$
$F\therefore F^-$	1.911	1.916	1.936	1.931	1.939	0.785	1.913	1.909	1.930	1.928	1.934	0.76
$Cl\therefore Cl^-$	2.675	2.653	2.667	2.673	2.677	0.765	2.642	2.586	2.597	2.613	2.619	0.77
$Br\therefore Br^-$	2.908	2.876	2.876	2.889	2.894	0.765	2.915	2.836	2.852	2.865	2.870	0.77
$I\therefore I^-$	3.322	3.267	3.274	3.295	3.299	0.765	3.296	3.186	3.193	3.215	3.221	0.765
$F\therefore Cl^-$	3.036	2.050	2.054	2.073	2.202	0.77	3.020	2.054	2.059	2.074	2.177	0.775
$F\therefore Br^-$	3.045	2.174	2.182	2.187	2.259	0.77	3.238	2.174	2.184	2.191	2.249	0.77
$F\therefore I^-$	2.329	2.344	2.356	2.351	2.352	0.77	2.308	2.302	2.315	2.314	2.313	0.77
$Cl\therefore Br^-$	2.795	2.748	2.756	2.768	2.780	0.75	2.773	2.705	2.723	2.731	2.737	0.77
$Cl\therefore I^-$	2.971	2.913	2.918	2.936	2.950	0.765	2.937	2.857	2.862	2.881	2.887	0.77
$Br\therefore I^-$	3.111	3.062	3.067	3.086	3.091	0.765	3.095	3.003	3.010	3.031	3.036	0.77

TABLE 2: Vibrational Frequencies (cm^{-1}) for the Dihalogen Anion Radicals

	BS1					BS2					
	UHF	MP2	PMP2	MP4	CCSD(T)	UHF	MP2	PMP2	MP4	CCSD(T)	exptl
$F\therefore F^-$	476	486	462	461	460	475	480	456	484	456	459,[a] 450[b]
$Cl\therefore Cl^-$	245	244	244	238	228	252	264	253	249	249	249[b]
$Br\therefore Br^-$	155	154	154	156	150	145	156	155	152	147	148[b]
$I\therefore I^-$	102	108	104	102	103	101	113	108	107	107	110 ± 2,[c] 115[b]
$F\therefore Cl^-$	64	688	698	629	363	67	707	706	657	375	
$F\therefore Br^-$	75	536	532	498	333	52	507	499	502	345	
$F\therefore I^-$	316	312	300	302	295	313	319	308	311	306	
$Cl\therefore Br^-$	199	216	210	211	199	196	215	207	204	203	
$Cl\therefore I^-$	169	191	192	186	174	172	191	192	187	186	
$Br\therefore I^-$	125	135	136	132	127	123	136	136	129	129	

[a] Reference 18. [b] Reference 3. [c] Reference 4.

in all cases slightly too short with deviations on the order of 0.02−0.03 Å (0.04 Å for I_2^-), probably due to spin contamination as can be judged from the rather large $\langle S^2\rangle$ values as compared to the expected 0.75 value. Indeed, the PMP2 results are consistently better, with maximal errors of 0.02 Å. The MP4 results are even better and never depart from the accurate values by more than 0.01 Å. The magnitudes and the tendencies of the MP*n* errors are the same in both basis sets. On the other hand, the calculated values for the equilibrium bond lengths are more or less basis set dependent, depending on the halogen. Thus, Cl_2^- is much more sensitive to basis set improvement than F_2^-, as expected since chlorine is more polarizable than fluorine, a property that requires diffuse high-rank polarization functions to be computationally reproduced. The effect is less clear in Br_2^-, probably because the 6-311+G(3df) itself is far from being complete for bromine, and the same remark holds for the pseudopotentials used for I_2^-. Be it as it may, the calculation of accurate spectroscopic parameters for the anions involving heavy halogen atoms would require very large basis sets and passes the scope of the present study.

Interestingly, even the modest UHF level is found to be rather reliable as far as equilibrium distances *of symmetrical species* are concerned, and quite close to CCSD(T) results. This good agreement with higher levels, which may appear as counterintuitive in view of the known complete failure of the Hartree−Fock level to reproduce bonding energies of three-electron bonds[24,25,37] (vide infra), has however already been noticed for a series of three-electron-bonded radical cations and demonstrated to be general in symmetrical cases.[37] Briefly summarized, the qualitative study of the dynamic electron correlation that is at work in a three-electron bond shows that a UHF dissociation energy curve is essentially correct for symmetrical species provided the symmetry is imposed to the wave function at all interatomic distances, from equlibrium all the way to infinite separation. As this symmetry condition is naturally met at short distances, it follows that UHF-calculated and accurately calculated dissociation energy curves of symmetrical three-electron-bonded species have locally the same shape in the vicinity of the equilibrium distance, leading to nearly similar optimized distances and vibrational frequencies.

In sharp contrast to the above results, some rather uneven performances are observed for the MP*n*-calculated bond lengths in unssymmetrical cases. In the BS1 basis set, the bond lengths of two molecules, FBr^- and FCl^-, are severely underestimated at the MP2 level, by 0.09 Å in the first case and as much as 0.15 Å in the second. The error is not related to spin contamination, as the PMP2 values are practically no better, nor to basis set quality, as the errors are only slightly reduced in the BS2 basis set (0.08 and 0.13 Å, respectively). In such circumstances, the standard answer is to push the level of theory to higher Møller−Plesset orders, but remarkably, the MP4 level does not perform much better than MP2, whatever the basis sets. These poor performances of MP*n* calculations are indicative of severe inadequacies of the calculated orbitals, as further indicated by the nonsensical equilibrium bond lengths that are calculated at the UHF level for FBr^- and FCl^-. On the other hand, the bond lengths of the other unsymmetrical dihalogen anions, namely, FI^-, $ClBr^-$, ClI^-, and BrI^-, are fairly well reproduced at the MP2 and PMP2 levels, and very well at the MP4 level.

B. Vibrational Frequencies. Hand in hand with the above results, the MP*n* performances for the vibrational frequencies (displayed in Table 2) closely follow the ups and downs of the performances for bond lengths. In both basis sets, the agreement between MP2- and CCSD(T)-calculated frequencies is generally good for symmetrical molecules. Some exceptions (e.g., F_2^-) are due to spin contamination and are well corrected at the PMP2 level, and the MP4-calculated frequencies are close to the MP2 values. The agreement of the MP*n*- and CCSD(T)-calculated frequencies is still good for FI^-, $ClBr^-$, ClI^-, and BrI^-, i.e., those molecule that are unsymmetrical but the bond lengths of which are correctly reproduced at the MP*n* levels. On the other hand, the MP*n* errors on the vibrational frequencies are dramatic for FBr^- and FCl^-. At the MP2 level, the frequencies are

TABLE 3: Dissociation Energies (kcal/mol) for the Dihalogen Anion Radicals

	BS1					BS2							
										CCSD(T)			other ab initio calculations
	UHF	MP2	PMP2	MP4	CCSD(T)	UHF	MP2	PMP2	MP4	w/so[a]	so[b]	exptl	
$\mathrm{F}\therefore\mathrm{F}^-$	3.0	26.2	29.4	25.8	27.3	2.8	26.9	30.2	27.4	28.3		28.5,[c] 30.2[d]	25.7[c]
$\mathrm{Cl}\therefore\mathrm{Cl}^-$	12.6	24.7	25.5	24.4	24.6	13.5	29.1	29.9	28.3	28.1		31.8[d]	
$\mathrm{Br}\therefore\mathrm{Br}^-$	18.5	31.6	30.9	29.6	29.6	14.1	27.9	28.5	27.2	27.0	23.5	27.0,[e] 27.9[d]	23.3[f]
$\mathrm{I}\therefore\mathrm{I}^-$	14.4	24.4	24.8	23.4	23.5	13.9	26.0	26.2	24.9	24.7	17.4	23.5,[g] 24.3[d]	20.9[h]
$\mathrm{F}\therefore\mathrm{Cl}^-$	1.8	23.7	25.3	24.2	29.5	2.1	29.0	30.9	28.0	28.6			
$\mathrm{F}\therefore\mathrm{Br}^-$	2.2	31.5	33.1	31.5	32.6	1.7	32.5	34.0	33.1	32.2			
$\mathrm{F}\therefore\mathrm{I}^-$	3.6	34.0	35.1	33.8	34.5	3.4	35.8	36.7	35.8	36.1	28.9		
$\mathrm{Cl}\therefore\mathrm{Br}^-$	14.8	25.7	26.4	25.5	25.7	14.2	26.9	27.6	26.6	26.5	23.0		
$\mathrm{Cl}\therefore\mathrm{I}^-$	14.7	23.8	24.2	23.2	23.4	14.9	24.2	24.7	23.5	23.3	16.1	22.3[i]	19.2[h]
$\mathrm{Br}\therefore\mathrm{I}^-$	15.3	24.3	24.7	23.4	23.5	13.9	24.0	24.4	23.0	22.8	15.5	23.5[i]	

[a] Without spin−orbit corrections. [b] Spin−orbit corrected. [c] Reference 18. [d] Reference 3. [e] Huber, K. P.; Herzberg, G. *Molecular spectra and molecular structure. IV. Constants of diatomic molecules*; Van Nostrand Reinhold: New York, 1979. [f] Reference 19. [g] Reference 4. [h] Reference 22. [i] D_e obtained from the ZPE-corrected experimental D_0 value from the NIST Standard Reference Database Number 69, November 1998 Release. ZPE corrections from our calculated frequencies (CCSD(T)/BS2).

overestimated, relative to the CCSD(T) level, by factors of 1.90 and 1.61, repectively, for these two molecules, in the smallest basis set. Far from improving things, the PMP2 level proves even worse than MP2, while the MP4 level still overestimates the frequencies by factors of 1.73 and 1.54, respectively. The tendencies in the largest basis set are exactly the same. Besides, it is noteworthy that our highest level of calculation, CCSD(T) in the BS2 basis set, provides vibrational frequencies in excellent agreement with available experimental values.

C. Dissociation Energies. The dissociation energies of the $\mathrm{X}\therefore\mathrm{Y}^-$ anions, as calculated at various computational levels, are displayed in Table 3. Expectedly, the UHF level is found to be totally inadequate in this respect, as has already been noted in the case of three-electron-bonded cations,[24,25,37] and does not deserve further comments. On the other hand, the MP2 and MP4 levels of calculation prove satisfactory for symmetrical species, in both basis sets, as predicted from the qualitative analysis. Both orders of perturbation are in good agreement with each other and with CCSD(T) results, with deviations never exceeding 2 kcal/mol.

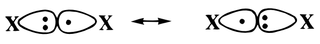
It can be seen in Table 3 that our best level of calculation, CCSD(T) in the BS2 basis set, yields some calculated dissociation energies in excellent agreement with available experimental values, if spin−orbit corrections are omitted. This agreement, as already noted by some authors,[22] is fortuitous for the heaviest molecules of the series, and falls off as first-order spin−orbit corrections are included, as expected since very large basis sets must be used for bromine and iodine to better reproduce the polarizabilities of these atoms and provide accurate dissociation energies.

For the unsymmetrical cases that have proved problematic in the preceding calculations, namely, $\mathrm{F}\therefore\mathrm{Cl}^-$ and $\mathrm{F}\therefore\mathrm{Br}^-$, one might have expected the Møller−Plesset dissociation energies to be too small (inadequate orbitals leading to increased MP*n* energies). As a matter of fact, the only bonding energy that is found significantly too small at the MP2 and MP4 levels is that of $\mathrm{F}\therefore\mathrm{Cl}^-$ in BS1, while the other results for $\mathrm{F}\therefore\mathrm{Cl}^-$ and $\mathrm{F}\therefore\mathrm{Br}^-$ are surprisingly good. It thus turns out that the Møller−Plesset errors affect bonding energies less than the other spectroscopic parameters, a point that will be discussed later.

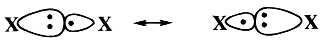
To summarize, the MP*n* levels of calculation yield reasonable geometries, frequencies, and dissociation energies for all symmetrical dihalogen anions, in both basis sets. On the other hand, some dissymmetrical species are well described at these levels while some are not. $\mathrm{F}\therefore\mathrm{Cl}^-$ and $\mathrm{F}\therefore\mathrm{Br}^-$ are found significantly too short, while their vibrational frequencies are greatly overestimated, at the MP2, PMP2, and MP4 levels. Last, the dissociation energy of $\mathrm{F}\therefore\mathrm{Cl}^-$ is found too small. While the success of the Møller−Plesset method was expected for symmetrical anions, the situation is rather confused for some dissymmetrical species. It is clear that the above results cast doubt on the validity of MP*n* calculations as applied to such species, but does the warning apply to *all* dissymmetrical three-electron-bonded anions, or can one find some rules to predict in which case MP*n* can be trusted or must be avoided? For this to be done, it is necessary to analyze in detail the Møller−Plesset failure, so as to understand why this method fails in some cases while it succeeds in others. As the above MP*n* errors are expectedly related in some way to the symmetry-breaking artifact (in this case a near-symmetry- or pseudo-symmetry-breaking artifact), which is generally discussed in valence bond terms, the analysis will be best carried out by means of a qualitative valence bond model.

IV. A Qualitative Valence Bond Model

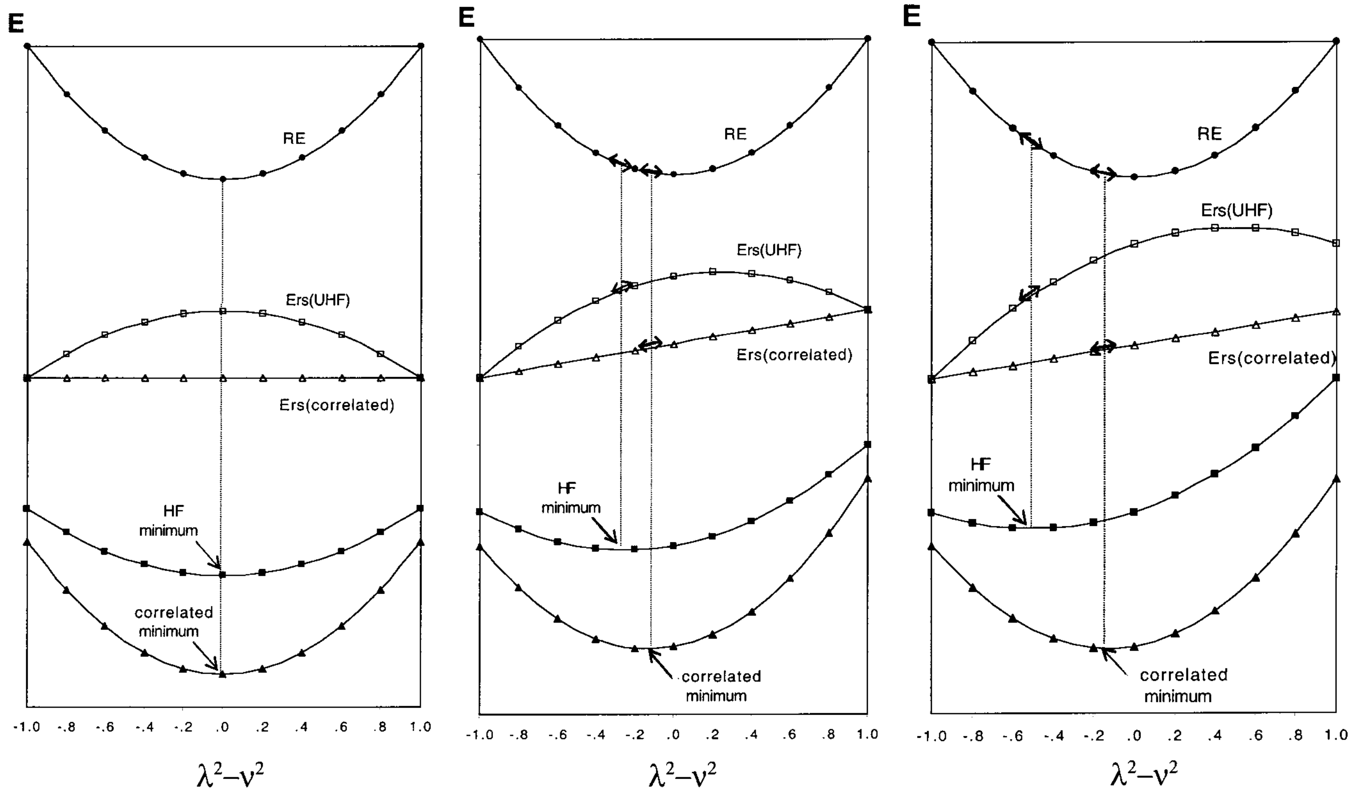
A. Why Do Dissymmetrical Species Cause Problems? The nature of three-electron bonding and the effect of electron correlation are best illustrated by considering the symmetric $\mathrm{X}\therefore\mathrm{X}^-$ case, in the framework of valence bond theory. It should first be noted that the Hartree−Fock wave function can always be expanded, by a simple mathematical operation, into its valence bond components, displaying in the present case the expected combination of resonating structures **1** ↔ **2**, as has been shown recently.[37] It follows that the Hartree−Fock description of a symmetric three-electron bond presents a qualitatively correct physical picture, and that no left−right electron correlation is needed, at variance with the two-electron bond case. Yet, the Hartree−Fock level dramatically underestimates the three-electron bonding energies, owing to a subtle built-in constraint that makes all the orbitals of **1** equivalent to those of **2**, while a better wave function would allow the orbitals of the anionic fragments to be different (i.e., larger) from those of the neutral fragments, leading to two resonating structures, each having its specific set of orbitals, as in **1′** ↔ **2′**. It has



1 **2**



1' **2'**



(a) (b) (c)

Figure 1. Qualitative variations of the energy of a three-electron-bonded anion as a function of the delocalization of the negative charge in the UHF determinant (see eq 1 in the text): (●) resonance energy; (□) summed energies of the two VB structures, at the UHF level; (△) summed energies of the two VB structures, at the correlated level; (■) total energy at the UHF level; (▲) total energy at the correlated level. The slopes of the various curves at critical abscissas are emphasized by angular brackets.

recently been shown that this effect,[37] by which the orbitals instantaneously adapt to the charge fluctuation in the resonating picture, closely corresponds to the differential electron correlation that is associated with the breaking or formation of the three-electron bond. Note that although only the active orbitals (those involved in the X∴X bond) are drawn in the above schemes, *all* the orbitals of X^- must be different from those of X in **1′** or **2′**. In the VB framework, going from **1** ↔ **2** to **1′** ↔ **2′** can be accomplished in a direct way as in the BOVB method[38] (BO standing for “breathing orbitals”), or in an indirect way by performing a CI including **1** and **2** and their monoexcited structures obtained by substituting an occupied atomic orbital for a virtual one.[38c] In the MO framework, the equivalent CI would include all the monoexcitations from the $\sigma_g^2\sigma_u$ and $\sigma_g\sigma_u^2$ configurations.[38c] Two points are noteworthy: (i) the appropriate CI space is included in the standard CISD space, made of the single and double excitations from the Hartree−Fock determinants; (ii) the correlated wave function that mimicks the orbital optimization will include a lot of excited configurations, each having a small coefficient, an ideal situation for perturbation theories.[39] Here are the basic reasons the simple MP2 level is expected to perform well as a general rule, and to yield results in agreement with MP4 or higher levels of theory.

Let us now consider the energy *E* of a wave function that represents the mixture of the two resonating structures **1** and **2** in the general X∴Y^- case, with the respective weights λ^2 and ν^2:

$$E = \lambda^2 E(\mathbf{1}) + \nu^2 E(\mathbf{2}) + \mathrm{RE} \qquad \lambda^2 + \nu^2 = 1 \qquad (1)$$

where *E*(**1**) and *E*(**2**) are the energies of structures **1** and **2**, respectively, and RE is the resonance energy arising from their mixing. The first two terms can be gathered in a single variable, E_{RS} (the weighted energies of the resonance structures, i.e., the energy of the system if there were no resonance energy), and it is interesting to visualize separately the variations of E_{RS} and RE as the wave function represents a delocalized situation ($\lambda^2 = \nu^2$) when both resonance structures contribute and the charge is equally divided between both centers, or a localized situation ($\lambda^2 \gg \nu^2$ or $\nu^2 \gg \lambda^2$) when only one resonance structure is important. These variations are schematized in the three diagrams of Figure 1, in which the delocalization is characterized by $\lambda^2 - \nu^2$ in the abcissa.

Thus, from the left-hand side of each diagram all the way to the right-hand side, the wave function (whatever its level, correlated or Hartree−Fock) is supposed to represent structure **1** alone ($\lambda^2 = 1$), then a mixture of **1** and **2** ($\lambda^2 = \nu^2$), and last structure **2** alone ($\nu^2 = 1$).

Let us consider the symmerical case first (Figure 1a). In this case the left- and right-hand parts of the diagram represent symmetry-broken situations, while the (correct) symmetry-adapted situation finds its place in the central part of the diagram. At the correlated level (e.g., in the BOVB wave function), both **1** and **2** have their optimal specific set of orbitals at each point of the diagram, so that E_{RS}(correlated) is a constant and displays a horizontal line. The situation is different at the Hartree−Fock level: while the orbitals are ideally optimized at both extremes of the diagram to fit the unique resonance structure, in the middle of the diagram the unique set of orbitals is a compromise that fits neither **1** nor **2**, so that E_{RS}(HF) displays a maximum. This bump is at the origin of the (considerable) Hartree−Fock error on the dissociation energies of three-electron bonds, and results from a competition between resonance energy and the so-called “orbital size effect”:[40] delocalization improves resonance, but at the expense of poorly describing each individual resonance structure.

The total energy curve in orbital rotation space is of course the sum of the RE and E_{RS} curves. The behavior of the RE curve is the same at both the Hartree–Fock and correlated levels: the resonance energy is at its best when the two resonance structures have equal weights, in the middle of the diagram. As a consequence, the RE curve (which we will consider to be the same at both the Hartree–Fock and correlated levels) displays a minimum. At the Hartree–Fock level, the curvature of E_{RS}(HF) is in general less sharp than that of RE, so that the total energy is minimal in the middle of the diagram, leading to a set of optimized orbitals that display the correct delocalized charge distribution. Thus, the symmetric situation is favorable in that the Hartree–Fock wave function displays about the same electronic density as the correlated wave function, so that this single-reference determinant is a priori reasonable and can be safely used as a starting point for the subsequent Møller–Plesset procedure.

Let us now consider a heteronuclear bond, $X\therefore Y^-$, and suppose that the two fragments X and Y have different electronegativities, e.g., EA(Y) > EA(X) (Figure 1b). At the correlated level, the E_{RS}(correlated) curve is still a straight line, but it now displays a slope that reflects the different energies of structures **1** and **2**. As for the RE curve, it is unaffected by the different stabilities of the resonance structures and still displays a minimum in the middle of the diagram. Adding the two curves leads to a minimal energy that is reached when the RE and E_{RS} curves have their slopes opposite in sign and equal in magnitude, at a point on the abcissa that determines the final charge distribution in the molecule (correlated minimum in Figure 1). Turning to the Hartree–Fock level, the E_{RS}(HF) curve can be deduced from the preceding E_{RS}(HF) curve of Figure 1a by adding point by point this latter curve to the inclined straight line E_{RS}(correlated) of Figure 1b, thus assuming the Hartree–Fock error to be the same in both situations at each point of the abcissa. It follows from this construction that the E_{RS}(HF) slope is necessarily *larger*, in absolute value, than the RE slope at the abcissa of the correlated minimum, and that the Hartree–Fock minimum for the total energy is left-shifted with respect to the correlated level (HF minimum in Figure 1b). As a consequence, the orbitals that result from the Hartree–Fock optimization are inappropriate, as leading to a reference determinant that does not display the correct electron density, overlocalizing the charge with respect to the correlated level. This defect is only incompletely overcome by the Møller–Plesset process, leading to higher energies than if appropriate orbitals had been used.[41]

What happens if the bond is slightly stretched out of its equilbrium geometry? The E_{RS} curves are unaffected, while the resonance energy diminishes, because the two fragments have a diminished overlap. It follows that the RE curve flattens while the E_{RS}(HF) and E_{RS}(correlated) curves remain the same. This inevitably results in an increase of the Hartree–Fock error,[42] leading to a concomitant increase of the Møller–Plesset error which is therefore *distance-dependent*. This means that the quality of the orbitals worsens as the bond is stretched, with the consequence that the MP2 or MP4 energy will be more and more upshifted, relative to the exact energy profile, as the bond is elongated. This error on the dissociation energy curve is expected to result in two consequences: (i) the bond length will be found too short and (ii) the vibrational frequency corresponding to the stretching mode will be found too large.

TABLE 4: Electron Affinities of the Halogen Atoms X and Differential UHF Errors on the Atomic Electron Affinities in an $X\therefore Y^-$ Molecule Anion[a]

	BS1		BS2		
	UHF	CCSD(T)	UHF	CCSD(T)	exptl[b]
		EA (X)			
F	29.5	71.1	27.5	74.2	78.4
Cl	57.0	71.6	55.4	80.0	83.4
Br	57.3	72.9	55.6	77.0	77.5
I	55.5	67.0	54.0	67.6	70.5
		ΔΔEA(X,Y)[c]			
$F\therefore Cl^-$	27.1		22.1		
$F\therefore Br^-$	26.0		25.3		
$F\therefore I^-$	30.1		33.0		
$Cl\therefore Br^-$	−1.1		3.3		
$Cl\therefore I^-$	2.9		11.0		
$Br\therefore I^-$	4.0		7.7		

[a] Energies are in kilocalories per mole. [b] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry, *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1 and references therein. [c] Differential UHF error on the electron affinities of X and Y, calculated by means of eqs 2 and 3 in the text.

All the above discussion has been illustrated in the case of Figure 1b, in which we have supposed that structures **1** and **2** have different energies but that this difference is correctly reproduced at the Hartree–Fock level. This is of course not always the case, owing to the fact, among others, that the Hartree–Fock error on electronegativities may widely vary from one fragment to another. The Hartree–Fock level may thus either underestimate or exaggerate the energy difference of **1** and **2**, leading in the latter case to an increased tilting of the E_{RS}(UHF) curve relative to E_{RS}(correlated) as illustrated in Figure 1c. In fact, as will be seen below, it is only in this latter case that significant MP*n* errors will be found. As one can see, a spectrum of situations may be encountered, but in all cases the MP*n* error is predicted to be related to the same inadequacy of the reference UHF determinant: its erroneous description of the sharing out of the charge between the two fragments that are three-electron-bonded. In such a case, a sophisticated method such as CCSD(T) has the definite advantage over perturbation methods to be much less sensitive to the quality of the starting orbitals.

B. Discussion of the Computational Results. As yet the qualitative valence bond analysis predicts that dissymmetrical three-electron-bonded anions are subject to errors at the MP*n* levels while symmetrical systems are not, and explains why the errors consist in (i) bond lengths being found too short and (ii) vibrational frequencies being found too large. It remains to be understood why the errors occur in some systems and not in others, and, more importantly, to be seen whether the validity of one given MP*n* calculation can be ascertained by some easy mean, without having to launch into high-level computations.

Several factors govern the relative energies of the $\ddot{X}^-\ \dot{Y}$ vs $\dot{X}\ddot{Y}^-$ VB structures, among which the relative electron affinities of X and Y atoms are expected to play the major role, at least for the lighter atoms of the series, where the effects of atomic polarizabilities are presumably not predominant. If, for example, X has a larger electron affinity than Y, then the $\ddot{X}^-\dot{Y}$ VB structure will be lower in energy than $\dot{X}\ddot{Y}^-$, as in Figure 1b. However, it can be seen in Table 4 that the differences in electron affinities are rather small for the halogen series (X = F, Cl, Br, I), whether experimental or accurately calculated values are considered. More important therefore than the electron affinities themselves are the UHF errors on these quantities, which can be quite significant (see Table 4). The UHF error, noted $\Delta\text{EA}(\text{X})$, on the electron affinity of X is calculated by reference to an accurate calculation, here CCSD(T), in the same basis set:

$$\Delta\text{EA}(\text{X}) = \text{EA}_{\text{UHF}}(\text{X}) - \text{EA}_{\text{CCSD(T)}}(\text{X}) \tag{2}$$

Inaccurate MP*n* results are to be expected when the UHF errors are very different for X and Y. Indeed, if, for example, the electron affinity of X is found to be more erroneous (i.e., more underestimated) than that of Y at the UHF level, then the $\ddot{\text{X}}^{-}\dot{\text{Y}}$ VB structure will be disfavored relative to $\dot{\text{X}}\ddot{\text{Y}}^{-}$ and the charge will be overlocalized on Y at this level, relative to experiment or to accurate computational levels. In such a case, the root cause for the UHF inadequacy and the subsequent MP*n* error is the *differential* UHF error in the calculated electron affinity of X and Y, which is defined as follows:

$$\Delta\Delta\text{EA}(\text{XY}) = \Delta\text{EA}(\text{X}) - \Delta\text{EA}(\text{Y}) \tag{3}$$

Now that we have tentatively spotted some general cases in which the MP*n* levels are likely to be unreliable, can one get a specific clue indicating that a given calculation is effectively in error? In other words, how can one *measure* the extent to which the UHF determinant is inadequate as a reference determinant for subsequent MP*n* calculations? As the problem originates in an erroneous sharing out of the negative charge at the UHF level, the simplest way to get a quantitative index for the UHF inadequacy is to compare the UHF- and MP2-calculated values for the net charges of the X and Y fragments. Let q_x and $1 - q_x$ be the net charges of the X and Y fragments, respectively, as calculated at the UHF level, while q_x' and $1 - q_x'$ are the net charges arising from the MP2 calculation. Calling $|\mathbf{1}\rangle$ and $|\mathbf{2}\rangle$ the valence bond structures $\ddot{\text{X}}^{-}\dot{\text{Y}}$ vs $\dot{\text{X}}\ddot{\text{Y}}^{-}$, the valence bond content of the UHF and MP2 wave functions, namely, Ψ_{UHF} and Ψ_{MP2}, can be expressed as in eq 4. An

$$\Psi_{\text{UHF}} = q_x|\mathbf{1}\rangle + (1 - q_x)|\mathbf{2}\rangle \tag{4a}$$

$$\Psi_{\text{MP2}} = q_x'|\mathbf{1}\rangle + (1 - q_x')|\mathbf{2}\rangle \tag{4b}$$

approximate expression (neglecting the $\langle\mathbf{1}|\mathbf{2}\rangle$ term) for the overlap between the UHF and MP2 valence bond (VB) representations is given by the index *S* in eq 5. It is clear that

$$S = \frac{q_x q_x' + (1 - q_x)(1 - q_x')}{[q_x^2 + (1 - q_x)^2]^{1/2}[q_x'^2 + (1 - q_x')^2]^{1/2}} \tag{5}$$

the resemblance of the UHF and MP2 wave functions in terms of the sharing out of the charge is measured by *S*, which is equal to unity if the net charges are identically estimated at both levels, and takes smaller values if the UHF and MP2 levels differ in this respect. Therefore, a large value of $1 - S$ is an indication that the UHF and MP2 electron densities are in poor agreement with each other, and that the MP*n* calculations will display systematic deviations of bond lengths and frequencies in proportion to $1 - S$ if our qualitative model is correct.

Let us now put the above qualitative considerations through the test of numerical data. The electron affinities of the halogen atoms, as calculated at the UHF and CCSD(T) levels, as well as the differential UHF errors for the various dihalogen anions and values of the $1 - S$ factor are displayed in Table 4. All calculated electron affinities underestimate the electron affinities relative to experiment. The agreement between experimental values and CCSD(T) values is better in the BS2 basis set than in the BS1 basis set, while the UHF values are in error by 1−2 eV in both basis sets. This latter error is however not uniform, being much larger for fluorine than for the other halogens, leading to large differential errors as displayed in the lower part of Table 4.

TABLE 5: Calculated Net Charges for the X Fragment in $X\therefore Y^-$ and Values of the $1 - S$ and $1 - S'$ Indices for the Dihalogen Anion Radicals

	BS1				BS2			
	q_x[a]	q_x'[b]	$1 - S$[c]	$1 - S'$[d]	q_x[a]	q_x'[b]	$1 - S$[c]	$1 - S'$[d]
$F\therefore Cl^-$	0.503	0.904	0.218	0.324	0.534	0.895	0.175	0.276
$F\therefore Br^-$	0.597	0.907	0.118	0.208	0.625	0.903	0.092	0.178
$F\therefore I^-$	0.749	0.800	0.003	0.078	0.767	0.796	0.001	0.074
$Cl\therefore Br^-$	0.578	0.493	0.014	0.121	0.576	0.565	0.000	0.104
$Cl\therefore I^-$	0.672	0.587	0.013	0.113	0.678	0.656	0.001	0.095
$Br\therefore I^-$	0.611	0.58	0.002	0.101	0.611	0.617	0.000	0.101

[a] Natural population analysis of the UHF wave function. [b] Natural population analysis of the MP2 wave function. [c] From eq 6. [d] From eq 8.

On the whole, it appears that the MP*n* errors are related in some way to the importance of the differential UHF errors on the fragments' electron affinities, as expected. Large $\Delta\Delta$EA values (22−33 kcal/mol) are indeed found for $F\therefore Cl^-$ and $F\therefore Br^-$, for which MP*n* results are inaccurate, while smaller $\Delta\Delta$EA values are found for $Cl\therefore Br^-$, $Cl\therefore I^-$, and $Br\therefore I^-$ that pose no particular problem. On the other hand, $F\therefore I^-$ is well described at the MP*n* levels despite its high $\Delta\Delta$EA value. An explanation for this apparent anomaly might come from the high polarizability of iodine, which possibly makes the relative energies of the $\dot{\text{F}}\ddot{\text{I}}^{-}$ and $\ddot{\text{F}}^{-}\dot{\text{I}}$ VB structures have nothing to do with the electron affinities of the fragments, and these energies are rather ruled by other factors. Be it as it may, the various effects that rule the sharing out of the charge at the UHF level result in an electron density which agrees or conflicts with that calculated at higher levels, as characterized by the 1 − S index.

The net charges for the X and Y fragments have been calculated by means of the standard natural population analysis, known to be more reliable than the Mulliken population analysis, and are shown in Table 5. Roughly speaking, the discrepancy between UHF- and MP2-calculated net charges is inferior to 10% for $F\therefore I^-$ and $Br\therefore I^-$, is somewhat larger (only in BS1) for $Cl\therefore I^-$ and $Cl\therefore Br^-$, and becomes quite large for the two remaining species, irrespective of the basis set. The values of $1 - S$ are reported side by side with the MP*n* errors relative to the CCSD(T) level in terms of X−Y bond lengths and stretching frequencies. It is found that the $1 - S$ quantity, which can be considered as a direct measure of the inadequacy of the UHF determinant, exhibits a remarkable correlation with the MP*n* error. Focusing on the calculations performed in BS1, the $1 - S$ index takes low values, smaller than 0.004, for $F\therefore I^-$ and $Br\therefore I^-$, two species that are rather accurately described at the MP2 level, with errors on the optimized bond lengths in the range 0.01−0.03 Å, which is quite satisfying if one recalls that bond lengths in the symmetric cases are found consistently too short by ca. 0.02 Å at the MP2 level. Slightly larger errors, 0.03−0.04 Å, are found for $Cl\therefore I^-$ and $Cl\therefore Br^-$, which exhibit values for $1 - S$ in the range 0.013−0.014. The largest errors, respectively, 0.085 and 0.152 Å, are found for $F\therefore Br^-$ and $F\therefore Cl^-$, and follow the order of the calculated $1 - S$ values, 0.12 and 0.22. Similar correlations are found with the results obtained in the BS2 basis set. More specifically, one can establish an empirical linear relationship between the $1 - S$ index and the MP2 error on the bond length:

$$\Delta R_{\text{eq}}\ (\text{Å}) = 0.546\ (1 - S) + 0.020 \tag{6}$$

where ΔR_{eq} is the quantity by which the MP2 bond length is underestimated relative to the CCSD(T) level. As applied to the series of dissymmetrical dihalogen radicals, eq 6 is able to predict the 12 values for the MP2 errors with an accuracy of ±0.013 Å, irrespective of the basis set that has been used. It is even possible to define an empirical expression that has a better predicting power than eq 6, at the cost of some extra complexity, by taking into account the overlap $\langle \mathbf{1}|\mathbf{2} \rangle$ between the two VB structures, a term which is neglected in the expression of S in eq 5. This leads to an improved expression for the S index, now called S' in eq 7, where γ is an empirically adjusted

$$S' = S + \gamma(q_x + q_x' - 2q_x q_x') \tag{7}$$

parameter that represents the unknown overlap $\langle \mathbf{1}|\mathbf{2} \rangle$. A new expression for ΔR_{eq} arises, eq 8, which is now able to reproduce the 12 MP2 errors on the X−Y bond lengths to an amazing accuracy of ±0.006 Å.

$$\Delta R_{eq}\ (\text{Å}) = 0.5816(1 - S') - 0.0313 \tag{8}$$

Similar, although more qualitative, correlations with the $1 - S$ or $1 - S'$ indices are obiously found for the MP2 errors on the stretching frequencies, since the latter have been found to be closely connected to the errors on bond lenghs. As for the dissociation energies, it has already been noted that they appear to be less affected than geometries and bonding frequencies by the UHF inadequacy. Yet, we believe this good agreement of MP*n* bonding energies with higher levels to be fortuitous. Indeed, the dissociation product of the $\mathrm{F}{\therefore}\mathrm{X}^-$ anion (X = Cl, Br) is of the type $\dot{\mathrm{F}}\ddot{\mathrm{X}}^-$, while the ground state of the bonded molecule is a mixture of the $\dot{\mathrm{F}}\ddot{\mathrm{X}}^-$and $\ddot{\mathrm{F}}^-\dot{\mathrm{X}}$ VB structures. If for some reason the MP*n* levels favor the latter VB structure with respect to the former, then this error tends to lower the ground state relative to the dissociation product. Examination of the MP*n* electron affinities of F, Cl, and Br shows that this is indeed the case. For example, the MP2/BS1 electron affinity of fluorine amounts to 78.5 kcal/mol, which is significantly higher than the CCSD(T) value and even larger than experiment. On the other hand, the electron affinities of chlorine and bromine, respectively, 73.5 and 75.2 kcal/mol at the same level, are less overestimated, clearly favoring $\ddot{\mathrm{F}}^-\dot{\mathrm{C}}\mathrm{l}$ over $\dot{\mathrm{F}}\ddot{\mathrm{C}}\mathrm{l}^-$ and $\ddot{\mathrm{F}}^-\dot{\mathrm{B}}\mathrm{r}$ over $\dot{\mathrm{F}}\ddot{\mathrm{B}}^-$. The same tendencies appear at the MP4 level and in the BS2 basis set. This artifact tends to increase the energy of the dissociation products relative to the molecule, thus counterbalancing the bonding energy decrease that was expected on the basis of the qualitative analysis above. These two sources of errors, which appear to fortunately cancel out in most cases, both disappear in symmetrical systems.

C. Trusting or Distrusting Møller−Plesset Calculations for Three-Electron-Bonded Radical Anions: A Thumb Rule. As shown from the qualitative considerations that have been developed in Section IV.A, there are some good theoretical reasons to trust Møller−Plesset calculations, even at second order, in the case of symmetrical three-electron-bonded anions. On the other hand, the unsymmetrical analogues are potentially subject to systematic errors in some well-defined cases that are easily recognized by considering some simple information that is routinely provided by the standard ab initio programs. The two above statements can be gathered in the following thumb rule, which is worth considering as a practical safeguard to check the validity of a computational investigation: *Optimized geometries, vibrational frequencies, and dissociation energies of three-electron-bonded radical anions can be calculated at the MP2 and MP4 levels and deemed reliable provided the UHF and MP2 population analyses yield comparable results, say within 10%, as regards the sharing out of the charges among the two fragments. If not, one expects the equilibrium distance of the three-electron bond to be found too short, while the corresponding stretching frequency should be found too high.*

TABLE 6: Electron Affinities EA(X)[a] of the Constituent Fragments of Some Typical Three-electron-bonded Organic Anions

	UHF/BS1 (this work)	exptl		UHF/BS1 (this work)	exptl
OH	−6.47	42.2[b]	SCH_3	15.36	42.9[c]
SH	26.17	53.3[c]	CF_3	9.68	42.4 ± 4[d]

[a] All energies in kilocalories per mole. [b] Celotta, R. J.; Bennet, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740. [c] Janousek, B. K.; Reed, K. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 3125. [d] Bartmess, J. E.; Scott, J. A.; McIver, R. T. *J. Am. Chem. Soc.* **1979**, *101*, 6047.

Owing to its physical basis, the above rule is expected to be general and to extend beyond the restricted domain of dihalogen anion molecules. Practically, some difficulties can be anticipated for systems composed of two fragments which have very different electron correlation requirements for their electron affinity to be calculated, leading to large ΔΔEA values. This may happen, for example, when one fragment has compact orbitals while the other has more diffuse ones. More generally, a large UHF error on the electron affinity is expected for a fragment that can only offer a confined space for an additional electron, thus making correlation effects particularly important. Finally, it is important to note that the above thumb rule is proposed on the basis of a two-structure VB model, and therefore cannot be extended to electronic systems that require more than two mesomeric structures for their qualitative description in VB terms. Such cases are encountered when, for example, one or both fragments have a delocalized electronic structure.[43] In the same way, the above analysis applies to simple three-electron bonds and not to multiply bonded systems. These limitations being placed, let us now apply the above rule to attempt some predictions on some unsymmetrical radical anions of chemical interest.

V. Application to Some Three-Electron-Bonded Organic Anions

Candidates for fragments that could possibly form three-electron-bonded anions are to be searched among good electron acceptors, displaying comparable electron affinities. HS and SCH_3 are well-known to be prone to form such interactions. The hydroxyl radical, HO, has an electron affinity comparable to that of SH (42.2 vs 53.3 kcal/mol experimentally). While the $\mathrm{HO}{\therefore}\mathrm{OH}^-$ isomer is unstable and collapses to hydrogen-bonded forms because of the large polarity of the O−H bond, a three-electron-bonded form of the type $\mathrm{HO}{\therefore}\mathrm{SR}^-$ can be thought of. The CF_3 radical also has an electron affinity (42.4 kcal/mol) in the same range as that of RS or OH, and has been shown to form three-electron bonds in $\mathrm{HS}{\therefore}\mathrm{CF_3}^-$ or $\mathrm{H_3CS}{\therefore}\mathrm{CF_3}^-$ radicals.[11] The list is of course by no means exhaustive. To restrain oneself to the above-cited examples, any combination between the HO, HS, H_3CS, and F_3C fragments can a priori lead to stable three-electron-bonded anions.

The electron affinities of these four radicals, as calculated at the UHF level in the 6-31+G* basis set (BS1) are displayed in Table 6 and compared with experimental values.

It appears that, if all UHF values are largely underestimated, the errors relative to experiment display considerable variations. While the electron affinities of $HS^\bullet$, $H_3CS^\bullet$, and $F_3C^\bullet$ are calculated with roughly constant errors on the order of 1 eV,

TABLE 7: Calculated Net Charges for the X Fragment in X∴Y⁻ and Values of the 1 − *S* and 1 − *S*′ Indices for the Organic Radical Anions

	q_x[a]	q_x'[b]	$1 - S$[c]	$1 - S'$[d]
HO∴SH⁻	0.288	0.711	0.304	0.429
HO∴SCH$_3$⁻	0.574	0.839	0.099	0.195
HO∴CF$_3$⁻	0.575	0.733	0.041	0.140
HS∴SCH$_3$⁻	0.598	0.505	0.017	0.123
HS∴CF$_3$⁻	0.533	0.493	0.003	0.110
H$_3$CS∴CF$_3$⁻	0.459	0.466	0.000	0.106

[a] Natural population analysis of the UHF wave function. [b] Natural population analysis of the MP2 wave function. [c] From eq 6. [d] From eq 8.

that of HO• is calculated with twice this error, and does not even display the correct sign. These tendencies are reasonable and expected (see above) since the negative charge in HO⁻, which has compact first-row orbitals, is more confined than it is in HS⁻ or H$_3$CS⁻. As for the fragment F$_3$C•, the UHF error on its electron affinity is intermediate between that of HO• and that of the other two radicals. From these data, one can tentatively expect that the largest MP2 errors on the optimized geometries will be found for HO∴SH⁻ and HO∴SCH$_3$⁻.

The geometries of the six possible three-electron-bonded anion radicals that can be made out of the four fragments above have been optimized at the MP2 level, in the 6-31+G* basis set (BS1), and the net charges (cumulated for each fragment) have been calculated at the UHF and MP2 levels. The results for the net charges, displayed in Table 7, are very contrasted. H$_3$CS∴CF$_3$⁻ and HS∴CF$_3$⁻ have their UHF- and MP2-calculated net charges in reasonable agreement, within 10%, and can thus be expected to be accurately described at the MP2 level, according to the above thumb rule. The agreement worsens for HS∴SCH$_3$⁻ and HO∴CF$_3$⁻,with a discrepancy of 20−30% between the UHF and MP2 values, leading to the prediction that the bond lengths for these two species will be found somewhat too short at the MP2 level, while the stretching frequencies (more specifically the force constants for the stretching of the three-electron bond) will be found too large. An MP2 error of the same type, but still larger, is predicted for HO∴SCH$_3$⁻ for which the UHF vs MP2 discrepancy for the calculated net charges is close to 50%. Last, a huge MP2 error is predicted for HO∴SH⁻, which displays completely different net charges at the UHF and MP2 levels.

Figure 2 shows the structures of the six radical anions, together with selected geometrical data and force constants, as fully optimized at the MP2 level and fully or partially optimized at the CCSD(T) level. The quality of the MP2 results, in terms of geometries and force constants, runs from excellent to very poor, depending on which system is considered. Thus, the MP2 bond lengths of H$_3$CS∴CF$_3$⁻ and HS∴CF$_3$⁻ are found to be quite close to the CCSD(T) values, only 0.01−0.02 Å too short, an excellent agreement if one recalls that MP2 bond lengths are found systematically slightly too short in symmetrical systems. The MP2 force constants are also reasonably accurate for these two species, leading to stretching frequencies within 4% of the CCSD(T) values. Next in accuracy come the HS∴SCH$_3$⁻ and HO∴CF$_3$⁻ systems with MP2 errors of 0.04−0.05 Å on the bond lengths, and nonnegligible overestimations of the force constants. Last, large MP2 errors are found for the two remaining systems, especially HO∴SH⁻ for which the bond length is 0.21 Å too short at this level, while the relative orientation of the two fragments, which is related to the strength of the three-electron bond, is also very poor. As for the force constant, it is more than 3 times too large, leading to a stretching frequency that would be overestimated by a factor of 1.75. All this closely follows the predictions that have been made above on the basis of calculated net charges. Moreover, the MP2 errors on the bond lengths of these organic systems are found to quantitatively correlate with the 1 − *S*′ index in eq 8, just as the errors on the dihalogens. This correlation is illustrated in Figure 3, which displays the whole set of MP2 errors that have been found in the 18 calculations of dissymmetrical systems that have been performed in the present work, in the BS1 or BS2 basis set, as a function of 1 − *S*′. It is clear that a nice linearity appears, meaning that the MP2 errors in dissymmetrical radical anions do not happen by accident but are on the contrary physically rooted and predictable.

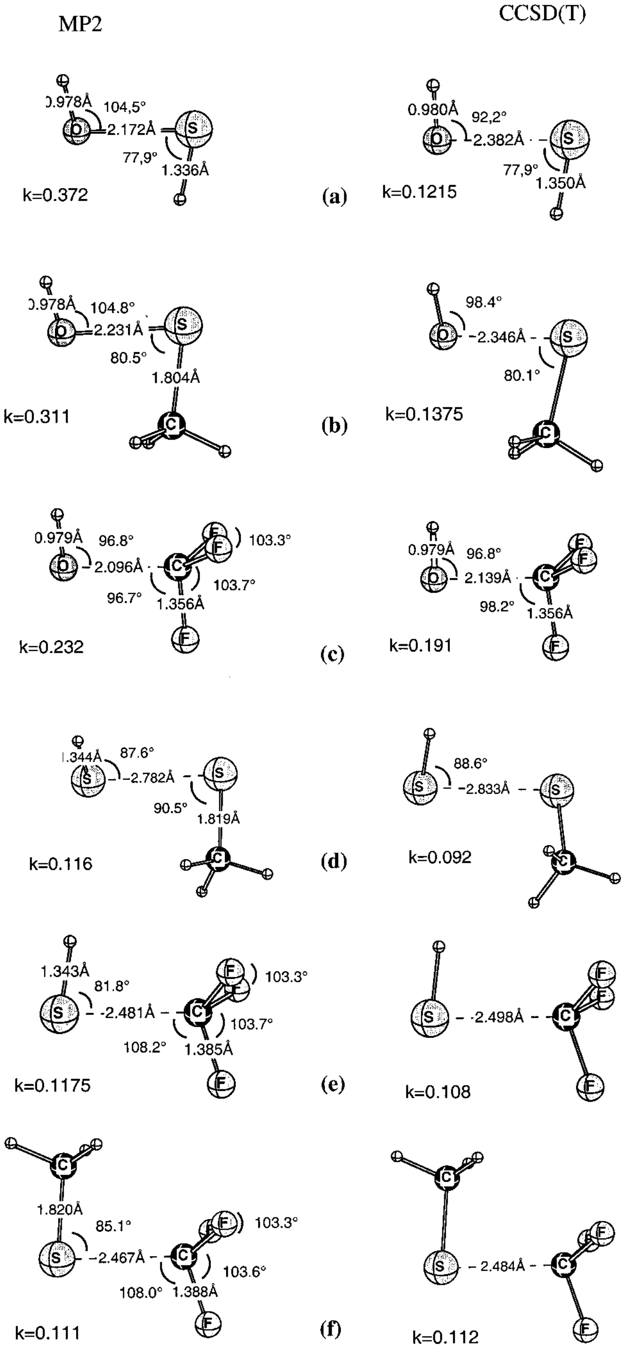


Figure 2. Geometries of (a) HO∴SH⁻, (b) HO∴SCH$_3$⁻, (c) HO∴CF$_3$⁻, (d) HS∴SCH$_3$⁻, and (e) H$_3$CS∴CF$_3$⁻, as optimized at the MP2 and CCSD(T) levels in the BS1 basis set. At the CCSD(T) level, the only parameters that are reoptimized relative to the MP2 geometry are those indicated.

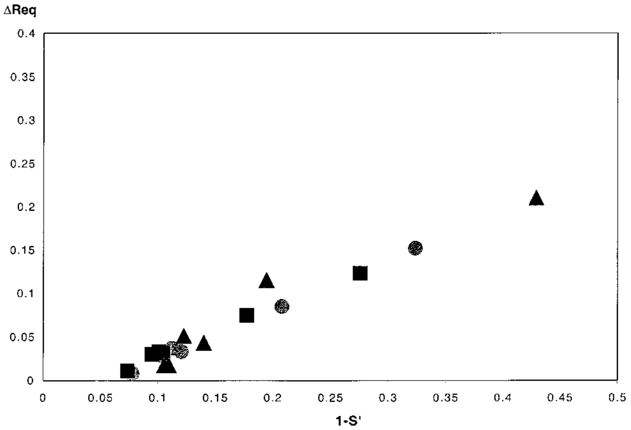


Figure 3. ΔR_{eq}, the MP2 error on the interfragment bond length, against the $1 - S'$ index (eq 8), for the whole series of unsymmetrical radical anions calculated in this work: (●) dihalogens in BS1; (■) dihalogens in BS2; (▲) organic radical anions in BS1.

VI. Conclusion

A qualitative model, based on a valence bond reading of MO wave functions for three-electron-bonded species, vindicates the often assumed fact that Møller−Pesset calculations offer a good description of symmetrical homonuclear three-electron bonds by providing fairly accurate equilibrium bond lengths, stretching frequencies, and dissociation energies. By contrast, the same model predicts that these optimistic conclusions cannot be extended blindly to isoelectronic systems devoid of left−right symmetry, and may break in some cases of *dissymmetrical* three-electron-bonded anions. The present calculations show that such systems are indeed potentially problematic, as MP2 or even MP4 results can display considerable errors on the optimized geometries and stretching frequencies. This warning is all the more relevant as the lowest of our MP*n* levels, MP2 in basis set BS1, is precisely the standard level for geometry optimization and better than standard for calculations of vibrational frequencies in the G2 procedure. Thus, among a series of dissymmetrical dihalogen anions, calculated in two different basis sets, completed by a set of three-electron-bonded organic anions, some errors peaking to 0.21 Å have been found in three-electron bond lengths at the MP2 level, while some vibrational frequencies are overestimated by a factor of almost 2.

The reason for the Møller−Plesset failure in such cases lies in a severe inaptitude of the UHF level to represent the sharing out of the negative charge among the two fragments. This inadequacy results in a set of optimized molecular orbitals that is poorly adapted to the subsequent perturbation calculation, and carries over to the MP2 and MP4 levels. Such situations have a chance to be encountered whenever the UHF errors on the electron affinities of the two fragments happen to be widely different.

The occurrence of the UHF inadequacy, and therefore of the MP*n* error, can fortunately be accurately detected by examining the net charges of the two fragments, as calculated by means of a standard natural population analysis performed at both the UHF and MP2 levels. The MP2 errors, relative to the accurate CCSD(T) level, on the interfragment bond lengths and on the stretching frequencies are shown to be systematic and predictable, as linearly related to a simple function of the fragments' net charges. There follow some simple thumb rules: (i) The MP2 and MP4 levels are predicted to perform well for symmetrical three-electron-bonded anions, and provide equilibrium geometries, vibrational frequencies, and dissociation energies that are in good agreement with each other and with higher levels of computation. (ii) Unsymmetrical three-electron-bonded anions $X\therefore Y^-$ subdivide into two cases. If the MP2-calculated net charges for the X and Y fragments remain comparable to the UHF-calculated ones, then the MP2 and MP4 levels should be reliable for the study of the $X\therefore Y^-$ system. If on the contrary the two sets of net charges widely differ from each other, then the MP*n* levels should lead to errors that consist of systematically biased geometries and frequencies for $X\therefore Y^-$, the X−Y bond length being found too short and the corresponding vibrational frequency too high.

The above rules—and in particular the optimistic conclusions for the MP2 description of symmetrical systems—are limited to simple three-electron bonds and do not extend to multiply bonded systems nor to delocalized three-electron-bonded systems that must be represented by more than two mesomeric structures. This restriction being placed, no exception to these rules has been found among the 26 calculations of symmetrical or dissymmetrical species that have been performed in this work.

What then are the best alternative computational methods in cases where the MP*n* levels are expected to fail? DFT might be thought of, as in such methods the orbitals are determined by taking electron correlation into account, thus avoiding the inappropriate orbitals arising from the Hartree−Fock level. Unfortunately, DFT methods have been shown to perform very poorly for three-electron bonds,[26] with the exception of the BHLYP functional that is better than the others but still not very reliable. On the other hand, a valence bond method like BOVB[38] completely avoids the competition between orbital size effects and resonance, which is the root cause of the UHF and subsequent MP*n* problems. However, this method is not applicable to large systems for reasons of computational cost, like any method dealing with nonorthogonal orbitals, owing to the well-known *n*! problem. Work is presently in progress, in our laboratory, for defining small MCSCF expansions that would reproduce the valence bond results in the framework of molecular orbitals. In the meantime, difficult cases such as those that have been defined above require CCSD(T) or other high computational levels.

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(43) Although the present study is devoted to anions, the F_4^+ system can be used to illustrate this limitation of the thumb rules that predict simple three-electron bonds to be well described at the MP2 level. F_4^+ is stabilized with respect to F_2 and F_2^+ by a three-electron bond of the type $(F_2\therefore F_2)^+$. Now F_2^+ itself is a delocalized system which has two mesomeric forms. It follows that $(F_2\therefore F_2)^+$ has a total of four mesomeric forms, so that the thumb rules do not apply. As a matter of fact, the MP2 description of the C_{2h} conformer of F_4^+ is totally misleading. For detailed results and discussions, see: Hiberty, P. C.; Berthe-Gaujac, N. *J. Phys. Chem. A* **1998**, *102*, 3169.