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**AB INITIO CALCULATION
OF THE IONIZATION POTENTIALS AND HYPERFINE SPLITTING CONSTANTS
OF THE RADICAL ANIONS FCl^- AND Cl_2^-**

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Employing a CI wavefunction with a DZ+(2d) basis set, the isotropic hyperfine splitting constants for the F and Cl nuclei in the gas-phase radical anions FCl^- and Cl_2^- were evaluated. The ionization potentials are calculated as 2.10–2.27 eV for FCl^- and 2.22–2.28 eV for Cl_2^- , the latter comparing well with the experimental value of 2.32–2.38 eV.

The accurate evaluation of molecular electron affinities (EAs) for neutral species (conversely, ionization potentials of anions) and hyperfine splitting constants (hfs) for radicals are currently difficult problems for computational chemistry. For EAs, the difficulty arises mainly from the non-conservation of electron pairs in going from the neutral molecule to the anion. This can easily lead to an unbalanced treatment of the correlation energies in the neutral and the ion [1]. A recent systematic study [2] of the EAs of small doublet radicals (open shell for neutrals and closed shell for anions) showed that even at full fourth order in Møller–Plesset perturbation theory with large basis sets, the differences between calculated and experimental values still remain large (up to 0.5–0.7 eV). Nevertheless, the situation in radical anions (e.g. closed shell for the neutrals and open shell for the anions) may be somewhat better [3].

For the hfs constants, it has been shown that these are often inadequately evaluated by standard basis sets [4]. Reliable prediction requires large CI calculations. However, most ab initio studies to date have focused on neutral and cationic radicals (see for

example refs. [5,6]). Little is known on the theoretical determination of this property for radical anions [3,5].

Recently, a number of small radical anions have been generated and trapped as free ions in dilute neon matrices at low temperature [5]. Their magnetic properties have subsequently been determined by means of electron spin resonance (ESR) spectroscopy. In this context, accurate theoretical hfs values for these species in the gas phase may be useful for the interpretation of matrix data. In this communication, we wish to report a preliminary assessment of ab initio calculations in determining both the ionization potentials (IP) and hfs constants of simple radical anions. As a test case, the diatomic halogen ions FCl^- and Cl_2^- were considered. The F_2/F_2^- system has been studied in some detail in a previous work [3].

Firstly we examine the theoretical determination of the adiabatic IPs (i.e. the EAs) of FCl and Cl_2 . Calculations were performed with a variety of different basis sets ranging from the split-valence plus sp-diffuse and d-polarization functions 6-31+G(d) [7] through a double-zeta plus sp-diffuse and d-polari-

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zation functions DZ+(2d) [8] to a basis including f-polarization functions 6-31+G(2df) [7]. The bond length of each species was optimized at second order in Møller–Plesset perturbation theory (MP2) [9] using the 6-31+G(d) basis set. In each case, the energy difference between the ground states of the neutral molecule and the radical anion was obtained at the Hartree–Fock, second- through fourth-order MP perturbation theory [9] and configuration interaction (CI) levels. For the perturbation calculations, the unrestricted formalism (UHF, UMP) was employed for the anions. In the CI calculations which used the DZ+(2d) basis set, the CI matrix included all configurations generated from single and double excitations from all valence shell orbitals to all virtual orbitals. These were selected by perturbation theory with an energy threshold of 10^{-6} hartree. The CI calculations for the anions were based on a restricted open-shell Hartree–Fock wavefunction [10]. Tables 1 and 2 list the calculated energies and EAs for Cl_2 and Cl_2^- , respectively.

As with F_2/F_2^- [3], extension of the basis set and/or inclusion of correlation energy only slightly change the computed EA of Cl_2 . The two effects act in the opposite direction: inclusion of higher polarization functions such as a second set of d-functions or a set

of f-function always decreases the EA (by ≈ 0.15 eV) whereas inclusion of correlation energy tends to increase it (table 1). The larger the basis set, the smaller the correlation correction. In addition, higher-order perturbation theory (UMP3, UMP4) does not affect the UMP2 values. This is in line with a previous conclusion [2] for cases in which the UHF wavefunctions have low spin contamination ($\langle S^2 \rangle_{\text{UHF}} = 0.78$ for Cl_2^-).

The RCI values are comparable with the UMP ones bearing in mind that the basis set used is not the same. Overall, our best UMP value of 2.28 eV and RCI value of 2.22 eV for the EA of Cl_2 compare quite favourably with experimental values of 2.32 ± 0.1 [11] and 2.38 ± 0.1 eV [12]. For a comparison, note that the EA of F_2 previously calculated at similar levels (2.8 eV at RCI and 3.0 eV at UMP) also compares well with the experimental values, which are in the range 2.96 to 3.08 eV [3].

With regard to the computed EAs for FCI (table 2), a similar trend in the polarization and correlation effects occurs. Our best values, namely 2.10 eV at UMP and 2.27 eV at RCI, are probably underestimates; based on the above results we predict an EA of 2.4 ± 0.2 eV for this species.

Some molecular properties calculated using the

Table 1

Total energies (hartree) for Cl_2 and Cl_2^- and electron affinities (eV) of Cl_2 at different levels of theory

Method	$E(\text{Cl}_2)$	$E(\text{Cl}_2^-)$	EA(Cl_2)
UHF/6-31+G(d)//UHF/6-31+G(d) ^{a)}	-918.91469	-919.00852	2.55
UMP2/6-31+G(d)//MP2/6-31+G(d) ^{b)}	-919.17502	-919.26457	2.44
UMP3/6-31+G(d)//MP2/6-31+G(d)	-919.20014	-919.28901	2.42
UMP4SDQ/6-31+G(d)//MP2/6-31+G(d)	-919.20216	-919.29091	2.42
UMP4SDTQ/6-31+G(d)//MP2/6-31+G(d)	-919.20840	-919.29641	2.40
UHF/6-31+G(2d)//MP2/6-31+G(d)	-918.92305	-919.00968	2.36
UMP2/6-31+G(2d)//MP2/6-31+G(d)	-919.22093	-919.31314	2.51
UHF/6-31+G(2df)//MP2/6-31+G(d)	-918.93011	-919.01091	2.20
UMP2/6-31+G(2df)//MP2/6-31+G(d)	-919.28417	-919.36785	2.28
RCISD/DZ+(2d)//MP2/6-31+G(d) ^{c)}	-919.15558	-919.23597	2.19
RCISDQ/DZ+(2d)//MP2/6-31+G(d) ^{d)}	-919.18618	-919.26772	2.22
Expt.			2.32 ^{e)} , 2.38 ^{f)}

^{a)} The HF/6-31+G(d) bond lengths are 1.993 Å (Cl_2) and 2.675 Å (Cl_2^-).

^{b)} The MP2/6-31+G(d) bond lengths are 2.018 Å (Cl_2) and 2.652 Å (Cl_2^-) using the full set of orbitals.

^{c)} CI dimensions and C_0 coefficients are 3153 and 0.9509 for Cl_2 , and 7438 and 0.9501 for Cl_2^- , respectively (energy threshold $T=10^{-6}$ au).

^{d)} Including Davidson's correction for quadruple excitations.

^{e)} Ref. [11]. ^{f)} Ref. [12]. For a previous SCF calculation, see ref. [13].

Table 2

Total energies (hartree) and electron affinities (eV) of FCl at different levels of theory

Method	$E(\text{FCl})$	$E(\text{FCl}^-)$	EA(FCl)
UHF/6-31+G(d)//UHF/6-31+G(d) ^{a)}	-558.82741	-558.91424	2.36
UMP2/6-31+G(d)//UMP2/6-31+G(d) ^{b)}	-559.14327	-559.21577	1.97
UMP3/6-31+G(d)//UMP2/6-31+G(d)	-559.15142	-559.22475	1.99
UMP4SDQ/6-31+G(d)//UMP2/6-31+G(d)	-559.15928	-559.23236	1.99
UMP4SDTQ/6-31+G(d)//UMP2/6-31+G(d)	-559.16795	-559.23985	1.96
UHF/6-31+G(2d)//UMP2/6-31+G(d)	-558.82778	-558.90399	2.07
UMP2/6-31+G(2d)//UMP2/6-31+G(d)	-559.19273	-559.27503	2.24
UHF/6-31+G(2df)//UMP2/6-31+G(d)	-558.83350	-558.90485	1.94
UMP2/6-31+G(2df)//UMP2/6-31+G(d)	-559.24610	-559.32340	2.10
RCISD/DZ+(2d)//UMP2/6-31+G(d) ^{c)}	-559.10724	-559.17528	1.85
RCISDQ/DZ+(2d)//UMP2/6-31+G(d) ^{d)}	-559.13385	-559.21726	2.27

^{a)} The HF/6-31+G(d) bond lengths are 1.614 Å (FCl) and 3.036 Å (FCl⁻).^{b)} The MP2/6-31+G(d) bond lengths are 1.668 Å (FCl) and 2.049 Å (FCl⁻) using the full sets of orbitals.^{c)} CI dimensions and C_0 coefficients are 4250 and 0.9555 for FCl and 7808 and 0.9550 for FCl⁻, respectively (energy threshold $T=10^{-6}$ au).^{d)} Including Davidson's correction for quadruple excitations $\Delta E_Q = \Delta E_{SD}(1 - C_0^2)$.

Table 3

A comparison of calculated molecular properties for FCl and FCl⁻, and Cl₂ and Cl₂⁻ using CI wavefunctions

Property ^{a)}	FCl(¹ Σ ⁺)	FCl ⁻ (² Σ ⁺)	Cl ₂ (¹ Σ _g ⁺)	Cl ₂ ⁻ (² Σ _u ⁺)
dipole moment ^{b)}	0.4120	0.6125	0.0	0.0
quadrupole moment ^{b)}				
$Q_{xx} = Q_{yy}$	-0.4432	2.5899	-1.1199	6.6286
Q_{zz}	0.8864	-5.1798	2.2398	-13.2572
second moment ^{c)}				
$\langle x^2 \rangle = \langle y^2 \rangle$	-13.0245	-15.1556	-18.8927	-21.2236
$\langle z^2 \rangle$	-12.1381	-20.3354	-16.6530	-34.4808
electric field gradient ^{c)}				
$q_{zz}(\text{F})$	4.2462	1.8890	-	-
$q_{zz}(\text{Cl})$	7.2667	3.2553	5.6622	2.7549
spin density ^{c)}				
$\rho(\text{F})$	-	0.3938	-	-
$\rho(\text{Cl})$	-	0.4103	-	0.2515
hyperfine splitting constant ^{d)}				
$a(\text{F})$	-	591.1	-	-
$a(\text{Cl})$	-	64.2	-	39.4

^{a)} With RCISD/DZ+(2d) wavefunctions using the MP2/6-31+G(d)-optimized geometries given in tables 1 and 2.^{b)} Calculated at center of mass in au. ^{c)} In au. ^{d)} In G.

RCISD wavefunctions are presented in table 3. The second moment of the charge distribution in each radical anion is about twice as large as in the corresponding neutral. This diffuse character can also be seen in their large quadrupole moments with respect to the neutrals. The electric field gradient at the F

and Cl nuclei are markedly reduced ($\approx 50\%$) in the ions.

Of particular interest are the spin density (ρ) and the isotropic hyperfine splitting constants (a) at F and Cl nuclei. The spin density at each nucleus is defined as:

$$\rho(A) = \langle \Psi | \sum_i \delta(r_i - R_A) 2\hat{S}_{zi} | \Psi \rangle$$

and the isotropic coupling is given by:

$$a(A) = \frac{8}{3}\pi (g_e/g_0) g_A \beta_A \rho(A).$$

All symbols have their standard meaning. The hfs constant (G) and the spin density (au) are connected by

$$a(^{19}\text{F}) = 1501.0\rho(\text{F}),$$

$$a(^{35}\text{Cl}) = 156.5\rho(\text{Cl}).$$

At the RCISD/DZ+(2d) level, the isotropic hyperfine splitting constants are: $a(\text{F}) = 591.1$ G and $a(\text{Cl}) = 64.2$ G in FCl^- and $a(\text{Cl}) = 39.4$ G in Cl_2^- at their UMP2/6-31+G(d) equilibrium distances. At a similar level (RCISD/DZP+(d)) $a(\text{F})$ in F_2^- was calculated to be 520.0 G [3]. It is known that a values are not particularly sensitive to the basis sets employed. Thus, both hyperfine couplings in the heteropolar anion FCl^- are larger than those in the homonuclear diatomic species. For F_2^- , a value of $a(\text{F}) = 280.2$ G was obtained from the neon matrix experiment [14]. Such a large difference between computed and observed values may be accounted for by specific conditions inherent to the matrix experiments.

As a preliminary attempt to check this, the dependence of the isotropic coupling constant on the bond distance was also examined. As seen in table 4, this quantity is very sensitive to the bond length. For example, the $a(\text{F})$ value in FCl^- is reduced from 591.1 to 497.0 G when the F-Cl distance is reduced by 0.2 au. A similar pattern is observed for the $a(\text{Cl})$ values: the shorter the bond distance, the smaller the hyperfine coupling. Under matrix conditions, a radical anion may easily be frozen in its vertical neutral structure. In this context, the observed matrix a value is probably much smaller than the gas-phase value which is often associated with significant relaxation of the geometry. The F_2^- case (see above) is typical in this respect.

In summary, the results described above indicate that the ionization potentials of diatomic halogen radical anions (i.e. the electron affinities of neutral closed-shell molecules) can be accurately evaluated at a computationally reasonable level of theory such

Table 4

Spin densities (ρ) and hyperfine splitting constants (a) in FCl^- and Cl_2^- radical anions calculated at different bond distances near equilibrium ^{a)}

Δr (au)	ρ (au)		a (G)	
	F	Cl	^{19}F	^{35}Cl
+0.2	0.4704	0.4865	706.1	76.1
0.0	0.3938	0.4103	591.1	64.2
-0.2	0.3311	0.3424	497.0	53.6

Δr (au)	ρ (au)	a (G)
Cl_2^-	Cl	^{35}Cl
+0.4	0.7687	120.3
0.0	0.2515	39.4
-0.4	0.1828	28.6

^{a)} With RCISD/DZ+(2d) wavefunctions using the MP2/6-31+G(d)-optimized geometries given in tables 1 and 2.

as UMP2/6-31+G(2d) (provided the spin contamination is low). The error is found to be about 0.1–0.2 eV with respect to the experimentally estimated values. On the other hand, isotropic hyperfine splitting constants computed using RCISD wavefunctions may provide useful information on the real structure of the radical anions under matrix conditions.

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