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MRSDCI studies of low-lying electronic states of the CF_2^+ ion

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Summary. The equilibrium geometries, excitation energies, force constants and vibrational frequencies for four low-lying electronic states $X\,^2A_1$, $^2B_1$, $^2B_2$ and $^2A_2$ of the CF_2^+ ion have been calculated at the MRSDCI level with a double zeta plus polarization basis set. Our calculated excitation energies for these states and vibrational frequencies for the ground state are in good agreement with experimental data via photoelectron spectroscopy of the CF_2 radical (carbene). The electronic transition dipole moments, oscillator strengths for the $^2B_1 \rightarrow X\,^2A_1$ and $^2B_2 \rightarrow X\,^2A_1$ transitions, radiative lifetimes for the $^2B_1$ and $^2B_2$ states and the spin properties for the $X\,^2A_1$ state are calculated based on the MRSDCI wavefunctions.

Key words: MRSDCI – Excitation energy – Oscillator strength – Radiative lifetime – Hyperfine coupling constant

1. Introduction

The CF_2 radical (carbene) is believed to be created in the upper atmosphere by the photodissociation of chlorofluormethanes, and is an important intermediate in discharge environments containing CF_4, which is widely used as a source of F atoms and as a process gas in plasma etching applications. Theoretical and experimental investigations on the CF_2 radical have been widely made by many authors [1–7]. However there have been few studies of its ion states, i.e., the electronic states of the CF_2^+ radical cation. In recent years, there has been an increasing interest in understanding the chemistry of CF_2^+ since it may exist in the upper atmosphere, and little is known of its geometries and spectroscopic properties. In 1974, Dyke et al [8] studied the CF_2^+ ion via photoelectrom spectroscopy (PES) of the CF_2 radical, and obtained some vibrational frequencies and transition energies for the ground and excited states of the CF_2^+ ion. In 1979, Andrews and Keelan [9] obtained the asymmetric stretch frequency of the ground state of CF_2^+ from their IR spectrum.

In the literature, there are no reported experimental data for the geometries of the ground and excited states of the CF_2^+ ion. However, there are several theoretical studies for the ground and excited states of the CF_2^+ ion [10, 11]. In

1985, Koch and Frenking [10] performed *ab initio* calculations on the ground state at different levels (from UHF/4-31G to MP2/6-31G*). They obtained optimized geometric parameters, and the optimized values for the bond length range from 1.204 to 1.243 Å and for the angle from 124.3 to 124.9°. Hrovat and Borden [11] calculated the geometry of the excited state $^2A_2$ at the MCSCF level with a $9s5p1d/3s2p1d$ basis set, and also discussed dissociation properties of CF_2^+ ($^2A_2$).

We have studied four low-lying electronic states of the CF_2^+ ion, $X\,^2A_1$, $^2B_1$, $^2B_2$, and $^2A_2$, by means of multi-reference single and double excitation configuration interaction (MRSDCI) calculations with a double zeta plus polarization (DZ + P) basis set. In this paper, we report the optimized equilibrium geometries, calculated excitation energies, force constants and vibrational frequencies for these electronic states. We also report electronic transition properties for the $^2B_1 \rightarrow X\,^2A_1$ and $^2B_2 \rightarrow X\,^2A_1$ transitions and the hyperfine coupling constants for the ground state $X\,^2A_1$. These calculated results will be compared with available experimental data.

2. Details of calculations

The AO basis for CF_2^+ consists of the ($9s$, $5p$) cartesian gaussian basis for C and F in the [$4s$, $2p$] contraction, given by Dunning [12], augmented by uncontracted d-functions (6-term cartesian d's) with exponent 0.75 for carbon and 0.90 for fluorine [13], yielding a total of 48 contracted basis functions.

The MRSDCI calculations were performed using the program package MELDF [14] on a VAX 8350 computer.

In all calculations, we used the SCF (ROHF) orbitals, different ROHF orbitals were chosen for different electronic states. All ROHF orbitals include occupied and virtual orbitals. Before CI, the SCF (ROHF) virtual orbitals were transformed into K-orbitals [15], which have been shown to mimic frozen natural orbitals of the system, thus improving the convergence of CI. In the MRSDCI calculations, all the single excitations from the (multi-) reference configurations were included, as well as the most important double excitations, as selected by second-order perturbation theory [16] with a selection threshold $T = 10$ μh. The reference space in our MRSDCI calculations for the chosen states consisted of $6 \sim 7$ configurations, generated from selected space-orbital products whose coefficients are not less than 0.05, as listed in the next section. The energy values are denoted by E and E (full CI) corresponding to the MRSDCI energy at the configuration selection threshold T and the energy estimated according to the Davidson formula (full CI) [14].

In our study, we assume that the CF_2^+ ion has a C_{2v} geometry in each of the four electronic states. Therefore, only two geometric parameters, bond length R(C–F) and bond angle $\angle$F–C–F, were considered in searching for the optimized geometries by a simple fitting procedure. The force constant (k_1 and k_δ) and fundamental frequency (symmetric (ν_1), asymmetric (ν_3) stretching and bending (ν_2) vibrational frequencies) calculations were performed by means of a simple approach, described and tested for NF_2, OF_2^+ and BF_2 in [17–19], based on the assumption of valence forces [20]. Such an approach requires only a dozen single energy calculations and predicts quite accurate force constants (k_1 and k_δ) and fundamental frequency (ν_1, ν_2, and ν_3) values for XY_2 molecules [17–19].

3. Results and discussion

3.1 The $X\,^2A_1$ state

The ground state $X\,^2A_1$ was calculated as the lowest root in the secular equation for the A_1 irreducible representation of the C_{2v} group. The reference space in the MRSDCI calculations for the $X\,^2A_1$ state consisted of 6 configurations, generated from the following five space-orbital products (listed according to space symmetry, not the orbital energy level ordering):

(1) $(1a_2)^2(1\sim 4b_2)^2(1b_1)^2(1\sim 5a_1)^2(6a_1)^1$;

(2) $(1\sim 4b_2)^2(1\sim 2b_1)^2(1\sim 5a_1)^2(6a_1)^1$;

(3) $(1a_2)^2(1\sim 4b_2)^2(1b_1)^1(2b_1)^1(1\sim 5a_1)^2(6a_1)^1$;

(4) $(1a_2)^2(1\sim 4b_2)^2(2b_1)^2(1\sim 5a_1)^2(6a_1)^1$;

(5) $(1a_2)^2(1\sim 2b_2)^2(4\sim 5b_2)^2(1b_1)^2(1\sim 5a_1)^2(6a_1)^1$,

the first one being the most important. The total number of configurations was about 14 000. The total contribution to the final wavefunction from the reference set is $\sum_p^{ref} C_p^2 = 0.92$. The CI energies at our optimized geometry of the $X\,^2A_1$ state are $E = -263.76595$ and E (full CI) $= -263.82221$ h. The optimized values for the bond length and angle are shown in Table 1. In 1985, Koch and Frenking [10] calculated the equilibrium geometry of the $X\,^2A_1$ state of the CF_2^+ ion at the UHF/4-31G, UHF/6-31G* and MP2/6-31G* levels and their values for the bond length at these three levels ere significantly different, but for the bond angle were similar (see Table 1). Our MRSDCI value for the bond angle is very close to the MP2/6-31G* value, and our value for the bond length is only 0.01 Å shorter than the MP2/6-31G* one. We believe that our optimized geometry is more accurate than previous MP2/6-31G* and other *ab initio* calculations although there are no

Table 1. Optimized geometric parameters and (adiabatic and vertical) excitation energies for four low-lying electronic states of the CF_2^+ ion

State	R(C–F) (Å)	∠F–C–F (°)	T_e (eV)	
			Adiabatic	Vertical
$X\,^2A_1$	1.222	124.5	0.0	0.0
UHF/4-31G[a]	1.243	124.9		
UHF/6-31G*[a]	1.204	124.3		
MP2/6-31G*[a]	1.232	124.4		
$^2B_1(^2\Pi_u)$	1.232	180.0	2.799(2.857)[b]	2.992(3.012)[b]
$^2B_2$	1.370	86.0	4.658(4.459)[b]	4.931(4.725)[b]
				expt. 4.982 ± 0.030[c]
$^2A_2$	1.401	97.6	5.673(5.375)[b]	6.023(5.824)[b]
MCSCF/(9s5p1d/3s2p1d)[d]	1.356	95.1		
				expt. 5.977 ± 0.124[c]

[a] [10]

[b] Values in parentheses were evaluated from the estimated full CI energies

[c] [8] (vertical excitation energies)

[d] [11]

experimental data for comparison. In our *ab initio* calculations, electron correlation energy was well considered using the MRSDCI method with a DZ + P basis set, and the MRSDCI/DZ + P calculations considered electron correlation energy better than the MP2/6-31G* one. In general, the geometries (and spectroscopic properties) at the MRSDCI/DZ + P level are accurate, see for example [18, 19, 21–28].

The force constants of the $X\,^2A_1$ state, calculated on the MRSDCI/DZ + P energy surface by means of the valence force assumption, are listed in Table 2. The vibrational frequencies calculated from our predicted force constants are also in Table 2. Our calculated vibrational (fundamental) frequency values of bending mode ν_2 and asymmetric stretch mode ν_3 are in good agreement with experimental data [8, 9].

The spin properties of the $X\,^2A_1$ state of the CF_2^+ ion have been calculated based on the MRSDCI wavefunction at the optimized geometry using the same program package MELDF. The calculated isotropic (a) and anisotropic (A) hyperfine coupling constants from the atoms (assuming $C = {}^{13}C$ and $F = {}^{19}F$) are given in Table 3.

3.2 The $^2B_1$ state

This state was treated as the lowest root in the secular equation for the B_1 irreducible representation. The reference space in the MRSDCI calculations for this state consisted of 7 configurations, generated from the following five selected

Table 2. Calculated force constants (k) and vibrational frequencies (ν) for four low-lying electronic states of the CF_2^+ ion

State	k_1 (mdyn/Å)	k_δ (mdyn · Å)	k_δ/l^{2a} (mdyn/Å)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})
$X\,^2A_1$	8.22877	1.86007	1.24562	1259	656	1599
					expt. 650 ± 40[b]	1588[b]
$^2B_1$	5.23082	2.14647	1.41418	1025	684	1395
$^2B_2$	6.64706	2.07134	1.10360	1349	519	1211
$^2A_2$	6.95263	2.86195	1.45810	1304	606	1317

[a] l, optimized bond length R(C–F)
[b] [8, 9]

Table 3. Calculated isotropic (a) and anisotropic (A) coupling constants for the atoms ($C = {}^{13}C$ and $F = {}^{19}F$) in the $X\,^2A_1$ state of the CF_2^+ ion

	a (G)	$A_\parallel$ (G)	$A_\perp$ (G)
C	412.6	455.4	553.3
F	149.3	302.1	103.7

space-orbital products:

(1) $(1a_2)^2(1\sim 4b_2)^2(1b_1)^2(2b_1)^1(1\sim 5a_1)^2$;

(2) $(1a_2)^2(1\sim 3b_2)^2(1b_1)^2(2b_1)^1(1\sim 3a_1)^2(4a_1)^1(5a_1)^2(6a_1)^1$;

(3) $(1a_2)^2(1\sim 3b_2)^2(1b_1)^2(2b_1)^1(1\sim 5a_1)^2(7a_1)^2$;

(4) $(1a_2)^2(1\sim 4b_2)^2(1b_1)^2(2b_1)^1(1\sim 4a_1)^2(7a_1)^2$;

(5) $(1a_2)^2(1\sim 4b_2)^2(1b_1)^2(2b_1)^1(1\sim 4a_1)^2(5a_1)^1(7a_1)^1$,

the first one being the most important. The total number of configurations was about 10 000. The total contribution to the final wavefunction from the reference set is $\sum_p^{ref} C_p^2 = 0.92$. The optimized values for the bond length and angle are 1.232 Å and 180.0°, respectively. It is obvious that the CF_2^+ ion at this state is linear, and $CF_2^+(^2B_1)$ correspond to $CF_2^+(^2\Pi_u)$. It is noted that the predicted bond lengths for the $^2B_1(^2\Pi_u)$ and $X\,^2A_1$ states are similar while the angles are considerably different, which indicates that the bending vibrational mode of the $^2B_1(^2\Pi_u)$ state will be excited in the $X\,^2A_1 \rightarrow {}^2B_1(^2\Pi_u)$ transition. This phenomenon should be observed in future experiments.

Our predicted adiabatic excitation energy for $X\,^2A_1 \rightarrow {}^2B_2(^2\Pi_u)$, as the difference of the CI energies at the corresponding optimized geometries of these two states, is 2.799(2.857) eV (value in parentheses was evaluated from the estimated full CI energies). We also calculated the vertical excitation energy for $X\,^2A_1 \rightarrow {}^2B_2$ at the $X\,^2A_1$ state equilibrium conformation, which is 2.992(3.012) eV.

For the $X\,^2A_1 \rightarrow {}^2B_1(^2\Pi_u)$ transition that is electron dipole allowed, we calculated the electronic transition properties based on the MRSDCI wavefunctions, using the same package program. The calculated values for the square of the electronic transition dipole moment, the oscillator strength for the absorption (taking $\Delta E = 2.799$ eV (corresponding to adiabatic excitation) and 2.992 eV (corresponding to vertical excitation), respectively), and the radiative lifetime (adiabatic and vertical transition) for the $^2B_1(^2\Pi_u)$ state are given in Table 4.

For the $^2B_1(^2\Pi_u)$ state, the force constants and vibrational (fundamental) frequencies have been calculated and shown in Table 2.

3.3 The $^2B_2$ state

This state was treated as the lowest root on the secular equation for the B_2 irreducible representation. The reference space in the MRSDCI calculations for

Table 4. Calculated values of the properties dependent upon the electronic transition dipole moment (R_e) for the $^2B_1 \rightarrow X\,^2A_1$ and $^2B_2 \rightarrow X\,^2A_1$ band systems

	Transition dipole moment $\Sigma\lvert R_e\rvert^2$ (a.u.)	Oscillator strength f_e (a.u.)	Radiative lifetime τ (ns)
$^2B_1 \rightarrow X\,^2A_1$	0.44414(0.46124)[a]	0.01523(0.01691)[a]	193(152)[a]
$^2B_2 \rightarrow X\,^2A_1$	0.12412(0.11324)[a]	0.00708(0.00680)[a]	150(139)[a]

[a] Values in parentheses correspond to vertical excitation and were calculated taking vertical excitation energies

this state consisted of 7 configurations, generated from the following five selected space-orbital products:

(1) $(1a_2)^2(1\sim 3b_2)^2(4b_2)^1(1b_1)^2(1\sim 6a_1)^2$;

(2) $(1a_2)^1(1\sim 4b_2)^2(1b_1)^2(2b_1)^1(1\sim 4a_1)^2(5a_1)^1(6a_1)^2$;

(3) $(1a_2)^2(1\sim 3b_2)^2(4b_2)^1(1\sim 2b_1)^2(1\sim 5a_1)^2$;

(4) $(1a_2)^2(1\sim 3b_2)^2(4b_2)^1(5b_2)^2(1b_1)^2(1\sim 5a_1)^2$;

(5) $(1a_2)^2(1\sim 4b_2)^{(}5b_2)^1(1b_1)^2(1\sim 4a_1)^2(5a_1)^1(6a_1)^1$,

the first one being the most important. The total number of configurations was about 17 000. The total contribution to the final wavefunction from the reference set is $\sum_p^{ref} C_p^2 = 0.91$. The optimized values for the bond length and angle are 1.370 Å and 86.0°, respectively. The calculated adiabatic excitation energy for the $X\,^2A_1 \rightarrow {}^2B_2$ transition is 4.658(4.359) eV, which is slightly smaller than the experimental value of 4.982 ± 0.030 eV obtained from PES of the CF_2 radical (carbene) [8]. It is noted that the experimental value is vertical excitation energy. At the MRSDCI/DZ + P level, we also calculated the vertical transition energy at the ground state equilibrium conformation to be 4.931(4.725) eV, which is close to experimental value of 4.982 ± 0.030 eV.

For the $X\,^2A_1 \rightarrow {}^2B_2$ transition (electron dipole allowed), the electronic transition properties have also been calculated based on the MRSDCI wavefunctions and are shown in Table 4. The calculated radiative lifetime for the $^2B_2$ state is smaller than that of the $^2B_1$ state.

The calculated force constants and vibrational frequencies for the $^2B_2$ states are presented in Table 2.

The instability of $CF_2^+(^2B_2)$ to asymmetric distortion ($F + CF^+$) has been studied at the MRSDCI/DZ + P level, we found that the energy of $CF_2^+(^2B_2)$ at asymmetric distortion ($F + CF^+$) is higher than that at the C_{2v} symmetry, i.e. the CF_2^+ ion at the $^2B_2$ state is stable.

3.4 The $^2A_2$ state

This state was treated as the lowest root in the secular equation for the A_2 irreducible representation. The reference space in the MRSDCI calculations for this state consisted of 7 configurations, generated from the following five selected space-orbital products:

(1) $(1a_2)^1(1\sim 4b_2)^2(1b_1)^2(1\sim 6a_1)^2$;

(2) $(1a_2)^1(1\sim 4b_2)^2(1b_1)^1(2b_1)^1(1\sim 6a_1)^2$;

(3) $(1a_2)^2(1\sim 4b_2)^2(5b_2)^1(1b_1)^1(1\sim 5a_1)^2(6a_1)^1$;

(4) $(1a_2)^1(1\sim 4b_2)^2(1\sim 2b_1)^2(1\sim 5a_1)^2$;

(5) $(1a_2)^1(1\sim 4b_2)^2(2b_1)^2(1\sim 6a_1)^2$,

the first one being the most important. The total contribution to the final wavefunction from the reference set is $\sum_p^{ref} C_p^2 = 0.91$. The optimized values for the bond length and angle are 1.401 Å and 97.6°, respectively. In 1985, Hrovat and Borden [11] calculated the geometry of the $^2A_2$ state at the MCSCF level with a $9s5p1d/3s2p1d$ basis set, which are presented in Table 1 for comparison. There is a large discrepancy for the optimized geometric parameters of the $^2A_2$ state between our work and [11]. Our $9s5p1d/4s2p1d$ (DZ + P) basis set is similar to $9s5p1d/3s2p1d$ one, the large discrepancy for the optimized geometric parameters of the $^2A_2$ state must be caused by the difference of MRSDCI and MCSCF methods. In our MRSDCI/DZ + P calculations, we optimized the (MRSD)CI energy including sigma and pi-space using the multireference configurations generated from above 5 space-orbital products while Hrovat and Borden [11] optimized only the pi-space MCSCF energy. Since MRSDCI/DZ + P calculations consider electron correlation effect better than MCSCF/($9s5p1d/3s2p1d$), we believe that our results are more accurate than those of [11].

In 1985, Hrovat and Borden [11] also studied the dissociation properties of the $CF_2^+(^2A_2)$, and discussed the symmetry-breaking problems. They found that the $CF_2^+(^2A_2)$ easily dissociate to $F + CF^+$ and this dissociation is exothermic. We also studied the instability of $CF_2^+(^2A_2)$ to asymmetric distortion $(F + CF^+)$ at the MRSDCI/DZ + P level, but we found that $CF_2^+(^2A_2)$ is stable in comparison with asymmetric distortion $(F + CF^+)$ although later is exothermic.

The predicted excitation energy from $X\,^2A_1$ to $^2A_2$ is 5.673(5.375) eV, which is slightly smaller than experimental vertical one of 5.977 ± 0.124 eV [8]. Our calculated vertical excitation energy for $X\,^2A_1 \rightarrow {}^2A_2$ is 6.023(5.824) eV which is in good agreement with previous experimental value.

For the $^2A_2$ state, the calculated force constants and vibrational frequencies are shown in Table 2.

4. Conclusion

The equilibrium geometries, excitation energies, force constants and vibrational frequencies for the four low-lying electronic states, $X\,^2A_1$, $^2B_1$, $^2B_2$, and $^2A_2$ of the CF_2^+ ion have been calculated at the MRSDCI level with a DZ + P basis set.

Our calculated excitation energies for these electronic states are in agreement with available experimental data obtained via PES of the CF_2 radical. Our calculated vibrational frequencies for the ground state are in good agreement with experiment.

Some electronic transition properties for the $^2B_1 \rightarrow X\,^2A_1$ and $^2B_2 \rightarrow X\,^2A_1$ transitions and the spin properties for the $X\,^2A_1$ state are calculated based on the MRSDCI wavefunctions.

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