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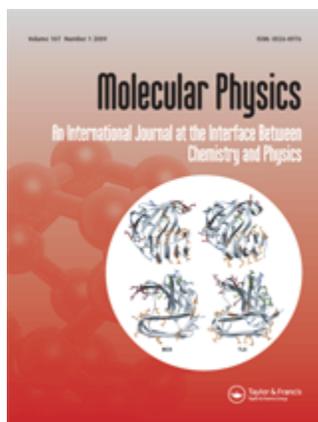
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An MRCI investigation of the electronically excited states of difluorocarbene and its monovalent ions

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Abstract

The MRCI/CBS computational protocol was employed to describe the low-lying electronic states of CF_2 in excellent agreement with experiment. Also of interest for modeling the fluorocarbon plasmas are the difluorocarbene ions, and the geometries, adiabatic excitation energies and orbital characteristics of their electronically excited states were established. Most of the transitions leading to the excited states were found to be mono-electronic and, for the dipole-allowed ones, the oscillator strengths and radiative lifetimes were predicted to aid in the spectroscopic studies.

Keywords:

carbenes; excited states; ab initio; MRCI; CBS

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1. Introduction

Multi-reference configuration interaction methods are well-suited for an accurate characterization of molecules in their electronically excited states [1]. We devised the computational protocol, which combines the multiconfigurational-reference internally-contracted configuration interaction (MRCI) [2] technique with extrapolations of the energies to the complete basis set (CBS) limit, and is capable of a highly accurate description of valence electronic states of both neutral and charged species [3]. Most recently we applied this approach to obtain the bond lengths r_e , bond angles θ and adiabatic excitation energies T_e of NF_2 , NF_2^+ and NF_2^- [4] to facilitate the modeling of the NF_3 plasma. Due to its vast chemical and technological significance, the CF_2 molecule was the subject of numerous experimental and theoretical investigations (*cf.* Part 3.1), while much less is known about CF_2^+ and CF_2^- . In particular, the informations describing the geometries and adiabatic electronic transitions in the difluorocarbene ions were obtained only by ab initio calculations or are missing (see Parts 3.2 and 3.3). We employ here the above-mentioned computational strategy to obtain the r_e , θ and T_e data for a number of electronic states of difluorocarbene and its monovalent ions. We compare our results against the experimental and high-level computational data wherever available, and we describe the 2^2A_2 , 2^2B_1 and 2^2B_2 states of CF_2^+ and 1^2A_2 , 1^2B_2 , 2^2A_2 , 2^2B_1 and 2^2B_2 states of CF_2^- for the first time. We also predict the oscillator strengths and radiative lifetimes for all the allowed transitions.

2. Computational methods

The geometries of the investigated electronic states were obtained using the procedure we described in detail in ref. [3] and only briefly summarize here. The implementation of the MRCI approach [5], [6] was combined with the standard aug-cc-pVQZ basis set [7] (240 basis functions). After a Hartree-Fock calculation, the multiconfigurational self-consistent

field (MC SCF) step described in references [8], [9] was performed with averaging over three states from each of the irreducible representations of the C_{2v} point group (the case of the ${}^2\Pi_u$ state of CF_2^+ was treated in the D_{2h} , instead of the non-Abelian $D_{\infty h}$, point group in an analogous way). The natural orbitals were generated and the full-valence (12 active orbitals) configuration interaction was subsequently performed for the electronic states of interest (the calculations involved up to 19 electrons, 14259 configuration state functions and 11.3×10^6 variational parameters). For each of the states, a series of energy-calculations were performed over suitably chosen grids and the geometries were extracted using SURVIBTM [10] (the output files can be obtained from the corresponding author upon request). The MRCI/aug-cc-pVQZ geometries thus obtained were subjected to the single-point energy calculations using an analogous MRCI protocol, but with the correlation of all occupied orbitals (1s on C and F in addition to the valence orbitals). The family of the augmented correlation-consistent polarized core-valence X -tuple basis sets, [11] aug-cc-pCVXZ, where X is the cardinal number associated with each basis set: $X = 2$ (double- ζ , DZ), 3 (TZ), 4 (QZ), was used. This resulted in calculations with up to 327 basis functions, 77598 configuration state functions and 107×10^6 variational parameters. The estimates of the energies in the complete basis set limit E_{CBS} were obtained using the mixed Gaussian/exponential form [12] as given by Equation (1).

$$E(X) = E_{CBS} + b \exp[-(X-1)] + c \exp[-(X-1)^2] \quad (1)$$

Resulting E_{CBS} data were employed to calculate the adiabatic excitation energies T_e as the differences between the E_{CBS} of the excited and the corresponding ground state. Also for the MRCI/aug-cc-pVQZ geometries, the oscillator strengths f_{ij} of the allowed transitions were obtained from the MRCI vertical excitation energies T_v^j and the electronic transition dipole moments in the length form M_{ij} for the transitions between the excited state j and the ground state i as follows:

$$f_{ij} = \frac{2}{3} T_v^j |\mathbf{M}_{ij}|^2 \quad (2)$$

Subsequently, the radiative lifetimes τ (in seconds) were estimated using Equation (3) (with T_v^j and \mathbf{M}_{ij} in atomic units).

$$\tau = \frac{3.1123 \times 10^{-11}}{T_v^{j^2} f_{ij}} \quad (3)$$

In addition, the oscillator strengths and radiative lifetimes were obtained for the MRCI/aug-cc-pVQZ geometries applying the standard aug-cc-pVDZ basis set [7] together with the equation-of-motion coupled-clusters singles, doubles and triples method (EOM-CCSDT) [13] in the frozen-core approximation (the implementation described in ref. [14]). The MRCI and EOM-CCSDT calculations were performed in Molpro 2006.1 [15] and NWChem 5.0 [16], respectively.

3. Results and discussion

3.1 The difluorocarbene, CF_2

Difluorocarbene is often the principal carbon-bearing component in fluorocarbon plasmas, which are used for a variety of material processing applications [17]. It also plays an important role as the intermediate in chemical reactions, with a markedly different behavior of its singlet and triplet electronic states [18]. As a consequence, the CF_2 molecule in the ground and excited states was studied by a number of spectroscopical and theoretical methods (see [19] for a recent review). Significantly, Cai [20] calculated the geometries of the X^1A_1 , 1A_2 , 3A_2 , 1B_1 , 3B_1 , 3B_2 states and the corresponding adiabatic excitation energies using the MRCISD/TZ+2P approach, and collected the available experimental and older ab initio results. Table 1 compares our MRCI data with those obtained by Cai and with their experimental counterparts. In spite of an application of rather limited active spaces and of relatively small basis set in [20], the computed values agree fairly well. Thus, the bond

lengths, bond angles and excitation energies differ at most by ca. 5 pm, 2° and one third of eV, respectively (*cf.* Table 1). Importantly, the computational results closely match the measured values, the biggest discrepancy being the 0.14 eV difference between the MRCI/CBS and the experimental adiabatic excitation energy of the 3B_1 state (Table 1).

Table 1

The MRCISD/TZ+2P approach was also applied to predict the oscillator strength and radiative lifetime of the $1^1B_1 \rightarrow X^1A_1$ transition [20]. Interestingly, the results substantially differ from the MRCI and EOM-CCSDT values obtained using the aug-cc-pVDZ basis set (see Table 2). We note in passing that our MRCI calculations are almost unaffected by the choice of the basis set (the aug-cc-pV5Z result for f and τ are 0.0408 and 20.73 ns accordingly, to be compared to their aug-cc-pVDZ counterparts of 0.0413 and 20.68, respectively), and the EOM-CCSDT computations are too demanding to study the basis set dependence of the results.

Table 2

The MRCI calculations reveal the details of the electronic transitions leading to the excited states. The configuration of the ground (X^1A_1) state of the CF_2 in its MRCI/aug-cc-pVQZ geometry is

$$(1b_2)^2 (1a_1)^2 (2a_1)^2 (3a_1)^2 (2b_2)^2 (4a_1)^2 (3b_2)^2 (5a_1)^2 (1b_1)^2 (1a_2)^2 (4b_2)^2 (6a_1)^2 (2b_1)^0,$$

with the MRCI/aug-cc-pVQZ reference coefficient of 0.921. Table 3 characterizes the 1A_2 , 3A_2 , 1B_1 , 3B_1 , 3B_2 excited states of CF_2 in terms of their configurations and occupational numbers of the orbitals involved in the corresponding excitations. Clearly, all these states are dominated by one-electron transitions (see Table 3).

Table 3

3.2 The difluorocarbene cation, CF_2^+

The geometries and excitation energies of CF_2^+ were studied by MRSDCI/DZP calculations in ref. [21], which also summarizes previous work on this molecule. We applied the same technique, which successfully described the CF_2 molecule, to investigate the X^2A_1 , 1^2A_2 , 2^2A_2 , 1^2B_1 , 2^2B_1 , 1^2B_2 and 2^2B_2 electronic states of CF_2^+ . The configuration of the ground state (the reference coefficient of 0.924) is predicted to be

$$(1b_2)^2 (1a_1)^2 (2a_1)^2 (3a_1)^2 (2b_2)^2 (4a_1)^2 (3b_2)^2 (1b_1)^2 (5a_1)^2 (1a_2)^2 (4b_2)^2 (6a_1)^1 (2b_1)^0,$$

and in Table 3 the configurations of the excited states are presented with respect to it. As was the case of CF_2 , all the investigated transitions are essentially monoelectronic (cf. Table 3). It can be inferred from Table 4 that our geometries and adiabatic excitation energies are quite similar to those provided by the MRSDCI/DZP calculations [21]. However, the MRSDCI/DZP oscillator strengths and radiative lifetimes differ significantly from both the MRCI and EOM-CCSDT data (see Table 2), probably due to the limited excitation manifold employed in ref. [21].

Table 4

3.3 The difluorocarbene anion, CF_2^-

We are not aware of any systematical investigation of electronically excited states of CF_2^- (the experimental and best theoretical data characterizing the ground state are given in Table 5, and a density functional theory-based description of the first excited state was presented [22]). To fill this gap, we searched for stable structures of the first two electronic states in each of the irreducible representations of the C_{2v} point group and estimated the resulting MRCI/CBS adiabatic excitation energies. Six excited states were located, which are summarized in Table 5. The oscillator strengths and radiative lifetimes of the dipole-allowed

transitions were predicted (see Table 2). According to the MCSCF/aug-cc-pVQZ natural orbitals, the configuration of the ground state (the 2B_1 symmetry) was found to be

$$(1b_2)^2 (1a_1)^2 (2a_1)^2 (3a_1)^2 (2b_2)^2 (4a_1)^2 (3b_2)^2 (5a_1)^2 (1b_1)^2 (1a_2)^2 (4b_2)^2 (6a_1)^2 (2b_1)^1.$$

Its reference coefficient as provided by the MRCI/aug-cc-pVQZ is 0.935, with the occupational number of the $2b_1$ natural orbital equal to 0.998. The single-electron replacements leading to the $1\ {}^2A_1$, $1\ {}^2B_2$, $1\ {}^2A_2$, $2\ {}^2A_2$ excited states are specified in Table 3 together with the two-electron excitations forming the $2\ {}^2B_2$ state. The electronic configuration of the $2\ {}^2B_1$ state contains a significant contribution from the ground state (*cf.* Table 3).

Table 5

4. Conclusions

The MRCI-based computational protocol was employed to describe the low-lying electronic states of CF_2 in excellent agreement with experiment. Also of interest for modeling the fluorocarbon plasmas are the difluorocarbene ions and hence the MRCI/aug-cc-pVQZ geometries and orbital characteristics of the $X\ {}^2A_1$, ${}^2\Pi_u$, $1\ {}^2A_2$, $1\ {}^2B_2$, $2\ {}^2A_2$, $2\ {}^2B_1$ and $2\ {}^2B_2$ states of CF_2^+ and the $X\ {}^2B_1$, $1\ {}^2A_1$, $1\ {}^2A_2$, $1\ {}^2B_2$, $2\ {}^2A_2$, $2\ {}^2B_1$ and $2\ {}^2B_2$ states of CF_2^- were established. The adiabatic excitation energies of all the species were extrapolated to the CBS limit. The transitions leading to the excited states were found to be mono-electronic (with the exception of the $X\ {}^2B_1 \rightarrow 2\ {}^2B_2$ of CF_2^-) and, for the dipole-allowed ones, the oscillator strengths and radiative lifetimes were predicted to aid in the spectroscopic studies.

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Table 1. The computational and experimental results for the low-lying electronic states of CF₂. See the text for details.

State	r_e (pm)	θ (°)	T_e (eV)
X ¹ A ₁	129.60 ^a	104.90 ^a	–
	129.80 ^b	104.80 ^b	
	130.0 ^c	104.94 ^c	
³ B ₁	131.47 ^a	119.21 ^a	2.594 ^c
	130.16 ^b	119.10 ^b	2.4236 ^b
			2.4579 ^e
¹ B ₁	131.86 ^a	122.02 ^a	4.753 ^c
	132.34 ^b	122.04 ^b	4.6396 ^b
	132 ^e	122.30 ^e	4.6160 ^f
³ A ₂	153.32 ^a	74.43 ^a	6.674 ^c
	150.79 ^b	73.50 ^b	6.3094 ^b
¹ A ₂	154.09 ^a	74.31 ^a	6.700 ^c
	152.32 ^b	73.42 ^b	6.5250 ^b
³ B ₂	156.04 ^a	88.88 ^a	7.725 ^c
	151.21 ^b	86.92 ^b	7.7594 ^b
			7.8430 ^g

^a The MRCI/aug-cc-pVQZ value (this work).

^b The MRCISD/TZ+2P value from ref. [20].

^c The MRCI/CBS value (this work).

^d The experimental value from ref. [23].

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3 ^e The experimental value from ref. [24].
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5 ^f The experimental value from ref. [25].
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8 ^g The experimental value from ref. [26].
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Table 2. The oscillator strengths f and the radiative lifetimes τ calculated for the MRCI/aug-cc-pVQZ geometries by various methods. See the text for details.

Molecule	Transition	f	τ (ns)
CF ₂	1 ¹ B ₁ → X ¹ A ₁	0.04079 ^a	21 ^a
		0.03769 ^b	23 ^b
		0.02003 ^c	54 ^c
CF ₂ ⁺	1 ² B ₁ → X ² A ₁	0.00843 ^a	143 ^a
		0.00745 ^b	158 ^b
		0.01691 ^d	152 ^d
	2 ² B ₁ → X ² A ₁	0.00855 ^a	47 ^a
	1 ² B ₂ → X ² A ₁	0.00373 ^a	63 ^a
		0.00430 ^b	92 ^b
	0.00680 ^d	139 ^d	
	2 ² B ₂ → X ² A ₁	0.00715 ^a	8 ^a
CF ₂ ⁻	2 ² B ₁ → X ² B ₁	0.00454 ^a	20 ^a
	1 ² A ₁ → X ² B ₁	0.00362 ^a	29 ^a
	1 ² A ₂ → X ² B ₁	0.00721 ^a	10 ^a
	2 ² A ₂ → X ² B ₁	0.00388 ^a	10 ^a

^a The MRCI/aug-cc-pVDZ value (this work).

^b The EOM-CCSDT/aug-cc-pVDZ value (this work).

^c The MRCISD/TZ+2P value from ref. [20].

^d The MRCISD/DZP value from ref. [21].

Table 3. The leading MRCI/aug-cc-pVQZ reference configurations and the orbital characteristics of the excited states. See the text for details.

Molecule	State	Configuration ^a	Coefficients of the natural orbitals
CF ₂	³ B ₁	0.932 (6a ₁ → 2b ₁)	1.002 (6a ₁), 1.002 (2b ₁)
	¹ B ₁	0.919 (6a ₁ → 2b ₁)	1.007 (6a ₁), 1.006 (2b ₁)
	³ A ₂	0.874 (4b ₂ → 2b ₁) – 0.265 (3b ₂ → 2b ₁)	1.038 (4b ₂), 1.001 (2 b ₁), 1.952 (3b ₂)
	¹ A ₂	0.909 (4b ₂ → 2b ₁)	1.038 (4b ₂), 1.002 (2b ₁)
	³ B ₂	0.897 (1a ₂ → 2b ₁)	1.074 (1a ₂), 0.996 (2b ₁)
CF ₂ ⁺	1 ² B ₂	0.908 (4b ₂ → 6a ₁)	1.900 (6a ₁), 1.039 (1a ₂)
	1 ² A ₂	0.894 (1a ₂ → 6a ₁)	1.900 (6a ₁), 1.039 (1a ₂)
	2 ² B ₁	0.814 (1b ₁ → 6a ₁) – 0.244 (6a ₁ → 2b ₁)	1.208 (1b ₁), 1.694 (6a ₁), 0.226 (2b ₁)
	2 ² A ₂	0.908 (4b ₂ → 2b ₁)	1.038 (4b ₂),

			1.005 (2b ₁)
	2 ² B ₂	0.651 (3b ₂ → 6a ₁) – 0.613 (1a ₂ → 2b ₁)	1.967 (3b ₂), 1.479 (6a ₁), 1.546 (1a ₂), 0.523 (2b ₁)
CF ₂ ⁻	1 ² A ₁	0.940 (2b ₁ → 7a ₁)	0.061 (2b ₁), 0.997 (7a ₁)
	1 ² B ₂	0.940 (2b ₁ → 5b ₂)	0.075 (2b ₁), 0.998 (5b ₂)
	2 ² B ₁	0.565 (6a ₁ → 7a ₁) – 0.555 (6a ₁ → 7a ₁) – 0.510 (the ground state)	1.533 (6a ₁), 0.453 (7a ₁), 0.996 (2b ₁)
	1 ² A ₂	0.947 (6a ₁ → 5b ₂)	0.999 (6a ₁), 0.998 (5b ₂)
	2 ² A ₂	0.941 (6a ₁ → 5b ₂)	1.002 (6a ₁), 0.997 (5b ₂)
	2 ² B ₂	0.744 (6a ₁ 2b ₁ → 7a ₁ 5b ₂) + 0.558 (6a ₁ 2b ₁ → 7a ₁ 5b ₂)	1.164 (6a ₁), 0.048 (2b ₁), 0.828 (7a ₁), 0.998 (5b ₂)

^a Excitations given relative to the reference configurations described for the respective molecules in Part 3.

Table 4. The computational results for the low-lying electronic states of CF_2^+ . See the text for details.

State	r_e (pm)	θ ($^\circ$)	T_e (eV)
$X \ ^2A_1$	121.47 ^a	124.82 ^a	–
	122.2 ^b	124.5 ^b	
$1 \ ^2B_1$ ($^2\Pi_u$)	122.86 ^a	180.0	2.985 ^c
	123.2 ^b		2.799 ^b
$1 \ ^2B_2$	137.22 ^a	84.14 ^a	4.552 ^c
	137.0 ^b	86.0 ^b	4.658 ^b
$1 \ ^2A_2$	139.56 ^a	95.69 ^a	5.554 ^c
	140.1 ^b	97.6 ^b	5.673 ^b
$2 \ ^2B_1$	145.42 ^a	104.56 ^a	7.272 ^c
$2 \ ^2A_2$	136.48 ^a	93.01 ^a	7.404 ^c
$2 \ ^2B_2$	145.78 ^a	96.91 ^a	8.033 ^c

^a The MRCI/aug-cc-pVQZ value (this work).

^b The MRCISD/DZP value from ref. [21].

^c The MRCI/CBS value (this work).

Table 5. The computational and experimental results for the low-lying electronic states of CF_2^- . See the text for details.

State	r_e (pm)	θ ($^\circ$)	T_e (eV)
$X \ ^2B_1$	143.77 ^a	98.99 ^a	–
	145.09 ^b	100.079 ^b	
	145 ± 2^c	99 ± 2^c	
$1 \ ^2A_1$	128.22 ^a	106.00 ^a	0.819 ^d
$1 \ ^2B_2$	163.19 ^a	82.17 ^a	3.393 ^d
$1 \ ^2A_2$	130.06 ^a	118.52 ^a	3.471 ^d
$2 \ ^2B_1$	130.90 ^a	116.59 ^a	3.710 ^d
$2 \ ^2A_2$	129.83 ^a	121.78 ^a	5.859 ^d
$2 \ ^2B_2$	120.90 ^a	126.05 ^a	8.131 ^d

^a The MRCI/aug-cc-pVQZ value (this work).

^b The CCSD(T)/6-311+G(2d) value from ref. [27].

^c The experimental value from ref. [28].

^d The MRCI/CBS value (this work).