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REGULAR ARTICLE

Electronic spectrum of F_2CO: theoretical calculations of vertical excitation energies and intensities

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Abstract In this work, the linear response formalism with a triples-corrected CCSD reference wave function, LR-CCSDR(3), is applied to the calculation of vertical excitation energies of singlet states of the F_2CO molecule. A basis set of atomic natural orbitals augmented with a series of Rydberg functions has been used in the calculations. A large number of electronically excited states were calculated, and the valence, Rydberg, or mixed character of the states were investigated. In addition, the molecular quantum defect orbital (MQDO) method has been used to determine transition intensities involving Rydberg states. Excitation energies and transition intensities for Rydberg states with $n > 3$ are reported for the first time.

Keywords F_2CO · Vertical excitation energies · Rydberg-valence interactions · Oscillator strengths

1 Introduction

Carbonyl halides are known to play an important role in the photochemistry of the Earth's upper atmosphere. Carbonyl fluoride, F_2CO, considered the most stable of carbonyl halides, is formed in the oxidation of radicals originating from the photolysis of chlorofluorocarbons [1, 2]. Rinsland et al. [3] were the first to detect F_2CO in the stratosphere, where a significant increase in its concentration has been observed [4]. However, a very recent study [5] reveals that, in the last years, the F_2CO growth rate is decreasing due to the stabilization of the CFC-12 tropospheric concentration and to the decrease in the CFC-11 atmospheric abundance. Carbonyl fluoride has been shown to be the second most abundant stratospheric fluorine reservoir [6]. Moreover, this compound is considered to be an alternative gas to conventional C_2H_6 for chemical vapor deposition chamber cleaning due to its low global warming potential [7].

Relatively a few experimental works are found in the literature on the UV spectroscopy of carbonyl fluoride, even though it must be understood to comprehend the photochemistry of this molecule. The most complete measurement of the electronic spectrum of F_2CO was done by Workman and Duncan [8] long ago. They reported that at least four electronic transitions occur down to 10.2 eV in the far-ultraviolet region and discussed their nature in relation to transitions in similar molecules. These authors were not able to identify the bands corresponding to transitions to higher energies. Although Workman and Duncan [8] claimed that more studies at higher resolution are needed, it is hard to find experimental works other than one by Judge and Moule [9], in which the vibrational structure of the first observed electronic transition was analyzed. This situation is likely due to the difficulties in the experimental measurements caused by the high reactivity of the F_2CO.

On the theoretical part, the UV spectrum of F_2CO has been less investigated than formaldehyde, H_2CO. Obviously, replacing electron-rich fluorine atoms for hydrogens complicates the spectrum and its interpretation. Some of the low-lying excited states of F_2CO have been studied by Vasudevan and Grein [10] employing ab initio methods based on self-consistent field (SCF) and configuration

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interaction (CI) approaches. A much larger number of excited states, including valence and Rydberg ones, were examined in a multi-reference single and double excitation (MRD-CI) study by Grein [11], which provides excitations to the lowest member ($n = 3$) of the Rydberg series. Other theoretical studies in carbonyl fluoride analyzed only the two lowest lying excited states [12, 13]. No calculations seem to have been performed to date on Rydberg states with $n > 3$ even though their presence in the spectrum of F_2CO has been predicted [11].

Since so little detailed information is available for a molecule of potential impact in atmospheric chemistry, further theoretical investigations are highly desirable. The presence of a high density of excited states, very likely of Rydberg character, in the electronic spectrum of F_2CO has been suggested [10]. It should be noted here that in the electronic spectrum of other carbonyl compounds, high Rydberg series members have been observed. For example, in formaldehyde, ns, np, nd, and nf Rydberg series up to n equal to 5, 12, 12, and 9, respectively, have been analyzed [14]. The main aim of the present work is hence to fill some gaps in the information of the F_2CO spectrum by calculating vertical excitation energies (VEEs) in the 7.0–13.6 eV energy range. Special emphasis will be placed on the expected mixing of states of Rydberg and valence-shell character.

The linear response formalism with a triples-corrected CCSD reference wave function, LR-CCSDR(3), has proved to be reliable for the accurate study of the spectrum of formaldehyde [15]. It is applied here to calculate the vertical excitation energies of singlet states of carbonyl fluoride, where CO group is bonded to F, the highest electronegativity element. Rydberg states with $n > 3$ have also been analyzed and assigned in detail. In addition, transition intensities in terms of absorption oscillator strengths, or *f*-values, for some Rydberg transitions, have been calculated with the molecular quantum defect orbital (MQDO) method. This method, when applicable, yields accurate results for transitions involving Rydberg states and has proved its reliability in recent applications to two other carbonyl compounds [16, 17].

2 Methods of calculation

The vertical spectrum of the F_2CO molecule has been calculated with a coupled cluster linear response approach using a CCSD wave function as reference function [18, 19], and the effect of connected triples has been estimated using the CCSDR(3) method [20], as implemented in the DALTON code [21]. The CCSDR(3) method is correct to third order in the fluctuation potential for states dominated by single excitations [20]. The square radius mean value of the CCSD calculated states has been used as a help in assessing the consistency of state assignments.

F_2CO was treated as a planar C_{2v} molecule lying in the yz plane with the carbon–oxygen bond on the z-axis in all calculations. Experimental values [22] with $R_{CO} = 1.1720$ Å, $R_{CF} = 1.3166$ Å, and $<(FCF) = 107.6°$ were adopted for the ground state geometry.

A general atomic natural orbital (ANO) [23] basis set, with [6s5p3d2f] contractions for carbon, oxygen, and fluorine atoms, has been employed. For a proper description of the Rydberg states, the ANO basis was augmented with a single set of ANOs, generated for this particular system at equilibrium geometry, following the general technique proposed by Roos et al. [24] and using the optimized universal exponents by Kaufmann et al. [25]. A set of (8s8p8d8f) uncontracted ANO-like Rydberg functions allocated in the charge centroid of F_2CO^+ ground state was contracted to a [6s6p6d5f] basis. The exponents and coefficients for these basis functions are collected in Table 1.

Transition intensities were calculated with the MQDO method, which has been described in detail elsewhere [26]. This approach, based on a semiempirical model potential, has proven to be appropriate for dealing with molecular Rydberg states. The starting point of the MQDO formalism is to derive the radial part of the MQDO wave functions by analytically solving a one-electron Schrödinger equation involving a parametric potential. The angular part of the MQDO wave functions is expressed as a symmetry-adapted combination of the spherical harmonics, which form bases for the different irreducible representations of the molecular symmetry group. It does matter to mention that within the molecular quantum defect orbitals formalism, the transition integrals involved in the calculation of oscillator strengths have closed-form analytical expressions, which offers, in our view, an important computational advantage.

3 Results and discussion

At equilibrium geometry, the electronic configuration of the X $^1A_1$ ground state of carbonyl fluoride in the C_{2v} symmetry is $\ldots(1a_2)^2\ (8a_1)^2\ (4b_2)^2\ (2b_1)^2\ (5b_2)^2$. The highest occupied molecular orbital (HOMO), $5b_2$, behaves mainly as a $2p_y$ orbital of the oxygen atom and will be denoted as n_O. The $2b_1$ is a π (C–O) molecular orbital. The $4b_2$ is essentially a fluorine lone-pair and will be referred as $n_{b2}(F)$. The $8a_1$ is a σ (CF_2O) MO. Finally, $1a_2$ is an a_2 π orbital in the fluorine atoms and will be labeled by $\pi_{a2}(F)$ in this work.

The present calculated absorption spectrum of F_2CO corresponds to vertical transitions from the ground state to excited states below the first ionization potential, at

Table 1 Exponents and coefficients for the ANO Rydberg basis functions of F_2CO

Exponents	Coefficients					
s functions						
0.024624	0.386701	−0.522301	0.860546	−0.903352	2.792547	−4.442539
0.011253	0.046377	−1.330055	0.701982	0.042221	−5.985894	18.517188
0.005858	−1.272346	1.231898	−3.499997	4.027107	1.581893	−41.816355
0.003346	0.230224	−0.599374	1.752657	−4.048891	9.717670	60.595736
0.002048	−0.472848	1.275791	−0.056251	−1.457994	−11.890721	−57.787904
0.001324	0.399988	−0.926061	1.420174	0.858509	2.477481	37.917654
0.000893	−0.212569	0.480748	−0.620781	1.797393	1.246499	−19.000523
0.000624	0.052164	−0.118788	0.156787	−0.074662	0.500639	5.988944
p functions						
0.042335	0.255878	−0.093380	0.185760	−0.447400	1.412284	−2.126110
0.019254	0.711647	−0.295446	0.434448	−0.138280	−0.991947	5.480357
0.009988	0.266228	0.018364	−0.090276	0.365179	−1.702138	−6.411185
0.005689	−0.138460	0.638358	−1.098600	1.485257	1.694716	3.215764
0.003476	−0.266491	0.444546	−0.433779	−1.696134	1.513062	−2.819179
0.002242	0.049821	0.065277	0.937598	0.761606	−0.169610	10.417515
0.001511	−0.037941	0.007117	0.605071	−3.542072	−4.661921	−14.227111
0.001055	0.010124	−0.001351	0.097417	3.471230	3.415503	6.392788
d functions						
0.060540	0.053555	−0.091276	0.225611	−0.499224	0.918623	−1.727918
0.027446	0.228213	−0.276004	0.410114	−0.239919	−0.518820	3.456389
0.014204	0.402320	−0.348080	0.069694	0.061844	−0.512976	−3.343969
0.008077	0.320302	−0.033342	−0.352220	1.539101	0.357081	2.616827
0.004927	0.118767	0.406312	−0.779650	−1.964818	−1.625277	−5.761590
0.003175	0.017344	0.453845	0.392519	2.652695	7.901189	11.869091
0.002137	0.000523	0.193746	−0.212801	−5.092043	−11.591613	−11.914182
0.001491	0.000320	0.026704	1.017310	3.557615	5.621462	4.614800
f functions						
0.079070	0.001108	−0.010213	0.068152	−0.256517	1.157514	
0.035763	0.035364	−0.042428	0.293985	−0.343308	−0.496600	
0.018478	0.118240	−0.169508	0.226849	−0.564903	−0.289572	
0.010493	0.264340	−0.149371	0.676846	1.007645	−0.414265	
0.006395	0.332856	−0.569794	−1.459648	−1.184302	0.518556	
0.004117	0.280944	0.615676	2.457355	4.272804	1.803551	
0.002770	0.103447	−0.562234	−4.551695	−6.905762	−3.283420	
0.001931	0.032777	1.205555	3.058028	3.660635	1.597619	

13.6 eV. The assignment of the Rydberg or valence character for the different states is established through an analysis of the coupled cluster wave functions in terms of predominant configurations. Furthermore, the $\langle r^2 \rangle$ expectation value, that provides summarized information on how much the state extends in space, is used to identify the nature of the state. In particular, valence states or mixed valence-Rydberg states drop to smaller $\langle r^2 \rangle$ values, while monotonous increasing should be expected for Rydberg states. Another tool for assigning the Rydberg states comes from the analysis of the quantum defects associated with each of the Rydberg series. According to Sandorfy [27], the typical quantum defect values ranges from 0.9 to 1.2 for the ns series, from 0.3 to 0.6 for the np, less than 0.1 for the nd, and much smaller values for higher nl.

The quantum defect, δ, is related to the energy of a Rydberg state through the well-known expression:

$$E_{\mathrm{nl}} = \mathrm{IP} - \frac{1}{(n - \delta_{\mathrm{l}})^2}$$

where IP is the ionization potential and n represents the principal quantum number. In the spectral region studied here, the five highest occupied orbitals are involved. We have taken the vertical ionization potentials measured by photoelectron spectroscopy by Brundle et al. [28]. The reported values for the two first ionization potentials, $n_O \rightarrow \infty$ and $\pi \rightarrow \infty$, are 13.6 and 14.6 eV, respectively. As pointed out by these authors, the assignment of the observed bands in the 16–18 eV is not clear as the $8a_1$, $4b_2$, and $1a_2$ ionizations lie close together. They identified the bands at 16.6 and 17.2 eV as ionizations from the $8a_1$ and $4b_2$ molecular orbitals, respectively. In contrast, CI calculations of Grein [11] predict the $4b_2$ orbital to have lower vertical ionization potential than the $8a_1$. Consequently, Grein [11] proposed that the assignment of the bands at 16.6 and 17.2 eV suggested by Brundle et al. [28] should be interchanged so that the 16.6 eV IP would correspond to the $4b_2$ molecular orbital, and that of 17.2 eV to the $8a_1$ orbital. We have followed the latter proposal. Since no experimental vertical IP for the $1a_2$ ionization has been reported, we have adopted for it the value of 17.35 eV as reported by Grein [11].

The CCSD and CCSDR(3) vertical excitation energies of singlet states are given in order of increasing energy in Table 2. The CCSD square radius mean values and the quantum defects for Rydberg states calculated using the CCSDR(3) energies are included as well in the table. For comparative purposes, the results of two theoretical studies of the vertical spectrum of F_2CO found in the literature are also displayed. These include vertical energies computed at the CI and MRD-CI levels. Note that in the CI calculations of Vasudevan and Grein [10], the molecule is assumed to lie in the xz plane. Thus, their results for states of B_2 and B_1 symmetries, as showed in Table 2, correspond to those of B_1 and B_2, respectively, in their notation.

It seems apparent in Table 2 that inclusion of linked triples effects in the CCSDR(3) calculations leads to a systematic decrease in the CCSD excitation energies. The diminution amounts about 0.11 eV on average and brings the CC values close to the MRD-CI ones in most cases. Henceforth, we will refer along this section to LR-CCSDR(3) values of vertical energies.

As mentioned in the "Introduction", Workman and Duncan [8] identified four electronic transitions below 10.2 eV in the far-ultraviolet spectrum of carbonyl fluoride. Although the assignment of the first band is not in question, the other three observed bands have been subject of several contradictory interpretations.

The first electronic transition ranges from 5.22 eV to about 6.94 eV and consists of around 140 vibrational transitions. It is well established that this transition corresponds to the promotion of an electron from the nonbonding n_O orbital to an antibonding π^* orbital centered in the CO bond. Our calculations predict the lowest excited state to be a $n_O\pi^*$ $^1A_2$ valence state, so confirming the previous assignment. The second electronic transition, observed in the 7.02–7.66 eV energy region with maximum at 7.34 eV, is difficult to interpret in terms of electron structure [8]. On the grounds of the close similarity to the first transition, Workman and Duncan [8] suggested that the second excited singlet state is also of A_2 symmetry, resulting from an excitation from the lone-pair MO localized in the F atom to the a π^* molecular orbital. However, our results predict the $nb_2(F)\pi^*$ $^1A_2$ state to be at higher energy, 11.32 eV. On the other hand, Robin [29] claimed that the second transition in F_2CO can be assigned as either $n_O\sigma^*$ or $\pi\sigma^*$, although indicated that the possibility of this transition to be $n_O \rightarrow \pi^*$ cannot be definitely discarded. There is no evidence, in the present calculations, of the presence of any state arising from excitation into the σ^* valence-shell orbital in the lower energy region. The second transition has also been tentatively attributed to the triplet $\pi\pi^*$ [10, 11]. In order to confirm such assignment, we have calculated vertical excitation energies for the lower triplet states of carbonyl fluoride. At CCSD level of calculations, since CCSDR(3) is not implemented for triplet excitation energies, we have obtained the values of 7.03, 7.53, and 9.22 eV for the $n_O\pi^*$ $^3A_2$, $\pi\pi^*$ $^3A_1$, and n_O3s $^3B_2$, respectively. These results seem to support the assignment of the second band to the $\pi\pi^*$ $^3A_1$ state.

The third absorption system of F_2CO, beginning at 8.13 eV, shows a single progression of five broad bands. Though Workman and Duncan [8] admit that it can be assigned to the $n_O \rightarrow \sigma^*$ valence-shell excitation, they claim it can also be classified as the first member of a Rydberg series ($n_O \rightarrow 3s$). On the grounds of CI [10] and MRD-CI [11] results and of our calculations, an assignment to the $n_O \rightarrow 3s$ transition seems to be the most convincing. Nonetheless, it should be mentioned that a relevant mixing between the n_O3s $^1B_2$ Rydberg state and the $n_O\sigma^*$ $^1B_2$ repulsive state is found. A similar mixing had been reported in the MRD-CI results [11].

Workman and Duncan [8] found a fourth electronic transition, which is a continuous absorption, with a maximum lying near 9.67 eV and an oscillator strength of 0.15. These authors tentatively assigned it to the $\pi \rightarrow \pi^*$ transition of $^1A_1$ symmetry. Theoretical calculations [10, 11] agree with such assignment. In the present study, the lowest excited state $^1A_1$ is found at 10.19 eV, in excellent accord with the MRD-CI result (10.18 eV), and is characterized as an $\pi\pi^*$ valence state with an admixture of n_O3p_y Rydberg state. An additional support in assigning the fourth absorption system observed in the spectrum of F_2CO to the $\pi\pi^*$ $^1A_1$ state is the rather good agreement between the coupled cluster oscillator strength, $f = 0.19$ and the observed value of 0.15. It is worth noting that CI calculations [10] place the excitation energy of the $\pi \rightarrow \pi^*$ 0.7 eV higher than the CCSDR(3) and MRD-CI ones, probably

Table 2 Vertical excitation energies, eV, of F_2CO

State	CCSDR(3)[a]	CCSD[a]	$\langle r^2 \rangle$	δ	MRD-CI[b]	CI[c]
GS	0.00	0.00	66			
$n_O\pi^*\ ^1A_2$	7.31	7.36	66		7.35	6.87
$n_O3s\ ^1B_2$	9.30	9.45	71	1.2210	9.47	9.22
$\pi\pi^*\ ^1A_1$	10.19	10.35	67		10.18	10.89
$\pi3s\ ^1B_1$	10.39	10.55	70	1.2031	10.67	10.22
$n_O3p_x\ ^1A_2$	10.98	11.07	82	0.7212	10.86	10.63
$n_O3p_z\ ^1B_2$	11.14	11.25	86	0.6468	11.20	10.88
$n_O3p_y\ ^1A_1$	11.26	11.38	87	0.5869	11.25	
$\sigma\pi^*\ ^1B_1$	11.27	11.39	65		11.31	11.27
$n_{b2}(F)\pi^*\ ^1A_2$	11.32	11.56	65		11.72	
$n_O4s\ ^1B_2$	11.62	11.75	99	1.3799		
$n_O3d_{yz}\ ^1A_1$	12.04	12.15	104	0.0468	11.98	
$n_O3d_{xy}\ ^1B_1$	12.06	12.16	104	0.0265		
$n_O3d_{x^2-y^2}\ ^1B_2$	12.06	12.16	106	0.0250	11.88	
$n_O3d_{xz}\ ^1A_2$	12.08	12.17	106	0.0113	11.94	
$n_O3d_{z^2}\ ^1B_2$	12.08	12.18	107	0.0087	11.82	
$n_{b2}(F)3s\ ^1B_2$	12.16	12.35	75	1.2499		
$\pi3p_x\ ^1A_1$	12.20	12.34	84	0.6177	12.19	
$\pi3p_y\ ^1A_2$	12.32	12.44	97	0.5585		
$n_O4p_x\ ^1A_2$	12.34	12.44	141	0.7169		
$n_O4p_z\ ^1B_2$	12.38	12.48	160	0.6631		
$\pi3p_z\ ^1B_1$	12.42	12.56	86	0.5033	12.41	
$n_O4p_y\ ^1A_1$	12.44	12.54	170	0.5792		
$n_O5s\ ^1B_2$	12.48	12.61	174	1.5133		
$n_O4d_{x^2-y^2}\ ^1B_2$	12.64	12.79	168	0.2427		
$\pi_{a2}(F)\pi^*\ ^1B_2$	12.72	12.87	203			
$n_O4d_{yz}\ ^1A_1$	12.72	12.82	220	0.0665		
$n_O4f\ ^1B_2$	12.72	12.82	183	0.0641		
$n_O4d_{xy}\ ^1B_1$	12.73	12.82	204	0.0528		
$n_O4f\ ^1A_1$	12.73	12.82	183	0.0462		
$n_O4f\ ^1A_2$	12.73	12.82	186	0.0453		
$n_O4f\ ^1B_2$	12.73	12.82	182	0.0417		
$n_O4f\ ^1A_1$	12.73	12.83	185	0.0387		
$n_O4f\ ^1A_2$	12.74	12.83	184	0.0346		
$n_O4f\ ^1B_1$	12.74	12.83	209	0.0337		
$n_O4d_{xz}\ ^1A_2$	12.74	12.84	233	0.0155		
$n_O4d_{z^2}\ ^1B_2$	12.75	12.84	241	0.0071		
$\pi_F\ 3s\ ^1A_2$	12.76	12.93	84	1.3574		
$\pi4s\ ^1B_1$	12.78	12.93	96	1.2659		
$\sigma3s\ ^1A_1$	12.79	12.98	97	1.2427		
$n_O5p_x\ ^1A_2$	12.86	12.95	334	0.7270		
$n_O5p_z\ ^1B_2$	12.87	12.97	347	0.6919		
$n_O5p_y\ ^1A_1$	12.90	12.99	370	0.6075		
$n_O6s\ ^1B_2$	12.93	13.04	408	1.4872		
$n_O5f\ ^1B_2$	13.03	13.12	427	0.1146		
$n_O5d_{xy}\ ^1B_1$	13.04	13.13	459	0.0952		
$n_O5f\ ^1A_2$	13.04	13.13	433	0.0870		
$n_O5f\ ^1A_1$	13.04	13.13	428	0.0848		

Table 2 continued

State	CCSDR(3)[a]	CCSD[a]	$\langle r^2 \rangle$	δ	MRD-CI[b]	CI[c]
$n_O5d_{yz}\ ^1A_1$	13.04	13.14	509	0.0826		
$n_O5f\ ^1B_2$	13.04	13.13	429	0.0822		
$n_O5f\ ^1A_1$	13.04	13.13	430	0.0791		
$n_O5f\ ^1A_2$	13.04	13.13	431	0.0730		
$n_O5f\ ^1B_1$	13.04	13.13	477	0.0677		
$n_O5d_{x^2-y^2}\ ^1B_2$	13.04	13.14	520	0.0615		
$n_O5d_{xz}\ ^1A_2$	13.05	13.14	517	0.0468		
$n_O5d_{z^2}\ ^1B_2$	13.05	13.14	527	0.0365		
$n_O6p_x\ ^1A_2$	13.11	13.20	730	0.7592		
$n_O6p_z\ ^1B_2$	13.11	13.20	712	0.7427		
$n_O6p_y\ ^1A_1$	13.13	13.22	766	0.6478		
$n_O7s\ ^1B_2$	13.15	13.25	712	1.5315		
$n_O6d_{xy}\ ^1B_1$	13.23	13.32	720	−0.0149		
$n_O6d_{yz}\ ^1A_1$	13.23	13.32	727	−0.0277		
$n_O6d_{x^2-y^2}\ ^1B_2$	13.23	13.33	705	−0.0684		
$n_O6d_{xz}\ ^1A_2$	13.23	13.33	704	−0.0832		
$n_O6d_{z^2}\ ^1B_2$	13.24	13.33	677	−0.1445		
$\pi 3d_{x^2-y^2}\ ^1B_1$	13.28	13.42	104	−0.2113	13.26	
$\pi 3d_{xy}\ ^1B_2$	13.29	13.42	120	−0.2187		
$\pi 3d_{z^2}\ ^1B_1$	13.32	13.46	108	−0.2642	12.84	
$\pi 3d_{xz}\ ^1A_1$	13.33	13.46	170	−0.2686	13.25	

Square radius mean values are given in a.u

[a] This work

[b] Grein [11]

[c] Vasudevan and Grein [10]

due to an insufficient AO basis set. Note also that in the same CI calculations the $n_O3p_x\ ^1A_2$ and $n_O3p_z\ ^1B_2$ Rydberg states are placed below the $\pi\pi^*\ ^1A_1$ valence state, in contrast to the present coupled cluster and the MRD-CI calculations.

From their experience with heavily fluorinated molecules, Robin [29] predicts that the $\pi \rightarrow 3s$ Rydberg excitation should come approximately at 10.4 eV, just before the $n_O \rightarrow 3p$ band, expected at 11 eV. These estimated values are in good agreement with present calculated energies for the $\pi 3s$, 10.39 eV, and n_O3p Rydberg states, 10.98–11.26 eV. The CC calculations show that both $\pi 3s$ $^1B_1$ and $n_O3p_y\ ^1A_1$ states are perturbed by its interaction with the valence states, $\pi\sigma^*\ ^1B_1$ and $\pi\pi^*\ ^1A_1$, respectively. The next two states, at 11.27 and 11.32 eV, are clearly of valence character and they can be attributed to $\sigma\pi^*\ ^1B_1$ and $nb_2(F)\pi^*\ ^1A_2$, respectively, in coincidence with the assignments proposed by Grein. The coupled cluster VEE is in very good agreement with the MRD-CI one for the first of two states, but the CCSDR(3) energy value for the $nb_2(F)\pi^*\ ^1A_2$ state is 0.4 eV below MRD-CI result.

CC calculations place the second member of the n_Os Rydberg series, $n_O4s\ ^1B_2$, at 11.62 eV. This state could not be obtained by Grein [11] because the basis set used in its calculations contained only Rydberg functions for $n = 3$. For energies larger than 12.0 eV, as clearly seen in Table 2, the density of states becomes systematically higher with increasing energy, so that in some instances it was very difficult to establish the correct ordering of states. The n_O3d Rydberg states are calculated to occur in the 12.04–12.08 eV energy range. The $\langle r^2 \rangle$ and the quantum defects are consistent with states dominated by 3d Rydberg orbitals. It is surprising that the state $n_O3d_{xy}\ ^1B_1$ does not appear among the five lowest roots corresponding to $^1B_1$ states reported by Grein [11]. According to the present CC calculations, the leading configuration for the third state with $^1B_1$ symmetry is n_O3d_{xy}, with nearly pure Rydberg character. In both CCSD and CCSDR(3) calculations, the ordering of n_O3d components is $3d_{yz} < 3d_{xy} \sim 3d_{x^2-y^2} < 3d_{xz} \sim 3d_{z^2}$ whereas from the MRD-CI calculations is $3d_{z^2} < 3d_{x^2-y^2} < 3d_{xz} < 3d_{yz}$. It is apparent that the calculated splitting of the n_O3d components is too small to settle the state ordering of these components. Anyway, vertical energies are similar in both CCSDR(3) and MRD-CI calculations. Higher lying states belonging to the n_Od Rydberg series are essentially of Rydberg character, with the only exception of the $n_O4d_{x^2-y^2}$ $^1B_2$ state (12.64 eV) that will be analyzed below.

Just after the five 3d Rydberg states, at 12.16 eV, there appears a state with $^1B_2$ symmetry, which shows mixture of n_{b2}(F) 3s and $\pi_{a2}(F)\pi^*$ configurations, the former being the dominant configuration. In addition, its $\langle r^2 \rangle$ value is much closer to that expected for a 3s Rydberg state than that of a valence state, moreover, its quantum defect is typical of a 3s orbital. Thus, we attribute it to the first member of a Rydberg series originated in an excitation from a 2p orbital of fluorine atom.

We predict that the π3p Rydberg states are reached in the 12.20–12.42 eV region, in excellent agreement with MRD-CI results for the $\pi3p_x$ $^1A_1$ and $\pi3p_z$ $^1B_1$. Again, it is striking that the $\pi3p_y$ $^1A_2$ state was not reported by Grein [11]. This state seems to be mixing with a n_Op_x $^1A_2$ Rydberg state while the other two π3p states are of mostly pure Rydberg character. Such a mixing might be an explanation of the high value of $\langle r^2 \rangle$ for the $\pi3p_y$ $^1A_2$ state, 97 a.u., when compared to the values found for the other 3p orbitals, 82–87 a.u.

Particular attention deserves the group of three electronic states of B_2 symmetry calculated in the 12.48–12.72 eV energy range, which show strong mixing of Rydberg and valence character. Unfortunately, their assignments are not easy. The calculated coupled cluster amplitudes for the first state indicate strong mixing between the n_O5s Rydberg and the $\pi_{a2}(F)\pi^*$ valence configurations, the former having a larger weight. The configuration arising by the excitation of a π_{a2} orbital of F into the lowest energy valence orbital is also present in the description of the state at 12.64 eV. Since the main configuration is $n_Od_{x^2-y^2}$, we have assigned this state to the $n_O4d_{x^2-y^2}$ $^1B_2$ Rydberg state. The large mixing of the valence contribution in such state is made clear when its $\langle r^2 \rangle$ value (about 170 a.u.) is compared to the $\langle r^2 \rangle$ values for pure Rydberg n_O4d states, which are in the range 204–241 a.u., and those of the valence states, which are about 65 a.u. The anomalously high quantum defect for the $n_O4d_{x^2-y^2}$ $^1B_2$ state (0.2427) provides an additional evidence of the Rydberg-valence mixing. Unequivocal assignment for the third state, referred as $\pi_{a2}(F)\pi^*$ $^1B_2$ (12.72 eV) in Table 2, is difficult to make. A significant mixing among several configurations with the same symmetry occurs in such state, with a maximum coefficient for the $\pi_{a2}\pi^*$ valence configuration, but with a notable contribution from the $n_Od_{x^2-y^2}$ and n_Os Rydberg configurations, which could explain its high $\langle r^2 \rangle$ value when compared to a valence state. Another state that exhibits relevant mixing is that at 12.79 eV of $^1A_1$ symmetry, reported here for the first time. The dominant configuration is σ3s but the mixing with the closest n_04d_{yz} might explain its high value of $\langle r^2 \rangle$.

Referring to the π3d Rydberg states, our result (13.28 eV) for $\pi3d_{x^2-y^2}$ $^1B_1$ is in a very good agreement with that of Grein (13.26 eV). However, for the $\pi3d_{z^2}$ $^1B_1$ state a notable discrepancy is observed between CCSDR(3) and MRD-CI vertical energies, 13.32 and 12.84 eV, respectively. As can be seen from Table 2, CCSDR(3) calculations place the π4s $^1B_1$ state at 12.78 eV, close to the MRD-CI energy value for the $\pi3d_{z^2}$ $^1B_1$ state. From this fact and taking into account that the basis used by Grein is insufficient to obtain 4s Rydberg states, as this author admits, the state found in its calculations at 12.84 eV might be tentatively assigned to π4s $^1B_2$, instead of $\pi3d_{z^2}$ $^1B_2$.

According to the present coupled cluster calculations, the remaining members of the np, ns, and nd Rydberg series are essentially Rydberg in character. The two lowest members of the nf Rydberg series are also given in Table 2, as they appear more separated than the expected mean error (0.1–0.2 eV) of our VEE calculations.

The MQDO oscillator strengths for transitions of F_2CO, originating in the n_O orbital of the ground state and ending in a Rydberg state with ns or nd character, are reported in Table 3. In this work, CCSDR(3) vertical excitation energies have been taken for the MQDO calculations. In Table 3, the *f*-values have been grouped according to the different nl-components of the Rydberg series. It is our purpose to show that the MQDO calculations reflect the expected decrease in the magnitude of the oscillator strengths along a given Rydberg series, as the upper state becomes more excited. This fact can be understood on the grounds of a diminishing overlap of the wave functions corresponding to the initial and final states when the upper state is highly excited (and largely spreads on space) so that the resulting decrease in the transition integral is no compensated by the increase in transition energy.

To the best of our knowledge, the only data reported in the literature on *f*-values for F_2CO are those calculated by Grein [11] with the MRD-CI method. For comparative purposes, they are listed in Table 3. As one can see, there is an excellent agreement between MQDO and MRD-CI *f*-values for the X $^1A_1 \rightarrow n_O3d_{z^2}$ $^1B_2$ transition. For the X $^1A_1 \rightarrow n_O3d_{x^2-y^2}$ $^1B_2$ both calculations predict oscillator strengths of the same order of magnitude. However, for the X $^1A_1 \rightarrow n_O3d_{yz}$ $^1A_1$ transition, the MQDO *f*-value is about 9 times the MRD-CI value. The small value reported by Grein for this later transition, which is lower than that for the X $^1A_1 \rightarrow n_O3d_{z^2}$ $^1B_2$ transition, appears to be inconsistent with a d_{yz} component, since this orbital is

Table 3 Oscillator strengths for the $X \rightarrow n_Ond$ ($n = 3$–6) and $X \rightarrow n_Ons$ ($n = 4$–7) Rydberg transitions in F_2CO

Transition	MQDO[a]	MRD-CI[b]	Transition	MQDO[a]	MRD-CI[b]
$X \rightarrow n_O3d_{yz}\ {}^1A_1$	0.0089	0.001	$X \rightarrow n_O3d_{z^2}\ {}^1B_2$	0.0025	0.002
$X \rightarrow n_O4d_{yz}\ {}^1A_1$	0.0036		$X \rightarrow n_O4d_{z^2}\ {}^1B_2$	0.0009	
$X \rightarrow n_O5d_{yz}\ {}^1A_1$	0.0018		$X \rightarrow n_O5d_{z^2}\ {}^1B_2$	0.0005	
$X \rightarrow n_O6d_{yz}\ {}^1A_1$	0.0007		$X \rightarrow n_O6d_{z^2}\ {}^1B_2$	0.0001	
$X \rightarrow n_O3d_{xy}\ {}^1B_1$	0.0081		$X \rightarrow n_O4s\ {}^1B_2$	0.0253	
$X \rightarrow n_O4d_{xy}\ {}^1B_1$	0.0034		$X \rightarrow n_O5s\ {}^1B_2$	0.0084	
$X \rightarrow n_O5d_{xy}\ {}^1B_1$	0.0019		$X \rightarrow n_O6s\ {}^1B_2$	0.0039	
$X \rightarrow n_O6d_{xy}\ {}^1B_1$	0.0007		$X \rightarrow n_O7s\ {}^1B_2$	0.0021	
$X \rightarrow n_O3d_{x^2-y^2}\ {}^1B_2$	0.0080	0.006			
$X \rightarrow n_O4d_{x^2-y^2}\ {}^1B_2$	0.0051				
$X \rightarrow n_O5d_{x^2-y^2}\ {}^1B_2$	0.0017				
$X \rightarrow n_O6d_{x^2-y^2}\ {}^1B_2$	0.0005				

[a] This work

[b] Grein [11]

expected to have a larger overlapping with the nonbonding $2p_y$ orbital of the ground state than the d_{z^2} orbital does. Given the lack of comparable data, we take the decrease in the MQDO *f*-values as we advance toward higher transitions along a given Rydberg series as an indicator of the correctness of our results.

4 Conclusions

In the present work, the vertical electronic spectrum of carbonyl fluoride, for which experimental measurements are difficult to carry out, has been calculated with the highly accurate LR-CCSD and LR-CCSDR(3) methods. The classification of the spectrum of this molecule into Rydberg and valence states is difficult to make since states of the same symmetry of both categories lie in the same energy region. Their interaction leads to states of mixed valence-Rydberg character, as shown in the present study. A large number of excited electronic states of F_2CO have been investigated in the 7.0–13.6 eV region. Our results support previous theoretical assignments of the four transitions experimentally observed. Furthermore, the present study reports and assigns excitation energies for Rydberg states with $n > 3$. With the basis set and theory levels used in this work, we expect to have treated adequately the excitation to Rydberg states up to $n = 7$ for ns, $n = 6$ for np and nd, and $n = 5$ for nf Rydberg series. Moreover, predictions for a number of unobserved intensities for transitions involving Rydberg states have been calculated with the MQDO method. We would like to remark that contributions to the knowledge of the F_2CO spectrum in the UV region are needed in order to understand possible photochemical degradation pathways of this system.

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