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CASSCF and MR–CISD study of the n−4s and n−4pe Rydberg states of the CF_3Cl

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A B S T R A C T

The low-lying n−4s (S_2 and T_2) and n−4pe (S_3 and T_3) Rydberg states of the CF_3Cl have been studied at the CASSCF, MR–CISD, MR–CISD + Q and MR–AQCC levels using the mixed aug–cc–pVDZ/d–aug–cc–pVDZ and aug′–cc–pVTZ/d′–aug′–cc–pVTZ basis sets. Spin–orbit corrections for the singlet energies, vertical excitation energies and oscillator strengths have been computed. The effect of the inclusion of $K + L$ or only the K inner shell chlorine orbitals in the frozen core space at the post-CASSCF levels has also been discussed. Good agreement with available experimental and with previous high-level theoretical results has been achieved.

1. Introduction

The role of clorofluorcarbons (CFCs) as depleting agents of Earth's ozone layer in the atmosphere is well known [1–3] and is a subject of great concern [4–8]. CFC action as ozone depleters is connected to their photodissociation, which mainly yields atomic chlorine (Cl) and clorofluormethyl radicals, and the former catalyzes the cleavage of ozone molecules through chain reactions in the stratosphere [1]. These photodissociation channels involve excitation from chlorine lone pairs (n) to C— Cl antibonding (σ^*) orbitals [9] and lie in the UV region [10]. Although most of the CFCs molecules photodissociate while in the stratosphere, the surviving molecules can reach the ionosphere, where vacuum UV (VUV) is present, and thus can photodissociate through the action of that radiation. The Rydberg states play a very important role in the case of photodissociation through the action of VUV radiation [11].

Pitarch-Ruiz et al. [12] have calculated vertical excitation energies and oscillator strengths of several Rydberg states of the CF_3Cl molecule. The vertical excitation energies have been obtained from a linear response function approach with a coupled-cluster singles and doubles reference function in which the effect of connected triples has been estimated through the CCSDR(3) method [13]. The ANO basis set [14] with contraction [5s4p2d1f] for C and F and [6s5p2d1f] for Cl has been used. For this latter atom this basis set has been augmented with a series of 6s6p6d4f Rydberg functions. The obtained energies have been used in order to determine absolute photoabsorption oscillator strengths in the molecular adapted quantum defect orbital formalism (MQDO) [15,16].

Pitarch-Ruiz et al. [12] have computed vertical excitation energies from the ground state to the ns, np and nd ($n = 4, 5, 6$) and to the 4f Rydberg states. However, in the case of oscillator strengths the results concerning transitions to the np states are absent.

Our group has previously presented the highest level up to date *ab initio* results concerning the dissociation curves (along the C—Cl bond) for the ground and nσ^* states, as well as vertical excitation energies between these two states [9].

In this Letter vertical excitation energies, oscillator strengths and spin–orbit coupling between the first four singlet (S) and the first three triplet (T) states have been computed at the complete active space SCF (CASSCF) and multi-reference configuration interaction with singles and doubles (MR–CISD) [17] (including size-extensivity corrections) levels. To the best of our knowledge this is the first letter in which triplet energies and spin–orbit corrected energies for Rydberg states of this molecule have been computed, as well as the oscillator strength for the transition from the ground state to the n−4pe Rydberg state.

2. Computational details

The experimental geometry [18] of the CF_3Cl molecule has been used in all calculations. The ground state electronic configuration of the CF_3Cl molecule is given elsewhere [9]. Cs symmetry has been used, and the symmetry plane corresponds to the xy plane. The C—Cl bond almost coincides with the x axis. Therefore, the $3p_x$ lone pair orbital of the chlorine atom is involved in the formation of the σ and σ^* molecular orbitals with the *quasi-sp*^{3} hybrid orbital of the CF_3 radical. The ($3p_y$, $3p_z$) degenerate pair is designed as 3pe or n and they are the chlorine orbitals responsible for the nσ^* configuration. Thus, the nσ^* state is doubly degenerate and has E symmetry. The 4s and 4pe Rydberg orbitals have also been included in the present study.

The first step consists of a state-averaged CASSCF calculation [19] where the same weight is given to all states considered, that is, the ground state, the nσ^* state, the n−4s and n−4pe Rydberg

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states. This notation refers to the leading configurations involved in the first three excited states. For instance, n−4s stands for the Rydberg state whose main configuration corresponds to the n → 4s single excitations. Due to the equivalence between the p_y and p_z orbitals and because of the leading configurations obtained the n−4pe state has been considered fourfold degenerate, while the n−4s state is doubly degenerate (that is, of *E* symmetry). Actually, the n−4pe state is composed of three quasi-degenerate states, *E*, A_1 and A_2 (in C_{3v} notation). The quasi-degeneracy comes from the fact that the open-shell part of the leading configurations for these four states (two of Á symmetry and two of Á symmetry in Cs notation) have very similar weights and are of the same type, that is, $(3p_y)^1(4p_y)^1 + (3p_z)^1(4p_z)^1$ in the case of the two highest states of Á symmetry and $(3p_y)^1(4p_z)^1 + (3p_z)^1(4p_y)^1$ in the case of the two highest states of Á symmetry. Therefore, the energies of these four states have been averaged in the calculation of the excitation energies for the n−4pe state. One (Á, Á) pair corresponds to the doubly degenerate state *E* in C_{3v} symmetry. The other Á state becomes the A_1 state while the other Á state becomes the A_2 state in C_{3v} symmetry.

The active space for the CASSCF calculations consists of six electrons distributed, in all possible ways (consistent with spin and space symmetry) among the σ(C—Cl), σ*(C—Cl), 3pe (Cl lone pairs) and the 4s and 4pe Rydberg orbitals. These orbitals have, in C_{3v} notation, a_1, a_1, e, a_1 and e symmetries, respectively. In the case of the S states five Á and four Á states have been averaged, while for the T states four Á and four Á states have been averaged. In order to generate the configuration state functions (CSF) that are used as reference functions for the MR–CISD and multi-reference averaged quadratic coupled cluster (MR–AQCC) calculations the σ, σ* and the 3pe orbitals have been included in the complete active space (CAS), while the 4s and 4pe Rydberg orbitals have been included in the auxiliary (AUX) space and the restriction that up to single CAS → AUX excitations are allowed has been applied.

Two options for the frozen core (FC) orbitals have been tested. In one option the *K* shells of the C and F atoms along with the *K* + *L* shells of the Cl atom have been included in the FC space, while in the other option only the *K* shells of the C, F and Cl atoms have been included in that space. In the latter case the *L* shell of the Cl atom has been included in the doubly occupied space. The set of reference CSFS generated from the first option is called *ref1*, while the second option defines *ref2*. The final expansions for the MR–CISD and MR–AQCC wavefunctions are built from the reference CSFs and all single and double excitations thereof into all virtual orbitals. The symmetry of the reference CSFs is restricted to the state symmetry, and the interacting space restriction has been used [20].

Two types of combined basis sets have been used in this work: (i) aug–cc–pVDZ [21] for C and F and d–aug–cc–pVDZ [22] for Cl; (ii) aug′–cc–pVTZ for C and F and d′–aug–cc–pVTZ for Cl. This latter set is simply named d′–aug′–cc–pVTZ. The aug′–cc–pVTZ is built from the aug–cc–pVTZ basis set [23] simply by removal of the *f* function in the aug-set and, similarly, the d′–aug–cc–pVTZ basis set for Cl is built from the d–aug–cc–pVTZ basis set [22] through removal of the additional *f* function in the *d* (doubly augmented) set. Since in the CF_3Cl molecule the Rydberg molecular orbitals are very similar to those of the isolated Cl atom [24,25] the doubly-augmented orbitals (which are used to describe the Rydberg orbitals) have been centered on the Cl atom instead of the center of mass. The same approach has been used by Pitarch-Ruiz et al. [12].

The CI dimensions treated in this work vary from about 108×10^6 CSFs (MR–CISD/*ref1* with the d′–aug′–cc–pVTZ basis set) to 216×10^6 CSFs (MR–AQCC/*ref2* with the d′–aug′–cc–pVTZ basis set).

Size-extensivity corrections have been considered by means of the generalized Davidson method (MR–CISD + Q [26,27]) and the MR–AQCC approach [28,29]. Several MR–AQCC calculations of excited states showed intruder-states problems, which consists of additional CSFs (not included in the reference space) that obtained an unreasonably large weight. In order to solve this problem these individual CSFs (up to twelve) were included in the reference space as well. The COLUMBUS program system [30–33] was used for most of the calculations. The atomic orbitals (AO) integrals and AO gradient integrals were computed with program modules taken from DALTON [34]. Spin–orbit corrected singlet energies have been computed with the MOLPRO program system [35] using the Breit–Pauli (BP) operator [36]. The state-interacting method is employed, which means that the spin–orbit eigenstates are obtained by diagonalizing $\hat{H}_{el} + \hat{H}_{so}$ in a basis of eigenfunctions of $\hat{H}_{el}$. Due to the size of the system such calculations have been performed only at the CASSCF level with the aug–cc–pVDZ(C,F)/d–aug–cc–pVDZ(Cl) basis set.

3. Results and discussion

The spin–orbit corrected energies of the *S* Rydberg states differ from the uncorrected CASSCF energies by less than 0.009 eV with the combined aug–cc–pVDZ/d–aug–cc–pVDZ basis set. Although it has not been possible to perform spin–orbit calculations at the MR–CISD level and with the larger basis set, it is expected that the effect is not very different.

Table 1 shows the results of the vertical excitation energies for the *S* and *T* Rydberg states along with the oscillator strength (*f*) values (for the *S* states), weights of the main configurations and $< r^2 >$ (where $r^2 = x^2 + y^2 + z^2$) expectation values at the CASSCF, MR–CISD, MR–CISD + Q and MR–AQCC levels with the d′–aug′–cc–pVTZ basis set. These results have been obtained with the *ref1* reference space. As can be seen from this table the triplet energies at the CASSCF level are slightly higher than the corresponding singlet energies. As can be seen from all results the energies of the *S* and *T* Rydberg states are very close, at all computational levels. The optimized molecular orbitals obtained at the CASSCF level for the *S* states are slightly different from the corresponding optimized molecular orbitals obtained for the *T* states, since in the averaging procedure for a given spin multiplicity only states of that multiplicity are considered. Therefore, in a situation of quasi-degeneracy between *S* and *T* states one can obtain slightly lower energies for the *S* states. Only if the same set of molecular orbitals is used for both *S* and *T* states at the CASSCF level one must obtain lower energies for the *T* states even in a situation of quasi-degeneracy. The results show that upon inclusion of dynamic electron correlation such artificial behavior is eliminated. The $< r^2 >$ values at the CASSCF level already show the much greater diffuseness of the Rydberg states as compared to the ground state. The value of this property for the valence n−σ∗ state (not shown in the Table) is 93.8 a_0^2, which is close to the value of 97.4 a_0^2 obtained for the n−4s state, due to the great admixture between these two states (see Table 1). At the MR–CISD level this admixture is practically eliminated. On the other hand, the weights of the n−4s CSFs for the *T* states are considerably larger than the corresponding weights for the *S* states, at the CASSCF level (see Table 1). Thus at this level the n−4s *S* state has a much higher multiconfigurational character than the corresponding *T* state.

The excitation energies of all four Rydberg states change by at least 0.23 eV and at most 0.57 eV upon inclusion of dynamic electron correlation at the MR–CISD level (see Table 1). Thus, such effect is very important for the description of these Rydberg states. The inclusion of extensivity corrections at the MR–CISD + Q level leads to an increase of at most 0.19 eV for the excitation energies,

Table 1
CASSCF, MR–CISD, MR–CISD + Q and MR–AQCC results for the CF_3Cl molecule obtained with the d′–aug′–cc–pVTZ basis set and with the *ref1* reference space.

State	CASSCF[a]				MR–CISD[b]				MR–CISD + Q[c]	MR–AQCC[d]		
	Δ*E*	$<r^2>$	Weights[e]	f (x 10^2)	Δ*E*	$<r^2>$	Weights[e]	f (x 10^2)	Δ*E*	Δ*E*	$<r^2>$	Weights[e]
gs	0.00	71.1	0.96	–	0.00	72.3	0.83	–	0.00	0.00	73.9	0.76
n–4s(*S*)	9.09	97.4	0.54n4s + 0.43nσ*	11.58	9.45	114.8	0.79n4s	10.61	9.58	9.56	114.7	0.72n4s
n–4pe(*S*)	9.85	147.3	0.98n4pe	0.171	10.42	146.3	0.85n4pe	0.766	10.58	10.61	141.9	0.76n4pe
n–4s(*T*)	9.03	113.1	0.96n4s	–	9.26	113.2	0.84n4s	–	9.42	9.45	122.6	0.75n4s
n–4pe(*T*)	9.99	141.5	0.99n4pe	–	10.30	140.6	0.85n4pe	–	10.49	10.54	136.0	0.76n4pe

gs: ground state; (S): singlet; (T): triplet. The excitation energies and the $< r^2 >$ values are given in eV and in au (a_0^2), respectively. [a,b,c,d]Ground state energies (au): −795.84472; −796.78180; −796.91882; −796.95615; [e]Only weights of the CSFs which are larger than 0.1 are shown.

Table 2
MR–CISD, MR–CISD + Q and MR–AQCC results for the CF_3Cl molecule obtained with the d′–aug′–cc–pVTZ basis set and with the *ref2* reference space.

State	MR–CISD[a]				MR–CISD + Q[b]	MR–AQCC[c]		
	Δ*E*	$<r^2>$	Weights[d]	f (x 10^2)	Δ*E*	Δ*E*	$<r^2>$	Weights[d]
gs	0.00	72.3	0.84	–	0.00	0.00	74.05	0.76
n–4s(S)	9.45	114.8	0.79n4s	10.65 (12.86)[e]	9.58	9.66 (9.67)[e]	113.3	0.72n4s
n–4pe(S)	10.42	146.3	0.85	0.764	10.58	10.68 (10.72)[e]	140.4	0.75n4pe
n–4s(T)	9.26	112.6	0.84	–	9.42	–	–	–
n–4pe(T)	10.30	139.8	0.85	–	10.49	–	–	–

gs: ground state; (S): singlet; (T): triplet. The excitation energies and the $< r^2 >$ values are given in eV and in au (a_0^2), respectively. [a,b,c]Ground state energies (au): −796.81018; −796.95068; −796.99725. [d]Only weights of the CSFs which are larger than 0.1 are shown. [e]reference [12].

and the effect is similar for all four states (see Table 1). By taking into account the more accurate extensivity corrections as obtained through the MR–AQCC method one can see that the excitation energies change by at most 0.05 eV as compared to the MR–CISD + Q values. The effect of dynamic electron correlation on the oscillator strength values is much larger for the n–4pe state than for the n–4s state (see Table 1).

In Table 2 the results obtained with the *ref2* reference space are shown. Through comparison between the two tables one can clearly see that the inclusion of the *L* shell of the Cl atom in the doubly occupied orbitals (instead of the inclusion in the FC orbitals) for generating the reference CSFs (at post-CASSCF levels) has a very small effect, at all computational levels (compare Tables 1 and 2). Therefore, both *S* states are well described, even with the smaller *ref1* reference space. For the other properties the effect is also very small (compare Tables 1 and 2). This result is very important for speeding up calculations concerning potential energy surfaces for this molecule, a work which is being developed in our group.

There is a good agreement of our results for the oscillator strength concerning transition from the ground state (gs) to the n–4s state, obtained with both reference spaces at the MR–CISD level with the value of 0.1286 given in Ref. [12], obtained with the MQDO method using CCSRD(3) energies. There is also a good agreement of our values of 0.1158, 0.1061 and 0.1065 (obtained at the CASSCF, MR–CISD/*ref1* and MR–CISD/*ref2* levels, respectively) with the experimental value of 0.1625 ± 0.032 obtained by Au et al. [37] through a high-resolution dipole (e,e) technique. This result gives us confidence on the values of 0.766×10^{-2} and 0.764×10^{-2} obtained for the gs → n–4pe transition at the MR–CISD/*ref1* and MR–CISD/*ref2* levels, respectively. To the best of our knowledge the value of the oscillator strength for this transition has not been published, but the value of the oscillator strength in the region between 10.18 and 10.95 eV has been measured by Au and King et al. [37,38] and the corresponding values are 0.0865 [37] and 0.119 [38]. The vertical excitation energies obtained by Pitchard-Ruiz et al. [12] are in excellent agreement with our results obtained at the MR–AQCC/*ref2* level for the n–4s and n–4pe states, that is, 9.66 and 10.68 eV, respectively (see Table 2). The most recent experimental results are 9.69 and 10.64 eV [37] and also show a very good agreement with our results.

The singlet–triplet gap is 0.19 and 0.12 eV for the n–4s and n–4pe states, respectively, at the MR–CISD/*ref1* level. Inclusion of extensivity corrections at the MR–CISD + Q/*ref1* level slightly decrease these values to 0.16 and 0.09 eV. At the MR–AQCC/*ref1* level these gaps further decrease to 0.11 and 0.07 eV. Through comparison between Tables 1 and 2 one can see that the effect of including the chlorine *L* shell in the doubly occupied orbitals for generating the reference CSFs is practically negligible for the singlet–triplet gap at both MR–CISD and MR–CISD + Q levels.

4. Conclusions

The low-lying n–4s (S_2 and T_2) and n–4pe Rydberg (S_3 and T_3) states of the CF_3Cl have been studied at the CASSCF, MR–CISD, MR–CISD + Q and MR–AQCC levels using the mixed aug–cc–pVDZ/d–aug–cc–pVDZ and aug′–cc–pVTZ/d′–aug’–cc–pVTZ basis sets. Spin–orbit corrections for the singlet energies, vertical excitation energies and oscillator strengths have been computed. The spin–orbit corrected energies of the *S* Rydberg states differ from the uncorrected singlet energies by less than 0009 eV at the CASSCF level with the aug–cc–pVDZ/d–aug–cc–pVDZ basis set. The effect of the inclusion of *K* + *L* (*ref1*) or only the *K* inner shell chlorine orbitals in the FC space (*ref2*) is practically negligible for the excitation energies of all four states at all post-CASSCF levels. The same holds for the other properties.

The inclusion of extensivity corrections at the MR–CISD + Q level (for the *ref1* reference space) slightly decrease the singlet–triplet gap for both n–4s and n–4pe states. At the MR–AQCC/*ref1* level there is a further decrease of these gaps to 0.11 and 0.07 eV (see Table 1). The effect of including only the chlorine *K* shell or both the *K* + *L* shells in the FC space is almost negligible at both MR–CISD and MR–CISD + Q levels (compare Tables 1 and 2).

The calculations performed in this work represent the highest level *ab initio* calculations for the n–4s and n–4pe Rydberg states of the CF_3Cl molecule. Our highest level results (that is, at the MR–AQCC/*ref2* level) for the vertical excitation energies of these two states are 9.66 and 10.68 eV and are in very good agreement with the previous results obtained by Pitchard-Ruiz et al. [12] using the CCSDR(3) method [13] and with the experimental results obtained by Au et al. [37] (see Table 2). Our highest level results (that is, at the MR–CISD/*ref1* and MR–CISD/*ref2* levels) for *f* are 0.1061 and 0.1065 for the gs → n−4s transition and are in good agreement with the value of 0.1286 obtained by Pitchard-Ruiz et al. using the MQDO method [12] and with the value of 0.1625 ± 0.032 obtained from the most recent experimental result provided by Au et al. [37]. The *f* values for the gs → n−4pe transition are 0.766×10^{-2} and 0.764×10^{-2} at the MR–CISD/*ref1* and MR–CISD/*ref2* levels, respectively. The value of *f* for this transition has not been reported previously.

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