J. Phys. Chem. A **2007,** *111,* 3321−3325

Excitation Energies and Photoabsorption Oscillator Strengths of the Rydberg Series in CF_3Cl. A Linear Response and Quantum Defect Study

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Received: January 10, 2007; In Final Form: March 5, 2007

Vertical excitation energies of the CF_3Cl molecule have been obtained from a response function approach with a CC reference function to determine absolute photoabsorption oscillator strengths in the molecular-adapted quantum defect orbital formalism (MQDO). The present work covers more highly excited Rydberg states than have been experimentally reported. Assessing of the reliability of the present calculations is provided through a comparative analysis between the results of the molecule and the Cl atom. This can be used to allow for predictions of the same type of properties in other analogous systems.

1. Introduction

Halogenated methanes have important applications in many areas of technology, ranging from the fabrication of semiconductors by plasma etching to their use as refrigerants.[1] However, the harmlessness of these compounds, which make them so attractive for lab-based technology, is lost as they diffuse into the stratosphere where they undergo solar UV photodissociation. For chlorinated methanes, the free Cl atoms liberated in this process are of major significance in the catalytic depletion of stratospheric ozone.[2] Growing attention is paid to the oscillator strengths of these molecules even higher into the continuum, as these properties may help for easy identification of dissociation channels.

The UV and vacuum-UV photochemistry of these molecules has aroused much interest given that an understanding of the decay dynamics of valence and Rydberg states of the neutral molecule as well as excited valence states of the parent molecular ion can provide useful information for atmospheric modelers. Although the UV photodissociation of many of the freons has been extensively studied, there has been less work on the vacuum-UV photodissociation processes that occur.

The characterization of the lower-lying states of polyatomic molecules, populated by absorption in the vacuum ultraviolet region is no easy task, either theoretically or experimentally. In this paper, we seek to aid the assignment and analysis of the electronic spectrum of CF_3Cl, for which excitation energies as well as related absolute oscillator strength data are very scarce in the literature. In the present work, vertical excitation energies of the CF_3Cl molecule are inferred from a response function approach with a coupled cluster reference function.[3] The calculated excitation energies cover more highly excited Rydberg states and give more detailed description of these states than previous experimental data. These predictions provide optimal parameters for the determination of absorption oscillator strengths with the use of the molecular-adapted quantum defect orbital method (MQDO).[4] A comparison with the experimental data available in the literature has been applied. However, given that available comparative data are scarce, the correctness of our results has been additionally assessed by a comparative analysis of the quantum defects and intensities of analogous transitions in both the CF_3Cl molecule and the isolated Cl atom. Similarities in the intensities of analogous electronic transitions in the molecule and Cl atom might be anticipated on the grounds of that Rydberg orbitals of the molecule are essentially lone-pair atomic orbitals centered on Cl atom in its ground state.[5] We expect the comparative analysis of the results for the molecule and the atom to provide information on the character of the molecular Rydberg states, in addition to helping assess the reliability of the present calculations.

2. Methods and Computational Details

2.1. Ab initio Calculations. Two kinds of ab initio calculations are performed in this study. First, vertical excitation energies of the CF_3Cl system at the experimental geometry are obtained by means of a coupled cluster linear response approach with a linked triples-corrected coupled cluster singles and doubles (CCSD) wave function as reference function[6−8] and the effect of connected triples estimated using the CCSDR(3) method.[3] For systems that can be properly described by simple reference methods, triples-corrected coupled cluster methods give excitation energies that differ in around 0.1 eV from the full CI values.[3] The 1s core orbitals were kept frozen in all the electronic correlation calculations. Coupled cluster (CC) and linear response coupled cluster (LR-CC) calculations were carried out with the use of the DALTON program,[9] in which the above-mentioned algorithms are implemented.

Second, one-photon transition intensities were calculated with the molecular-adapted quantum defect orbital (MQDO) approach.[4] The MQDO approach, formulated to deal with mo-

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10.1021/jp070210z CCC: $37.00

lecular Rydberg transitions, has been described in detail elsewhere.[4] In this method, a model one-electron Hamiltonian with a parametric potential is employed. The radial quantum defect orbitals are the analytical solutions of the corresponding Schrödinger equation. The angular counterparts are linear combinations of spherical harmonics chosen so that the complete MQDO molecular orbitals provide basis functions for the irreducible representations of the pertinent molecular symmetry group. The energy data used by the MQDO method are provided by the CC calculations, whereas the ionization potential of the lowest cation has been taken from experimental values.[10,11]

2.2. Basis Set. We have used a basis set of atomic natural orbitals (ANO)[12] with contraction [5s4p2d1f] for carbon and fluorine and [6s5p2d1f] for the chlorine atom. For carbon and fluorine atoms, this basis set is of similar quality than the Dunning's correlation consistent aug-cc-pVTZ basis. This basis can be considered large enough to treat the valence character of the system at equilibrium geometry. In addition, the ANO set has been augmented with a series of 6s6p6d4f Rydberg functions allocated on the chlorine atom and built by following the technique proposed by Roos et al. to generate a universal Gaussian basis set.[13] Specific coefficients have been obtained for the Rydberg function basis set for the particular CF_3Cl system. It can be assumed that in CF_xCl_y systems, the Rydberg molecular orbitals (and consequently, the corresponding Rydberg series of states) are essentially similar to those of the Cl isolated atom.[5,14] To mimic this behavior, especially for the highest terms, the Rydberg orbitals of the augmented basis set have been centered on the Cl atoms instead of the center of masses.

3. Results and Discussion

3.1. Ab initio Transition Energies. The electronic configuration of the outermost valence MOs of CF_3Cl in the C_{3v} symmetry is[10,15] ... $(3a_1)^2(2e)^4(4a_1)^2(3e)^4(4e)^4(1a_2)^2(5a_1)^2(5e)^4$: X^1A_1.

The HOMO (5e) essentially contains the lone pair electrons located on the chlorine atom.[10] The ionization energy (IP) of the outer valence orbital 5e, adopted for the present calculations, is 13.08 eV as measured by high-resolution HeI and HeII photoelectron spectroscopy (PES) by Cvitas et al.[10]

At shorter wavelengths, the absorption spectra of CF_3Cl is dominated by sharp and rather strong bands, which have been assigned to electronic transitions arising from the lone pairs of Cl and ending in ns, np, or nd Rydberg states.[5,16−19] In particular, the first peak at 9.7 eV has been determined to be a strong transition to the $(5e)^{-1}4s$ Rydberg state.[5,17] A weak shoulder about 10.6 eV has been assigned, in this case, to a transition to the $(5e)^{-1}$ 4p Rydberg state.[5,17] Another strong peak has been reported at 11.6 eV and assigned to a transition to the $(5a_1)^{-1}4s$, $(5e)^{-1}3d$, or $(5e)^{-1}5s$ Rydberg states.[5,17] Finally, a peak at 12.10 eV has been determined to be a transition to the $(5e)^{-1}4d$ or $(1a_2)^{-1}4s$ Rydberg states.[17] These experimental assignments are summarized in Table 1.

Given that the ground state of CF_3Cl exhibits C_{3v} symmetry, one might consider the np and nd states, respectively, as giving rise to the following set of Rydberg series: np$e$, npa_1, nd$eI(dx^2 - y^2, dxy)$, nd$eII(dxz, dyz)$, and nd$a_1(dz^2)$. In no case were experimentalists able to resolve these different Rydberg series. Consequently, in the present work, we aim at calculating the corresponding excitation energies to the np and nd Rydberg series, as mentioned above. The nsa_1 Rydberg series and the first few members of the nf Rydberg series are also investigated.

TABLE 1: Vertical Excitation Energies (eV) for the Rydberg Series of CF_3Cl

state	CCSD[a]	CCSDR(3)[a]	expt.[b]	expt.[c]	expt.[d]	expt.[e]	expt.[f]
4sa_1	9.81	9.67	9.68	9.69		9.68	9.60
5sa_1	11.64	11.48					
6sa_1	12.31	12.15					
4pe	10.87	10.72	10.65	10.64	10.7	10.59	10.60
5pe	12.05	11.89					
6pe	12.48	12.31					
4pa_1	10.98	10.80					
5pa_1	12.08	11.91					
3deI[g]	11.69	11.53					
4deI[g]	12.33	12.16	12.10				
3deII[h]	11.64	11.48					
4deII[h]	12.30	12.14	12.10				
3da_1	11.78	11.62	11.61	11.60		11.58	11.51
4da_1	12.37	12.21					
4fe	12.28	12.12					
4fe	12.29	12.13					
4fe	12.30	12.14					
4fa_1	12.30	12.14					
4fa_2	12.30	12.15					

[a] This work. [b] King and McConkey.[17] [c] Au et al.[16] [d] Biehl et al.[19] [e] Gilbert et al.[5] [f] Jochims et al.[18] [g] eI $(dx^2 - y^2, dxy)$. [h] eII (dxz, dyz).

The presently calculated vertical excitation energies, together with all the known experimental values, are displayed in Table 1. Our assignment of the "n" values to the Rydberg states has been made following the criteria described by Gilbert et al.[5] These authors based their assignment on the fact that the large atomic orbitals entering the Rydberg orbital in the molecular orbital description belong to the atom around which the initial orbital in the related photoexcitation process is mainly concentrated. This assumption appears to be reasonable, because the structure of a molecule in a Rydberg state usually resembles the structure of the related ion yielded by the ionization limit.

It seems apparent in Table 1 that inclusion of linked triples in the CCSDR(3) calculations has a significant effect in the magnitude of all excitation energies that are shifted in approximately −0.16 eV. This shift leads to a better approximation to the experimental measurements. The effect of triple excitations acts on average as a systematic error correction of about 0.15 eV that corresponds to a 1.3−1.4% shift in all the range of excitation energies. In the present case, the CCSDR(3) energies are surely more accurate than their CCSD counterparts. However, in a recent work on the CH_4 system[20] also combining CC energy data with the MQDO method, the effect of the linked triples was only of about 0.02−0.03 eV. The increasing relevance of these effects can be related to the number of correlated electrons and, more roughly, to the period in the periodic table. However, the occurrence of several lone pairs on the same atom, as happens in halogens, can also lead to highly correlated effects, as happens, for example, in the F_2 system.[21,22] On the other hand, the influence of an enlargement of the basis set is negligible, as we have checked that using a larger aug-cc-pVTZ basis[23] varies our results by around 0.03 eV, well below the expected error of the method. Nevertheless, a smaller basis such as aug-cc-pVDZ is known to be inadequate.[24]

Regarding experimental measurements, the peak assignment appears, in some cases, not quite straightforward. As mentioned above, more than one Rydberg state is assigned to a given energy value in most cases. We have presently attempted not to assign more than one peak to a given excitation. This is reflected in Table 1. More specifically, the experimental peak observed at about 11.6 eV was assigned to several states ($(5a_1)^{-1}4s$, $(5e)^{-1}3d$, or $(5e)^{-1}5s$ Rydberg states[5,17]). According to our calculations, this peak can be assigned to the $(5e)^{-1}3da_1$ Rydberg state, unequivocally. Our energy is in close agreement with experiment (see Table 1). For the $(5e)^{-1}5sa_1$ Rydberg state, we have obtained excitation energy equal to 11.48 eV.

Also, for the $(5a_1)^{-1}4s$ state, the calculated CCSDR(3) value is 11.86 eV, slightly greater than the observed value, 11.6 eV (by the way, this value is not included in Table 1 because we are dealing only with those Rydberg states that converge to the first ionization potential).

Considering now the observed peak at 10.65 eV, it has presently been assigned to a 4p Rydberg orbital, as has the experimental assignment. However, we have been more specific, giving to it the character of 4p*e*. This is in agreement with the predictions by Yen et al.[25] After a spectral study of the Cl/Cl* photofragmentation, these authors strongly suggest that the upper state around 118 nm is the 4p(e) Rydberg orbital, which is connected to the ground state via a parallel transition moment.

Finally, we have assigned the peak observed at 12.10 eV to a 4d Rydberg state either of character *eI* or *eII*. These are, respectively, obtained at 12.16 and 12.14 eV, in the present calculations. They should be too close to one another to be discriminated at the experimental level.

It is apparent that assignments so far performed lead to quantum defects in consistency with their values generally expected for Rydberg series deriving from ns, np, and nd orbitals of the third-row atoms. A more detailed discussion of this feature follows.

Given that the experimentally observed energy levels correlate only with the first terms of the different Rydberg series, only for the first terms of each Rydberg series (s, p, d, ...) is it possible to compare our results to experimental values. A thorough analysis of the resulting quantum defects has been achieved by including a comparison to those corresponding to the isolated chlorine atom. Then, given the analogies between the outer valence electronic structure of the CF_3Cl molecule and that of the Cl atom in the ground states, the reliability of our calculations can be established.

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

$$T_n = \mathrm{IP} - h\upsilon_n = \frac{R}{(n-\delta)^2}$$

where IP is a molecular ionization potential, υ_n is the frequency of the absorbed photon, R is the Rydberg constant, n is an integer, and δ is the quantum defect. The magnitude of δ can be seen as reflecting the degree to which the upper orbital penetrates the molecular core; increasing penetration increases the electron binding energy and hence the term value T_n. It also reflects departure from simple H-atom behavior and varies with the quantum number "*l*".

Table 2 displays the quantum defects and term values for the different Rydberg series studied. Those corresponding to the molecule were derived from the calculated CCSD and CCSDR(3) vertical excitation energies. For the atom, the quantum defects have been extracted from the tabulated energy levels and ionization energies.[26]

An inspection of Table 2 leads us to conclude that the use of CCSDR(3) energies yields quantum defects in better accord with those of Cl than CCSD energies do. The CCSDR(3) values are more reliable not only in magnitude but also in their systematic trends along each Rydberg series, as can be observed for the nsa_1 series. The CCSDR(3) energies are of superior quality than the CCSD energies, as expected. Accordingly, in the remainder of our calculations referring to the properties object of this section, we have considered the CCSDR(3) energies only.

TABLE 2: Term Value (T_n) and Quantum Defects (δ) for the Rydberg Series of CF_3Cl and Cl Atom

	CCSD[a]		CCSDR(3)[a]			Cl[b]	
CF_3Cl	T_n	δ	T_n	δ	Cl	T_n	δ
4sa_1	3.27	1.96	3.41	2.00	$4s^2P$	3.74	2.09
5sa_1	1.44	1.93	1.60	2.08	$5s^2P$	1.63	2.11
6sa_1	0.77	1.80	0.93	2.18	$6s^2P$	0.90	2.11
4p*e*	2.21	1.52	2.36	1.6	$4p^2D$	2.46	1.65
4pa_1	2.1	1.45	2.28	1.56	$4p^2P$	2.38	1.61
5p*e*	1.03	1.37	1.19	1.62	$5p^2D$	1.17	1.58
5pa_1	1.00	1.31	1.17	1.59	$5p^2P$	1.01	1.34
6p*e*	0.60	1.27	0.77	1.8	6p	0.71	1.63
3d*eI*[c]	1.39	−0.13	1.55	0.04	$3d^2F$	1.63	0.11
3d*eII*[d]	1.44	−0.07	1.6	0.08	$3d^2D$	1.67	0.14
3da_1	1.30	−0.24	1.46	−0.05	$3d^2P$	1.56	0.05
4d*eI*[c]	0.75	−0.26	0.92	0.15	4d	1.01	0.34
4d*eII*[d]	0.78	−0.18	0.94	0.20			
4da_1	0.71	−0.38	0.87	0.05			

[a] This work. [b] Moore.[26] [c] *eI* ($dx^2 - y^2$, dxy). [d] *eII* (dxz, dyz).

The δ values in Table 2 reveal that in each Rydberg series, important similarities occur in the magnitude of the quantum defects of the two species (isolated Cl atom and molecule) because, as mentioned above, the Rydberg orbitals of the molecule are essentially atomic orbitals centered on Cl. A very similar spectroscopic behavior of the Cl atoms when they are free and when bound within the molecule is clearly noticed. This behavior is probably due, at least partly, to the feature anticipated by Gilbert et al.[5] and confirmed by the present calculation, concerning the large size of the atomic orbitals entering the molecular Rydberg orbital. The former are orbitals that belong to the atom, around which the electron that departs in the related photoexcitation process is mainly concentrated.

It is may be worth noticing that for the states which exhibit a "d" character, a change of 0.1 in δ occurs when dealing with the 4d Rydberg state, in comparison with that of the 3d state. This change may be related to differences in excitation energies of about 0.5 eV. Hence, the errors happen to be significantly larger than the ones expected, even at the LR-CCSD level (see Table 1). The same feature is observed in the free chlorine atom. A plausible explanation is that, as the spin−orbit coupling scheme in the Cl atom changes from LS to $j_c l$ from the 3d to the 4d state, the electron spin coupling scheme may vary as well in the molecule as n increases from the Russell−Saunders scheme for low n values to separate core (Ω_c)−optical electron (ω) (Ω_c ,ω) coupling when n is large. It might also happen that the interactions between molecular states differing in both n and l, for example, an nd state will be nearly isoenergetic with the $(n + 1)$s state because they will have very similar term values T_n. If the two molecular states have the same symmetry under the point group of the molecular core, they will strongly interact.

3.2. MQDO Oscillator Strengths. The oscillator strengths have been calculated with the MQDO method using the CCSDR(3) energies in Table 1. The oscillator strength values are collected in Tables 3 and 4 together with the earlier MQDO results[27] based on extrapolated quantum defects. In general, the oscillator strengths obtained from the CCSDR(3) energies are greater than previous ones. In Table 3, the MQDO absorption oscillator strengths for the electronic transitions originating in the ground 3p*e*(X^1A_1) state are collected together with the experimental data available in the literature. We have also included in the first two columns of Table 3 the oscillator strengths calculated with the LR-CCSD approach and with the MQDO method (CCSD energies). They are on the same order but of lower magnitude than the values in columns three and

TABLE 3: Oscillator Strengths for the $3pe(X\,^1A_1) \rightarrow nsa_1$, nda_1, $ndeI$, and $ndeII$ Transitions of CF_3Cl

transition	CCSD[a]	MQDO[b]	MQDO[c]	MQDO[d]	expt.
$3pe(X\,^1A_1) - 4sa_1$	0.0776	0.0919	0.1286	0.1191	0.1625 ± 0.032[e] 0.1516 ± 0.015[f] 0.220 ± 0.088[g] ~ 0.1503[h]
$3pe(X\,^1A_1) - 5sa_1$	0.0189	0.0181	0.0389	0.0225	
$3pe(X\,^1A_1) - 6sa_1$	0.0062	0.0023	0.0171	0.0087	
$3pe(X\,^1A_1) - 3da_1$	0.0050	0.0067	0.0116	0.0120	
$3pe(X\,^1A_1) - 4da_1$	0.0014	0.0025	0.0074	0.0060	
$3pe(X\,^1A_1) - 3deI$[i]		0.0556	0.0908		
$3pe(X\,^1A_1) - 4deI$[i]		0.0209	0.0560		
$3pe(X\,^1A_1) - 3deII$[j]	0.0189	0.0328	0.0518		
$3pe(X\,^1A_1) - 4deII$[j]	0.0010	0.0130	0.0304		

[a] CCSD this work [b] MQDO, this work using CCSD energies [c] MQDO, this work using CCSRD(3) energies [d] MQDO[27] [e] Au et al.[16] [f] Suto and Lee[28] [g] King and McConkey[17] [h] Doucet et al.[29] [i] eI ($dx^2 - y^2$, dxy) [j] eII (dxz, dyz).

TABLE 4: MQDO Absorption Oscillator Strengths for $4pe$-nsa_1, $4pa_1$-nsa_1, nsa_1-$n'pa_1$, nsa_1-$n'pe$ Transitions for CF_3Cl

transition	MQDO[a]	MQDO[b]
$4pe$-$5sa_1$	0.3040	0.2415
$4pe$-$6sa_1$	0.0118	0.0290
$4pa_1$-$5sa_1$	0.3122	
$4pa_1$-$6sa_1$	0.0079	
$4sa_1$-$4pa_1$	0.3225	0.2942
$4sa_1$-$5pa_1$	0.0059	
$4sa_1$-$4pe$	0.6226	0.5884
$4sa_1$-$5pe$	0.0073	
$5sa_1$-$5pa_1$	0.4590	0.4152
$5sa_1$-$5pe$	0.9143	0.8303

[a] MQDO, this work using CCSRD(3) energies. [b] MQDO.[27]

TABLE 5: Absorption Oscillator Strengths for Analogous Transitions in CF_3Cl and the Isolated Cl Atom

	CF_3Cl			
transition	MQDO[a]	MQDO[b]	transition	Cl
$3pe(X^1A_1)$-$4sa_1$	0.1286	0.1191	$3p\,^2P$-$4s\,^2P$	0.1603
$3pe(X^1A_1)$-$3da_1,eI,eII$	0.1532		$3p\,^2P$-$3d\,^2(P,D)$	0.1448
$4pe$-$5sa_1$	0.3040	0.2415	$4p\,^2P$-$5s\,^2P$	0.3026
$4pa_1$-$5sa_1$	0.3122		$4p\,^2S$-$5s\,^2P$	0.3097
			$4p\,^2D$-$5s\,^2P$	0.2862
$4sa_1$-$4pa_1,e$	0.9451	0.8971	$4s\,^2P$-$4p\,^2(S,P,D)$	0.9362
$5sa_1$-$5pa_1,e$	1.3733	1.2455	$5s\,^2P$-$5p\,^2(S,P,D)$	1.2626

[a] MQDO, this work using CCSRD(3) energies. [b] MQDO.[27]

four, which have been obtained with the MQDO but using the CCSDR(3) energies and the experimental data, respectively. The comparison with the several experimental values reported for the oscillator strength of the $3pe(X^1A_1)$-$4sa_1$ transition suggests a reliability of the results using the MQDO method with the CCSDR(3) energies, whose calculation is very efficient.

To provide additional results that may be of the same potential usefulness, we have also calculated oscillator strengths for other electronic bands that originate from different excited states, as collected in Table 4. As one could expect for a non-perturbed Rydberg series, the oscillator strengths diminish when the final state in the transition changes from the *nl* state to the $(n + 1)l$ state.

The only comparative oscillator strengths that we have found in the literature correspond to the $3pe(X^1A_1) \rightarrow 4sa_1(^1E)$ transition in CF_3Cl. The present results conform well with the most recent measurements, performed with a high-resolution dipole (e,e) technique, by Au et al.[16] A general agreement of the present calculations with the comparative data is apparent,[16,17,28,29] and more so if we take into account their estimated uncertainties, also written in Table 3. Anyway, our values seem somehow underestimated.

Given the lack of experimental values, we take the comparison to the Cl atom exhibited by the oscillator strengths as an assessment of the adequacy of the MQDO approach for the calculation of the spectral transition intensities. The intensities for this atom have been obtained through the relativistic quantum defect orbital (RQDO) method.[30,31] The results are collected in Table 5. Because the atom possesses spherical symmetry higher than that of molecules, the state described by a given *nl* notation in an atom is symmetry-split in the molecule. On the other hand, there may be several different terms and multiplets arising from a given outer *nl* atomic electron configuration. In such cases, the comparison should be made between the resulting *f*-values of an *nl*-*n′l′* "supermultiplet" in the atom and the sum of the intensities of all *nl*-*n′l′* transitions that comprise all the different irreducible representations involved in the molecule. A "supermultiplet"[32] is the group of multiplets with different *L* values but the same spin multiplicity that arise from a given electron configuration in an atom.

Inspection of Table 5 reveals the similarities in the magnitude of the oscillator strengths for equivalent transitions in the isolated halogen atom and its parent molecule. In particular, it is noticeable that in those cases in which MQDO calculations can be achieved with measured excitation energies, the MQDO values calculated with CC energies conform better in magnitude with those of the atom, with the only exception being the 5s−5p transition. Hence, we can expect that a similar behavior will hold in the other cases (3p−3d and 4p−5s). The agreement in these cases between the molecular f-values and the ones obtained for the isolated Cl atom values is apparent in Table 5. The set of values reported in this table, as a whole, can be taken as an additional check of the MQDO procedure that we have followed in the present work and help to assess the reliability of the values reported in Tables 3 and 4.

4. Conclusions

As a summary of our analysis, we may point out that both the presently calculated vertical excitation energies and oscillator strengths are consistent with the scarce values obtained from the measurements. Clear similarities in the spectral properties of CF_3Cl and Cl are apparent. A similar behavior of the lower excited states of CF_3Cl and those of Cl atom has been disclosed. This feature lends substantial usefulness, not only because it allows the prediction of the same type of properties in other molecular species that exhibit analogies with the electronic structure of CF_3Cl, but it can also be taken as a good tool for assessing the reliability of our theoretical approach in molecules containing third period atoms. In addition, the present results for the molecular Rydberg transitions conform better with the f-values of the isolated Cl atom, for a number of transitions, than the earlier MQDO results calculated with quantum defect extrapolated from the experimental energies do.

To conclude, we expect that the data supplied by the present calculations might help future interpretations of the electronic spectra of the studied Rydberg radical in a spectral region for which the states have not been yet assigned.

Acknowledgment. The present work has been supported by European FEDER funds and Spanish projects MEC (CTQ2004-07768-C02/BQU), the J.C.L. (VA047A06 and VA016B06), GV (GV-INFRA03-047). A.M.V. also acknowledges her research agreement awarded by the "Ramon y Cajal" program from the Spanish MEC, and FSE.

Supporting Information Available: The auxiliary file contains a table that shows the coefficients for the Rydberg function basis set for the CF_3Cl system, optimized with the technique proposed by Roos et al., as reported in the text. The general exponents used for this system are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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