

Low-Lying Rydberg States of HCl

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Vertical excitation energies belonging to some different Rydberg series of hydrogen chloride have been determined with a coupled-cluster theoretical approach. These excitation energies have allowed us to calculate electric dipole transition intensities in HCl and allow additional assessment of the calculation approach presently used to provide an adequate description of the valence and Rydberg states of HCl. The molecular quantum defect orbital has been applied to the calculation of oscillator strengths. In particular, new insight is given on the assignment of states as the $R^1\Pi$, the $^1\Delta(4d\pi$ and $5p\pi)$, the $^1\Sigma^+(4d\pi)$, and the $nd\delta(^1\Pi, ^1\Phi)$ and $4f$ states.

Introduction

The importance of hydrogen chloride in astrophysics has long been known. HCl has been observed in dense clouds of the interstellar medium^{1–3} and as a minor constituent of Venus's atmosphere.⁴ This compound is also present in Earth's stratosphere, from which it can only be removed through certain chemical reactions and by photodissociation.^{4,5} The interest in the study of molecules such as HCl in interstellar clouds lies in the fact that the physical conditions prevailing in the interstellar gas may be inferred from the output.⁶ If this information happens to be reliable, some existing modeling of the chemical evolution of such clouds may be tested and employed.⁶ These circumstances have triggered extensive experimental and theoretical investigations on HCl-related topics. In addition to the interest the spectral behavior of HCl offers from a physical standpoint, its strong polar nature is also interesting because it may have some influence in the absorption pattern of this molecule.

The first reported experimental observations of the rather complex absorption of HCl in the VUV spectral region are due to Price.⁷ This author observed the strongest transitions in photoabsorption measurements.⁷ Further photoabsorption studies have revealed that HCl seems to exhibit a weaker structure at excitation energies between 9.6 and 11.7 eV.^{8–10} More recently, electron impact experiments on HCl have been reported by Shawn et al.¹¹ and by Wang et al.¹² York and Comer¹³ have also studied the spectrum of HCl with an electron energy-loss spectrometer, finding a large number of transitions which had not been reported previously. These authors attributed these transitions to electric dipole-allowed transitions, different from those of our study. Jureta et al.,¹⁴ after analyzing the spectra of HCl with a high-resolution threshold electron spectrometer, suggested some assignments of state symmetries. A comprehensive study of the excited electronic states of HCl has been reported by Green et al.,¹⁵ as a result of their observations with a resonance-enhanced multiphoton ionization ((2 + 1) REMPI) and time-of-flight techniques. The most recent data concerning the spectral features of HCl have been reported by Kravan and Wang,¹⁶ who used a (3 + 1) REMPI technique. These authors

supplied, for the first time, observations and analyses of certain electronic states of HCl which are not accessible in one- and two-photon spectral measurements.

As to the theoretical studies of HCl, Hirst and Guest¹⁷ and Bettendorf et al.,¹⁸ independently, reported what seem to be the only *ab initio* calculations on the excited states of HCl that can be, as far as we know, found in the literature. Hirst and Guest,¹⁷ employing *ab initio* methods based on self-consistent field (SCF) and configuration interaction (CI) approaches, investigated some of the low-lying excited states of HCl. The aforementioned report by Bettendorf et al.¹⁸ also included some *ab initio* calculations on HCl, which involved MCSCF and CI treatments. These authors focused on providing a description of the influence that vibrational stretching had on the properties of electronic states of HCl.

The ground state of HCl consists of a completely filled shell of electrons, and hence most excited states are expected to exhibit rather similar Rydberg characteristics as those of the corresponding ion when the core structure is either $^2\Pi$ or $^2\Sigma^+$.¹⁸ The electron configurations and corresponding states of major interest to the present work result from the addition of an $n\lambda$ electron to the $(\sigma^2\pi^3)X^2\Pi_{1/2}$ core. In the *ab initio* calculations reported in refs 17 and 18, no $n\lambda$ configurations with $n > 4$ were considered. In this work, we intend to help in the assignment and analysis of the electronic spectrum of HCl, involving Rydberg states with $n > 4$ and energies in the vicinity of 12 eV.

Following the same procedure used previously for a number of closed shell systems,^{19,20} in the first part of the present study we have computed vertical excitation energies (VEE) of the HCl molecule using a response function approach with a coupled cluster (CC) reference function.^{21,22} Calculations have been performed at the equilibrium geometry, since we mainly aim at obtaining both VEE and transition properties for a fairly large number of Rydberg states of HCl. The oscillator strengths for electric dipole-allowed transitions have been determined with the molecular quantum defect orbital method (MQDO).²³ In some previously studied open shell (ArH)²⁴ or closed shell

TABLE 1: Exponents and Coefficients of the ANO Basis Functions Used in the Calculations of Rydberg Functions in HCl

exponents			coefficients		
s Functions					
0.005858	1.468843	-1.576298	3.505787	-9.568938	10.940019
0.003346	0.485634	2.049467	-7.167094	36.523905	-52.708021
0.002048	-2.353830	-1.496749	7.589472	-72.007043	123.917086
0.001324	2.829886	3.751622	-13.104898	104.517452	-182.899114
0.000893	-3.262435	-4.006511	18.035726	-120.445550	191.252117
0.000624	2.626516	3.091008	-13.222758	96.043769	-147.542523
0.000449	-1.291654	-1.479069	6.363170	-45.116512	73.682108
0.000332	0.290527	0.327418	-1.416796	10.137721	-16.242309
p Functions					
0.009988	0.077494	-3.739190	2.813284	-2.647325	
0.005689	0.648901	8.142003	-7.719818	8.462194	
0.003476	0.054888	-13.759461	11.355354	-12.721375	
0.002242	0.628827	20.843649	-16.764927	16.291258	
0.001511	-0.825561	-23.264312	20.842164	-21.539605	
0.001055	0.781793	18.707528	-16.317341	18.367837	
0.000759	-0.443591	-9.436465	8.405206	-8.030956	
0.000560	0.113582	2.210372	-1.989330	2.192782	
d Functions					
0.014204	0.964501	-1.246255	1.041490	-1.499746	
0.008077	-1.025190	1.568585	-1.608038	3.221706	
0.004927	2.519170	-2.848141	2.258267	-4.415286	
0.003175	-3.276228	5.261067	-5.002044	7.925340	
0.002137	3.873623	-5.312563	5.525908	-10.831371	
0.001491	-3.176406	4.741330	-3.803155	8.670105	
0.001072	1.673756	-2.523300	2.805792	-6.283222	
0.000790	-0.413191	0.635285	-0.562139	3.545847	
f Functions					
0.018478	0.213835	-0.264000	0.567240		
0.010493	0.067880	-0.009006	-0.304299		
0.006395	0.673433	-0.707834	0.807964		
0.004117	-0.216348	0.644188	-1.158132		
0.002770	0.691373	-0.447593	0.033937		
0.001931	-0.480111	1.160037	0.117793		
0.001387	0.286457	-0.205975	-0.980726		
0.001022	-0.076070	0.188094	1.677133		
g Functions					
0.022792	0.033750	-0.193944			
0.012930	0.043732	-0.048595			
0.007874	0.174021	-0.557470			
0.005067	0.201633	0.332046			
0.003407	0.340209	-1.003975			
0.002374	0.218375	1.435748			
0.001705	0.129580	-1.101631			
0.001256	0.051948	1.164904			

(SH₂)²⁵ molecules, other *ab initio* methods of MR-SDCI character were chosen instead of the present CC approach. Nevertheless, for closed shell systems, CC calculations can supply a larger number of excited states by incorporating a significant and well balanced fraction of the dynamic correlation, at lower computational costs.

Methods and Computational Details

All energy calculations have been carried out using Dalton program²⁶ at the coupled cluster (CC) level. A CCSD wavefunction was employed as a reference function to obtain excitation energies,^{27,28} determined from the corresponding linear response function and corrected for the effect of connected triple excitations estimated through the use of a CCSDR(3) method.²² The CCSDR(3) method used is correct to the third order in the fluctuation potential for states dominated by single excitations.²² Core electrons were kept frozen in all calculations.

A general atomic natural orbital (ANO)²⁹ basis set, with [6s5p3d2f] contractions for chlorine and [5s4p3d] for hydrogen atoms, has been employed. For a proper description of the Rydberg states, the basis set has been augmented with a single

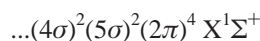
set of atomic natural orbitals, generated for this particular system (HCl) at its equilibrium geometry by following the technique proposed by Roos et al.³⁰ and using the optimized universal exponents by Kaufmann et al.³¹ To this end, a set of Rydberg primitive functions (8s8p8d8f8g) allocated in the charge centroid of the ²Π (HCl⁺) state of the ionic core was contracted to a 5s4p4d3f2g Rydberg basis. The exponents and coefficients for these basis functions are reported in Table 1. Note that the coefficients correspond to unnormalized orbitals. The somehow unusually large values of some coefficients occurring in the highest Rydberg s functions are required for generating a noticeable electron density far away from the basis center due to the small (i.e., very diffuse) exponent values as reported in column 1. In particular, for the present work, the absolute maxima of the radial density functions of the Rydberg s functions occur in the range of 15 to 60 a.u.

It is amply accepted for Rydberg states to be labeled with atom-like *nl* notation, generally followed by its symmetry symbol in the molecule. The use of a single ANO Rydberg basis set facilitates this labeling work and the corresponding characterization of calculated states.

The MQDO approach has been broadly used to successfully determine one-photon transition intensities in molecular Rydberg transitions. For example, we have recently calculated oscillator strengths for transitions involving a number of molecular Rydberg states for several compounds of relevance in the Earth's atmosphere and in astrophysical regions.^{32–34} The starting point of the MQDO formalism²³ is to derive the radial part of the MQDO wavefunctions by analytically solving the corresponding Schrödinger equation, formulated in terms of a model one-electron Hamiltonian with a parametric potential. The angular part of the molecular Rydberg orbitals is a linear combination of spherical harmonics, selected in such a way that the complete MQDO MO's form basis functions for each of the pertinent irreducible representation of the molecular symmetry group, $C_{\infty v}$ in the case of HCl. The radial transition moments also turn out to be closed-form, analytical expressions, which offer an important computational advantage.

Results

The outer electronic configuration of the ground state of HCl may be written as



where the molecular orbital and state notations correspond to the $C_{\infty v}$ symmetry group. The outermost occupied molecular orbital MO in the ground state, that is the 2π MO, is mainly an atomic Cl 3p orbital holding an electron lone-pair.³⁵ When HCl absorbs radiation, the main excitation arises from this orbital. As a consequence, the equilibrium geometry is not very different in the Rydberg excited states from that of the ground state. In addition, some other MOs of HCl exhibit a rather large influence in their composition and behavior of atomic orbitals centered on Cl. This feature helps estimate some characteristic of the HCl molecule, which is rather convenient when the calculated excitations must be assigned to one or other particular Rydberg series. Kilcoyne et al.³⁶ have remarked that much of the atomic character of HCl arises from the sizeably important contribution of the Cl atom in the electronic structure of this molecule. In HCl, the hydrogen atom behaves only as a relatively minor perturbation to the total electronic structure. As to the cationic core of HCl, the ground state of HCl^+ is formed by removing a 2π electron from the ground state of the molecule, which leads to states that are split into $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ symmetries by spin-orbit coupling.

Various low-lying excited states in HCl result from excitation into the antibonding σ^* MO ($A^1\Pi$). The single-configuration Rydberg states may be described by the product of the wavefunctions of the cationic core and the Rydberg electron, e.g., $[\dots](5\sigma)^2(2\pi)^3n\lambda$. An inspection of the CCSD wavefunction reveals that the Rydberg states of HCl have been mainly created by single excitations that arise from the 2π MO of the HCl to virtual MOs which possess a high degree of ns , np , nd , and nf Rydberg MOs.

Considering what seem to be major features in the absorption spectrum of HCl, we have studied each of the following Rydberg series: $ns\sigma$ ($^1\Pi$), $np\sigma$ ($^1\Pi$), $np\pi$ ($^1\Delta$, $^1\Sigma^+$, $^1\Sigma^-$), $nd\sigma$ ($^1\Pi$), $nd\pi$ ($^1\Delta$, $^1\Sigma^+$, $^1\Sigma^-$), and $nd\delta$ ($^1\Pi$, $^1\Phi$). Additionally, the energy positions and symmetry classification of the 4f states has been found. The present tentative assignments of the “ n ” values of the excitations obtained via CC calculations has been made through a careful analysis of the quantum defects associated with each of the studied Rydberg series of HCl, on the assumption that the Rydberg MOs are centered on atomic Cl.

The quantum defects, δ , have been calculated according to the well-known formula:

$$E_{nl} = \text{IP} - \frac{1}{2(n - \delta)^2} \quad (1)$$

where IP is the experimental ionization energy, determined with electron energy-loss measurements by York and Comer.¹³ Both IP and E_{nl} are expressed here in Hartrees.

In Table 2, the presently calculated excitation energies for the Rydberg states are displayed, together with the corresponding theoretical values reported by Hirst and Guest¹⁷ and Bettendorf et al.¹⁸ A variety of experimental excitation energies, derived from observation and analysis of the 0–0 spectral bands, have also been included in the table. These experimental data are the result of some low-energy electron impact experiments,^{11–13} optical absorption measurements,^{8–10} and high-resolution threshold electron spectrometry,¹⁴ as well as from resonance-enhanced multiphoton ionization (2 + 1) and (3 + 1) REMPI techniques.^{15,16}

Nonetheless, we have found some inconsistencies in the assignment of some electronic states of HCl, when these result from different experimental analyses. In particular, the assignments by Ginter and Ginter¹⁰ are very different from those reported by Douglas and Greening.⁹ In Table 2, and further in this paper, the state symbols proposed by Ginter and Ginter¹⁰ have been chosen. The Rydberg orbitals involved at each state are also reported in the table.

The inclusion of linked triples in the CCSDR(3) calculation systematically reduces the CCSD excitation energies as clearly apparent in Table 2. The presence of several lone pairs on the same constituent atom, as in the case of the halogens, is an important source of electron correlation.^{20,37,38} The reduction of the CCSD excitation energies turns out to be about 0.05 eV, slightly larger than the effect in CH_4 that amounts to 0.02–0.03 eV.¹⁹

The splitting of the $X^2\Pi_{3/2,1/2}$ states due to spin-orbit coupling in one of the 2π electrons, i.e., the active electron, is about 0.08 eV for HCl.¹² The mean absolute value of our theoretical errors amounts to 0.07 eV, very much the same order of magnitude as that of the spin-orbit splitting. As a consequence, one can assume that the lack of inclusion of spin-orbit correction cannot be expected to introduce a noticeably large correction. The energy values and the general ordering of the spin-orbit split states have made it possible for us to perform a clear-cut assignment. Spin-orbit coupling should be unavoidably important in the next hydrogen halide, HBr.

The well known $V^1\Sigma^+(\sigma \rightarrow \sigma^*)$ state has not been included in Table 2, because at the geometry at which the calculations were performed, the VEE of the $V^1\Sigma^+$ happened to be higher than the other calculated states. For example, Bettendorf et al.¹⁸ obtained a VEE of about 12.25 eV. On the other hand, the $V^1\Sigma^+$ state is substantially dependent on the internuclear distance.^{17,39–41} It is not, then, surprising that the VEE for this state and the 0–0 band origin (9.45 eV, according to Hirst and Guest¹⁷) exhibit a large difference in value.

The lowest singlet state considered in our calculations is the repulsive $A^1\Pi$ state, the presence of which may be due, as remarked by different authors,^{17,18,42} to a $\pi \rightarrow \sigma^*$ excitation, with valence character. We obtain the following CC results: 7.89 eV at the CCSD level and 7.81 eV at CCSDR(3). This state has not been included in Table 2 because of its non-Rydberg character. No matter, this excitation serves the purpose of showing the rather good agreement with other vertical theoretical

TABLE 2: Vertical Excitation Energies for the Rydberg Series of HCl Converging to the $^2\Pi_{1/2}$ Cationic Core, HCl^+

Rydberg orbital	state	CCSD ^a	CCSDR(3) ^a	expt	theor ⁱ	theor ^j
4s σ	C ¹ Π	9.69	9.62	9.607 ^{b,d,e}	9.67	9.752
5s σ	M ¹ Π	11.12	11.07	11.24 ^{b-e}		
6s σ	¹ Π	11.84	11.79	11.937, ^e 11.923, ^f 11.933 ^g		
4p σ	D ¹ Π	10.22	10.16	10.227 ^b	10.00	10.137
5p σ	R ¹ Π	11.54	11.49	11.462 ^b		
6p σ	¹ Π	12.03	11.98			
4p π	F ¹ Δ	10.30	10.25	10.272, ^{b,c} 10.29 ^e	9.96	10.027
5p π	¹ Δ	11.57	11.51	11.60 ^b		
6p π	¹ Δ	12.04	11.98			
4p π	G ¹ Σ^-	10.36	10.30	10.318, ^c 10.33 ^e	10.00	10.068
5p π	¹ Σ^-	11.58	11.52			
6p π	¹ Σ^-	12.04	11.99			
4p π	E ¹ Σ^+	10.46	10.40	10.387, ^{b,c} 10.381, ^d 10.38 ^e	10.08	10.170
5p π	¹ Σ^+	11.60	11.55			
6p π	¹ Σ^+	12.03	11.98			
3d π	I ¹ Δ	11.02	10.97	10.983, ^b 11.030 ^c	10.91	
4d π	¹ Δ	11.78	11.73	11.809 ^b		
5d π	¹ Δ	12.13	12.08			
3d π	H ¹ Σ^+	11.09	11.03	10.996, ^b 10.995 ^{c,d}	10.87	11.088
4d π	¹ Σ^+	11.81	11.76	11.786 ^b		
5d π	¹ Σ^+	12.13	12.08			
3d π	¹ Σ^-	11.05	10.99		10.92	
4d π	¹ Σ^-	11.79	11.73			
5d π	¹ Σ^-	12.13	12.08			
3d δ	L ¹ Φ	11.19	11.13	11.156 ^h		
4d δ	¹ Φ	11.86	11.81			
5d δ	¹ Φ	12.17	12.12			
3d δ	K ¹ Π	11.23	11.18	11.119 ^{b,c}		
4d δ	¹ Π	11.89	11.84			
3d σ	N ¹ Π	11.42	11.37	11.162, ^{b,c} 11.171, ^d 11.165 ^e	10.80	
4d σ	¹ Π	11.97	11.92	11.845 ^d		
4f σ	1P	11.86	11.81			
4f τ	¹ Σ^+	11.86	11.81			
4f π	¹ Δ	11.87	11.81			
4f τ	¹ Σ^-	11.87	11.82			
4f δ	¹ Φ	11.87	11.82			
4f δ	1P	11.88	11.82			
4f ϕ	¹ Δ	11.88	11.83			
4f ϕ	¹ Γ	11.88	11.83			

^a This work. ^b Green et al.¹⁵ ^c Ginter and Ginter.¹⁰ ^d York and Comer.¹³ ^e Jureta et al.¹⁴ ^f Wang et al.¹² ^g Shawn et al.¹¹ ^h Kravan and Wang.¹⁶ ⁱ Bettendorf et al.¹⁸ ^j Hirst and Guest.¹⁷

values: 7.84 eV by Bettendorf et al.,¹⁸ and 7.93 eV by Hirst and Guest,¹⁷ as well as the relatively large effect of the triples correction for this state.

The first few states of each Rydberg series reported in Table 2 agree within 0.06 eV with the experimental values. Errors for the other states are commonly smaller than 0.1 eV. When other theoretical calculations exist, it is clear from Table 2 that the present CC calculations lead to much better accordance in the excitation energies, showing that an update of these results is actually needed. An independent way to assess the accuracy of the present calculations is provided by the calculation of the quantum defects associated to the different Rydberg series. The allowed Rydberg series have been deduced from a thorough analysis of the CCSD and CCSDR(3) quantum defects. These values amount to ~ 2 , ~ 1.7 and $0.1-0.3$, for the ($ns\sigma$), ($np\pi$), ($np\sigma$), and ($nd\sigma$, $nd\pi$, $nd\delta$) Rydberg series, respectively, and are consistent with the expected range for the quantum defects of ns , np , and nd Rydberg series in the chlorine atom.

Some states remain somewhat open for debate. Let us mention, as a first example, the electronic configuration of the $n = 5$ Rydberg state belonging to the ($\sigma^2\pi^3$) $np\sigma$ series, namely R¹ Π . Green et al.¹⁵ have reported the energy at which the R¹ Π state lies, 11.462 eV. A quantum defect approximately equal to 1.844 is obtained for $n = 5$. Lefebvre-Brion et al.⁴³ have assigned this state to a ($\sigma^2\pi^3$) $4d\sigma$ configuration on the grounds of the quantum defect determined by themselves, with a value

approximately equal to 0.8. The present calculations hint at characterizing the R¹ Π state as a $5p\sigma^1\Pi$ Rydberg state, for which the present CCSD and CCSDR(3) VEEs are in good agreement with the corresponding measurements by Green et al.¹⁵ Also, the quantum defect, equal to 1.8, agrees with the quantum defect belonging to a “p” state of the chlorine atom. Moreover, we have found in our calculations that the $4d\sigma$ Rydberg state lies at higher energy.

Our results confirm some other assignments though, such as those made by Green et al.¹⁵ of their measurements performed with a (2 + 1) REMPI technique. For example, we have assigned the peak at 11.60 eV to the lowest vibrational level ($v' = 0$) of a Rydberg ¹ Δ state (correlated with the X² $\Pi_{1/2}$ ionic core), with a quantum defect that turns out to be equal to 1.672, so that we had no other choice than assigning this quantum defect to a $5p\pi$ state.

Another relevant case is the spectral band centered at 11.809 eV, that Green et al.¹⁵ assigned to the ¹ Δ -X(0,0) system and which is probably associated with a $4d\pi$ Rydberg state, given that a quantum defect equal to 0.346 is provided.

In other cases, our results appear to clarify some discrepancies. The $v' = 0$ vibrational level belonging to a ¹ Σ^+ state, was also identified by Green et al.¹⁵ to appear at 11.786 eV. According to these authors, the observed state is probably a member of the $4d$ or $5p$ Rydberg complexes of HCl. The $5p\tau$ -(¹ Σ^+) state has been found in this work to lie at lower energies.

TABLE 3: Oscillator Strengths for the $(X^1\Sigma^+) \rightarrow ns\sigma(^1\Pi)$, $nd\sigma(^1\Pi)$, $nd\delta(^1\Pi)$, and $nd\pi(^1\Sigma^+)$, Transitions of HCl

transition	MQDO ^a	MQDO ^b
$X^1\Sigma^+ - 4s\sigma(^1\Pi)$	0.1421	0.1714
$X^1\Sigma^+ - 5s\sigma(^1\Pi)$	0.0750	0.1034
$X^1\Sigma^+ - 6s\sigma(^1\Pi)$	0.0350	0.0304
$X^1\Sigma^+ - 3d\pi(^1\Sigma^+)$	0.0304	0.0319
$X^1\Sigma^+ - 4d\pi(^1\Sigma^+)$	0.0098	0.0078
$X^1\Sigma^+ - 5d\pi(^1\Sigma^+)$	0.0011	0.0001
$X^1\Sigma^+ - 3d\delta(^1\Pi)$	0.1054	0.1192
$X^1\Sigma^+ - 4d\delta(^1\Pi)$	0.0609	0.0732
$X^1\Sigma^+ - 3d\sigma(^1\Pi)$	0.0101	0.0119
$X^1\Sigma^+ - 4d\sigma(^1\Pi)$	0.0070	0.0089

^a MQDO, this work using CCSD energies. ^b MQDO, this work using CCSDR(3) energies.

Therefore, we assign it to the $4d\pi(^1\Sigma^+)$ Rydberg state with a quantum defect of about 0.3–0.4, which conforms to that expected for a 4d state in the Cl atom.

No earlier theoretical data, as regards the $nd\delta(^1\Pi)$, 1Φ) Rydberg series, seem to exist in the literature. The presently calculated energies for the first member of the series ($n = 3$), which is associated with the $L^1\Pi$ and $K^1\Pi$ states, appear to be in fairly good accord with photoabsorption measurements and with the recent $(3 + 1)$ REMPI observations of Kravan and Wang.¹⁶ No comparative data have been found in the literature as regards the $n > 3$ complex.

Li et al. reported MRD-CI calculations of the three lowest lying $1^3\Pi$ and $3\Sigma^+$ states where some nonadiabatic coupling and spin-orbit interactions between different states were taken into account.⁴⁴ Unfortunately, direct comparison with the present results is difficult because these authors did not report sufficient details of their ground state results. A rough estimate of their VEE value for the $(4s)$ $1^1\Pi$ state can be obtained from the reported T_{00} value. It should amount to ~ 9.71 eV, close to the CCSDR(3) value for this state that we find at 9.62 eV and the experimental value at 9.607 eV.

References to nf Rydberg states are scarce in the literature. In Table 2, we have given the 4f manifold of states of HCl, classified according to their respective symmetries. However, it is apparent that all these states fall together in a small range of 0.02 eV (11.81–11.83), which is smaller than the precision of our methodology.

The MQDO approach has been used to calculate the oscillator strengths for transitions arising from the ground state and ending in a few different Rydberg series, as displayed in Table 3. As already mentioned, the electric dipole length approximation of the transition operator has been chosen for the present calculation, the excitation energies are of CC quality, and the ionization potential is that determined by York and Cormer,¹³ i.e., 12.825 eV.

Inspection of Table 3 reveals that the MQDO calculations exhibit the expected decrease in the magnitude of the oscillator strengths, as the excitation of the upper state becomes greater, along a given Rydberg series. This feature can be understood on the grounds of a diminishing overlap of the wavefunctions corresponding to the states involved in a particular transition, which becomes so substantial when the upper state is highly excited that the resulting decrease in the transition integral is no longer compensated by the accompanying increase in transition energy.

As an additional assessment of the reliability of our procedure, we have compared the intensities of transitions that may refer to as “analogous” in HCl and Cl, which according to literature^{36,41} should be similar. The oscillator strengths for the latter have been obtained with the relativistic formulation of the

RQDO method.^{45,46} We have calculated the $3p^2P-4s^2P$ and $3p^2P-3d^2(P,D)$ “supermultiplet” transitions in Cl. As broadly used, the term “supermultiplet” consists of the group of multiplets that arise from a given electronic configuration in an atom. A different L-value is assigned to each of the multiplets that are selected according to their spin multiplicity.⁴⁷ The atomic “supermultiplet” intensities may, and usually have, a comparable magnitude with that obtained by adding up the individual intensities of all the $nl-n'l'$ transitions with the same spin multiplicity comprising all the different irreducible representations involved in the molecular symmetry group. It may then be expected the $3p^2P-4s^2P$ transition of the Cl atom to compare with the transition intensity associated with the $X^1\Sigma^+ - 4s\sigma$ excitation in HCl, and also, the $3p^2P-3d^2(P,D)$ transition in Cl should be comparable to the sum of the intensities corresponding to the $X^1\Sigma^+ - 3d\pi$, $X^1\Sigma^+ - 3d\delta$, and $X^1\Sigma^+ - 3d\sigma$ transitions in HCl. The RQDO total oscillator strengths for the $3p^2P-4s^2P$ transition of Cl, which happened to be equal to 0.1603, conforms quite well to the MQDO oscillator strength values of 0.1421 and 0.1714, obtained with the presently determined CCSD and CCSDR(3) energies, respectively. For the $3p^2P-3d^2(P,D)$ supermultiplet of the Cl atom, the RQDO-calculated f -value is 0.1448, which is in fair accord with the magnitude of the f -values equal to 0.1459 and 0.1630, obtained through the sum of those for the individual transitions using the CCSD and CCSDR(3) energies, respectively. These features might be interpreted as a further confirmation of the remarks made by Kilcoyne et al.,³⁶ in the sense that the Rydberg states of the HCl molecule mainly arise from the chlorine atom lone pair.

Concluding Remarks

To the best of our knowledge, some of the highest energy transitions we have calculated have never been the object of experimental or theoretical work. The comparison of potentially observed, still unassigned new spectral features with the presently supplied intensity data may help clarify the nature of the Rydberg structure of HCl and, hence, help also in the assignments of potential experimental work in the future. These last remarks particularly refer to the presently included, in the previous section, discussion on the states of HCl characterized by $n > 4$, as well as by having detected the presence of 4f Rydberg states in HCl.

The complex and time-consuming CC theoretical calculation employed in this work, combined with the simple but effective MQDO methodology, is a powerful tool to study some complete series of Rydberg states in HCl that were unstudied previously. Additionally, our technique may supply good-quality transition intensities.

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