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An *ab initio* treatment of the x-ray emission spectra of the HCl molecule

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Abstract. *Ab initio* calculations for the energy and absolute transition rates of x-ray transition processes associated with the hydrogen chloride molecule have been undertaken at the relaxed Hartree-Fock level. Data for K-, L_1- and L_{23}-shell x-ray emission spectra are presented. Comparison with atomic calculations is used to show that the molecular effect is manifested most clearly in transitions involving the 5σ bonding molecular orbital. The spectra are, however, dominated by intra-atomic effects. Participator and spectator satellite transitions associated with an initial K-shell hole and a 3π excited valence electron are also considered. The energy and transition rate results for spectator satellites associated with the $[1\sigma]3\pi$ resonant excited neutral state are close to those determined for the normal K_α and K_β processes. The 3π participator satellite is predicted to be at higher photon energy with 10% of the main K_β spectator line intensity.

1. Introduction

High-resolution x-ray emission spectra (XES) of molecules provide one basis for the elucidation of the electronic properties of excited and ionised molecules (Nordgren *et al* 1982, Pettersson *et al* 1985, Rubensson *et al* 1985, La Villa 1982, Deslattes 1986). Theoretical interpretations of XES have been based upon semiempirical or *ab initio* approaches (Manne 1970, Ågren and Nordgren 1981, Ågren and Arneberg 1983, Ågren *et al* 1984, Larkins and Rowlands 1986, Rowlands and Larkins 1986, Phillips and Larkins 1986). Previous research by our group, cited above, has shown that multicentre (interatomic) terms and electronic relaxation effects can make a major contribution to absolute transition probabilities involving valence electrons. In some cases these changes occur without significantly affecting relative intensities when compared with predictions from the use of a one-centre localised transition model. However, it would seem that the breakdown of a one-centre intra-atomic model is more severe when modelling valence molecular x-ray emission processes than for molecular Auger processes involving valence electrons (Larkins 1987).

In this paper we report the *ab initio* results for the energy and intensity of x-ray transition processes associated with the hydrogen chloride molecule based upon the use of a relaxed orbital Hartree-Fock model. Decay processes resulting from initial holes in the 1σ (K_α and K_β emission), 2σ (L_1 emission) and 3σ, 1π (L_{23} emission) core orbitals are considered. The results are compared with atomic chlorine rate calculations (Scofield 1974a, b) and the limited experimental K_β data for the HCl molecule (Gilberg 1970, La Villa 1982). The molecular effect is manifested most clearly in transitions involving the 5σ bonding molecular orbital.

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The energy and intensity of transitions associated with the $[1\sigma]3\pi$ resonant excited state of the neutral HCl molecule are also reported. The results obtained for spectator satellites are close to those determined for the normal K_α and K_β emission processes. The participator satellite is at higher energy and has an intensity of about 10% relative to the main spectator line. Extension of the model to include other electron correlation effects is in principle possible, but very complex for molecules. Some insight into the difficulties involved can be gained from the configuration interaction studies previously undertaken for the satellite structure associated with the isoelectronic atomic argon system (Dyall and Larkins 1982).

The theory is briefly reviewed in § 2. Results for the various hole state processes are presented in § 3. An analysis of the findings including a comparison with atomic data and the limited experimental information is presented in § 4.

2. Theoretical considerations

To characterise x-ray emission from an initial to a final state it is necessary to calculate the transition energy, E_{if} and the transition probability given in atomic units by the Einstein A coefficient

$$A_{if} = \tfrac{4}{3}E_{if}^3\alpha^3|\boldsymbol{M}_{if}|^2 \tag{1}$$

where α is the fine-structure coefficient and $\boldsymbol{M}_{if}$ the transition moment

$$\boldsymbol{M}_{if} = \langle\Psi_f|\boldsymbol{\mu}|\Psi_i\rangle. \tag{2}$$

Ψ_f and Ψ_i represent the wavefunctions for the final and initial states respectively, while $\boldsymbol{\mu}$ is the electric dipole operator for all N particles of charge Z_i in the system:

$$\boldsymbol{\mu} = \sum_i^N Z_i\boldsymbol{d}_i. \tag{3}$$

In this work the formally equivalent length and velocity forms of the dipole operator have been considered:

$$\boldsymbol{d}_i = \boldsymbol{r}_i \qquad \text{(length)} \tag{4a}$$

$$\boldsymbol{d}_i = (1/E_{if})\boldsymbol{\nabla}_i \qquad \text{(velocity)}. \tag{4b}$$

In the relaxed orbital approach SCF calculations are performed separately for the initial and final states with the consequence that the two wavefunctions are not necessarily orthogonal. In the single determinantal framework used here, equation (2) can be solved by the method of Lowdin (1955).

Appropriate observation of spin and spatial symmetry allows equation (2) to be expressed as (Phillips and Larkins 1986)

$$\langle\Psi_f|\boldsymbol{\mu}|\Psi_i\rangle = \sum_k^K\left(\prod_{l\neq k} D_l\right)\sum_i^{n_k}\sum_j^{n_k}\{\langle\phi_i^k|\boldsymbol{\mu}|\phi_j^k\rangle D_k(ij)\} \tag{5}$$

where K is the number of spin and spatial symmetry blocks, D_l is the determinant of molecular orbital overlap integrals of block l, the ϕ are one-electron molecular spin orbitals and $D_k(ij)$ is the cofactor of block k formed by eliminating the ith row and jth column from D_k. For relaxed orbital calculations, where the states are not necessarily orthogonal, the transition moment M_{if} is dependent on the choice of origin of the coordinate system, and so we have chosen the coordinate system at the centre of mass consistent with the work of Yoshimine *et al* (1973). The theory involved in the present calculations has been discussed in more detail elsewhere (Phillips and Larkins 1986).

Hydrogen chloride is a linear molecule with the ground-state electronic configuration

$$1\sigma^2, 2\sigma^2 3\sigma^2 1\pi^4, 4\sigma^2 5\sigma^2 2\pi^4.$$

X-ray emission processes follow from ionisation in the K shell of the chlorine atom (1σ orbital) and from ionisation in the L shell of the chlorine atom, 2σ, 3σ and 1π orbitals.

For the normal or diagram K emission processes we may have core-core K_α transitions, or core-valence K_β transitions:

$$\mathrm{HCl}^+[c_\mathrm{K}] \rightarrow \mathrm{HCl}^+[c_\mathrm{L}] + h\nu \qquad (\mathrm{K}_\alpha \text{ emission})$$

or

$$\mathrm{HCl}^+[c_\mathrm{K}] \rightarrow \mathrm{HCl}^+[v] + h\nu' \qquad (\mathrm{K}_\beta \text{ emission})$$

where c_L corresponds to 2σ, 3σ or 1π, and v to 4σ, 5σ or 2π, and [ ] denotes a hole. For the L emission processes we have L_1 core (2σ)-valence and L_{23} core ($3\sigma, 1\pi$)-valence transitions:

$$\mathrm{HCl}^+[c_{\mathrm{L}_1}] \rightarrow \mathrm{HCl}^+[v] + h\nu'' \qquad (\mathrm{L}_1 \text{ emission})$$

$$\mathrm{HCl}^+[c_{\mathrm{L}_{23}}] \rightarrow \mathrm{HCl}^+[v] + h\nu''' \qquad (\mathrm{L}_{23} \text{ emission}).$$

For a given mode of initial hole state ionisation the relative importance of the various processes depends upon the initial ionisation cross sections as well as the de-excitation rates. The radiative pathways must compete with the non-radiative pathways for decay. The latter are more dominant for molecules containing first- and second-row atoms.

A related process, which has recently become amenable to experimental investigation through the use of synchrotron radiation, arises from resonant excitation of the neutral ground-state molecule. In this case the molecule is not ionised but the core electron is selectively excited into an unoccupied (virtual) molecular orbital:

$$\mathrm{HCl}[-] \rightarrow \mathrm{HCl}[c]\phi$$

where ϕ is a virtual orbital. De-excitation can then proceed via two mechanisms.

In the *participator* process the electron in the virtual orbital fills the core hole, while in the *spectator* process the core hole is filled by one of the valence orbitals, i.e.

$$\mathrm{HCl}[c]\phi \rightarrow \mathrm{HCl}[-] + h\nu' \qquad (\text{participator})$$

$$\mathrm{HCl}[c]\phi \rightarrow \mathrm{HCl}[v]\phi + h\nu'' \qquad (\text{spectator}).$$

Results are reported here for participator and spectator emission where an electron in the 1σ core orbital has been excited to the 3π lowest unoccupied molecular orbital. Lines from such processes may manifest themselves in K- and L-type emission spectra.

The calculations reported here were carried out in the C_{2v} subgroup of the $C_{\infty v}$ point group with a neutral molecule internuclear separation of 1.275 Å (2.409 au) (Rank *et al* 1965). The geometry was optimised for the $[1\sigma]$ state and was found to be 2.395 au. The changed geometry had no effect on the transition moments since intra-atomic contributions dominate. A problem was encountered in attempting to calculate the $[n\pi]3\pi$ state, which in C_{2v} symmetry can be expressed as $nb_1^{3/2}$, $3b_1^{1/2}$, $nb_2^{3/2}3b_2^{1/2}$. While it is theoretically possible to obtain a single determinantal treatment of such a state (Carbo and Riera 1978), we cannot handle so many open shells within a single calculation.

The hydrogen basis set, $(5s)\rightarrow[3s]$ was taken from Dunning (1970) augmented by a p function of exponent 1.0. This was used with the $(12s9p)\rightarrow[6s4p]$ chlorine basis of McLean and Chandler (1980), to which was added a diffuse s function ($\alpha_s = 0.08$), a diffuse p function ($\alpha_p = 0.05$) and a d function ($\alpha_d = 1.0$), taken from Ogilvie *et al* (1980).

3. Results

3.1. *K emission diagram lines*

The energy and intensity results of the x-ray calculations for the K_α and K_β emission spectra based on a relaxed Hartree-Fock model are shown in table 1. The results of relativistic Hartree-Fock relaxed (ΔSCF) average energy calculations for atomic chlorine (Dyall 1987) and the relaxed orbital relativistic Hartree-Fock transition rate calculations of Scofield (1974b) are also presented. The molecular rate calculations are presented from both the length and velocity forms of the dipole operator (equation (4)), while the atomic rates from Scofield are for the length form. The length and velocity forms agree within about 7% of each other. The exception is the $[1\sigma]$-$[2\sigma]$

Table 1. K emission spectra of HCl. Relaxed Hartree-Fock calculations.

Process	Final hole state	E_{if}[a] (eV)	A_L (10^{-6} au)	A_V (10^{-6} au)	% A_L
Molecular HCl					
$[1\sigma]$ K_α	$[2\sigma]$	2551.9	0.2	0.0	0.0[b]
	$[3\sigma]$	2621.6	664.4	617.9	50.2[b]
	$[1\pi]$	2621.7	1322.3	1228.8	100.0[b]
K_β	$[4\sigma]$	2801.0	1.7	1.3	1.5[c]
	$[5\sigma]$	2814.0[d]	42.5	39.3	35.9[c]
	$[2\pi]$	2818.4[d]	118.5	109.1	100.0[c]
Atomic Cl					
[1s]	$[2p_{1/2}]$	2621.1[e]	690.9[f]		50.5[g]
	$[2p_{3/2}]$	2621.7	1367.1		100.0
	$[3p_{1/2}]$	2818.6	55.9		50.5[h]
	$[3p_{3/2}]$	2818.6	110.2		100.0

[a] Relative to the energy of HCl^+ $[1\sigma]$, −356.0890 Hartree. The ground-state energy of HCl with the same basis is −460.0954 Hartree.

[b] Intensities relative to the $[1\sigma]$-$[1\pi]$ rate set equal to 100.0.

[c] Intensities relative to the $[1\sigma]$-$[2\pi]$ rate set equal to 1000.0.

[d] Corresponding experimental energies estimated from published spectrum of Gilberg (1970) to be 2813.2 and 2817.0 eV, respectively.

[e] Dyall (private communication), average energy including higher-order terms.

[f] After Scofield (1974b). Relaxed relativistic Hartree-Fock calculations.

[g] Intensities relative to the $[1s]$-$[2p_{3/2}]$ set equal to 100.0.

[h] Intensities relative to the $[1s]$-$[3p_{3/2}]$ set equal to 100.0.

transition, but both rates are very small since the transition corresponds to a forbidden [1s]-[2s] transition in the atomic case. Similar behaviour was observed in previous work (Phillips and Larkins 1986) in those cases where the transition probabilities were small. The relative rates (column 5) are presented only for the length form since there is close agreement with the relative rates using the velocity form. The experimental K_α spectrum for HCl has not been reported, but the K_β spectrum has been reported by Gilberg (1970).

3.2. K emission satellite lines

The energy and intensity for the various x-ray transitions associated with the $[1\sigma]3\pi$ resonant initial state are shown in table 2. While there is only one participator line which is associated with the K_β spectrum, there are spectator lines for the K_α and K_β spectra. The energies of the spectator lines are within 0.2 eV of the related diagram line and the intensities are very similar. While it has not been possible to calculate the $[n\pi]3\pi$ states, on the evidence available for the $[n\sigma]3\pi$ states, the results would be expected to be very similar to those involving the $[n\pi]$ single-hole states. Hence the relative intensities of the satellite lines (column 5) have been calculated on this basis. The energy shift for the participator satellite is 10.0 eV to higher energy from the main $[1\sigma]$-$[2\pi]$ diagram line.

Table 2. K emission 3π satellite spectra of HCl. Relaxed Hartree-Fock calculations.

Process	Final hole state	E_{if}[a] (eV)	A_L (10^{-6} au)	A_V (10^{-6} au)	% A_L
Spectator $[1\sigma]3\pi$	$[2\sigma]3\pi$	2551.8	0.3	0.0	0.0[b]
	$[3\sigma]3\pi$	2621.5	664.7	618.1	50.3[b]
	$[1\pi]3\pi$	NA	NA	NA	(100)[b]
	$[4\sigma]3\pi$	2800.8	1.8	1.2	1.5[c]
	$[5\sigma]3\pi$	2813.8	41.9	38.8	35.3[c]
	$[2\pi]3\pi$	NA	NA	NA	(100)[c]
Participator $[1\sigma]3\pi$	[–]	2828.4	11.5	10.6	9.7[c]

[a] Relative to the energy of HCl $[1\sigma]3\pi$, −356.1509 Hartree.

[b] Intensity relative to $[1\sigma]3\pi$-$[1\pi]3\pi$ rate assumed equal to $[1\sigma]$-$[1\pi]$ rate (see text).

[c] Intensity relative to $[1\sigma]3\pi$-$[2\pi]3\pi$ rate assumed equal to $[1\sigma]$-$[2\pi]$ rate (see text).

3.3. L_1 emission diagram lines

The energy and intensity for the various L_1 x-ray transitions are shown in table 3 along with the atomic chlorine data. The atomic transition energies are based upon relativistic relaxed Hartree-Fock calculations (Dyall 1987) and the transition rates are from the frozen orbital relativistic Hartree-Slater work of Scofield (1974a). The molecular length and velocity values agree within about 22% for the main transitions. For the 'forbidden'-type $[2\sigma]$-$[4\sigma]$ transition (atomic 2s→3s type) the rates, while small, differ significantly from the length to the velocity form.

Table 3. L_1 emission spectra of HCl. Relaxed Hartree-Fock calculations.

Process	Final hole state	E_{if}[a] (eV)	A_L (10^{-6} au)	A_V (10^{-6} au)	% A_L
Molecular HCl					
normal	[3σ]	69.7	0.49	0.38	10.4[b]
L_1-L_{23}	[1π]	69.8	0.99	0.77	20.9[b]
L_1-M	[4σ]	249.2	0.08	0.04	1.7[b]
	[5σ]	262.2	1.66	1.29	35.1[b]
	[2π]	266.5	4.73	3.72	100.0[b]
Atomic Cl					
L_1-L_{23}	[$2p_{1/2}$]	70.6[c]	0.29[d]		10.5[e]
	[$2p_{3/2}$]	71.2	0.63		22.8[e]
L_1-M_{23}]	[$3p_{1/2}$]	268.0	1.43		51.8[e]
	[$3p_{3/2}$]	268.0	2.76		100.0[e]

[a] Relative to the energy of the HCl^+ [2σ] state, −449.8697 Hartree.

[b] Intensities relative to [2σ]-[2π] rate set equal to 100.0.

[c] Dyall (private communication), average energy including higher-order terms.

[d] After Scofield (1974a). Frozen orbital relativistic Hartree-Slater calculations.

[e] Intensities relative to the [2s]-[$3p_{3/2}$] rate set equal to 100.0.

3.4. L_{23} emission diagram lines

The L_{23} emission rates and transition energies for HCl are presented in table 4. The 3σ and 1π hole states, which are predominantly of chlorine 2p character, are within 0.09 eV of each other. The length and velocity rates for the main transitions agree

Table 4. L_{23} emission spectra of HCl. Relaxed Hartree-Fock calculations.

Process	Final hole state	E_{if} (eV)	A_L (10^{-6} au)	A_V (10^{-6} au)	% A_L
Molecular HCl					
L_{23}-M	[4σ]	179.5[a]	0.94	0.71	100.0[c]
[3σ]	[5σ]	192.5[a]	0.001	0.013	0.1[c]
	[2π]	196.8[a]	0.0005	0.0008	0.0[c]
[1π]	[4σ]	179.4[b]	0.70	0.57	100.0[d]
	[5σ]	192.4[b]	0.11	0.09	16.4[d]
	[2π]	196.7[b]	0.01	0.0005	0.7[d]
Atomic Cl					
L_2-M_1	[3s]	182.1[e]	0.64[f]		
L_3-M_1	[3s]	181.6	0.65		

[a] Relative to the energy of the HCl^+ [3σ] state, −452.4313 Hartree.

[b] Relative to the energy of the HCl^+ [1π] state, −452.4346 Hartree.

[c] Intensities relative to [3σ]-[4σ] rate set equal to 100.0.

[d] Intensities relative to [1π]-[4σ] rate set equal to 100.0.

[e] Dyall (private communication), average energy including higher-order terms.

[f] After Scofield (1974a). Frozen orbital relativistic Hartree-Slater calculations.

within about 24%. The [3σ]-[5σ] transition is predicted to be weak (<0.1%) relative to the main line, but the corresponding [1π]-[5σ] transition is more significant at 16.4% of the main line. The atomic rates for L_2-M_1 and L_3-M_1 transitions are almost equal; however, the total [3σ]-[v] molecular rate is 115% of the total [1π]-[v] molecular rate. For the 'forbidden'-type [3σ]-[2π] and [1π]-[2π] transitions (atomic 2p-3p type) the variation between the calculated length and velocity form rates in percentage terms are more significant, but the absolute rates are very small.

4. Discussion

4.1. K emission diagram lines

The molecular K transition rates for HCl (table 1) are closer to Scofield's value for atomic chlorine than to those for the united atom limit, namely atomic argon. This results from the limited polarisation of the chlorine L-shell electrons by the hydrogen atom in the molecule and the dominance of the intra-atomic contribution to the total XES rate. The relative intensities for the K_α[3σ] to [1π] ratio is 1:2 consistent with the statistical ratio based upon orbital electron population distribution.

The calculated K_β energies are within 1.5 eV of experiment. The [1σ]-[4σ] transition rate is only 1.5% of the main K_β line. A Mulliken population analysis for the neutral molecule shows that the 4σ orbital has 90% Cl 3s character with a 10% H 1s character. The [1σ]-[2π] transition has the highest rate because the 2π orbital has mainly Cl 3pπ lone pair character. The 5σ orbital is the bonding orbital in the molecule. It has 59% Cl 3pσ character with a 32% H 1s character. The [1σ]-[5σ] transition rate is only 36% of the [1σ]-[2π] rate compared with 50% for the ratio of the atomic transitions. The intensity expected if the [1σ]-[5σ] transition were purely atomic in nature has been reduced by the admixture of hydrogen character to the 5σ orbital. The predicted intensity ratio between transitions involving [5σ] and [2π] final hole states is 36:100. The experimental ratio has been estimated to be 35:100 from the published spectrum of Gilberg (1970). However, the published spectrum contains a significant contribution from satellite lines, therefore a direct comparison between theory and the existing experimental data cannot be confidently made, although the two ratios are in close agreement. Both depart from the statistical ratio of 50:100.

In much previous work on theoretical x-ray emission spectra, use has been made of the one-centre and frozen orbital models (Larkins and Rowlands 1986, Ågren *et al* 1984 and references therein). For a molecule such as HCl where the electron density is almost entirely on one centre, both approximations are expected to be reasonable. Calculations show that the frozen orbital and one-centre methods give essentially identical results in all cases. For K_α processes the frozen orbital absolute transition probabiliities are in good agreement with the relaxed results given in table 1. For example, for the [1σ]$\rightarrow$[1π] transition A_L is 1322.27×10^{-6} au in the relaxed case and 1285.26×10^{-6} au in the frozen case.

The relative intensities of the $K_\beta$valence orbital transitions in the two more approximate models also agree well with the relaxed values. The [5σ] transition is predicted to have between 34 and 35% of the intensity of the [2π] line in the frozen and one-centre approaches, compared with 36% in the relaxed case. However, the absolute transition probabilites of the valence transitions are only two thirds of those calculated using the relaxed orbital technique.

Previous work has shown that absolute intensities are consistently underestimated using such approximations. It should also be noted, despite the success of the frozen orbital and one-centre models in this case, that caution must be used when applying such techniques, because it is expected that the frozen orbital and especially the one-centre approximations will fail when applied to more complicated molecules than HCl with substantial electron delocalisation (Phillips and Larkins 1986).

The K_β/K_α branching ratio for the HCl molecule is 8.2:100 while that for atomic chlorine is 8.6:100. The relative lowering of the molecular value is due to 5σ delocalisation effects, since the 5σ orbital is the bonding orbital with substantial H 1s character as discussed earlier.

4.2. K emission satellite lines

The 3π spectator results (table 2) for the excited neutral molecule are interesting in that both the energies and transition probabilities are essentially identical to the normal XES case (table 1). Such similarity can be explained by the fact that HCl has very little covalence associated with either the 1σ or 3π orbitals. The occupancy of the 3π orbital in the spectator case clearly has very little effect on the molecular electron density distribution since the 3π orbital is highly localised on the chlorine. It is not expected that this will be the case in more complicated covalent molecules with more than one heavy atom.

The participator satellite strength is about 10% of the main spectator line (table 2) which is assumed to have the same transition rate as the main diagram line. Furthermore, the participator:spectator satellite branching ratio for de-excitations involving valence electrons is 1:14. In order to make a comparison between the intensity of diagram and satellite lines a knowledge of the relative population of the initial hole states is required. This value will depend upon the details of the excitation process. Using synchrotron radiation it should be possible to differentiate between diagram and satellite processes since theory predicts a difference of 1.7 eV between the energy required for the $1\sigma \rightarrow 3\pi$ resonant excitation and 1σ ionisation.

4.3. L emission diagram lines

The results of calculations where the initial state has a hole in the Cl 2s orbital (2σ) are shown in table 3. The relative intensities follow the same ratios as in the K spectrum, namely that transitions involving $[3\sigma]$ and $[1\pi]$ final hole states have a 1:2 ratio, and the transitions involving $[5\sigma]$ and $[2\pi]$ final hole states have a 35:100 ratio. However, the absolute rates for x-ray transitions involving a 2σ initial hole are one to two orders of magnitude less than the absolute rates for transitions involving a 1σ initial hole. The branching ratio for L_1-L_{23} to L_1-M transitions is 23;100 (L) for the HCl molecule compared with a ratio of 22:100 for atomic chlorine.

The $[3\sigma]$-$[4\sigma]$ transition dominates the L_{23} radiative de-excitation (table 4) involving 3σ initial hole state. However, the $[1\pi]$-$[4\sigma]$ transition has only 75% (L) (80%, V) of the rate of the $[3\sigma]$-$[4\sigma]$ pathway, while in the atom it is predicted that the L_2 and L_3 holes will be filled at equal rates. The $[1\pi]$-$[5\sigma]$ transition is also important, providing 16.4% of the de-excitation relative to the $[1\pi]$-$[4\sigma]$ transition, but the $[3\sigma]$-$[5\sigma]$ process is negligible. The total radiative rate for the filling of the 1π hole is 87% (L) (91% V) of the total rate for filling the 3σ hole. The differences are due to symmetry effects. Interatomic effects involving the 36% hydrogen 1s orbital component of the 5σ molecular orbital are considered to be dominant for the 'forbidden' transitions with the $Cl_{2p\pi} \rightarrow H_{1s}$ contribution being much more important than the $Cl_{2p\sigma} \rightarrow H_{1s}$ contribution. In order to compare the data in table 4 with any experimental measurement it may be necessary to assume that the 3σ and 1π orbitals have the same ionisation cross section values and that the total branching ratios are equal.

From the transition energy values in table 2 it is possible to deduce the values for the corresponding 3π spectator lines in the L_1 emission spectrum. The spectator values are within a few tenths of an electron volt of the diagram lines.

The $[2\sigma]3\pi$ participator line is at 276.6 eV, which is 10.1 eV higher in energy in the spectrum than the $[2\sigma]$-$[2\pi]$ main diagram line. It has a transition rate which is 7% of the main line. The creation of $[3\sigma]3\pi$ and $[1\pi]3\pi$ states correspond to forbidden atomic p–p type transitions and therefore the probability of such resonant states is expected to be negligible. However, selective resonant excitation into the 6σ virtual orbital is allowed and de-excitation of $[3\sigma]6\sigma$ and $[1\pi]6\sigma$ states will produce spectator and participator satellite lines in the L_{23} spectrum.

5. Conclusion

The x-ray emission processes for the HCl molecule are dominated by intra-atomic effects; hence there is a strong parallel with the predictions for atomic chlorine. Only transitions involving the 5σ orbital show evidence of molecular effects due to electron delocalisation. K- and L-shell 3π spectator satellites have similar energies and transition rates to the parent diagram transitions. Selective core-hole excitation is required to separate the two spectra. The K_β and L_1 x-ray emission spectra provide complementary information on valence electron structure to the L_{23} emission spectrum.

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