

X-ray Emission Spectra of Some Carbon-containing Molecules*

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Abstract

Ab initio molecular orbital calculations for the energy and intensity of X-ray transitions associated with the carbon monoxide, hydrogen cyanide and carbon dioxide molecules have been calculated at the Hartree-Fock level. It is demonstrated that in general the absolute transition probabilities are sensitive to the inclusion of electronic relaxation effects and interatomic transition moment contributions. It is concluded that calculations for molecular X-ray emission phenomena should be undertaken at least at the multicentre relaxed Hartree-Fock level to achieve a realistic basis for comparison with experiment. Total carbon-K X-ray rates do not show a strong variation with changes in the molecular environment. The total rates are of a similar magnitude to those reported for the atom. The calculated carbon-K fluorescence yield is also similar in both the carbon atom and the CO₂ molecule.

1. Introduction

Recent studies of high resolution X-ray emission spectra for molecules have provided much data which can be used to elucidate the electronic properties of excited and ionised molecules (Nordgren *et al.* 1982; Pettersson *et al.* 1985; Rubensson *et al.* 1985; Deslattes 1986). From the theoretical viewpoint, interpretations have been based upon semi-empirical or *ab initio* approaches (Manne 1970; Ågren and Nordgren 1981; Ågren and Arneberg 1983; Ågren *et al.* 1984). Good agreement with relative experimental intensities has been reported in several instances using a one-centre localised transition model. This agreement has been taken to imply that interatomic transition moment contributions are negligible. Recent work (Larkins and Rowlands 1986; Rowlands and Larkins 1986) and data presented in this paper show that such a conclusion is generally not justified as multicentre terms can make a significant contribution to absolute transition probabilities.

In this paper our earlier *ab initio* work (Rowlands and Larkins 1986) has been extended. The X-ray emission processes associated with carbon monoxide, carbon dioxide and hydrogen cyanide molecules have been calculated using frozen orbital and relaxed orbital Hartree-Fock models. In the latter case, the dipole length moment is origin dependent because the molecule is charged. The results are in reasonable agreement with experiment.

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2. Theory.

The process involved in X-ray emission is one in which a molecule, initially in a state corresponding to a core orbital vacancy (hole), undergoes a radiative transition to a final state of lower energy, with emission of an X-ray photon. Such a process can arise subsequent to core ionisation of a neutral molecule. In such a case the X-ray emission arises from a transition between two states of a singly ionised molecule.

The probability of an X-ray transition is given in atomic units by the Einstein A coefficient

$$A_{if} = \frac{4}{3} E_{if}^3 \alpha^3 |M_{if}|^2, \quad (1)$$

where E_{if} is the transition energy, α is the fine structure constant and M_{if} is the transition moment.

In the dipole approximation (Manson 1976)

$$M_{if} = \langle \Psi_f | \boldsymbol{\mu} | \Psi_i \rangle, \quad (2)$$

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

$$\boldsymbol{\mu} = \sum_i^N Z_i \mathbf{d}_i, \quad (3)$$

and where Z_i is the charge of the particle.

In this work both the length and velocity forms of the dipole operator have been used:

$$\mathbf{d}_i = \mathbf{r}_i \quad (\text{length form}), \quad (4)$$

$$\mathbf{d}_i = (1/E_{if}) \nabla_i \quad (\text{velocity form}). \quad (5)$$

The formally equivalent acceleration form has not been considered.

In the Born–Oppenheimer approximation the state function Ψ is separated into nuclear and electronic parts

$$\Psi = \Psi_N \Psi_e. \quad (6)$$

The dipole operator can also be expressed as a sum of nuclear and electronic components,

$$\boldsymbol{\mu} = \boldsymbol{\mu}_N + \boldsymbol{\mu}_e = \sum_J^M Z_J \mathbf{d}_J - \sum_j^n \mathbf{d}_j, \quad (7)$$

where there are M nuclei and n electrons in the system. The negative sign arises from the charge of the electron. Substituting (6) and (7) into (2), we obtain

$$M_{if} = \langle \Psi_N^f | \Psi_N^i \rangle \langle \Psi_e^f | \boldsymbol{\mu}_e | \Psi_e^i \rangle + \langle \Psi_e^f | \Psi_e^i \rangle \langle \Psi_N^f | \boldsymbol{\mu}_N | \Psi_N^i \rangle. \quad (8)$$

In the fixed nuclei approximation with no geometric relaxation, the initial and

final nuclear wavefunctions are assumed to be identical and are represented as delta functions, or point charges. If there is no vibrational motion, we have

$$\langle \Psi_N^f | \Psi_N^i \rangle = 1. \quad (9)$$

The nuclear dipole term becomes

$$\langle \Psi_N^f | \mu_N | \Psi_N^i \rangle = \sum_{J=1}^M Z_J R_J \quad (\text{length form}), \quad (10a)$$

$$= 0 \quad (\text{velocity form}), \quad (10b)$$

where R_J is the position vector of nucleus J . In the following discussion we consider only the length form.

If the wavefunctions are orthogonal then the second term in (8) vanishes since the overlap $\langle \Psi_e^f | \Psi_e^i \rangle = 0$ and only the electronic dipole term remains,

$$M_{if} = - \left\langle \Psi_e^f \left| \sum_j^n r_j \right| \Psi_e^i \right\rangle. \quad (11)$$

If, however, the Ψ_e^f and Ψ_e^i are non-orthogonal, the transition moment is given by

$$M_{if} = - \left\langle \Psi_e^f \left| \sum_j^n r_j \right| \Psi_e^i \right\rangle + \langle \Psi_e^f | \Psi_e^i \rangle \sum_J^M Z_J R_J. \quad (12)$$

For charged molecules (12) is dependent on the choice of origin of the coordinate system (Yoshimine *et al.* 1973). This is readily illustrated by considering the electronic and nuclear position vectors r_j and R_J respectively, which are defined relative to an origin O . It is possible to define vectors r'_j and R'_J with respect to a new origin r_c , such that

$$r_j = r'_j + r_c, \quad R_J = R'_J + r_c. \quad (13)$$

Then, we have

$$\begin{aligned} \mu &= \mu_N + \mu_e = \sum_J^M Z_J R_J - \sum_j^n r_j, \\ &= \sum_J^M Z_J (R'_J + r_c) - \sum_j^n (r'_j + r_c). \end{aligned} \quad (14)$$

Substituting into (12), we obtain

$$M_{if} = M'_{if} + \langle \Psi_e^f | \Psi_e^i \rangle \left\{ \left(\sum_J^M Z_J - n \right) r_c \right\}, \quad (15)$$

where M'_{if} is the transition moment relative to the new origin, and the second term contains the origin dependence, which is a function of the electronic overlap between the two states and the molecular charge. For orthogonal states or neutral molecules

the second term in (15) disappears. However, in relaxed orbital calculations, where the states are not necessarily orthogonal, this is not the case and we have chosen the coordinate origin at the centre-of-mass, consistently with the work of Yoshimine *et al.* (1973).

The molecular state functions Ψ_e have been approximated in this work by a single Slater determinant ψ of one-electron molecular spin-orbitals ϕ determined via the restricted Hartree-Fock scheme:

$$\Psi_e \approx \psi = |\phi_1(1)\phi_2(2)\dots\phi_n(n)|. \quad (16)$$

A relaxed orbital approach was used so that the Hartree-Fock wavefunctions are separately calculated for the initial and final states. Since ψ_i and ψ_f are not necessarily orthogonal, the dipole matrix element is given by the formally simple but computationally complicated expression (Löwdin 1955)

$$\langle \psi_f | \mu | \psi_i \rangle = \sum_i^n \sum_j^n \langle \phi_i^f | \mu | \phi_j^i \rangle D_{if}(ij), \quad (17)$$

for normalised wavefunctions ψ_i and ψ_f , where D_{if} is the determinant of molecular orbital overlap integrals (Hurley 1976). The cofactor $D_{if}(ij)$ is $(-1)^{i+j}$ times the determinant formed by removing the i th row and j th column from D_{if} . Henceforth, the subscript 'if' and superscripts 'i' and 'f' are omitted, it being understood that the first function in a matrix element refers to a final state orbital.

In principle, solution of (17) leads to the calculation of n^2 determinants of order $(n-1)$. However, the problem can be factored by appropriate observation of spin and spatial symmetry so that (17) can be expressed as

$$\langle \psi_f | \mu | \psi_i \rangle = \sum_k^K \left(\prod_{l \neq k}^K D_l \right) \sum_i^{n_k} \sum_j^{n_k} \{ \langle \phi_i^k | \mu | \phi_j^k \rangle D_k(ij) \}, \quad (18)$$

where K is the number of spin and spatial symmetry blocks, with n_k electrons in block k , and $D_k(ij)$ is the appropriate cofactor. That is, within each block the cofactor expression analogous to (17) is evaluated and multiplied by the product of determinants of the other blocks. This procedure is repeated for each symmetry block k .

To illustrate the advantages of (18), we consider hole state transitions of CO^+ , which involve 13 spin orbitals. Using (17), one must calculate 169 determinants of order 12, while (18) results in 25 determinants of order 4 and 16 determinants of order 3. A further simplification arises if the determinants D_k are non-singular, whereby the cofactors can be evaluated using the Jacobi ratio theorem (McWeeny and Sutcliffe 1969)

$$D_k(ij) = (S_k^{-1})_{ji} D_k, \quad (19)$$

where S_k is the matrix whose determinant is given by D_k . Thus, within each block, only one inversion has to be performed instead of calculating n^2 determinants.

In certain circumstances, one of the sub-determinants D_m may be singular. Then, the product term on the right-hand side of (18) is nonzero only when $k = m$. In this case the matrix element is evaluated only over the one block and, in fact, most of the

cofactors within that block will also be zero. This is always the case for atoms and the matrix element expression can be considerably simplified (Quiney and Larkins 1984). However, for molecules this is not generally the case, and care must be exercised when applying such simplifications in particular cases. In previous work (Rowlands and Larkins 1986), expressions similar to those used by Quiney and Larkins (1984) were applied to the calculation of transition moment matrix elements for CO, with the result that only the leading term in the expression was explicitly accounted for.

It should be noted that an equivalent and possibly more efficient procedure for obtaining matrix elements between non-orthogonal wavefunctions is the corresponding orbital transformation of King *et al.* (1967), whereby the wavefunctions are transformed into a new, orthogonal basis. At the Hartree-Fock level and for the molecules considered here, the problems are so small that they can be very efficiently solved with contemporary digital computers, and it was not considered that substantial improvements would be achieved by applying the transformation, since only one matrix inversion (19) is necessary compared with one matrix diagonalisation using the corresponding orbital method.

The matrix element evaluation is much simplified in the frozen orbital method where both states are calculated in the same molecular orbital basis, usually the ground state molecular orbitals, and are orthogonal by virtue of the different occupations of the two states. In this case the transition matrix element reduces to a single molecular orbital integral

$$\langle \psi_f | \mu | \psi_i \rangle = \langle \phi_i^f | \mu | \phi_j^i \rangle, \quad (20)$$

where ϕ_i and ϕ_j are the molecular orbitals with different occupations in the two states. The frozen orbital method has the disadvantage that rearrangement of the molecular orbitals on ionisation (i.e. relaxation) is neglected.

A further commonly used approximation is the one-centre approximation (Manne 1970; Ågren and Nordgren 1981; Ågren and Arneberg 1983) which has only been used in the calculation of relative intensities by these workers. The molecular orbital ϕ is expressed as a linear combination of atomic orbitals χ ,

$$\phi_i = \sum_k C_k^i \chi_k = \sum_{\nu} \sum_l^{n_{\nu}} C_{l\nu}^i \chi_{l\nu}, \quad (21)$$

with n_{ν} such orbitals centred on each atom ν .

In calculating the matrix element (20) it is assumed in the one-centre approximation that the transition moment is dominated by terms centred on one atom A:

$$\langle \phi_i | \mu | \phi_j \rangle = \left\langle \sum_l^{N_A} C_{lA}^i \chi_{lA} \left| \mu \right| \sum_{l'}^{N_A} C_{l'A}^j \chi_{l'A} \right\rangle. \quad (22)$$

The validity of the one-centre approximation has been discussed previously (Rowlands and Larkins 1986; Larkins and Rowlands 1986) especially in its applicability to the calculation of absolute intensities, and further evidence is presented here to point out the shortcomings of this approximation.

3. Results and Discussion

(a) Carbon Monoxide

Carbon monoxide in its ground state has the electronic configuration

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

Core ionisation results in a hole in one of these orbitals, denoted here by $[n\sigma]$ or $[1\pi]$. The calculations reported here were carried out in the Abelian C_{2v} subgroup of the $C_{\infty v}$ point group with the neutral molecule internuclear separation of 2.132 a.u. (1 a.u. = 52.9177 pm).

For the relaxed orbital treatment, molecular orbitals were obtained for each of the hole states while, for the frozen orbital calculations, ground state molecular orbitals were used. In the frozen orbital case, relaxed state transition energies were used in most cases.

In calculating the transition probabilities for $[n\sigma] \rightarrow [1\pi]$ transitions, a degeneracy factor of 2 has been included because the 1π hole state is described by two degenerate Slater determinants.

Five different basis sets were used. In the first calculation, the 9s5p uncontracted basis set of Huzinaga *et al.* (1971) was used, to facilitate comparison with previous work (Rowlands and Larkins 1986). In the second calculation, this basis was replaced by the similar 9s5p set of Dunning (1970) for which contraction coefficients are readily available. This 9s5p set was contracted to 5s3p in the third case. The remaining two bases investigate the effect of polarisation functions.

Table 1. Basis set dependence of the total electronic energy of the ground state and $[1\sigma]$ and $[2\sigma]$ hole states of CO

(1) State	(2) H ^B 9s5p	(3) D ^C 9s5p	(4) Energy (h) ^A D ^C 5s3p	(5) D ^C 5s3p1d	(6) D ^C 6s4p2d
GS	-112.7014	-112.7012	-112.6984	-112.7678	-112.7750
$[1\sigma]$	-92.7822	-92.7821	-92.7610	-92.8494	-92.8606
$[2\sigma]$	-101.7452	-101.7450	-101.7305	-101.8418	-101.8493

^A Hartree units (1 h = 3.808×10^{-4} kJ mol⁻¹).

^B Basis set of Huzinaga *et al.* (1971).

^C Derived from the basis set of Dunning (1970).

The energies of the ground state and the $[1\sigma]$ and $[2\sigma]$ hole states are shown in Table 1 for the various basis sets. Both the Dunning and Huzinaga *et al.* basis sets give energies to within 2×10^{-4} h. Contraction of the basis raises the ground state energy by 0.003 h, while the $[1\sigma]$ and $[2\sigma]$ core-hole state energies are raised by 0.021 and 0.015 h respectively. The core hole states will be most affected by contraction since the contraction involves basis functions with large exponents. In column 5, d functions of exponent 0.75 and 0.85 (Dunning and Hay 1977) have been added to C and O respectively. This addition lowers the energy substantially, by between 0.07 and 0.11 h, being more important for the hole states. In the final basis, one diffuse s function and p function, taken from Dunning and Hay (1977), were added to both C and O. Furthermore, the single d function was split according to Dunning (1971) into two d functions (C, $\alpha_d = 1.845, 0.547$; O, $\alpha_d = 2.091, 0.619$) which were left

uncontracted. This results in a (10s 6p 2d) \rightarrow [6s 4p 2d] basis. The addition of these extra functions has very little effect on the total energy, being at most 0.011 h. In view of this last result there seems to be little point in further augmentation with polarisation functions, although an optimisation of the d function may be in order. Despite the slight rise in energy on contraction it was decided to work with the contracted basis in the interests of computational efficiency. Calculations beyond this level of accuracy require the inclusion of configuration interaction (CI) to account for correlation effects.

Table 2. Basis set dependence of the de-excitation energies (eV) and transition probabilities ($\times 10^6$ a.u.) of the O-K and C-K spectra of CO
Relaxed SCF (self-consistent field) calculations

(1) Final state hole	(2) Co- efficient	(3) H ^A 9s5p	(4) D ^B 9s5p	(5) D ^B 5s3p	(6) D ^B 5s3p1d	(7) D ^B 6s4p2d	(8) Expt ^C
O-K spectrum							
[3 σ]	E_{if}	502.05	502.05	502.48	503.30	503.26	—
	A_L	1.701	1.702	1.703	1.227	1.186	
	A_V	1.353	1.352	1.340	0.997	0.967	
[4 σ]	E_{if}	522.25	522.25	522.75	522.21	522.06	522.74
	A_L	5.929	5.924	5.877	6.628	6.705	
	A_V	5.415	5.413	5.309	5.853	5.921	
[1 π]	E_{if}	526.51	526.50	526.97	526.74	526.64	525.7
	A_L	34.690	34.700	34.116	33.789	33.754	
	A_V	30.218	30.219	29.369	29.094	29.055	
[5 σ]	E_{if}	528.48	528.47	528.97	528.58	528.46	528.4
	A_L	2.102	2.104	2.067	1.918	1.910	
	A_V	1.677	1.677	1.634	1.533	1.529	
C-K spectrum							
[3 σ]	E_{if}	258.16	258.16	258.41	258.60	258.67	—
	A_L	0.507	0.507	0.527	0.469	0.470	
	A_V	0.542	0.542	0.552	0.478	0.479	
[4 σ]	E_{if}	278.36	278.36	278.68	277.52	277.47	—
	A_L	0.019	0.019	0.013	0.016	0.010	
	A_V	0.003	0.003	0.002	0.001	0.001	
[1 π]	E_{if}	282.62	282.62	282.90	282.04	282.05	278.0
	A_L	3.796	3.796	3.713	3.618	3.606	
	A_V	3.155	3.155	3.064	2.978	2.976	
[5 σ]	E_{if}	284.58	284.58	284.90	283.89	283.87	282.01
	A_L	3.327	3.328	3.233	3.262	3.265	
	A_V	2.670	2.690	2.609	2.600	2.612	

^A Basis set of Huzinaga *et al.* (1971).

^B Derived from basis set of Dunning (1970).

^C Pettersson *et al.* (1985).

The de-excitation energies and the length and velocity forms of the relaxed transition probabilities (A_L and A_V respectively) are tabulated against the basis set in Table 2. The results are essentially unchanged for the two uncontracted basis sets and will not be discussed further. The de-excitation energies uniformly increase by about 0.1% on contraction of the basis (see column 5). For the O-K spectrum both the length

and velocity transition probabilities decrease slightly on contraction, the maximum change being of the order of 2% for the $[1\pi]$ state. On the other hand, in the C-K spectrum, the $[3\sigma]$ A coefficients increase slightly, while the $[1\pi]$ and $[5\sigma]$ coefficients decrease, the changes being of the order of 3–4%.

The addition of d functions decreases the de-excitation energies for all transitions except for the $[1\sigma] \rightarrow [3\sigma]$ and $[2\sigma] \rightarrow [3\sigma]$ transitions where E_{if} increases by 0.82 and 0.19 eV respectively. The E_{if} decreases by over 1 eV for the $[2\sigma] \rightarrow [4\sigma]$ transition. The A_L and A_V are substantially affected by the addition of d functions to the basis. For the $[1\sigma] \rightarrow [3\sigma]$ transition A_L decreases by 27%, while for $[1\sigma] \rightarrow [4\sigma]$, it increases by 13%; similarly $[2\sigma] \rightarrow [3\sigma]$ decreases by 12%. The transitions to $[1\pi]$ and $[5\sigma]$ states, however, are affected to a much smaller extent by this change to the basis.

The further augmentation of the basis shown in column 7 has very little effect on the energies or transition probabilities, with the single exception of the $[1\sigma] \rightarrow [3\sigma]$ transition where A_L and A_V decrease by about 3%. This result, together with the total energies shown in Table 1, provides evidence that the basis set is saturated with respect to diffuse and polarisation functions.

Of further interest in Table 2 is a comparison of A_L and A_V . They agree to within 20% for all the transitions and the relative ratio is also fairly constant for all the different bases. That is, A_L and A_V change by the same relative amount as the basis set is changed.

The de-excitation energies for the O-K spectrum agree well with experiment, considering that a Hartree-Fock treatment has been used, the maximum discrepancy being less than 1 eV. The C-K results, however, are less satisfactory, especially for the $[2\sigma] \rightarrow [1\pi]$ transition, where there is a discrepancy of 4 eV. Inclusion of both core and valence correlation effects are required to improve the agreement with experiment.

It is interesting to discuss the effect of errors in E_{if} on the transition probabilities. From equations (1)–(5), we have

$$A_L \propto E_{if}^3, \quad A_V \propto E_{if}. \quad (23, 24)$$

Therefore, the percentage error in A_V from the energy calculation is equal to the percentage error in E_{if} , while for A_L it is three times this amount. Considering the $[2\sigma] \rightarrow [1\pi]$ transition, where the calculated best E_{if} is in error by 1.8%, then the calculated A_L will be in error by 5.4% from this source.

In this context it is useful to discuss the frozen orbital transition probabilities shown in Table 3. These have been calculated with the relaxed orbital de-excitation energies for the appropriate basis set, instead of, as is usually the case, with the Koopmans energies from the frozen orbital calculation. The Koopmans energies are all higher than the relaxed energies, but what is interesting is that they are all higher by a uniform 3.5%. This means that the absolute probabilities will be higher by 10% for the length form when using Koopmans' energies, but that the *relative* intensities will be unchanged, the percentage error being the same for all transitions.

The absolute transition probabilities in the various approximations calculated with the largest basis set are shown in Table 3 for all transitions together with the total transition probability. The length and velocity forms are in good agreement for all three models. Considering first the total probability of transition to an oxygen

Table 3. Comparison of CO transition probabilities with the 6s4p2d basis from one-centre approximation, frozen orbital and relaxed orbital calculations

Final state hole	A_L (10^{-6} a.u.)			A_V (10^{-6} a.u.)		
	One-centre	Frozen	Relaxed ^A	One-centre	Frozen	Relaxed ^A
O-K spectrum						
[3 σ]	0.632	1.042	1.186	0.731	0.895	0.967
[4 σ]	7.096	8.309	6.705	6.884	7.461	5.921
[1 π]	17.436	19.653	33.754	16.764	17.496	29.055
[5 σ]	1.963	2.107	1.910	1.888	1.905	1.529
Total	27.127	31.111	43.555	26.267	27.757	37.472
C-K spectrum						
[3 σ]	0.189	0.610	0.470	0.240	0.504	0.479
[4 σ]	0.076	0.188	0.010	0.082	0.158	0.001
[1 π]	1.185	1.793	3.606	1.168	1.516	2.976
[5 σ]	1.423	1.985	3.265	1.385	1.728	2.612
Total	2.874	4.576	7.351	2.875	3.906	6.068

^A Centre-of-mass chosen as origin for calculation.

Table 4. The CO relative intensities in the various approximations calculated with the 6s4p2d basis

Final state hole	Length form			Velocity form			CI ^A	Expt ^B
	One-centre	Frozen	Relaxed	One-centre	Frozen	Relaxed		
O-K spectrum								
[3 σ]	0.04	0.05	0.04	0.04	0.05	0.03	0.03	—
[4 σ]	0.41	0.42	0.20	0.41	0.43	0.20	0.30	0.38
[1 π]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
[5 σ]	0.11	0.11	0.06	0.11	0.11	0.05	0.09	0.28
C-K spectrum								
[3 σ]	0.16	0.34	0.13	0.21	0.33	0.16	0.16	—
[4 σ]	0.06	0.10	0.0	0.07	0.10	0.0	0.04	—
[1 π]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
[5 σ]	1.20	1.11	0.91	1.19	1.14	0.88	0.82	0.59

^A Ågren and Arneberg (1983).

^B Ågren and Nordgren (1981), includes satellite contributions.

1 σ hole, it is seen that the one-centre and frozen orbital two-centre models are in good agreement, especially with the velocity dipole operator. However, when going to the relaxed treatment, the total probability increases by about 40%, and this increase is not uniform over all transitions. For example, the [1 σ] \rightarrow [4 σ] and [1 σ] \rightarrow [5 σ] transition probabilities decrease, while the [1 σ] \rightarrow [1 π] transition probability increases considerably.

In the case of the C-K spectrum, the one-centre model yields total probabilities substantially lower than in the frozen orbital calculations. This effect has been discussed previously (Rowlands and Larkins 1986). When relaxation is incorporated in this case the total probability increases by about 60%, this increase arising mainly from the [1 π] and [5 σ] states, while the probabilities of transition to the [3 σ] and [4 σ] states decrease, in the latter case becoming negligible.

Relative intensities were calculated in the ratio $A[n\sigma]/A[1\pi]$ and are collated in Table 4, together with other theoretical and experimental results. The length and velocity forms are in excellent agreement, especially for the O-K spectrum. In the O-K spectrum, the one-centre and frozen orbital relative intensities are also in excellent agreement. This is not the case, however, for the C-K spectrum, where agreement for the $[2\sigma] \rightarrow [3\sigma]$ transition is particularly poor. The relative intensities for both sets of transitions are substantially altered when relaxation is accounted for, with the intensities of all σ state lines dropping relative to the dominant π line. In the C-K case this brings the intensity of the $[2\sigma] \rightarrow [5\sigma]$ transition below that of the $[2\sigma] \rightarrow [1\pi]$ transition, in agreement with experiment. Generally, the relaxed SCF results agree only qualitatively with the published experimental results (Ågren and Nordgren 1981), the correct ordering but not the magnitude of the transition being predicted. Since the present experimental data are derived from interpretation of photographic plates and are known to also contain contributions from satellite lines (Werme *et al.* 1975), quantitative comparison must be made with caution. New experimental data based upon the use of tunable synchrotron radiation or coincidence studies would be valuable. Only then will it be possible to definitively unravel the contributions of resonance, shake-up and shake-off satellite lines from the diagram line spectrum. The latter has been the subject of these calculations. Our results, however, agree quite well with the relaxed SCF and limited CI results of Ågren and Arneberg (1983).

Further work is in progress to investigate the influence of correlation effects on absolute intensities along with the role of vibrational effects. It is clear from the analysis that relaxation effects are very important for X-ray emission from carbon monoxide. This point was established in earlier work (Rowlands and Larkins 1986), however, only electronic contributions were examined along with leading terms in the transition probability expression.

Table 5. Comparison of HCN X-ray emission transition probabilities

Final state hole	E_{if} (eV)	A_L (10^{-6} a.u.)			A_V (10^{-6} a.u.)		
		One-centre	Frozen	Relaxed ^A	One-centre	Frozen	Relaxed ^A
N-K spectrum							
[3 σ]	375.66	0.471	0.872	1.284	0.510	0.740	0.684
[4 σ]	386.34	0.0	0.001	0.234	0.0	0.0	0.279
[5 σ] ^B	394.02	4.182	4.956	6.264	3.957	4.391	5.865
[1 π]	394.85	6.126	7.218	14.173	5.737	6.305	11.818
Total		10.813	13.047	21.955	10.204	11.436	18.646
C-K spectrum							
[3 σ]	262.65	0.210	0.579	0.174	0.252	0.489	0.331
[4 σ]	273.33	0.720	1.211	1.491	0.723	1.037	0.951
[5 σ] ^B	281.00	0.407	0.760	0.522	0.421	0.655	0.531
[1 π]	281.83	2.503	3.172	6.108	2.310	2.697	5.069
Total		3.840	5.722	8.295	3.706	4.878	6.882

^A Centre-of-mass chosen as origin.

^B Note that the ordering of the [5 σ] and [1 π] states has changed here relative to the CO calculations.

(b) Hydrogen Cyanide

Hydrogen cyanide is isoelectronic with carbon monoxide and has a C–N bond length of 2.186 a.u. and a C–H bond length of 1.999 a.u. Similar to CO, all transitions are allowed by symmetry. Only one basis set was considered. The 5s3p1d carbon set used in the CO calculations was taken over and used with an analogous nitrogen set, where the d function exponent was 0.80 (Dunning and Hay 1977). The (5s) → [3s] hydrogen set (Dunning 1970) was augmented by a p function with exponent 1.0. With this basis the energy of neutral ground state HCN is predicted to be -92.897434 h, while the energy of the N(1s) hole state is -77.942670 h and the energy of the C(1s) [2 σ] state is -82.096006 h.

The absolute transition probabilities in the various approximations together with the transition energy are tabulated for each transition in Table 5. Considering the relaxed SCF results first, it can be seen that the length and velocity forms are in relatively good agreement for the more intense transitions but differ by a factor of almost two for transitions to the [3 σ] hole state. The effect of relaxation is most pronounced in transitions involving the [1 π] state, the transition probabilities in both the carbon and nitrogen spectra almost doubling with the inclusion of relaxation. Furthermore the [2 σ] → [3 σ] and [2 σ] → [5 σ] probabilities associated with the C–K spectrum decrease when relaxation is included. For the N–K spectrum the [1 σ] → [4 σ] transition, which has negligible intensity at the frozen orbital level, increases to 0.234(L) or 0.279(V) on relaxation of the wavefunctions. The one-centre model accounts for less than half of the total intensity obtained in the relaxed orbital calculations using the length formalism.

Table 6. The HCN relative intensities in the various approximations

Final state hole	Length form			Velocity form		
	One-centre	Frozen	Relaxed	One-centre	Frozen	Relaxed
N–K spectrum						
[3 σ]	0.08	0.12	0.09	0.09	0.12	0.06
[4 σ]	0.0	0.0	0.02	0.0	0.0	0.02
[5 σ]	0.68	0.69	0.44	0.69	0.70	0.50
[1 π]	1.0	1.0	1.0	1.0	1.0	1.0
C–K spectrum						
[3 σ]	0.08	0.18	0.03	0.11	0.18	0.07
[4 σ]	0.29	0.38	0.24	0.31	0.38	0.19
[5 σ]	0.16	0.24	0.09	0.18	0.24	0.10
[1 π]	1.0	1.0	1.0	1.0	1.0	1.0

The relative intensities of X-ray emission in HCN with respect to the [1 π] state are shown in Table 6. As observed for CO, the length and velocity forms are in good agreement. Considering the N–K spectrum, the one-centre and frozen orbital models are in good agreement, but in the relaxed calculation the [5 σ] transition is predicted to have a substantially lower intensity relative to [1 π]. In the carbon case there is no close agreement between the different models but the relaxed calculations show the various σ transitions to be significantly less important than in the frozen orbital calculations. We are not aware of any published experimental findings with which to compare these results.

(c) Carbon Dioxide

The experimental C–O bond length of 2.194 a.u. has been used along with the 5s3p1d basis set presented in Section 3a for the CO molecule. The calculated transition energies and X-ray transition probabilities for processes associated with an initial core hole on the carbon atom, $[2\sigma_g]$, are presented in Table 7. Calculations for the oxygen core hole require symmetry breaking or configuration interaction techniques to be applied; work on this problem is in progress. The conclusions to be drawn from the results are similar to those outlined for the HCN molecule. The absolute probabilities are sensitive to the inclusion of multicentre contributions and to electronic relaxation effects. The latter effect is most pronounced for the transition to the $[1\pi_u]$ final hole state. The total probability in the relaxed case is more than twice that calculated for the one-centre case; however, the relative intensities presented in Table 8 are in good agreement for the two cases. Indeed, the predictions of the one-centre model provided the best agreement with the limited experimental data. The findings for the present problem underline the inadequacy of making conclusions regarding the suitability of a particular model solely on the basis of relative intensity data.

Table 7. Comparison of C–K X-ray emission transition probabilities for CO₂

Final state hole	E_{if} (eV)	A_L (10^{-6} a.u.)			A_V (10^{-6} a.u.)		
		One-centre	Frozen	Relaxed ^A	One-centre	Frozen	Relaxed ^A
$[2\sigma_u]$	260.78	0.473	1.279	1.551	0.562	1.091	1.232
$[3\sigma_u]$	280.68	0.754	1.366	2.224	0.766	1.179	1.623
$[1\pi_u]$	281.05	1.886	2.668	5.413	1.815	2.278	4.627
Total		3.113	5.313	9.188	3.143	4.548	7.482

^A Centre-of-mass chosen as origin.

Table 8. The CO₂ C–K relative intensities in the various approximations

Final state hole	Length form			Velocity form			Expt ^A
	One-centre	Frozen	Relaxed	One-centre	Frozen	Relaxed	
$[2\sigma_u]$	0.25	0.48	0.29	0.31	0.48	0.27	—
$[3\sigma_u]$	0.40	0.51	0.41	0.42	0.52	0.35	0.43
$[1\pi_u]$	1.0	1.0	1.0	1.0	1.0	1.0	1.0

^A Nordgren *et al.* (1982).

(d) Influence of Chemical Effects

It is of interest to consider the influence of chemical effects on the total X-ray emission probabilities and the fluorescence yield associated with a particular initial hole state and the change in such quantities from the isolated atom to the molecular environment.

The total X-ray probabilities for C–K processes in the molecules CO, HCN and CO₂ from Tables 3, 5 and 7 respectively are 6.068×10^{-6} , 6.882×10^{-6} and 7.482×10^{-6} a.u. using the relaxed Hartree–Fock model and the velocity formalism. The total molecular X-ray transition probability is therefore not strongly dependent

upon the molecular environment, but it does show some increase with the number of valence electrons in the molecule. The degree of localisation of the emission as measured by the one-centre rate to the total frozen orbital rate was 73.6%, 76.0% and 69.1% for CO, HCN and CO₂ respectively. The values are considerably lower if expressed relative to the relaxed total rate.

For the isolated atoms several values for the total carbon-K X-ray emission probability exist in the literature. They have been determined using a frozen orbital model at various levels of approximation generally with the length form of the dipole operator. McGuire (1969) reported an atomic value of 8.24×10^{-6} a.u. using a model potential based upon the Herman-Skillman approximation. Walters and Bhalla (1971) obtained a value of 4.864×10^{-6} a.u. using a Hartree-Fock-Slater potential, while Scofield (1974) reported a value of 3.79×10^{-6} a.u. based upon a relativistic Hartree-Fock-Slater potential. These values, as a first approximation, may be compared with the length form, frozen orbital molecular values in Tables 3, 5 and 7. The C-K values of 4.576×10^{-6} , 5.722×10^{-6} and 5.313×10^{-6} a.u. for the CO, HCN and CO₂ molecules respectively are similar to the Hartree-Fock-Slater values. While recognising the difficulty of comparing values calculated by different models, it is reasonable to conclude that the X-ray transition rates are of a similar magnitude in the atom and the molecules. This is somewhat surprising in view of the importance of multicentre contributions to the molecular X-ray emission rates.

It is also possible to obtain a preliminary estimate of the influence of chemical effects on the fluorescence yields, ω_k . Richards and Larkins (unpublished work) have recently calculated the molecular Auger transition rates associated with the decay of a C-K hole in the CO₂ molecule using the *ab initio* procedure of Richards and Larkins (1984) to determine the continuum wavefunction without exchange. The total Auger rate was 1440×10^{-6} a.u. using a frozen orbital approximation. With the frozen orbital X-ray data in Table 7 and the formula

$$\omega_k = \Gamma_X / (\Gamma_X + \Gamma_A), \quad (25)$$

where Γ_X and Γ_A denote the total X-ray and Auger transition probabilities respectively, values of 0.0037 (length form) and 0.0031 (velocity form) were obtained for the fluorescence yield. These values are similar to the atomic value of 0.0024 calculated by Walters and Bhalla (1971) and the value of 0.0035 calculated by McGuire (1969). An experimental value of 0.003 for a carbon foil was reported by Toburen and Larkins (1972). The results support the conclusion that the fluorescence yield may not be strongly dependent upon molecular effects. We note, however, that in both of the previous studies the calculated total atomic Auger rate is significantly higher than the molecular value determined by Richards. Walters and Bhalla reported an atomic value of 20.59×10^{-4} a.u. and McGuire a value of 23.60×10^{-4} a.u. compared with the CO₂ value of 14.4×10^{-4} a.u. The difference may reflect the influence of delocalisation effects associated with the double hole final states or the lack of exchange interaction for the continuum electron in our Auger calculation. Further theoretical investigations are required in this area.

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