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Factors influencing the calculation of molecular X-ray emission spectra

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The importance of the choice of basis set, electronic relaxation, intra- and interatomic processes and vibrational effects related to the development of an acceptable *ab initio* molecular orbital model for the calculation of X-ray transition probabilities for molecules are examined with special reference to the carbon monoxide molecule. The length and velocity forms of the dipole transition operator have been used in the assessment. To calculate reliable intensities it is necessary to account for electronic relaxation effects and include interatomic contributions. Since some electronic transition moments show a strong dependence on bondlength variation the use of the adiabatic approximation separating electronic and vibrational effects must be used with caution.

Key words: X-ray emission — *Ab initio* calculations — Transition probabilities — Carbon monoxide

1. Introduction

The advent of experimental X-ray Emission Spectroscopy (XES) studies of excited molecules in the gas phase [1, 2] has resulted in spectra virtually free of intermolecular effects. Recent high resolution spectra [2–9] have provided data for theoretical interpretation. This involves the identification of transitions in terms of their energies and intensities. Ågren et al. [10] demonstrated that X-ray transition energies in small molecules can be obtained to within a few electron volts using Hartree–Fock SCF calculations, providing the effect of electronic relaxation is included by separately calculating the energies of the initial and final states.

The transition probabilities and hence the X-ray band intensity profiles of molecules such as CO, N_2, NO, O_2 and others have been discussed by researchers at various levels of sophistication [2-15]. The methods employed to calculate X-ray emission intensities predominantly involve the use of a one-centre model based on the initial work of Manne [11] to generate relative intensities which are then sometimes adjusted for vibrational effects [3, 10]. There has been little work reported on the validity of these calculations with respect to the methodology employed. Ågren and Nordgren [13] addressed this topic when they showed that relative intensity predictions made using the one-centre model and semi-empirical MO calculations were in quite good agreement with experiment and that more sophisticated calculations did not improve these results sufficiently to justify their use.

Ågren et al. [14, 15] have analysed the XES spectra of CO and N_2 in detail using configuration interaction wavefunctions built from molecular orbitals separately optimised for the initial and final states. However even these treatments have relied upon relative intensity comparisons to discuss features of the experimental spectra.

The subject of the present work is the role of absolute intensity values in assessing the relative merits of the various approximations normally made in theoretical XES calculations. The molecule chosen for study was carbon monoxide so as to complement the work of Ågren and Arneberg [14].

2. Theory

For molecules containing first row atoms an X-ray photon is emitted when an electron undergoes a transition from a core hole state to a valence hole state of the molecule. Carbon monoxide has five occupied sigma-type orbitals ($1\sigma \rightarrow 5\sigma$) and a pair of degenerate pi-type orbitals (1π). Core hole ionisation leads to the $CO[1\sigma]\,^2\Sigma^+$ or $CO[2\sigma]\,^2\Sigma^+$ state depending on whether the ionised electron is from what is basically an oxygen $1s$ orbital or a carbon $1s$ orbital respectively. Transitions between the $CO[1\sigma]\,^2\Sigma^+$ state and any one of the valence hole states ($CO[3\sigma]\,^2\Sigma^+$, $CO[4\sigma]\,^2\Sigma^+$, $CO[1\pi]\,^2\Pi$, or $CO[5\sigma]\,^2\Sigma^+$) lead to peaks in the O-K spectrum in the region of 525 eV. Transitions between the $CO[2\sigma]\,^2\Sigma^+$ state and any of the valence hole states lead to peaks in the C-K spectrum near 280 eV.

The probability of transition between states can be derived by time-dependent perturbation theory and is given in atomic units by the Einstein A coefficient

$$A_{if} = \tfrac{4}{3} E_{if}^3 \alpha^3 |\mathcal{M}_{if}|^2 \qquad (1)$$

where E_{if} is the energy of transition in a.u. and α is the fine structure constant and $\mathcal{M}_{if}$ is the transition moment.

In the dipole approximation [16] $\mathcal{M}_{if}$ is origin independent only when

$$\mathcal{M}_{if} = \langle \Psi_f | \Sigma d_j | \Psi_i \rangle \qquad (2)$$

Ψ_f and Ψ_i represent the final and initial orthonormal hole state wavefunctions respectively and d is the dipole operator for electron j.

The dipole operator has three formally equivalent representations known as the length, velocity and acceleration forms. In this work both the length and velocity forms have been used:

$$d_j = r_j \quad \text{length form} \tag{3}$$

$$d_j = \frac{1}{E_{ij}} \nabla_j \quad \text{velocity form} \tag{4}$$

Under the Born-Oppenheimer approximation the statefunctions, Ψ_i and Ψ_f, are normally written as the product of nuclear and electronic functions. That is,

$$\begin{aligned} \Psi_i &= V_i \Phi_i \\ \Psi_f &= V_f \Phi_f \end{aligned} \tag{5}$$

Then,

$$|\mathcal{M}_{if}|^2 = |\langle V_f | V_i \rangle|^2 |\langle \Phi_f | \Sigma d_j | \Phi_i \rangle|^2 \tag{6}$$

The squares of the nuclear function overlaps are the Franck-Condon factors often used in analysis of spectra [3, 10]. Only the electronic term has been considered in this paper. Another approximation inherent in this separation of nuclear and electronic functions is commonly called the adiabatic approximation. That is, the value of the electronic dipole element is assumed to be independent of nuclear position for bondlength variations within normal vibrational limits.

The molecular electronic state functions Φ_i, Φ_f, are normally expressed as linear combinations of determinants of one-electron orbitals under the molecular orbital approximation. The one-electron molecular orbitals are in turn expressed as linear combinations of atomic basis functions under the linear combination of atomic orbitals approximation (LCAO). In this work the one-electron molecular orbitals were determined self-consistently using the restricted Hartree-Fock method of Roothaan [17] over a basis set of Gaussian orbitals.

For the calculation of the transition moments between the molecular state functions two approaches can be used. In the frozen orbital approach the one-electron molecular orbitals in the initial and final states are considered to be identical so that the transition moment reduces to a single electron dipole element between the two one-electron orbitals involved in the transition. In the relaxed orbital approach the one-electron molecular orbitals are separately calculated for the initial and final states which means that the transition moment expression becomes a determinantal expression involving one-electron dipole elements which are origin dependent and overlap terms. For carbon monoxide the two required expressions are:

$[k\sigma] \to [m\sigma]$

$$|\mathcal{M}_{if}| = \det\left\{ \langle m\sigma | d | k\sigma \rangle \prod_{\substack{n=1 \\ n \neq m,k}}^{5} \langle n\sigma | n\sigma \rangle \right\} \det\left\{ \prod_{n=1}^{5} \langle n\sigma | n\sigma \rangle \right\} \langle 1\pi | 1\pi \rangle^4 \tag{7}$$

$[k\sigma]\rightarrow[1\pi]$

$$|\mathcal{M}_{if}|=\sqrt{2}\det\left\{\langle 1\pi|d|k\sigma\rangle\prod_{\substack{n=1\\n\neq k}}^{5}\langle n\sigma|n\sigma\rangle\right\}\det\left\{\prod_{n=1}^{5}\langle n\sigma|n\sigma\rangle\right\}\langle 1\pi|1\pi\rangle^{3} \tag{8}$$

In Eq. (7), only the leading determinant has been included. In calculating the one-electron dipole elements a full summation of terms over the whole basis set for each molecular orbital is readily carried out. However, in X-ray emission work in the past most theoretical calculations have been undertaken using a one-centre approach in which only basis set orbitals on the ionised atom are considered to contribute significantly to the transition intensity. To assess the validity of this approach for the frozen orbital case a separate summation was made, over the basis set orbitals on the ionised atom only, to obtain a "one-centre" contribution to the transition moment. This value was then compared with the full transition moment to assess the relative importance of the interatomic and intra-atomic contributions.

3. Results

The UIBMOL suite of restricted Hartree-Fock SCF programs, suitably modified, has been used to calculate the carbon monoxide one-electron molecular orbitals used to construct the molecular state functions [18]. The importance of several factors on the calculated values of the absolute intensities of X-ray transitions in the CO molecule have been assessed. They are:

(i) basis set dependence;
(ii) the use of the length or velocity dipole operator form;
(iii) frozen orbital or relaxed orbital Hartree-Fock representations;
(iv) single centre or multicentre approaches;
(v) bondlength dependence.

Relaxed calculations involving the CO$[4\sigma]\,{}^2\Sigma^+$ state were done using the CO$[5\sigma]\,{}^2\Sigma^+$ state molecular orbitals since interaction of the CO$[4\sigma]$ and CO$[5\sigma]$ configurations caused considerable convergence difficulties with the CO$[4\sigma]$ state.

Table 1. X-ray transition energies for the CO molecule (eV)

	C-*K* spectrum				O-*K* spectrum			
Final state	Koopmans'	CI [14]	Expt [8]	This work	Koopmans'	CI [14]	Expt. [8]	This work
$[3\sigma]$	267.48	256.5[a]	—	258.15	520.28	502.5[a]	—	502.03
$[4\sigma]$	288.28	277.69	—	278.22	541.08	523.53	522.74	522.09
$[1\pi]$	292.44	280.42	278.00	282.60	545.24	526.26	525.7	526.48
$[5\sigma]$	294.83	283.65	282.01	284.57	547.63	529.49	528.4	528.45

[a] Ågren et al. [14] have 4 different $[3\sigma]$ states

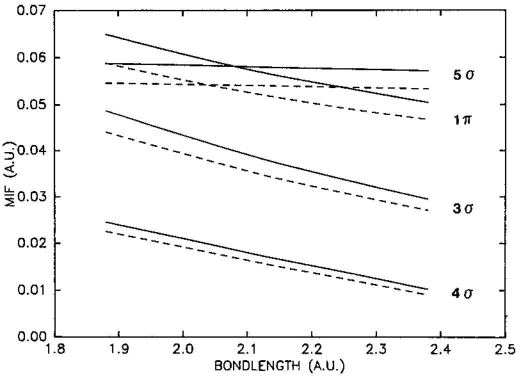

Fig. 1. Variation of the transition moment $\langle \Phi_f | \Sigma d_j | \Phi_{2\sigma} \rangle$ with internuclear distance. *L*: length form. *V*: velocity form

All calculations except where otherwise noted were performed using an uncontracted ($9s\,5p$) Gaussian basis from Huzinaga [19] at the neutral molecule geometry.

The calculated X-ray energies using the relaxed orbital representation are presented in Table 1 along with the theoretical values of Ågren et al. [14] and the experimental findings of Pettersson et al. [8]. The present results based upon transitions involving the CO[1σ] hole state are within 1 eV of experiment and previous calculations; however, for transitions involving the CO[2σ] hole state the discrepancy with experiment is as large as 4.6 eV. Transition energies based upon a frozen orbital approach, Koopmans' theorem, differ from experiment by as much as 20 eV and underline the importance of electronic relaxation effects.

The dependence of transition moment values on the various factors outlined above are presented in Tables 2–4 and Figs. 1 and 2.

4. Discussion

The lack of experimental absolute intensity data and the accompanying lack of theoretical absolute intensity values has meant that assessment of factors involved

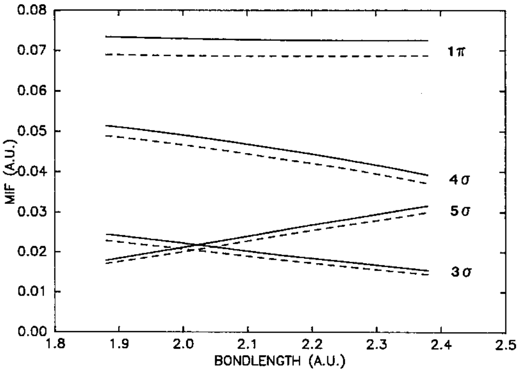

Fig. 2. Variation of the transition moment $\langle \Phi_f | \Sigma d_j | \Phi_{1\sigma} \rangle$ with internuclear distance. *L*: length form. *V*: velocity form

in calculating XES spectra has been limited to within the framework of relative intensities. Ågren and Nordgren [13] addressed the issue of the validity of the one-centre model and commented on other features such as orbital relaxation and basis set effects. Ågren and Arneberg [14] and Ågren et al. [15] also considered these factors without special emphasis in their detailed theoretical analyses of the spectra of CO and N_2 respectively.

However, absolute intensity data enable one to understand more clearly the importance of various factors involved in theoretical XES calculations. The sensitivity of the transition moment to the size of Gaussian basis set was investigated using uncontracted ($6s\,3p$), ($9s\,5p$) and ($11s\,7p$) sets from Huzinaga [19] on each atom. The values calculated using the length form of the dipole operator at a frozen orbital, neutral molecular level are shown in Table 2. The increase in basis flexibility from ($6s\,3p$) to ($9s\,5p$) leads to a significant change in the transition moment values for some transitions. The moment value change from the (9s 5p) basis to the (11s 7p) basis is much smaller. As a result the ($9s\,5p$) basis set was considered to be adequate and was used for all subsequent calculations.

Figures 1 and 2 illustrate the variation of the transition moment with bondlength for C-*K* and O-*K* spectra respectively. Values for each of the four allowed X-ray transitions in each spectrum were calculated at a frozen orbital level using neutral molecule orbitals in both the length and velocity forms. For each transition the length and velocity forms of the dipole operator agreed to within 10 per cent over the whole bondlength range.

The $[2\sigma]\rightarrow[5\sigma]$ and the $[1\sigma]\rightarrow[1\pi]$ transition moments in Figs. 1 and 2 respectively show little dependence on bondlength. It is concluded that they are dominated by one-centre contributions. However, the other transition moments show a strong dependence on bondlength. The transition moment for most transitions presented in Figs. 1 and 2 decreases with increasing bondlength. This trend reflects the reduced importance of two-centre contributions as the bond length increases. The notable exception is the O-*K* $[1\sigma]\rightarrow[5\sigma]$ transition for which the moment increases with increasing bondlength in the range investigated. This result is obtained because the one- and two-centre terms combine destructively. As the bond length increases the two-centre contribution diminishes. Since all transitions do not show the same bondlength dependence, changes in

Table 2. Basis set effect on $|M_{if}|$ for CO X-ray transitions associated with $[1\sigma]$ or $[2\sigma]$ initial hole states (length form (10^{-2} a.u.))

Final state	($6s\,3p$) O-*K*	C-*K*	($9s\,5p$) O-*K*	C-*K*	($11s\,7p$) O-*K*	C-*K*
$[3\sigma]$	1.926	3.785	1.965	3.788	1.964	3.788
$[4\sigma]$	4.547	1.616	4.608	1.710	4.609	1.708
$[1\pi]$	7.237	6.045	7.263	5.661	7.273	5.654
$[5\sigma]$	2.479	5.891	2.482	5.791	2.469	5.784

Table 3. Transition probability $|A_{if}|$ for C-*K* X-ray spectrum of the molecule CO (10^{-6} a.u.)

Final state	Frozen orbital One-centre *L*	*V*	Full moment *L*	*V*	Relaxed[a] Full moment *L*	*V*
[3σ]	0.215	0.269	0.635	0.527	0.630	0.698
[4σ]	0.090	0.094	0.162	0.134	0.012	0.052
[1π]	1.301	1.245	1.861	1.562	3.799	3.157
[5σ]	1.416	1.374	1.989	1.727	3.300	2.826
Total	3.022	2.982	4.648	3.950	7.740	6.733

[a] Electron term only, calculated with carbon atom as origin. Nuclear moment terms must be included to determine intensity

bondlength involved with core ionisation and vibrational excitations arising from the transitions themselves can lead to complex band shapes in the spectra. X-ray transitions have lifetimes near 10^{-12} seconds (see Tables 3, 4) which coincide with the timescale of a molecular vibration. The application of the Born-Oppenheimer approximation followed by Franck-Condon vibrational analysis, i.e. the adiabatic approximation, must therefore be used with caution.

The calculated electronic transition probabilities $|A_{if}|$ from Eq. (1) for the C-*K* and O-*K* spectra are presented in Tables 3 and 4, respectively. The effects of relaxation, the importance of two-centre transition moment terms and the length and velocity forms of the dipole operator are evaluated.

The importance of relaxation is demonstrated by comparing values in columns 4 and 6 and in columns 5 and 7 for the C-*K* spectrum, Table 3. The effect of relaxation on the total absolute transition probability is an increase of 67% for the length form and an increase of 70% in the velocity form. Most of this increase comes from the major transitions; $[2\sigma]\rightarrow[1\pi]$ (up to 104%, *L* and 102%, *V*) and $[2\sigma]\rightarrow[5\sigma]$ (66%, *L*, 64%, *V*). It should also be noted that the $[2\sigma]\rightarrow[3\sigma]$ transition is predicted to have significant intensity. In the experimental case this intensity may be spread over a broad energy range due to vibrational and correlation effects.

Table 4. Transition probability $|A_{if}|$ for O-*K* X-ray spectrum of the molecule CO (10^{-6} a.u.)

Final state	Frozen orbital One-centre *L*	*V*	Full moment *L*	*V*	Relaxed[a] Full moment *L*	*V*
[3σ]	0.894	0.902	1.257	1.099	1.343	1.464
[4σ]	6.602	6.343	7.778	7.006	9.409	8.260
[1π]	18.635	17.119	19.811	17.675	34.716	30.240
[5σ]	2.364	2.146	2.341	2.120	1.330	1.275
Total	28.50	26.51	31.19	27.90	46.80	41.24

[a] Electronic term only calculated with oxygen atom as origin. Nuclear moment terms must be included to determine intensity

In the O-*K* spectrum the total absolute transition probability increases by 50% in the length form and 48% in the velocity form (Table 4) with the inclusion of relaxation. Once again the major transition shows the most marked increase $-[1\sigma]\rightarrow[1\pi]$ up by 75% (L) and 71% (*V*). However, the $[1\sigma]\rightarrow[4\sigma]$ and $[1\sigma]\rightarrow[3\sigma]$ transitions are significant with absolute probability values which also increase with the inclusion of relaxation. An important finding however is that the $[1\sigma]\rightarrow[5\sigma]$ shows a decrease in value of 43% in the length form and 40% in the velocity form. Hence, as for the bondlength study, the transition involving the 5σ orbital displays the opposite trend towards electronic relaxation compared with the other transitions. In each case it is the transitions to outer valence hole states which are most affected by relaxation. It is concluded that orbital relaxation should be included in detailed model calculations of X-ray intensity values.

The importance of two-centre or 'crossover' transitions can be assessed by comparing values in columns 2 and 4 and in columns 3 and 5 in Tables 3 and 4. The interatomic terms, in general, make a more significant contribution to the transition processes in the C-*K* spectrum than in the O-*K* spectrum. In the C-*K* spectrum the one-centre contribution to the total transition probability is only 65% using the length form and 75% using the velocity form of the dipole operator. The interatomic terms have a significant influence on each of the separate transitions although this is not as apparent when only relative values are considered.

In the O-*K* spectrum the one-centre contribution to the total transition probability is higher (91% *L* and 95% *V*). There is a more significant contribution by the interatomic terms for the transitions to the inner valence hole states when compared with the dominant $[1\pi]$ line. For transitions involving the 3σ, 4σ and 1π orbitals inclusion of two-centre contributions increases the absolute transition probabilities. As previously, however, the 5σ orbital is the exception with the probability decreasing when the two-centre contribution is included.

This contrast between the two-centre contributions to the C-*K* and O-*K* spectra is evidence that the common practice of neglecting all but the one-centre terms is not always a valid approximation. The interatomic process makes a major contribution to the X-ray intensities observed in the C-*K* spectrum of CO. Since much of the recent XES research has been directed at carbon-containing molecules interatomic contributions should not be neglected in the spectral interpretation. Studies on other molecules will be discussed elsewhere.

The good agreement between the length and velocity forms of the dipole operator at the relaxed Hartree–Fock level provides a basis for confidence in the results. It is desirable to compute both dipole forms of the moment as an internal check on the reliability of the calculations.

5. Conclusions

Several factors related to the development of an acceptable model for the calculation of theoretical molecular X-ray emission spectra have been assessed in relation to the carbon and oxygen *K*-shell spectra of carbon monoxide. It has been shown that some of these factors do not affect all XES transitions in the same manner.

A Gaussian basis set $(9s, 5p)$ is considered to be adequate for XES calculations involving first row atoms. The sensitivity of some transition moments to bondlength variations typical of vibrational displacements indicates that the adiabatic approximation and in turn the Born-Oppenheimer approximation which separates nuclear and electronic motions need to be applied with some caution. Orbital relaxation between initial and final states was found to be very important, especially for the outer valence hole states. The commonly used one-centre, intra-atomic model was unsatisfactory especially when it is recognized that the addition of two-centre contributions can either decrease or increase the total probabilities depending upon the nature of the orbitals involved. Interatomic processes make a significant contribution to X-ray transitions involving an initial hole state on the carbon atom. The use of absolute rather than relative intensity data is a more suitable means of observing the effects of such factors. Absolute values also permit a direct comparison between the spectra from atoms and molecules and between XES spectra from an atom in different chemical environments. Further refinement of the study should include accounting for the nuclear moment term, for electronic correlation effects and nuclear geometry changes from the initial to the final hole state.

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