Core-hole Electronic Structure Studies on Molecules using Synchrotron Radiation*

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Abstract

Some recent developments in the study of core-hole photoabsorption, photoionisation, X-ray emission, Auger electron decay and photofragmentation processes for molecules are discussed. The emphasis is on the interpretation of experimental data obtained from synchrotron radiation studies. New insights which are being obtained through theoretical investigations into the electronic and nuclear properties of excited and ionised states of simple molecules are reviewed.

1. Introduction

Dedicated synchrotron radiation sources have been available for many years; however, only recently has there been major advances in photon energy resolution and photon flux levels. In the soft X-ray region resolution of the order $\Delta E \sim 50$ meV comparable with, or better than, the core-hole natural linewidth and vibrational spacings for a molecule can be achieved. Consequently, molecular features associated with X-ray induced core-hole excitation and subsequent de-excitation are being analysed in considerable detail, providing insight into molecular electronic and nuclear structure dynamics (Neeb *et al.* 1994; Eberhardt 1995).

The availability of high resolution soft X-ray radiation in the range 100–1000 eV enables researchers to probe the region around K-shell ionisation thresholds of first row atoms, L-shell thresholds for second row atoms and M-shell thresholds for third row atoms and the transition metals. Atoms from this region of the periodic table are important constituents of many molecules. Selective probing of site-specific atoms in different chemical environments through core-electron excitation to valence and to Rydberg states as well as to the continuum is possible through photoabsorption and associated photo-ion yield studies (Ma *et al.* 1991; Kosugi *et al.* 1992). Molecular spectral profiles are more complex than their atomic counterparts, principally because of vibrational effects and the possible influence of photodissociation. De-excitation spectra, X-ray and Auger electron, provide much information concerning the molecular electronic structure of excited and ionised states.

In this paper some recent developments in the study of core-hole photoabsorption, photoionisation, X-ray emission, Auger electron decay and fragmentation processes for molecules based upon synchrotron radiation studies will be reviewed with a particular focus on theoretical advances to elucidate electronic structure and nuclear dynamics.

2. Photoionisation and Core-hole Lifetimes

It is now possible to obtain vibrationally resolved core-hole photoelectron spectra for selected molecules from which an estimate of the core-hole inherent lifetime can be obtained by deconvolution of the experimental linewidth. Bozek *et al.* (1990, 1991) have endeavoured to characterise the effects of the chemical environment, vibrational splitting and ligand field splitting on photoelectron spectral profiles for selected silicon-containing and iodine-containing molecules and to deduce core-level lifetime widths. There can be ambiguities in the interpretation when the vibrational structure is complex and not adequately resolved (McColl and Larkins 1992).
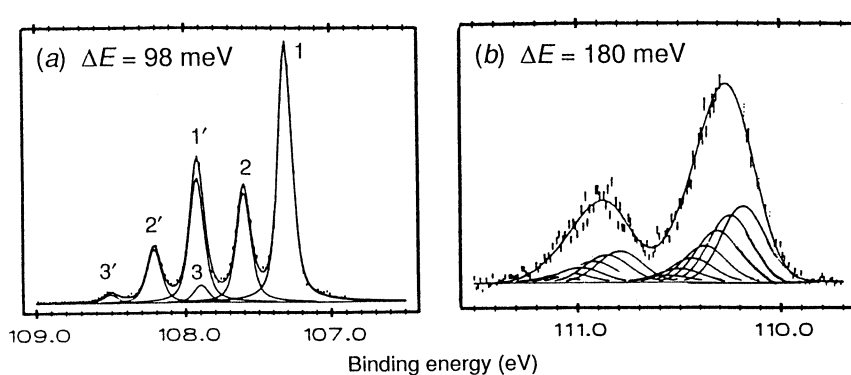

Fig. 1. Silicon 2p levels photoelectron spectra: (*a*) silane, SiH_4, vibrationally resolved; (*b*) tetrachloro silane, $SiCl_4$, vibrationally unresolved. [After Bozek *et al.* (1991).]

The Si 2p photoline for the SiH_4 molecule was vibrationally resolved with a total linewidth of 95 meV (Bozek *et al.* 1990). From this spectrum, shown in Fig. 1*a*, the Si 2p inherent linewidth ΔE was estimated to be 32 meV by assuming that only the Si–H stretching modes were populated to any extent during the core ionisation process. The calculated value based upon the total Auger rate Γ_A, using the relationship $\Delta E \approx \hbar\Gamma_A$, was 33 meV (McColl and Larkins 1992). However, for other silicon-containing molecules the reported experimental inherent linewidths were significantly larger than the predicted values. For example, the calculated Si 2p value for the $SiCl_4$ molecule was 32 meV compared with an experimental value of 119 meV (see Fig. 1*b*). The experimental overestimate was due to line-broadening contributions from a more complex vibrational structure than that assumed in the spectral analysis by the researchers. It has proved very difficult to obtain core-hole lifetimes for molecules from photoelectron spectra, except for the simplest molecules, since adequate resolution of overlapping vibrational modes has not been achieved.

Theoretical studies require a knowledge of the absolute Auger rate and in cases where the branching ratio is not dominated by the non-radiative de-excitation, the X-ray emission rate. In practice, in the soft X-ray region the core-hole inherent lifetime is dominated by the Auger rate. Absolute total Auger rates may be calculated using a direct method (Larkins 1990a) or by using a statistical model based upon knowledge of the Mulliken atomic orbital populations in the molecule (Walsh et $al.$ 1994a, 1994b). It is essential to take account of core-hole screening (Coville and Thomas 1991; Larkins 1994a). These approaches depend upon a knowledge of atomic Auger subshell rates. It may not always be adequate to use rates based upon Hartree–Fock or Dirac–Fock calculations. When dealing with low kinetic energy electrons a multi-configurational Hartree–Fock approach may be required to adequately account for correlation effects. This would appear to be the case for iodine-containing molecules (Larkins 1994b).

Some examples of core-hole lifetimes for selected carbon-containing molecules demonstrating the influence of chemical environment are shown in Table 1. The values are based upon a direct evaluation of the individual rates using INDO wavefunctions (Larkins 1990a) and the equivalent cores model. For the hydrocarbon series the C 1s inherent linewidths were insensitive to the chemical environment being in the range 98–104 meV. However, for molecules containing oxygen atoms the linewidth decreases as the electron withdrawing power of the substituents increases. The C 1s linewidth for the CO_2 molecule was reduced to 72 meV.

Table 1. Carbon core-hole inherent linewidths based upon Auger rate calculations

Molecule	Linewidth (meV)	Molecule	Linewidth (meV)
CH_4	104	CH_3OH	97
C_2H_6	102	$C^*H_3CH_2OH$	95
C_2H_4	102	$CH_3CH_2^*OH$	88
C_2H_2	98	CO	79
		CO_2	72

These results for the hydrocarbons would appear to be consistent with experimental photoabsorption observations (Ma et $al.$ 1989, 1991). The values shown in Table 1 are larger than those reported previously by Coville and Thomas (1991) because the atomic radial integrals from Chen et $al.$ (1990) have been used rather than the values by Walters and Bhalla (1971). Most inherent lifetime widths have been deduced from photoabsorption studies. Based on the limited evidence available, it is concluded that the theoretical values are in general good predictors of the true lifetime widths.

The importance of core-hole screening on lifetime widths is illustrated by the calculations for the N_2O molecule presented using ground state and core-hole, [c], wavefunctions (Table 2). A statistical model (Walsh et $al.$ 1994b) with ab $initio$ wavefunctions optimised for the various states (Meehan et $al.$ 1995) has been used. The increase in linewidth as a consequence of screening the core-hole is substantial ranging from 21% for the O atom to 63% for the central nitrogen (N_C) atom. There are clear differences for the central and terminal nitrogen atoms. A comparison of the inherent linewidths for the core-ionised state

Table 2.   Theoretical core-hole linewidths (meV) for excited and ionised states of the N_2O molecule

Initial state	N_T	N_C	O
Ground state	95[A]	65	152
[c]	132	106	184
[c] 3π	153	118	193
[c] 8σ	147	121	202

[A] Based on the formula ΔE (linewidth) $= \hbar\Gamma$ (Auger rate).

with the core-excited state reveals that the widths have increased for the resonant states ranging from 5 to 16%. Such changes may not be discernible in the analysis of most spectral profiles.

3. Photoabsorption and Resonant Excitation

By using variable photon energy high resolution photoabsorption, spectra for small molecules involving core-to-valence and core-to-Rydberg excitations may be studied. An understanding of the origin of such spectra can be a precursor to the interpretation of radiative and non-radiative de-excitation spectra and photofragmentation data.

Some recent examples are the work of Ma *et al.* (1991) (CO, CO_2, C_2H_2, C_2H_4, C_2H_6, NO, N_2O), Neeb *et al.* (1994) (O_2, N_2, CO), Schirmer *et al.* (1993) (H_2O, NH_3, CH_4) and Kosugi *et al.* (1992) (NO). Core excitation to valence and Rydberg states leads to vibrational excitation and in some cases geometry changes. However, for a range of simple molecules the fundamental features of Rydberg-state spectra are very similar.
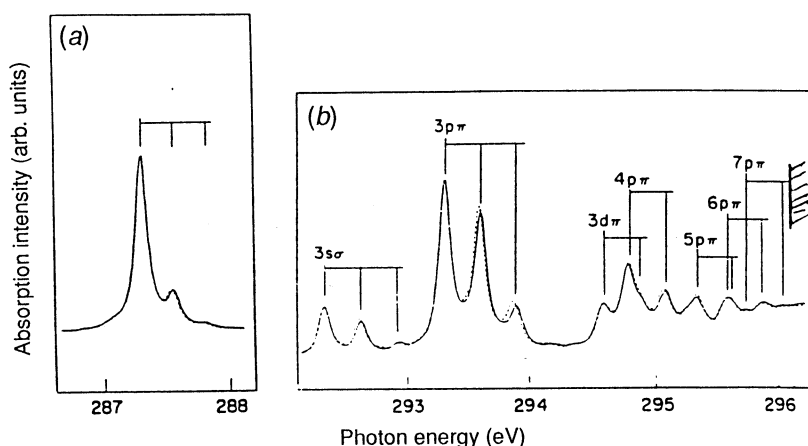

Fig. 2.   Photoabsorption spectra near the carbon K edge for $^{12}C^{16}O$ (solid curve) and $^{13}C^{18}O$ (dashed curve): (*a*) C $1\sigma \rightarrow 2\pi^*$; (*b*) C $1\sigma \rightarrow$ Rydberg state. [After Ma *et al.* (1991).]

The carbon K-shell photoabsorption spectra for $C^{12}O^{16}$ and $C^{13}O^{18}$ reported by Ma *et al.* (1991) are shown in Fig. 2. The two regions correspond to C 1s excitation (2σ orbital) to the antibonding $2\pi^*$ orbital and to the Rydberg states

below the ionisation threshold of 209·08 eV. Neeb *et al.* (1994) have analysed the $2\sigma \rightarrow 2\pi^*$ X-ray absorption peak including lifetime-vibrational interference effects and concluded that the lifetime width for the $2\sigma^{-1}2\pi^*$ state is 80 meV. Shaw *et al.* (1984) concluded that the value is 85 meV based upon electron energy loss studies. These values for the resonant states are very close to the values predicted for the ion state (79 meV Table 1). Our N_2O study (Table 2) supports the conclusion that there may not be a significant difference between the lifetime width for the resonant and the core-ionised states.

The detailed assignment of the Rydberg states identified in the photoabsorption spectra may require *ab initio* open-shell quantum mechanical calculations. Kosugi *et al.* (1992) analysed the NO ion yield and electron yield spectra following photoabsorption and were able to explain satisfactorily the principal features. Core-to-valence transitions were modelled by CI calculations using open-shell SCF orbitals, while for the core-to-Rydberg transitions a frozen ion-core approximation was used with Rydberg functions (Kaufmann *et al.* 1985, 1989) augmenting the basis set. This approach has recently been used to explain the photoabsorption spectrum of methane (Ueda, personal communication 1995). It is applicable to the interpretation of other small molecule systems where there is not a complex vibrational sub-structure accompanied by large geometry changes. When present these effects may result in energy shifts and to significant changes in peak shapes (Cederbaum and Tarantelli 1993). The manner in which the basis set is augmented by diffuse functions and the sophistication of the CI calculations are critical factors in the quality of the results obtained.

4. X-ray Emission Spectra

Synchrotron radiation-based studies of X-ray emission from gas phase molecules to date have been very limited (Flores-Riveros *et al.* 1985; Southworth *et al.* 1991) because of low branching ratios for radiative de-excitation pathways. For molecules containing first row atoms only condensed phase studies have been possible at variable photon energies (Wassdahl *et al.* 1990). There is experimental evidence, principally from a study of the solid CO_2 system, that the X-ray emission spectra profile may be a rich source of information on molecular excited states. The X-ray de-excitation spectra appear to show a greater sensitivity to excitation energy than the corresponding Auger electron spectra. With the introduction of third-generation synchrotron sources the prospects for the systematic study of X-ray emission phenomena from small molecules should gain renewed emphasis. Many of the deficiencies apparent in the present electron impact induced studies should be overcome.

There has been an amount of theoretical work directed at the interpretation of electron-induced molecular X-ray spectra (Ågren *et al.* 1984; Larkins 1990*b*). There have been very few studies for resonantly excited molecules (Flores-Reviros *et al.* 1985; Larkins 1994*b*). One example is the study of the X-ray emission spectra associated with core-ionised and core-excited atoms in the N_2O molecule using an *ab initio* molecular orbital approach (Meehan *et al.* 1995; Meehan and Larkins 1995). The emission is sensitive to chemical environment and to excitation energy. The emission spectra predicted to result from excitation of
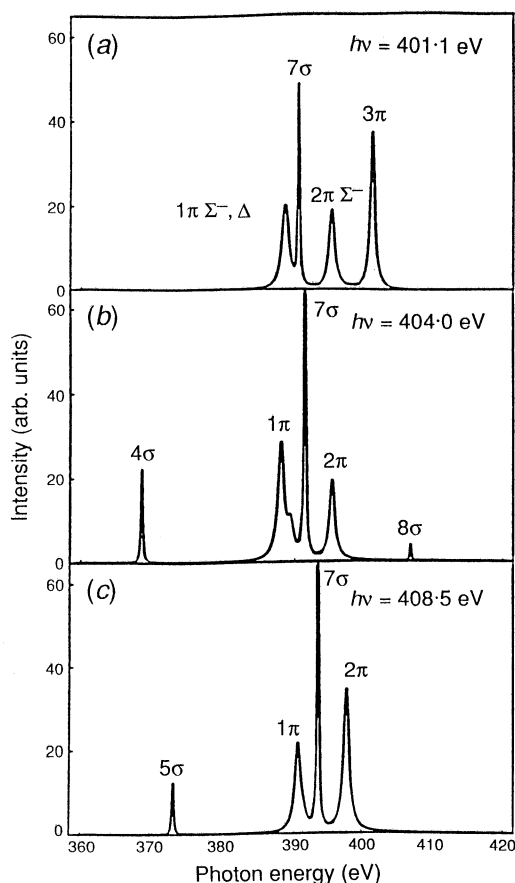
Fig. 3. Nitrogen K X-ray emission spectra associated with the terminal nitrogen atom N_T of the N_2O molecule: (a) N_T $3\sigma \rightarrow 3\pi$; (b) N_T $3\sigma \rightarrow 8\sigma$; and (c) N_T $3\sigma \rightarrow \epsilon\phi$. [After Meehan and Larkins (1995).]

a core electron on the terminal nitrogen (3σ orbital) to the 3π and 8σ valence orbitals as well as to the continuum are shown in Fig. 3. These spectra are calculated at the ground state geometry for the N_2O molecule. Over a relatively narrow energy range (401–410 eV) there is a very significant change in the emission spectrum corresponding to variations in the valence electron density distribution. Furthermore, it has been shown that these spectra may be quite sensitive to changes in geometry. The optimised geometry for the various initial states associated with a 3σ core hole are calculated to be as follows:

Ground state:

$$N_T \underset{}{\overset{2.183}{\rule{2cm}{0.4pt}}} N_C \underset{}{\overset{2.239}{\rule{2cm}{0.4pt}}} 0$$

$N_2O^+[3\sigma]$:

$$N_T^+ \underset{}{\overset{2.064}{\rule{2cm}{0.4pt}}} N_C \underset{}{\overset{2.050}{\rule{2cm}{0.4pt}}} 0$$

$N_2O[3\sigma](3\pi)$:

$$N_T^* \xrightarrow{\;2.193\;} N_C \xrightarrow{\;2.227\;} 0$$

$N_2O[3\sigma](8\sigma)$:

$$N_T^* \xrightarrow{\;2.031\;} N_C \xrightarrow{\;3.522\;} 0$$

A substantial destabilisation of the N_2O molecule is predicted to occur only for the $[3\sigma](8\sigma)$ excited state. The behaviour is different when the central nitrogen or terminal oxygen is excited (Meehan and Larkins 1995).

It is expected that X-ray emission spectra induced using a variable photon source will provide valuable information on the electronic, vibrational and nuclear structure of resonantly excited molecules. Spectral interpretation is likely to be more straightforward than the corresponding molecular Auger spectrum.

5. Auger Electron Spectra

Molecular Auger spectra are very complex for most molecules because of the large number of overlapping transitions associated with the two-hole final states which are possible. Nevertheless, considerable progress has been made in the interpretation of such spectra using a range of theoretical methods. Tarantelli and coworkers (see Tarantelli *et al.* 1992, 1993, 1994) have developed a two-particle Green's function algebraic diagrammatic construction formalism which has proved effective to directly calculate the energies of the final dicationic states. The approach is less rigorous for the calculation of Auger intensities and band shapes; however, the formalism developed has enabled very useful insights to be gained into spectral profiles. Relative intensities and the overall shape of the spectra are essentially determined by a statistical approach using the density of the final states and their local two-hole pole strength population. The consequences of geometry changes and vibrational effects are also included in an elegant and straightforward way (Cederbaum and Tarantelli 1993). The approach assumes that the singlet–triplet height ratio is $3:1$. Absolute total Auger rates are not obtained, hence it is not possible to obtain estimates of core-hole lifetimes. The method, while successful and very informative for many systems, does overlook some of the more detailed features of molecular Auger spectra which are not currently revealed in the broad experimental spectral profiles. Future high resolution coincidence studies at variable photon energies should provide such detail for selected small molecules.

Calculations using alternative approaches to obtain Auger intensities directly demonstrate that the assumption of a singlet–triplet height ratio of $3:1$ may not be valid (Larkins *et al.* 1993). Furthermore, Auger transition rates involving s and p electrons can be very different. For example, for atomic silicon the relative transition rates per transition for L_{23}–M_1M_1, L_{23}–M_1M_{23} and L_{23}–$M_{23}M_{23}$ transitions are not equal but are in the ratio $19:43:100$. For K–LL transitions, relative rates per transition display the reverse trend. For example, for the fluorine atom, $L_1L_1 : L_1L_{23} : L_{23}L_{23}$ transitions are in the ratio $100:25:45$. Relative intensities estimated on the basis of local two-hole pole strength populations

do not consider the differences in the atomic orbital character from ss to pp populations.

An alternative approach developed by our group (Larkins 1990a) has proved to be useful in gaining an overview of complex molecular Auger spectra, but it is deficient when valence electron correlation effects are strong.

The relative double-hole valence state energies for each two-hole multiplet (the two-particle states) are calculated using a single set of wavefunctions obtained from a calculation for the ground state of the molecule. In this respect, our approach and the basis of the energy calculations with the ADC method (Tarantelli *et al.* 1992) are consistent. We have usually used semi-empirical wavefunctions, but an *ab initio* approach is possible. The absolute Auger rates are calculated on the basis of a one-centre orbital-based model (Siegbahn *et al.* 1975) using wavefunctions appropriate for the initial screened core-hole state. There is therefore a fundamental difference to the calculation of the relative intensities required to construct the Auger-electron spectral profile between the approach of Tarantelli *et al.*, who use exclusively final state wavefunctions, and our approach, using initial state wavefunctions. We have modelled the molecular Auger process in two stages: inter-atomic electron rearrangement in the initial state (core-hole screening) followed by an intra-atomic Auger decay driven by the electron population associated with the screened initial state. Electron rearrangement in the presence of the two valence hole final state is considered to be less significant in influencing the c-vv Auger state.

Comparison of calculated and experimental inherent photo-linewidths in our work has led to the conclusion that an intra-atomic model is adequate provided the core-hole polarisation of the valence electrons is taken into account. The equivalent-cores model is a good first approximation to represent the hole screening effect.

When electron correlation effects are important the description provided by the approach outlined above for the energies of the final two-hole states is inadequate. Tarantelli *et al.* (1992) have shown that it is important to include configuration mixing with the excited 'shake-up type' states (i.e. mixing 2h states with 3h–1p states). This can be achieved through a configuration interaction or MCSCF approach, but computationally the task is more difficult than using the ADC approach. When correlated wavefunctions are necessary a redistribution of Auger intensity is to be expected without, in most cases, a significant change in the total transition probability.

More generally, when Auger spectra involving strongly correlated states are recorded at variable incident photon energies the intensity of correlation satellites may vary. To adequately model such effects initial and final state correlation wavefunctions will be required (Larkins *et al.* 1994). Green's function methods with a focus on final states and pole strengths cannot address such problems. More direct MC SCF procedures will need to be applied.

The approach we have used enables us to establish when electron correlation effects, which in a one-particle picture lead to satellites in the spectrum, are important. An example is the silicon 2p Auger spectrum for the SiF_4 molecule (Larkins *et al.* 1994). A comparison of the calculated and experimental Si L_{23}-VV Auger spectra is shown in Fig. 4. The presence of correlation satellites in the experimental spectrum is clearly evident. These may arise from both initial
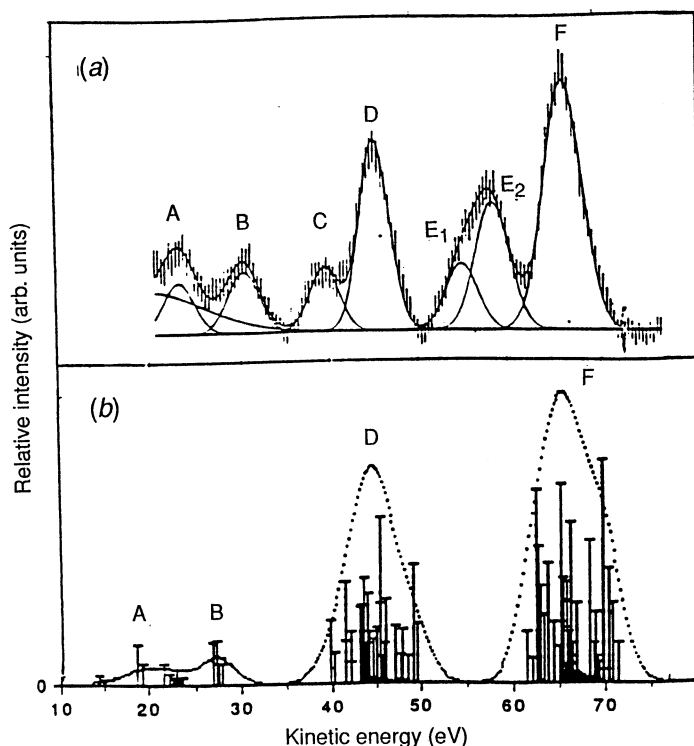
Fig. 4. Silicon L_{23}-VV Auger spectrum for the SiF_4 molecule: (a) experimental; (b) theoretical. [After Larkins *et al.* (1993).]

state and final state correlation contributions and vary in intensity with photon excitation energy.

Experimental studies undertaken to date on resonant spectator Auger processes surprisingly appear to indicate that the spectra are not very sensitive to the chemical environment or photon excitation energy. The oxygen autoionisation spectra for CO, CO_2 and OCS provide examples of the insensitivity to chemical environment (Carroll and Thomas 1989), possibly due to dissociative effects prior to de-excitation. The carbon Auger spectra of CO measured at photon energies near that required for double excitation (301 eV) provide an example of the insensitivity to excitation energy (Schmidtbauer *et al.* 1993). A further example is the Auger spectrum of CH_4 measured in the photon energy range 287–291 eV (Ueda *et al.* 1995). Such results are surprising and contrast with those expected for X-ray emission (Meehan *et al.* 1995). It is reasonable to expect that detailed electronic and vibrational structure changes do occur for the resonantly excited molecules, but the special features may be masked in the broad Auger spectral profiles due to the many overlapping final electronic states, to vibrational effects and to possible geometry changes.

Recently, a detailed study of the participator Auger spectra associated with the decay of the $1\sigma_u^{-1} 1\pi_g^3$ state of O_2 excited using energies in the narrow range 529·8 to 531·4eV has been reported (Neeb *et al.* 1994). It has been

elegantly demonstrated that the spectral profile is very sensitive to photon energy in this narrow energy range (Fig. 5). Interpretation of these spectra has required the application of lifetime-vibrational interference theory with an allowance for geometry changes and for different vibrational populations in the intermediate and final states. Potential energy curves of high quality need to be calculated for the various electronic states involved and then coupled with a suitable vibrational analysis. Eberhardt (1995) has also shown that the spectator Auger spectrum for oxygen is very sensitive to photon excitation energy. Detailed theoretical studies in this area are warranted.
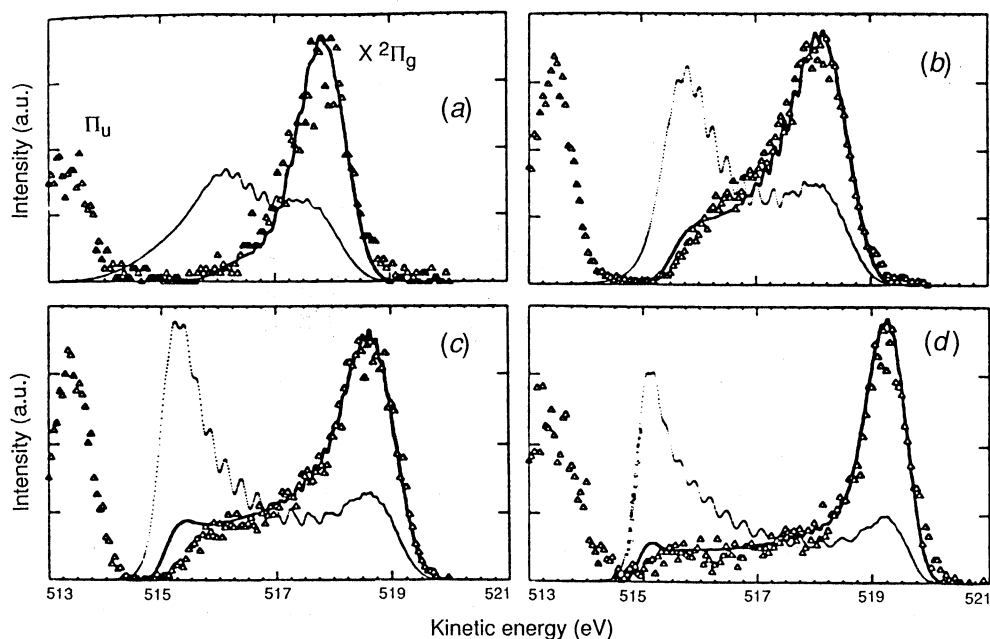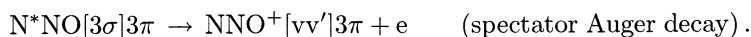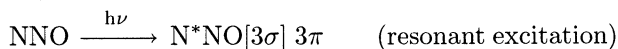

Fig. 5. Oxygen K participator Auger electron spectrum associated with the decay of the $[1\sigma_u]\,1\pi g$ state of the O_2 molecule. The excitation energies are (a) 529·8, (b) 530·4, (c) 531·0 and (d) 531·4 eV respectively. Experiment, triangles; theory with lifetime-vibrational interference effects, solid curves; without effects, dotted curves. [After Neeb *et al.* (1994).]

6. Photofragmentation Studies

The decay of a core-ionised molecule via radiative and non-radiative de-excitation or direct photoionisation processes can lead to multiply charged ions which may fragment into several components. Sophisticated multi-coincidence techniques pioneered by Eland *et al.* (1986) and Frasinsky *et al.* (1986) can be used to study the molecular fragmentation dynamics whereby the photon-induced emitted electron (PE) and the molecular ion fragments (PI) are measured in coincidence (CO), known as PEPIPICO. With present state-of-the-art electronics and the pulse characteristics of synchrotron radiation multiple coincidences of several particles (electrons, photons, ions) can be detected. Information concerning the

branching ratio between all the dissociation channels, the kinetic energy released with the fragments, the angular distribution of the fragments and the bond breaking sequence can be studied.

The N_2O molecule provides an interesting example of a PEPIPICO study. Morin *et al.* (1993) studied the dissociation dynamics following photon excitation corresponding to $N_T1s \to 3\pi$ (401 eV), $N_C1s \to 3\pi$ (405 eV), and core ionisation at 430 eV. Evidence is provided in the fragmentation patterns for dissociation to all possible single–single and single–double ion pair combinations (e.g. N_C^+/N_T^+, N_C^{2+}/O^+). It may have been expected that the resonant de-excitation would have produced only a singly charged final ion state, i.e.

$$NNO \xrightarrow{h\nu} N^*NO[3\sigma]\ 3\pi \qquad \text{(resonant excitation)}$$

$$N^*NO[3\sigma]3\pi \to NNO^+[vv']3\pi + e \qquad \text{(spectator Auger decay)}.$$

It has become apparent that valence Auger cascade processes (Becker *et al.* 1989; Armen and Larkins 1992) for atoms and molecules yield low kinetic energy electrons and multiply charged ions. Hence, further decay processes such as

$$NNO^+[vv']3\pi \to NNO^{2+}[vv''] + e \qquad \text{(valence Auger decay)}$$
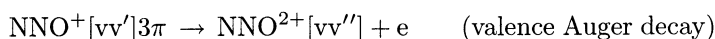
are possible. It was concluded by Morin *et al.* (1993) that the dissociation of core-excited N_2O should be explained by an impulse rather than a Coulomb-explosion model.

Murphy and Eberhardt (1988) studied the fragmentation of the N_2O molecule following O 1s ionisation and subsequent Auger decay. Coincidence data triggered by detecting specific Auger electron energies revealed that the distribution of ion fragments depended upon the different final double hole states created. A similar study by LeBrun *et al.* (1993) reported the fragmentation of N_2O following selective core excitation of the nitrogen atoms using the PEPIPICO technique. In this way an understanding of the potential energy curves and dissociation pathways for specific state doubly charged molecules can be obtained. The calculation of potential energy curves and a knowledge of the dominant de-excitation channels can be essential to assist the experimental interpretation.

7. Symmetry-resolved Studies

By using linearly polarised light the polarisation dependence of various decay channels after photoabsorption can be examined. For example, Kosugi *et al.* (1992) reported the symmetry-resolved ion yield spectra for the NO molecule following excitation near the nitrogen K edge. It is possible to distinguish between the consequences of $\sigma \to \pi(\Delta\Lambda = \pm 1)$ and $\sigma \to \sigma(\Delta\Lambda = 0)$ excitations from measurement of the angular distribution of the ion fragments produced. This technique is most valuable in determining orbital symmetry for molecules.

Angular resolved X-ray emission spectra, produced using the same principle, have been used to establish the symmetry of orbitals in the CF_3Cl molecule (Southworth *et al.* 1991). Examples of spectra obtained at emission angles parallel ($\theta = 0°$) and perpendicular ($\theta = 90°$) to the plane of polarisation of the radiation are shown in Fig. 6. The results obtained to date have been adequately explained
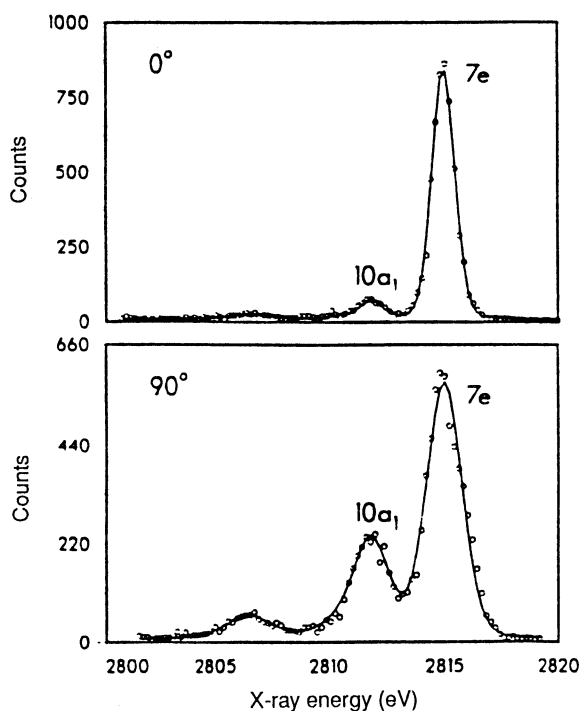
Fig. 6. Parallel-polarised Cl K-valence X-ray emission spectra from the CF_3Cl molecule recorded at emission angles $0°$ and $90°$ following $1a_1 \rightarrow 11a_1$ excitation. [After Southworth *et al.* (1991).]

using a classical model; however, for many molecules a quantum mechanical approach to the interpretation will be required.

8. Conclusion

Synchrotron radiation studies are proving to be a rich source of data regarding the electronic and nuclear properties of excited and ionised molecules. High quality *ab initio* calculations using correlated wavefunctions are required to interpret many of the features observed in high resolution.

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