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Core Excitation and Ionization of Molecules

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Abstract

A progress report is given on recent experimental studies of core excitation and inoization of free-molecules in the VUV and soft X-ray (50 to 2600 eV) by electron impact and X-ray photoabsorption (XAS) techniques. The current capabilities of inner shell electron energy loss spectroscopy (ISEELS) and XAS for gas phase studies are compared, with focus on: dipole versus non-dipole excitations, electric dipole oscillator strength determination, and bond length correlations. Recent studies of ionic fragmentation of molecules induced by tuned X-rays are discussed with regard to the possibility of site-selective fragmentation via core excited state. Using organometallic compounds as an intermediate, connections are made between the core excitation spectra of free molecules and those of surface absorbed molecules, as measured by near-edge X-ray absorption fine structure (NEXAFS) or reflection near-edge energy-loss fine structure (NEELFS) spectroscopies.

1. Introduction

Inner-shell excitation and ionization spectroscopies in the vacuum ultraviolet and soft X-ray are increasingly of interest for fundamental and applied studies of a wide range of materials. These applications frequently require studies of well-defined systems in order to assist spectral interpretation. Core spectroscopies of free molecules offer a nearly ideal testbed for such "calibration" studies: a very wide range of environments can be accessed; the electronic and geometric structure is either known or can be accurately calculated; the dynamics of core state creation, evolution and decay can be studied without the complications of multi-step, multi-site events that frequently complicate yield processes in solids. In this article I summarise recent core excitation studies of free molecules and the connections between such work and related condensed matter studies, principally surface chemisorption. Core hole creation events as probed by inner-shell electron energy loss spectroscopy (ISEELS) is emphasized and the relationship of ISEELS with X-ray absorption is discussed. Connections are also made between core excitation and various ion and electron spectroscopies used to characterise the decay of core states. Finally I describe the very exciting recent development of reflection EELS for core excitation of surface adsorbed molecules.

Studies of molecular core excitation and ionisation by X-rays have been reviewed by Koch and Sonntag [1] and, in wider context, by Brown [2]. More recently, Nenner and coworkers [3, 4] have described the wide range of synchrotron experiments which have been developed for optical studies of the dynamics of the ionic and electronic decay of core states of molecules. Core excitation by electron impact has been reviewed by Read [5], Brion [6, 7] and Hitchcock [8]. The latter three papers also describe (e, 2e) and (e, e + ion) coincidence spectroscopies and provide a probe of some aspects of the core state decay. A regularly updated bibliography of gas phase atomic and molecular core excitation studies [9] is available from the author.

2. Electron energy loss and X-ray absorption: A comparison

Inner shell electron energy loss spectroscopy (ISEELS) of gases has been carried out for about fifteen years. It complements X-ray absorption spectroscopy (XAS) for studies of electric-dipole inner-shell excitation, and in addition, has unique capabilities for studying electric-dipole-forbidden transitions which are inaccessible by optical techniques. The recent surge of interest in near-edge X-ray absorption fine structure (NEXAFS) core excitation spectroscopy of surface adsorbed molecules [10] has led to considerable interest in ISEELS of molecules as a guide to the assignment of NEXAFS spectra.

Fig. 1 shows a comparison on a term value scale (TV =IP - E, IP = ionization potential) of the K-shell spectrumof neon [11] with the N 1s spectra of NH₃ [12], N₂H₄ [13] and N_{2} [14], all recorded with dipole regime ISEELS and converted to an absolute oscillator strength scale. The X-ray absorption spectra of Ne [15] and N₂ [16] have also been recorded with essentially the same results. This figure illustrates many important features of molecular core excitation. As with other electronic spectroscopies, the majority of spectral features can be understood to arise from one electron promotions, i.e., transitions form the ground state to final states which can be described in terms of a single configurational wavefunction. Two electron processs (double excitation or simultaneous excitation and ionization) also contribute weakly, typically in the first 20 eV of the core ionization) also contribute weakly, typically in the first 20 eV of the core ionization continuum. Examples of these are the $(\underline{1s}, \underline{\pi}, \pi^{*2})$ states around 415 eV in N₂. The one-electron excitations can be divided into two classes: those with compact valence or those with more extended Rydberg final states. In contrast to valence electronic spectroscopy where many of the excited states are believed to have a large Rydberg character [17], core excitations often have strong valence-type character i.e., at the ground state internuclear separation the molecular orbital to which the core electron is excited has a small radial extent and is constructed from atomic orbitals of the same principle quantum shell as that of the occupied valence molecular orbitals (MOs). Thus, although the (1s, np) Rydberg states dominate the Ne 1s and NH₃ spectra, and weak $1s \rightarrow Rydberg$ transitions can be discerned in the spectra of N_2H_4 and N_2 , the valence-type σ^* (N-N) feature is very strong in the N 1s spectrum of N_2H_4 while the π^* and σ^* (N \equiv N) valence-type resonances dominate the N 1s spectrum of N₂. In general valence-type coreexcited states are more intense while Rydberg-type coreexcited states are weaker in larger molecules. Molecular size is a factor since the spatially extended Rydberg orbitals have limited overlap with the compact core orbitals. Coulomb, centrifugal or exchange barriers in the molecular potential



Fig. 1. Comparison on a term value scale of the *K*-shell spectrum of Ne with the N 1s spectra of NH₃, N₂H₄ and N₂, all recorded with dipole regime ISEELS and converted to an absolute oscillator strength scale. The NH₃ spectrum was digitized from the literature [12], all others were recorded at McMaster. The absolute energy scales are given along the top axes. Note that the N₂ spectrum is shifted relative to the absolute energy scale but is correctly plotted on the term value scale. The hatched regions indicate the expected shape of the σ^*_{NN} resonances while the dash-dot lines sketch the expected direct ionization continuum shape.

[18, 19] further diminish the intensity of transitions to Rydberg states and enhance those to valence-type coreexcited states by excluding spatially extended orbitals and localising compact orbitals. The dominant valence-type core excitation features can be discussed in terms of short-lived states, within a static molecular orbital model [20], or as resonances [21], a description emphasizing the photoionization dynamics. The latter picture is best suited to descriptions of core ionization continuum features, typically σ^* shape resonances. The former model gives a more intuitive description of discrete core excitations (i.e., features below the core *IP*), although the scattering description is also applicable since the discrete features are resonances in the underlying valence continuum.

Figure 2 presents a schematic of the inner-shell electron energy loss spectrometer (ISEELS) at McMaster that is used for survey studies of core excitation in gas phase molecules. This spectrometer uses fast incident electrons (> 2500 eV impact energy), small scattering angles (2°), and an unmonochromated electron beam which limits the resolution to 0.6 eV. Even so, the resolution of this instrument competes favourably with that of many current synchrotron radiation soft X-ray monochromators. A distinct advantage of electron



Fig. 2. Schematic of the McMaster inner-shell electron energy loss spectrometer (ISEELS). It is operated with 2° scattering angle and an electron kinetic energy after inelastic scattering of 2500 eV. The instrumental resolution is typically 0.6 eV FWHM.

impact over optical spectroscopy in the area of core excitation is that the resolution is constant over all energy losses when deceleration is used. The high resolution ISEEL spectrometer at the University of British Columbia (UBC) [22] employs a monochromated incident electron beam and routinely achieves better than 65 meV FWHM instrumental resolution for any core excitation below 1000 eV. By way of comparison, most grazing incidence soft X-ray monochromators are limited to 0.6 eV resolution at the C 1s (300 eV) and only 1.5 eV at the 0 1s (540 eV) edge. However the resolution advantage, that until recently has been enjoyed by ISEELS, will soon swing in favour of photoabsorption since extremely high resolution in the soft X-ray (< 50 meV) is now available with the development of DRAGON type monochromators using spherical optical elements [23]. High resolution is always of interest in all spectroscopies in order to distinguish closely spaced spectral features. However the intrinsically short lifetimes of core hole states limit the intrinsic linewidths to 50 meV or greater for core states above 100 eV. Thus state-of-the-arts ISEELS and XAS instruments are now capable of recording all potentially-resolvable core excitation features.

The first high resolution (< 0.1 eV FWHM) core excitation studies of molecules were carried out by ISEELS in the mid-1970's by King, Read and Tronc [24] at Manchester University, shortly followed by work at UBC [14, 25]. Recent high resolution ISEELS work includes studies of SO₂ [26], the vinyl halides [27, 28], MF_6 , (M = Te, Se) [29], ClF₃ [30] and Ni(CO)₄ [31] (see [9] for an up-to-date bibliography of molecular core excitation). As an example of the capabilities of high resolution ISEELS, Fig. 3 presents spectra of the (N 1s, π^*) ¹ Π and ³ Π states of N₂ recorded with 90 meV FWHM instrumental resolution 0° scattering angle and variable impact energy [32]. With impact energies above 1 keV and forward scattering the core loss spectra are dominated by spin-conserving, electric-dipole transitions. When the impact energy is reduced to values only fractionally larger than the threshold (typically less than 1.3 times the minimum energy needed to create the core state), exchange between the incident and target electron can occur, leading to excitation of spin-exchange transitions. King and coworkers have used low impact energies to study spin forbidden transitions in a number of molecules [32-34]. Such studies have shown that detectable (> 0.1 eV) singlet-triplet splittings are observed



Fig. 3. High resolution ISEELS (65 meV) of the $X^{\dagger}\Sigma^{+} \rightarrow {}^{\dagger}\Pi$, ${}^{3}\Pi$ (N1s, π^{*}) transitions in N₂ recorded with impact energies of 1300, 600, 500 and 460 eV (from Shaw *et al.* [32]).

only in core excitations to orbitals with an appreciable valence character. Not surprisingly, good spatial overlap of the core hole and the excited electron is needed to produce a sizeable exchange contribution to the state energy. This can be used to distinguish valence from Rydberg final states as was done in a study of COS and CS₂ by Harrison and King [34] in which features in the C 1s spectra previously assigned as Rydbergs [35] could be identified as having a sizeable singlet-triplet splitting and thus appreciable σ^* (C–S) valence character.

A further advantage of electron impact spectroscopy relative to X-ray photoabsorption is the capability of identifying non-electric dipole transitions via variable angle studies. The selection rules for inelastic electron scattering at high impact energy can be discussed in terms of a momentum transfer dependent, generalized oscillator strength (GOS, df(K)/dE for continuum states) which is related to the measured differential cross-section ($d\sigma/d\Omega$) by:

$$df(K)/dE = (E/2(k_0/k_1)K^2(d\sigma/d\Omega))$$

where E is the electronic transition energy, and k_0 , k_1 and K are the incident, scattered and transferred momenta. In the Bethe-Born approximation df(K)/dE can be expressed as a series expansion in the momentum transfer [36]:

$$df(K)/dE = df_0/dE + A \cdot K^2 + B \cdot K^4 + \cdots$$

where df_0/dE is the (continuum) optical oscillator strength (OOS) containing the electric dipole matrix element, A contains both quadrupole and monopole-octupole matrix ele-

ments, B contains higher order electric multipole terms, etc. This expression indicates that the GOS converges to the OOS in the limit of zero momentum transfer. The contributions of non-dipole excitations increase with increasing momentum transfer which occurs with larger scattering angle or lower impact energy. The momentum transfer under typical dipoledominated ISEELS conditions $(1-3 \text{ keV}, 0 < \theta < 2^\circ)$ is actually quite significant, amounting to 1.8 Å^{-1} at 300 eV(C 1s), 2.2 Å⁻¹ at 410 eV (N 1s) and 2.8 Å⁻¹ at 540 eV (O 1s) for 2.5 keV final electron energy and 2° scattering angle. At these K-values the A terms containing the quadrupole matrix element is given a greater weight than the dipole term (df_0) dE) in the Bethe-Born expansion of the GOS. Even so numerous direct comparison with optical studies indicate that the dipole contribution still dominates and that the relative intensities of the spectral features in dipole-regime electron energy loss and photoabsorption spectra are very similar. Electric dipole transitions still dominate ISEELS even at relatively large K values because of the very small spatial extent of the core orbitals. Due to the influence of the r^n -weighting on wavefunction overlap, the r^1 -weighted dipole $(\langle 1s|er|V^*\rangle)$ transition moment is much larger in general than the r²-weighted quadrupole ($\langle 1s|er^2|V^*\rangle$) transition moment [5] (V^* is the virtual valence orbital to which the core electron is excited). df_0/dE is expected to dominate the GOS up to $K \approx 1/R_c$, where R_c is the average radius of the core wavefunction [37]. Thus for example, non-dipole transitions in O 1s excitation are expected to be negligible until $K > 10 \,\text{\AA}^{-1}$.

Notwithstanding the above, there are a few cases where non-dipole core-excitations in ISEELS have been identified by angular studies or by comparison to optical spectra [38]. A dramatic example occurs in PCl₃ (Fig. 4) [39]. The $X^{1}A_{1} \rightarrow {}^{1}A_{2} \{ P2p_{3/2}(e), \sigma^{*}(P - Cl)(e) \}$ electric quadrupole transition has been detected under conditions where electric dipole transitions normally dominate. Of the six states created by P $2p(a_1, e) \rightarrow \sigma^*(\mathbf{P} - \mathbf{Cl})(a_1, e)$ excitations, that to the ${}^{1}A_{2}$ state is the only electric-dipole forbidden transition. The rapid variation with scattering angle of the 135.5 eV feature, along with its absence in the P 2p X-ray absorption spectrum of PCl₃ [40] indicate the electric quadrupole character of this transition. Interestingly, PF₃ has a very similar P 2p spectrum to that of PCl₃ and yet the corresponding feature is intense and does not change with scattering angle [39]. Either the non-dipole transition to ${}^{1}A_{2}$ turns on at very low K in PF₃ or the spectral pattern is different from that of PCl₃ and the $^{1}A_{2}$ state is not excited at all. Exceptions to the dipoledominated character of ISEELS such as the single state found in PCl₃ appear to be rather rare - in essentially all of the other 30 or-so molecules where 1:1 electron impact: photon impact comparisons are possible, the spectra are very similar.

Based on the Bethe-Born thoery [36], dipole-regime ISEEL spectra can be converted to approximate optical oscillator strengths. A systematic procedure for this is now used routinely [41]. This involves background subtraction to isolate signal from a single core edge, kinematic and transmission function correction, followed by normalization to calculated atomic oscillator strengths [42] in the far continuum (> 25 eV above the *IP*), where molecular resonance effects are negligible. This procedure allows systematic quantitative comparison of spectra from different core edges and different molecules. Although the same normalisation



Fig. 4. ISEELS of PC1₃ recorded with 1500 eV impact energy at the indicated scattering angles. The dipole forbidden transition in PCl₃ is indicated by the asterisk. The X-ray absorption spectrum of PCl₃ [40] is included for comparison. The sketch indicates the states derived from P $2p \rightarrow \sigma^*$ (P-Cl) excitation. Only the ${}^{1}A_{1} \rightarrow {}^{1}A_{2}$ transition is electric dipole forbidden in C_{3v}. (adapted from Sodhi and Brion [39]).

procedure can be applied to soft X-ray photoabsorption spectra, in many cases the derivation of accurate absolute intensities is more difficult with photon than with electron impact. A number of factors can be involved. In certain spectral regions problems arise with normalisation to the incident photon flux. This frequently occurs in the C 1s region (280-300 eV) where absorption of the X-rays by carbon contamination on optical surfaces is often so strong that stray light and higher order components dominate the photon flux delivered by the monochromator, resulting in greatly distorted spectra. When recording in a true absorption mode, it is often very difficult to use a pressure which is sufficiently low that the most intense features are not affected by absorption saturation and yet still have enough pressure for adequate statistical precision to detect weak features. Ion or electron yield detection is frequently used to minimize the absorption saturation problem. However there are often differences between yield and true absorption spectra. A major factor is an energy and/or state dependence of the degree of multiple ionisation. Since higher degrees of ionisation produce more ions and electrons, such changes distort

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the absorption spectra in favour of multiply ionized states. An example where these effects have been placed on a quantitative basis has been given in recent studies of the ionic decay of core-excited CO [43].

3. Absolute Oscillator Strengths as a Probe of Barrier Effects

A valuable aspect of the systematic derivation of absolute oscillator strengths (OS) from core excitation spectra is the ability to compare intensities of transitions to a common final orbital from different core levels in a single molecule and to compare corresponding transitions in related molecules. For example, $1s \rightarrow \pi^*$ oscillator strengths have been used to map the spatial distributions of π^* orbitals in the substituted carbonyls, HCONH₂, HCOOH and HCOF [44]. In agreement with a variety of calculations, the π^* (C=O) orbital in all three species was found to have a larger density on carbon than oxygen and about 6% contribution from X2p₂, (X = N, O, F).

Over the past three years ISEELS has been used to study the influence of perfluorination on unoccupied orbitals [41, 45-48]. In initial discussions perfluorinated compounds (SF₆, SiF₄, etc) were used to illustrate the effect of potential barriers [18]. However, the molecules examined in the early work were high symmetry species in which a central atom was almost fully enclosed by a cage of electronegative fluorine atoms. Studies of the core spectra of a



Fig. 5. Carbon 1s oscillator strengths derived from ISEEL spectra of C_6F_6 (IP = 294.1 eV), C_2F_4 (IP = 296.5 eV), C_2F_6 (IP = 299.8 eV) and CF_4 (IP = 301.9 eV). The spectra are plotted on a relative energy scale, aligned at their *IPs* with a vertical scaling in the ratio of 4:6:4:6 to correct for the different number of $C \ 1s \rightarrow \sigma^*$ (C-F) transitions. The shaded area is thus proportional to the intensity of $C \ 1s \rightarrow \sigma^*$ (C-F) on a per-transition basis (from [46]).

series of molecules in which there is progressive addition of fluorines at a single site allow a detailed examination of the evolution of a potential barrier. Comparison of the C 1s spectra of C_6F_6 , C_2F_4 , C_2F_6 and CF_4 (Fig. 5) is such an investigation [46]. The increase in the C 1s $\rightarrow \sigma^*$ (C-F) OS through this (CF . . . CF_2 . . . CF_3 . . . $CF_4)$ series is direct evidence for the development of a more complete potential barrier with more complete enclosure of a carbon atom by electronegative substituents. Recently Sze et al. [30] have recorded the Cl 2p, Cl 2s and F 1s spectra of ClF₃, these spectra exhibit both "normal" (visible Rydberg transitions, appreciable near-continuum intensity) and 'potential barrier' (strong valence resonance) features. The observations are most easily interpreted by postulating a highly anisotropic molecular potential barrier in this molecule. The photoionization dynamics of ClF₃ following core excitation should be particularly interesting.

In Fig. 6 the C 1s spectrum of 1,1,1-trifluorethane is compared to those of ethane [25, 49] and perfluoroethane [47]. The total ion yield spectrum of CH₃CF₃, reported previously [50], is similar but not identical to the oscillator strength spectrum shown in Fig. 6 – in particular the ion yield result has weaker C 1s (CH₃) relative to the C 1s (CF₃) features. The comparison presented in Fig. 6 further illustrate the relevance of the potential barrier model to core excitation spectra. The Rydberg transitions and near continuum which are strong in C 1s (CH₃) excitation in C₂H₆ and CH₃CF₃, are very weak in the case of C 1s (CF₃) excitation in CH₃CF₃ and C₂F₆. The C 1s $\rightarrow \sigma^*$ (C-F) transition around 295eV is more than twice as intense in C₂F₆ as in CH₃CF₃. The dip around 305 eV in C₂F₆ has been attributed to the exclusion of



Fig. 6. Comparison of the C 1s oscillator strength spectra of perfluoroethane [47], 1,1,1-trifluoroethane (new result) and ethane [49]. The hatched lines indicate the core ionization thresholds determined by XPS.

the low-energy continuum wave function from the region of the C 1s core orbital while the onset around 308 eV has been associated with the energy at which the core ejected electron becomes sufficient to pass over the top of the potential barrier associated with the fluorine cage [47].

4. Bond lengths from near edge features

For bonds between second row elements $(B \dots F)$ the $1s \rightarrow \sigma^*$ energies are rather sensitive to bond length, certainly much more so than the $1s \rightarrow \pi^*$ energies in unsaturated molecules. An example of this can be seen in the 11 eV difference in the term value of the N $1s \rightarrow \sigma^*$ (N–N) transition in N_2 and N_2H_4 (Fig. 1). Since term value scales correct for chemical shifts in the core orbital energy, changes in δ , the $1s \rightarrow \sigma^*$ energy relative to the core IP ($\delta = -TV$), reflect changes in σ^* orbital energies within a one-electron, frozen orbital picture. The bond length sensitivity of σ^* orbital energies has been documented in a variety of spectroscopies including core excitation [51], shape resonances in partial valence photoinoisation [52] and low energy electron scattering [53]. Recently simple multiple scattering [54] and quantum mechanical [55, 56] models have been developed to rationalise the strong bond length sensitivity of σ^* orbital energies. At the same time, concerns have been expressed about a number of marked exceptions to the empirical trends and the extent to which such bond length correlations depend on spectral assignments which have not been fully verified [57]. Although certain of these concerns have been answered [58], Lindle et al. [57] are correct in noting that studies of the electron and ion decay products following core excitation are very desirable in order to investigate whether spectral features assigned as σ^* shape resonances are indeed one electron excitations to (1s, σ^*) states. Recently, features in the core spectra of SF₆ and C₆H₆, previously attributed to oneelectron transitions have been shown to have a multi-electron excitation component [59-61]. However, when used with appropriate caution, the correlation of σ^* position and bond length has been useful both in spectral assignment and in bond length determination.

Intramolecular geometry changes associated with chemisorption have been measured by NEXAFS using the correlation between bond lengths and positions of $\sigma^*(C-C)$ shape resonances. An example of this is shown in Fig. 7 which plots the NEXAFS spectra of ethylene absorbed on a number of different metal surfaces [62]. The lower portion of the figure shows how the C-C bond lengths were derived from the observed σ^* resonance energies and gas phase calibration data. In each case the elongation of the C=C bond determined from the shift in the σ^* (C-C) resonance is qualitatively consistent with vibrational energy loss measurements as well as the relative reactivity of the different metal surfaces. The bond length stretch of $C_2 H_4$ on Cu (100) predicted from the σ^* position has been confirmed independently from analysis of the second shell C-Cu signal in the C 1s EXAFS [63].

The existence of a simple semiquantitative technique for determination of bond lengths from core excitation spectra has inspired searches for similar relationships in the core spectra of third row elements. A naive extrapolation of the second row trends [51] predicts that core excited resonances associated with σ^* orbitals involving third row atoms (Al to



Fig. 7. (a) Gas phase C 1s ISEELS of ethylene (π^* band truncated) compared with the normal incidence NEXAFS of monolayers of ethylene adsorbed on the indicated surfaces. In this geometry the NEXAFS spectra are sensitive to electronic excitations polarised parallel to the surface (i.e. $1s \rightarrow \sigma^*$ transitions in planar species flat on the surface) (from Stöhr et al. [62]. (b) Relationship between the absolute energy of the C $1s \rightarrow \sigma^*$ (C-C) transition and the C-C bond length, calibrated with gas phase results [51] and applied to derive the C-C bond lengths (in Å) for surface adsorbed ethylene that are indicated to the right of Fig. 7(a).

Cl) will be in the discrete with very large term values and that the bond length dependence (slope of the $\delta(R)$ line) might be expected to be relatively small. The S 1s and Cl 1s photoabsorption spectra of a number of molecules [64-67] have been studied recently to investigate this point. Analyses of these spectra via chemical systematics reveal that S $1s \rightarrow \sigma^*$ (S-X) energies are much less sensitive to bond length than O 1s $\rightarrow \sigma^*$ (O-X) energies. In Fig. 8 the δ -values for (S 1s, δ^* (S-X)) states are plotted against S-X bond length in comparison to correlations for (<u>O 1s</u>, σ^* (O-X)) states. The σ^* (S-X) resonances (X = C, OF) do appear in the discrete but at δ -values similar to those predicted by extrapolation of the corresponding σ^* (O-X) $\delta(R)$ curves to the region of S-X bond lengths. This is consistent with the chemical periodicity of atomic orbital energies - i.e the O 2p and the S 3p atomic orbitals which contribute to the σ^* orbitals have similar energies since Z_{eff} for these orbitals is similar. The S-X correlation lines are much shallower than the corresponding O-X



Fig. 8. Correlation of the negative term values ($\delta = E_{\sigma}^* - IP$) of O 1s $\rightarrow \sigma^*$ (O-X) and S 1s $\rightarrow \sigma^*$ (S-X) transitions with O-X and S-X bond lengths. The lines for the O-O and O-C curves are those reported previously [51], that for O-F is extrapolated from the Z-dependence reported in [51], while those for S 1s data are linear least squares fits. (adapted from [66], with deletion of the points for SF₄ and SOF₂ and re-evaluation of the S-F correlation line. The assignments of the S ls spectra of SF₄ and SOF₂ are currently under debate [71]).

lines, consistent with a weaker bond length dependence for resonances involving heavier atoms. Although there does not appear to be useful bond length sensitivity, this work has identified term values characteristic for specific types of $S \ 1s \rightarrow \sigma^*(S-X)$ transitions. This aspect has been used recently to aid studies of disulfide surface chemistry via S 1s near edge spectroscopy [68]. The present observation of a considerably lower *R*-dependence of the energies of molecular σ^* states associated with heavier atoms appears to be somewhat inconsistent with recent high-*Z* bond-length correlation interpretations of the near edge spectra of minerals [69] and ceramic superconductors [70].

A variety of schemes have been proposed for intramolecular bond length determination in surface adsorbates via σ^* resonance position. The simplest scheme would be to develop independently a set of bond length correlation curves for solids and surface adsorbates. However, this approach is hampered by the paucity of known structures for surface adsorbates. Thus, procedures to apply the gas phase $\delta(R, Z)$ correlation data to NEXAFS of surface absorbed molecules or molecular solids are of considerable interest. An issue of some concern is the correct choice of reference energy. In the case of the gas phase correlations, this is the core IP as determined by X-ray photoelectron spectroscopy. The ionization potential of a molecule adsorbed on a metal surface is invariably 5-10 eV lower than that of the corresponding free molecule. Part of this shift is the work function since condensed phase IPs are referenced to the Fermi rather than to the vacuum energy. However, much of the shift is related to the greater relaxation of core hole (ionized) states of semiconducting and conducting condensed phases because of the larger number of electrons available and their greater mobility, particularly in the case of a molecular monolayer on a metal surface.

In almost all cases studied to data, the positions of coreexcitation features of condensed molecules are essentially identical to those in the ISEEL or X-ray absorption spectrum

of the gas phase molecule, provided the molecular structure is unchanged in the condensed state. The independence of the excitation energy on phase (gas, solid or monolayer) can be explained by the self-shielding character of coreexcited states - i.e., the bulk of the shielding of the core hole is accomplished by the core excited electron so that the valence electron distribution is largely undisturbed. This occurs even for very short lived (1s, σ^*) continuum resonances, whose lifetime is typically $< 10^{-16}$ s, based on the resonance width. The similarity of $(\underline{1s}, \sigma^*)$ energies in gas and condensed phases suggests that absolute resonance energies can be combined into a single correlation for both gas and condensed phase molecules. This approach has been used with apparent success in several recent NEXAFS surface structure studies [72, 73] and has been illustrated in Fig. 7b. Furthermore, absolute (E) rather than relative (δ) energy correlations appear to be required even in the gas phase, whenever the molecule contains a highly polarisable species such as a metal atom. In such cases there can be significant differences between the relaxation energies of the core-excited and core-ionized states which invalidates the use of the "main line"IP (i.e. the lowest binding energy core ion state as detected by XPS) as a reference to convert two-electron $1s \rightarrow \sigma^*$ energies to approximate one-electron σ^* orbital energies. As an example, unless the difference in excited-state versus ion-state relaxation is taken into account, a bond



Fig. 9. Carbon 1s oscillator strengths on a per-carbonyl basis derived from ISEEL spectra of CO and four transition metal carbonyls. The Ni(CO)₄ spectrum, recorded elsewhere at 0.3 eV FWHM resolution [31], has been smoothed to match the lower resolution (0.6 eV FWHM) at which the other spectra were recorded [74, 76]. The hatched lines indicate the "main line" XPS *IPs.*

shortening rather than a bond lengthening is predicted based on the position of σ^* (C–O) resonances in the C 1s and O 1s spectra of transition metal carbonyls [74–76] (see Fig. 9).

5. Core excitation spectroscopy of organometallic compounds

The paucity of visible changes to core excitation spectra associated with the chemisorption bond has been a surprising aspect of comparisons between the NEXAFS spectra of chemisorbates and gas phase molecular core excitation spectra [77–79]. In some cases additional weak shoulders and pre-peaks have been noted in the NEXAFS spectra which may be excitations to unoccupied metal-adsorbate antibonding orbitals. We are currently carrying out systematic studies of the core excitation spectroscopy of organometallics in order to investigate the effects of metal-ligand bonding on unoccupied MOs as probed by core excitation. This work is constructing a bridge between the spectroscopy of free organic molecules and that of chemisorbates on metals.

In fig. 9 the C 1s specta of CO and four transition metal carbonyls are compared [31, 74, 76]. One finds that the C 1s (and O 1s) spectra of the metal carbonyls are very similar to those of CO. This is consistent with the NEXAFS spectra of chemisorbed CO. The strong similarity of the spectra of metal carbonyls and free CO indicates that the excitation is localised on a single carbonyl, rather than involving an excited state in which the core excited electron is delocalised over the full molecule. There are small differences between the carbon and oxygen 1s spectra of gas phase metal carbonyls and those of CO. These include: small shifts in the C 1s $\rightarrow \pi^*$ transition to higher and the O 1s $\rightarrow \pi^*$ transition to lower energy; suppression of Rydberg structure (consistent with the larger molecular size); additional weak features 2–4 eV above the main $1s \rightarrow \pi^*$ transition, which are assigned to C 1s (delocalised) transitions; and a reduction of the $1s \rightarrow \pi^*$ oscillator strengths. The shift in the $1s \rightarrow \sigma^*$ (C-O) transition to lower energy reflects the bond lengthening associated with the $d\pi$ backbonding electron donation into the π^* orbital. As noted in the preceding section, if the XPS 'main-line' IPs are used as a reference, the qualitatively incorrect conclusion is reached that the bond length contracts when CO is bonded to a metal.

In contrast to the metal carbonyls, the C 1s spectra of cyclopentadienes π -bonded to metals are dramatically different from that expected for free cyclopentadienyl. Fig. 10 presents the carbon 1s oscillator strengths of ferrocene, cobaltocene and nickelocene [80] in comparison to that of cyclopentadiene (C_5H_6) . Although the spectrum of the cyclopentadienyl anion or radical (C_5H_5) has not yet been recorded, it is expected to be dominated by a single strong $1s \rightarrow \pi^*(e_2'')$ transition around 286 eV. The metallocene spectra have a strong C $1s \rightarrow \pi^*$ transition around 287 eV which shifts in energy and intensity systematically with metal type. In addition all three metallocenes exhibit a peak at lower energy which is not expected to occur in the isolated cyclopentadienyl molecule. Detailed analysis, including comparison with extended Hückel calculations [80], shows that this first peak is associated with C 1s $\rightarrow e_{1g}(M \ 3d_{xz,yz})$ transitions. These spectra provide the first clear-cut examples of strong influences of metal bonding on molecular inner-shell spectra through the observation of ligand core excitations to



Fig. 10. Carbon 1s oscillator strengths derived from ISEEL spectra of cyclopentadiene, ferrocene, cobaltocene and nickelocene. The metallocene spectra are taken from Ref. [80].

anti-bonding metal-ligand orbitals. The location of these features supports several previous speculations [77–79] that core excitations to metal-ligand anti-bonding orbitals in chemisorbed molecules give rise to weak features occasionally seen as low energy shoulders on the π^* features of electronically unsaturated adsorbates.

Another theme of recent core ionization studies of organometallic compounds has been the extended fine structure (XFS) in the ligand and metal core ionisation continua. XFS of free molecules has been studied recently by both electrons (EXELFS [81]) and photons (EXAFS [82]) in order to provide experimental tests of calculated low-Z backscattering phases and amplitudes. The detailed studies by Letardi et al. [83] of the momentum transfer dependence of EXELFS of CF₄ and CO₂ have shown that non-dipole effects are negligible so that gas phase EXELFS recorded under typical ISEELS conditions can be analysed correctly with the EXAFS formalism. XFS of organometallic compounds provides useful models for surface EXAFS of chemisorbates. In Fig. 11 the extended fine structure (XFS) in the carbon 1s continuum of iron pentacarbonyl is shown along with the magnitude of the Fourier transform of the XFS. The three peaks in the radial distribution function correspond to the nearest neighbour oxygen and iron atoms and the carbon atoms of adjacent carbonyls. This identification of the neighbour atoms associated with the XFS components is supported by the similarity of the shapes of the experimental and calculated backscattering amplitudes. This comparison,



Fig. 11. Extended fine structure in the carbon 1s continuum of iron pentacarbonyl [84]. The background subtracted to obtain the central curve was a fit of the spectrum to $(a(E - b)^c)$, where a, b and c are adjusted parameters. The bottom curve is the magnitude of the Fourier transform of the central spectrum after it has been placed on a wavenumber scale and k^1 -weighted.

the procedures needed to obtain reliable background subtraction in the case of weak gas phase XFS, and several other examples have been described recently [84]. The ability to simultaneously detect both low-Z and high-Z backscattering signal in the carbon 1s spectrum of an organometallic compound allows one to estimate the intensity of the weak intramolecular signal in XFS of chemisorbed molecules [85]. As yet SEXAFS has not been able to detect the much weaker intramolecular component in the presence of the much stronger substrate signal.

6. Electron and ion studies of the decay of core-hole states of molecules

It is clear that studies of the creation of core excited states by electron or photon impact have a wide range of applications. At the same time, there are many questions concerning spectral assignment and the correlation of core-state production with the final state of a system that can only be answered by techniques that probe the intermediate and final electronic states and ionic fragments produced in the course of core hole decay. The question of the correct identification of particular spectral features as one-electron σ^* shape resonances instead of other types of states (double excitation, simultaneous excitation and core ionisation (shake-up) etc) [57] has already been alluded to. Photoelectron spectroscopy with variable photon energy provides partial photoionisation spectra which are very helpful in dissecting complex core-excitation spectra. This type of study has led to improved assignments in many molecules, including SF_6 [60, 86], CO [59, 87], C_2H_4 , C_6H_6 [60, 61], SiX₄ (X = H, F, Cl, CH₃) [88, 89]. Although electron emission spectra are most effectively measured by photoelectron spectroscopy using synchrotron radiation, some information, particularly about the electronic decay of strong $1s \rightarrow \pi^*$ resonances is being determined by electron impact (e, 2e) coincidence measurements [90–93]. The latter spectroscopy is a direct analog of autoionization resonance or de-excitation electron spectroscopy (DES), which has been applied to chemisorbed as well as free molecules [94, 95].

Photoionisation mass spectrometry (PIMS) and related studies of the ion production associated with core excitation can also give valuable insights into spectral assignments and the dynamics of core state decay. The early work in this area was done by electron-ion coincidence spectroscopy [96-98]. Such studies are now best carried out by synchrotron radiation, since PIMS is a non-coincidence technique. The addition of coincidence detection of energy selected electron(s) and mass-and energy-selected ion(s) produced by tuned photoionisation can be used to greatly extend PIMS and to obtain a rather complete picture of the core state dynamics [99]. Ion and electron spectroscopies have been used to identify the novel (and apparently rare) situations in which fragmentation occurs prior to core-hole electronic decay [4, 100]. In most cases both excited and ionised core states of molecules decay to multiply valence-ionized states which eventually produce several ion fragments. Such processes are best studied by photoion-photoion coincidence (PIPICO) techniques. The combination of PIPICO and normal photoionization mass spectrometry is being used to develop quantitative pictures of core state decay in several molecules including CO [32], CH₃CN and CF₃OOCF₃ [101] and N₂ [102].

Figure 12 presents the O 1s ISEEL spectrum of CF₃OOCF₃ [48] along with branching ratios for producing several molecular fragment ions following O 1s excitation and ionisation [101]. The partial ion yield data was derived from time-of-flight PIMS recorded under ion extraction conditions which have minimal kinetic energy discrimination. The indicated species constitute 50% of the ions produced, with the F^+ , O^+ and C^+ atomic ions accounting for essentially all of the remaining ion products. First one notes the extensive ionic fragmentation that typically follows core processes. In this case there are almost no doubly charged ionic fragments and yet doubly charged states dominate the electronic decay. These must undergo rapid dissociation into several energetic singly charged fragments (Coulomb explosion). Second there is some evidence for selectivity in the fragmentation processes, particularly at 534 eV where the intense O 1s $\rightarrow \sigma^*$ (O-O) feature decays with a strong preference to form CF_2^+ . Naively, since this core excitation is strongly localised in the region of the weak O-O bond (localised both by the O 1s orbital and the local character of the σ^* (O–O) orbital), one might expect copious production of CF_3O^+ , if the spatially localised character of the core excited state has an influence on the subsequent ionic fragmentation. It is possible that the observed enhanced CF_{2}^{+} yield is associated with secondary fragmentation of a primary CF_3O^+ fragment which itself does not have a sufficiently long lifetime $(> 2 \mu s)$ for detection. However, it is equally likely that the resulting ion yields are a complex mixture of the decay properties of many highly excited singly and doubly valence-ionised states to which essentially all core excited and



Fig. 12. (top) O 1*s* ISEEL spectrum of CF₃OOOCF₃. (bottom) Branching ratios for the production of the indicated framgent ions from CF₃OOCF₃ following photoionization. These results were derived from time-of-flight photoionization mass spectra recorded under high extraction field condition which have minimal kinetic energy discrimination. The PIMS were recorded with radiation from the ACO storage ring at LURE [101].

core-ionised states decay with more or less probability. The complexity of the PIPICO spectra supports this view [101]. Since it is these valence-ionized states that are the immediate precursors to the ionic fragmentation, which occurs on a 10^{-12} to 10^{-10} s time-scale, much longer than that of the Auger decay of the core hole ($< 10^{-14}$ s), the prospects for strong selectivity in bond breaking following core excitation seem unlikely [43, 101].

Measurements of ion kinetic energy distributions [102, 103] and ion angular distributions [104, 105] have been made for a few specific core states. Such information can be extremely valuable for identifying the core excited state, intermediate valence ionized states and for determining the electronic state of the product fragment ions. Angle-resolved fluorescence studies of single core-states complement the electron and ion spectroscopies. Such studies of molecules are just now appearing [106], commencing in the soft X-ray where fluorescence yields are larger. True state-to-state photoionisation dynamic studies are now possible in the X-ray region with modern synchrotron radiation spectroscopies.

7. NEELFS: NEXAFS in the home laboratory

A central theme throughout this paper has been the use of molecular core excitation spectroscopy as a means of understanding X-ray excited NEXAFS of condensed phases (surface adsorbates, polymers etc). In principle reflection electron energy loss spectroscopy can be used to study core excitation spectra of the condensed state. If reflection EELS of chemisorbed molecules is possible this will allow NEXAFS-type studies of surface adsorbates in the more comfortable, much more widely accessible and frequently better-equipped environment of the home surface science laboratory. We have recently developed an apparatus for such studies and have reported the first near-edge energy-loss fine-structure NEELFS spectra of chemisorbates [107]. Plural scattering events dominate the inelastic reflection of high energy electrons for a solid surface [108]. Thus an important question is whether or not the momentum transfer direction in the inelastic collision which produces the NEELFS signal is sufficiently well-defined to preserve a directional sensitivity to the electronic transition. Our very recent results on the coverage dependence of the N 1s spectrum of pyridine chemisorbed on Ag (100) and Ag (111) [109] give a conclusive and positive answer to that question. The N 1s NEELFS spectra of pyridine adsorbed on Ag (100) at 1, 2 and 5 Langmuir



Fig. 13. N 1s near edge energy loss fine structure (NEELFS) spectra of pyridine adsorbed on Ag (100) [109]. Each NEELFS spectrum was recorded in under one-half hour, with an incident beam current of ca. $0.1 \,\mu$ A mm⁻². The electron beam was shifted laterally on the surface every few minutes. Under these conditions, beam damage effects are believed to be minimal. The relative intensity scale, which is common for all three NEELFS spectra, is the ratio (in %) of the molecular adsorbate signal to the underlying background, which was subtracted by fitting to a power curve ($a(E - b)^c$). The exposures in langmuirs ($1 L = 10^{-6}$ Torr s⁻¹) are given. The N 1s ISEEL spectrum of gaseous pyridine is also plotted for comparison. The change from a π^* to a σ^* dominated spectrum tracks an orientational surface phase transition.

exposure are presented in Fig. 13. Suitable precautions were taken to ensure that beam damage effects were minimal. The N 1s ISEEL spectrum of gaseous pyridine [77] is also plotted for comparison. The change from a π^* to a σ^* dominated spectrum tracks a surface phase transition in which the pyridine molecule changes from an orientation predominantly parallel to the surface to one with a high tilt angle between the molecular and the surface planes. NEXAFS has been used to follow a corresponding orientational phase transition of pyridine on the Ag (111) surface [110]. With this development there now exists in non-synchrotron radiation laboratories, the capability to study the core excitation spectroscopy of a molecule both free and in the chemisorbed state.

8. Future directions

In the coming years dipole-regime gas phase ISEEL spectroscopy will be applied to more challenging systems such as molecular beams, transients, low-volatility species etc. Since the vapour pressure required for ISEELS is about an orderof-magnitude less than that needed for photoelectron spectroscopy (PES), the technique can be applied to the many transient species already studied by PES. At several institutions (Manchester, Maryland, McMaster, Monterotondo, Waterloo) variable angle ISEEL spectrometers are in existence or are being implemented. This will provide an appreciable expansion of systematic studies of non-dipole core-excitations and the momentum transfer dependence of inner-shell electronic excitations, a relatively unexplored area in which electron impact has unique capabilities. In the area of gas phase X-ray studies with synchrotron radiation, new beam lines using the principles of the DRAGON monochromator will become available, setting new standards for high-resolution soft X-ray spectroscopy. This, coupled with the much higher signal rates for yield experiments (as compared to techniques based on electron impact with coincidence detection schemes), will ensure that photon spectroscopies will dominate the VUV and soft X-ray physics of molecular core excitation in the coming years.

In the area of core excitation studies of surface adsorbed molecules, although NEXAFS is already a very popular spectroscopy with an increasingly large number of devotees, reflection electron energy loss spectroscopy [107] will likely experience rapid development and will play an important role in surface chemistry and physics. Parallel detection schemes will be essential to allow spectral acquistion in a time short compared to electron beam damage. Since the momentum transfer direction plays a role analogous to the electric vector in optical polarization studies, the dependence of the near edge spectrum on angle of incidence contains the same information as the polarization dependence of NEXAFS. This has been domonstrated by transmission EELS studies of anisotropic solids [111] but improved statistical precision is required before NEELFS of molecular adsorbates can be detected under large angle scattering where the spectrometer is less surface sensitive and the signal gets lost in the large, unstructured plural scattering background. With these improvements I expect that reflection EELS with variable incident angle will provide a lab-based technique that has the same capability as NEXAFS for determining the orientation of surface adsorbed species.

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