CARBON AND OXYGEN K-SHELL EXAFS OF GASES STUDIED BY ELECTRON ENERGY LOSS SPECTROSCOPY
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Abstract - EXAFS in the soft X-ray range from intramolecular, low Z backscattering has been investigated in the inner shell spectra of gaseous CO, CO₂, CF₄, C₆H₁₂, C₆H₆ and C₆F₆, recorded by inelastic electron scattering in the dipole regime. The O₁s continua of CO and CO₂ do not exhibit the oscillations recently reported by Yang et al (Phys. Lett A110 (1985) 301). The C₁s spectrum of CF₄ contains extended continuum features similar to those reported previously. The C₁s continua of C₆H₁₂, C₆H₆ and C₆F₆ exhibit weak extended continuum features which appear to be EXAFS although the analysis procedures used so far are not able to reproducibly extract accurate bond lengths.

I - INTRODUCTION

There is considerable interest at present in the application of soft X-ray EXAFS (100 to 1500 eV photon energies) for the solution of surface structural problems. To date, the majority of SEXAFS studies have investigated atomic adsorbates /1/. In the small number of molecular adsorbate studies reported only molecule-surface distances, but not intramolecular bond lengths, have been obtained from the extended fine structure. Although semiquantitative intramolecular bond lengths and details of the electronic structure can be obtained from the near edge spectrum /2/, the extraction of quantitative intramolecular bond lengths from SEXAFS remains an unattained, but extremely desirable goal. Measurements in free molecules containing second row elements (particularly carbon) allow one to study intramolecular EXAFS in the absence of surface backscattering contributions. Such studies provide an ideal means to explore the detection limits of intramolecular EXAFS in low Z molecules.

In earlier studies, continuum structure consistent with the C-C₁ bond in the C₁₂p and C₁s ISEELS of CCl₄ /3/ and with the C-F bond in the C₁s photoabsorption spectrum of CF₄ /4/ have been reported. Recently, Yang et al /5/ reported observations of oscillations in the ion photoyield spectra of the O₁s continuum of gaseous O₂, CO and CO₂ which they interpret and analyse as EXAFS. We have used inner shell electron energy loss spectroscopy (ISEELS) under dipole conditions to examine the C₁s and O₁s continua of CO and CO₂. As presented in Section III, the oscillations reported by Yang et al /5/ are not seen in our O₁s ISEELS data, which does not contain any recognizable extended fine structure.

In order to seek stronger EXAFS based on low Z backscattering, we have examined the ISEELS spectra of a number of molecules including CF₄, C₆H₆, C₆F₆ and C₆H₁₂. The C₁s ISEELS spectrum of CF₄ exhibits extended fine structure similar to that reported previously /4/ (section IV). Extended continuum structure is also observed in the C₁s spectrum of cyclohexane, benzene and hexafluorobenzene. The analysis of this data is presented in Section V along with a discussion of the limitations of the current EXAFS analysis procedures for weak signals.
The long-range, core excitation spectra were obtained by inelastic scattering of fast electrons, using 2.5keV final electron energy and 1-2° scattering angles. Under these conditions the momentum transfer is relatively small and electric dipole transitions dominate. Thus both the Bethe-Born theory of the scattering of fast, charged particles /6/ and comparisons to photoabsorption spectra for many molecules indicate that the ISEELS spectra may be interpreted in the same manner as photoabsorption spectra. One qualitative difference is that the spectral intensity decays faster with increasing energy loss (equivalent photon energy) than in photoabsorption. In the limit of zero momentum transfer the ISEELS spectra should be proportional to photoabsorption weighted by $E^{-3}$. Because of the finite momentum transfer the actual weighting is probably somewhere between $E^{-2}$ and $E^{-3}$. The samples studied in this work were obtained commercially and used without further purification, except for degassing liquids. The pressure in the collision cell is estimated to be $10^{-4}$ torr, sufficiently low so that there are no contributions from double scattering.

III - CO AND CO₂ - COMPARISON TO PHOTO-ION YIELD

The ISEELS spectra of CO and CO₂ from 540 to 900eV are shown in Fig. 1 in comparison to the photon ion yield spectra. It is clear that the oscillations between 600 and 700eV reported by Yang et al /6/ are not observed in our spectra. The only structure detectible in the ISEELS continua above the prominent $\sigma*$ resonances is a weak feature at 570eV in CO and one at 580eV in CO₂. Corresponding features are observed in the photon ion yield. These may be shake-up continua.

Since the ISEELS spectra are equivalent to photoabsorption except for a non-structured weighting factor of $E^{-n}$, $2<n<3$, our results indicate that the oscillations observed by Yang et al /6/ are artefacts. Two possible sources include incomplete normalization of the structured incident photon flux, or possibly distortion from the ion yield detection scheme. The latter seems more likely since the oscillations are much less apparent in the 01s spectrum of CO₂ recorded by Yang et al with true absorption procedures /7/.

We have also recorded the Cls continua of CO and CO₂ to high statistical precision. Oscillations are not observed in these spectra either, even at the level predicted by MS-Xα calculations /8/.

IV - CARBON TETRAFLUORIDE

The Cls ISEELS spectrum of CF₄ is plotted in Fig. 2 in comparison to the photoabsorption spectrum reported by Brown et al /4/. The additional $E^{-n}$ weighting is
apparent in the faster drop off of the ISEELS signal. The pattern of continuum features is similar in these two spectra and the absolute positions are in good agreement except for the broad maximum around 380 eV. The kX(k) spectrum extracted by subtracting a spline fitted background (Fig. 2) is plotted in Fig. 3 along with the transform magnitude. The derived distances from this analysis using the calculated C-F phase shift /9/, is 1.26 Å, somewhat shorter than the actual value of 1.32 Å. As with the C₆H₆, C₆F₆ and c-C₆H₁₂ data (Sect. V), the results were unacceptably dependent on the background subtraction procedure.

V - CYCLOHEXANE, BENZENE AND HEXAFLUOROBENZENE

The Cls continua of c-C₆H₁₂, C₆H₆ and C₆F₆ are shown in Fig. 4 along with the kX(k) isolated with a three section quadratic spline, and the transform magnitude. With this procedure the Fourier-filtered first shell phases and calculated phase shifts /9/ gave nearest neighbour distances of 1.47 Å (C₆H₁₂, R(C-C)=1.53), 1.40 Å (C₆H₆, R(C-C)=1.40) and 1.30 Å, 1.36 Å (C₆F₆, R(C-F)=1.32 Å, R(C-C)=1.40 Å). Although in this best-case analysis the results are in reasonable agreement with the known structures, results differing by up to 0.4 Å from these values were obtained if other, apparently reasonable background subtraction procedures were used. These procedures included: variations of the k-space spline-fit parameters (2-section quadratic, 2 and 3 section cubic); differentiation prior to spline fits; division by the smooth Cls continuum ISEELS signal of CH₄ prior to spline analyses; multiple 3-point smooths; and spline-fitting in energy rather than k-space. It appears that with any of these methods some of the X(k) signal arises from the subtracted background and that this signal produces Fourier components which badly overlap that of the real EXAFS. This is particularly true of the k-space spline procedures which are well known from other EXAFS studies to produce peaks in the 1-1.5 Å region of the transform. The
extreme weakness and the short k-space range of the low Z backscattering signal, coupled with the fact that the signal from short bond lengths falls in the same region as the spline artefacts, makes the analysis of soft x-ray EXAFS arising from low-Z backscatterers very difficult. Because of the sensitivity of the result to the background subtraction, it is not possible to evaluate the accuracy of the calculated phase shifts.

In summary, although these results indicate that weak extended fine structure from low-Z backscattering does occur in Cls-Fls continua, improved background subtraction procedures are needed for reliable data analysis. With this development, it appears that surface EXAFS will be able to measure intramolecular (C-C, C-O etc.) bond lengths given sufficiently precise photoyield spectra as may be provided by improved synchrotron radiation sources.

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Figure 4: ISEEELS spectra, isolated kX(k) signal (from a 3-section quadratic spline) and transform magnitudes for Cls of C\textsubscript{6}H\textsubscript{12}, C\textsubscript{6}H\textsubscript{6} and C\textsubscript{6}F\textsubscript{6}. (N.B. the π* resonances of C\textsubscript{6}H\textsubscript{6} and C\textsubscript{6}F\textsubscript{6} are truncated.)

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