High Resolution Gas Phase Photoelectron Spectra using Synchrotron Radiation. Selective Enhancement of the I 5p Cross Section in CF_3I due to Photoexcitation of I 4d Electrons

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Using monochromatized synchrotron radiation between 20 and 110 eV as the photoelectron source, we show that the I 5p lone pair intensity in CF_3I is selectively enhanced relative to other molecular orbitals when the I 4d core electrons are photoexcited.

Changes in relative photoionization cross sections between He I (21.2 eV), He II (40.8),[1] Y-M_ζ (132.3),[2,3] Zr-M_ζ (151),[4] Mg-K_α (1253.6), and Al-K_α (1486.6) have long been used as an aid in assigning photoelectron spectra of gas phase molecules. For example, it is well known that the valence *n*p ($n \geqslant 3$) cross sections of the rare gases and halogens drop dramatically above He I photon energies.[5] Such sharp drops in p cross sections have often been used as an aid in assigning the halogen lone pair molecular orbitals in gas phase molecules.[6—8]

The advent of synchrotron radiation sources has recently made it possible to study cross section changes continuously over a wide range of photon energies, and recent gas phase and solid state studies have shown that cross sections often do not vary smoothly with photon energy. For example, Gustaffson[9] has used synchrotron radiation to study cross section resonance features in the 20 to 50 eV region on SF_6, and these resonances are a powerful aid for assigning the symmetry of molecular orbitals. Carlson *et al.*[10,11] have recently used synchrotron radiation to study the large variations in the β asymmetry parameter and cross section variations from 13 to 90 eV. Minima in the halogen lone pair β values and cross sections were observed and characterized as Cooper minima. A number of recent solid state studies have shown resonance features in valence band intensities on scanning through a core level,[12—15] but such resonance features have not yet been characterized in a gas phase molecule.

In this communication, we show that the I 5p lone pair cross section does not fall continuously above the threshold for CF_3I, as indicated by the He I and He II spectra.[16] The large *relative* increase in I 5p cross section from 60 to 90 eV, which we observe, is shown to be due to interchannel coupling (or intersubshell interactions) on scanning through the intense I 4d cross section.

Photoelectron spectra were obtained using our Leybold–Heraeus LHS-11 photoelectron spectrometer mounted at the magic angle, and photons from the Canadian Synchrotron Radiation Facility (CSRF) at the Tantalus storage ring.[17,18] Valence band spectra of CF_3I (PCR Research Chemicals Inc.) were obtained at 0.8 Å monochromator band width and 50 eV analyser pass energy from 21 to 110 eV every 1—2 eV up to 50 eV and every 5 eV above 50 eV.

Spectra taken at 32, 41, and 80 eV (Figure 1) show the effect which is of immediate interest. The spectrum at 41 eV is very similar in quality and resolution to that obtained earlier with a He II source.[16] The first spin–orbit split peaks at 10.5 and 11.2 eV (peaks A) are due to I 5p lone pair electrons, while the second peak at 13.3 eV (peak B) is due to the C–I bonding molecular orbital.[16] Peaks A are much more intense than B at 21.2 eV;[16] but decrease rapidly above 26 eV until at 41 eV, they are much less intense than B (Figure 1). This relative decrease continues to 60 eV, at which energy peaks A begin to increase rapidly relative to B. Between 80 eV (Figure 1) and 90 eV, peaks A are more intense than B. At ≥100 eV, peak A becomes less intense than B once again.

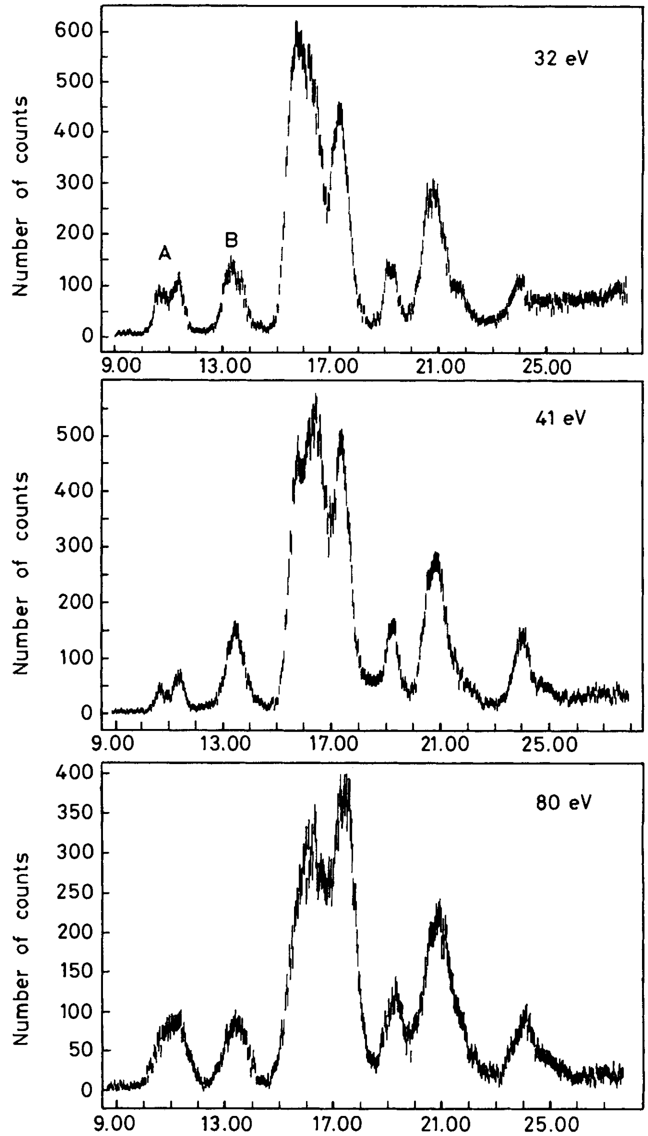

Figure 1. Photoelectron spectra of the valence band of CF_3I taken with monochromatized synchrotron radiation at 32, 41, and 80 eV photon energies.

This large change in the relative intensity of A follows the

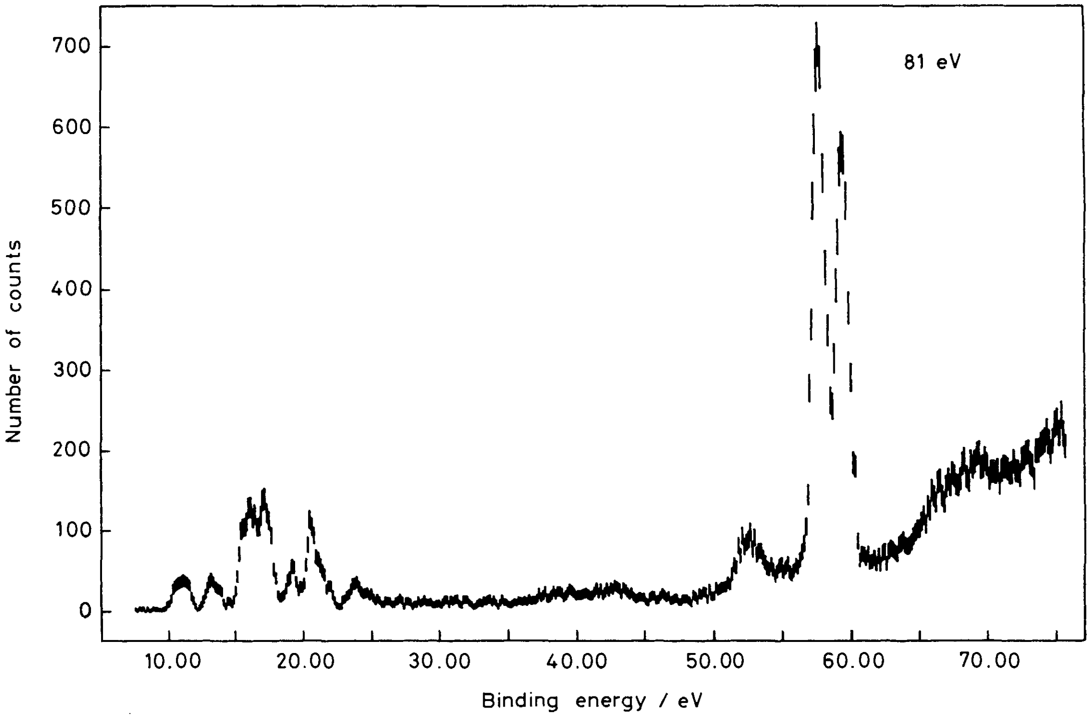

Figure 2. Photoelectron spectrum of CF_3I taken at 81 eV photon energy. Note the valence band region at *ca.* 10—25 eV binding energies (Figure 1), the weak F 2s peaks at *ca.* 40 eV, the intense I 4d peaks at *ca.* 60 eV, and the I NOO Auger peaks in the same region.

I 4d cross section rather closely. The I $4d_{5/2}$ peak has a binding energy of 57.81 eV (Figure 2); and like the Xe 4d level in Xe,[19] its cross section increases to a maximum about 30 eV above threshold.[20] Figure 2 shows that at 81 eV, the I 4d cross section is about an order of magnitude larger than the valence band cross sections. As has been shown both experimentally[21,22] and theoretically[23] for xenon, the enhancement of the 5p (and 5s) cross section on scanning through the 4d level is due to intersubshell interaction[23] (also called interchannel coupling[24]). The photoexcited I 4d electron either collides or interacts with an I 5p electron, such that all the kinetic energy obtained from the photon is imparted to the 5p electron. The I 4d electron then falls back into the 4d level, and the 5p electron is ionized with exactly the right kinetic energy.[24]

It is important to emphasize that the above many body effect should be a generally important mechanism for *selectively* enhancing valence band intensities at *known* core level energies when the cross section of the core level is large compared with valence band cross sections. It follows that this effect should be very useful for molecular orbital assignments. For example, the photon energy could be tuned to a known intense core level (*e.g.* 4d or 5d) to enhance the intensity of the molecular orbital with the largest atomic p character.

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