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C 1s and F 1s photoabsorption and subsequent electronic decay of CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4

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High-resolution electron yield spectra of CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4 are observed in the vicinity of C 1s and F 1s thresholds and interpreted with the help of *ab initio* SCF calculations. Resonance spectator and participant Auger spectra are observed following the C 1s and F 1s excitations of these molecules and discussed in terms of the characters of the orbitals of the electrons involved in the electronic decay. The electronic decay from the fragments is also observed for CH_2F_2, CHF_3, and CF_4 at the C $1s \to \sigma^*$ C–F antibonding excitation.

Brown et al. [1] observed C 1s absorption spectra of CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4 at a resolution of 0.4 eV, whereas Tronc et al. [2] observed the C 1s electron energy-loss spectra of CH_4 and CF_4 at a resolution of 70 meV. Schirmer et al. [3] and Remmers et al. [4] reinvestigated the C 1s absorption spectrum of CH_4 at a resolution of 60 meV but there has been no high-resolution data reported for CH_3F, CH_2F_2, and CHF_3. F 1s energy-loss spectra of CH_3F and CF_4 were observed by Brion and coworkers [5,6] but no F 1s spectra have been reported for CH_2F_2 and CHF_3.

We have thus carried out systematic investigation of C 1s and F 1s high-resolution spectra of CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4. We are interested in how the C 1s and F 1s spectra change or remain unchanged when the hydrogen atom is substituted with fluorine atoms one by one. We have also investigated for the first time the electronic decay following C 1s and F 1s excitations of these molecules.

The experiment was carried out on the 10-m grazing incidence monochromator in the undulator beamline BL-2B at the photon factory. The total electron yield spectra, equivalent to the absorption spectra, were measured using a channeltron detector without any energy analysis, at a photon resolution of $\sim$ 60 meV near the C K edge and $\sim$ 150 meV near the F K edge. The resonance Auger photoemission spectra were observed using

a 10-cm hemispherical electron energy analyser at a photon resolution of $\sim$ 0.6 eV and an electron resolution of about $\sim$ 0.7 eV near the C K edge and at a photon resolution of $\sim$ 1.5 eV and an electron resolution of $\sim$ 1.5 eV near the F K edge.

Figure 1 shows the total electron yield spectra of CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4 near the C 1s threshold. Most of the structures observed in the absorption spectra were assigned with the help of *ab initio* SCF calculations.

When the hydrogen atom is substituted with the fluorine atom one by one, a dramatic change appears in the spectra. First, we can see strong chemical shifts as we go from CH_4 to CF_4. This is because the fluorine atom is strongly electronegative. Next, the spectrum of methane is approximately Rydberg-like showing only sharp resonance features. All the structures observed in the CH_4 spectrum can be attributed to the npt_2, ndt_2, and $3sa_1$ Rydberg members and the associated vibrational levels. The spectrum of CF_4, on the other hand, shows a prominent broad feature overlapped with fine structure. The broad feature is the transition to the anti-bonding valence orbital trapped within the molecule whereas the fine structure corresponds to the transitions to the npt_2 and ndt_2 Rydberg orbitals. Between these two molecules we can see the gradual change from the dominance of Rydberg-like transitions to the dominance of valence-like transitions. Further
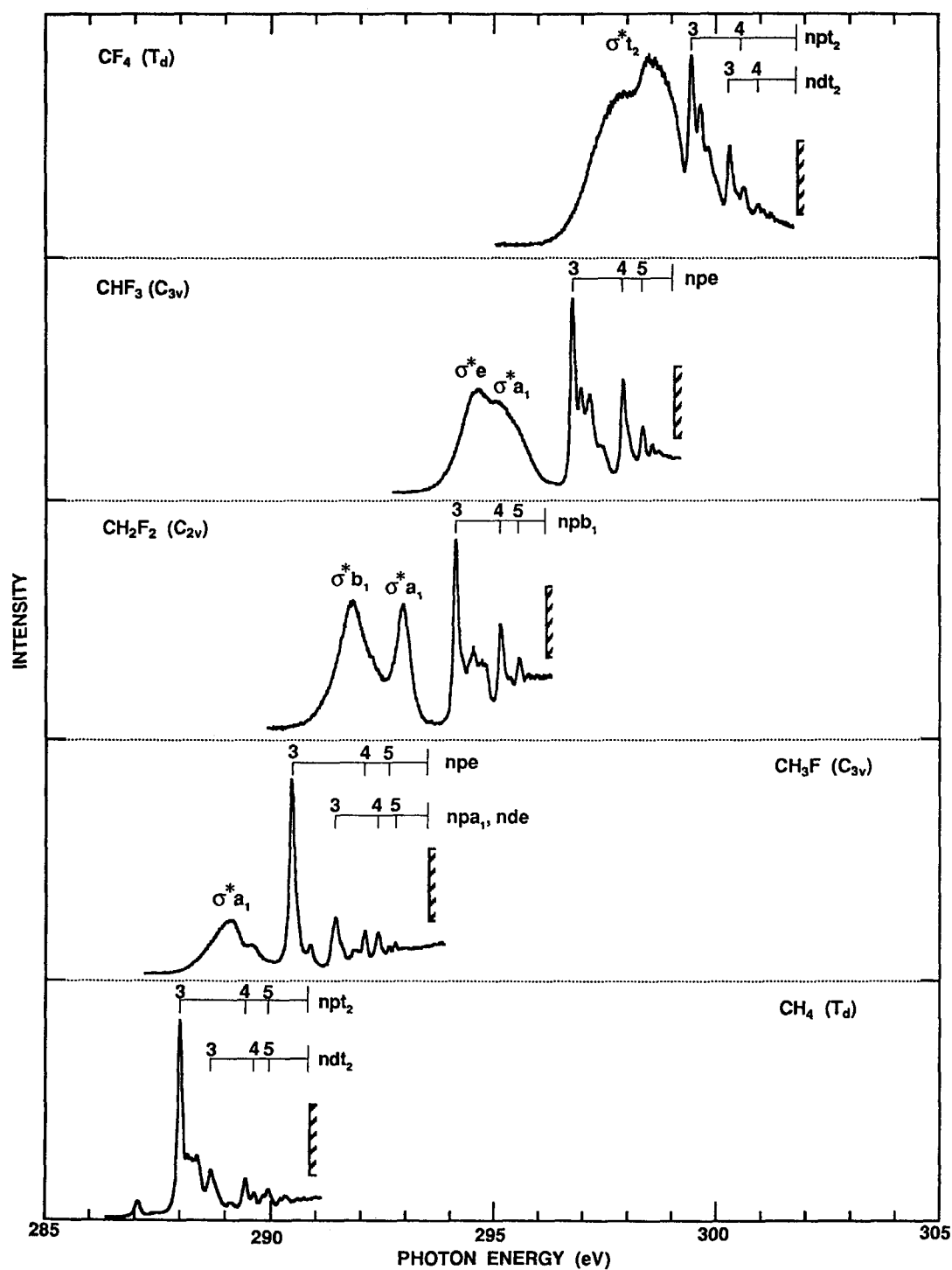
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Figure 1. Total electron yield spectra of CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4 in the vicinity of the C $1s$ threshold.
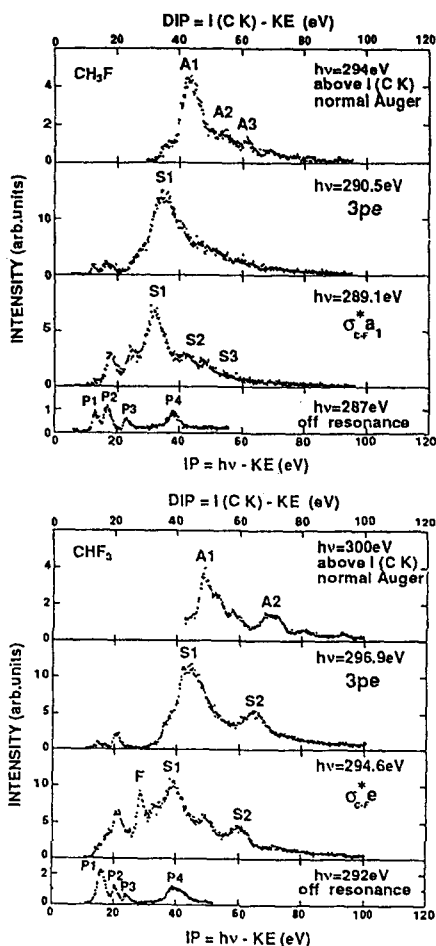
Figure 2. Electron spectra of CH_3F and CHF_3 recorded near the C 1s threshold. See the text for details.

Figure 3. Total electron yield spectra of CH_3F, CH_2F_2, CHF_3, and CF_4 in the vicinity of F 1s threshold.

detailed discussions for each molecule are given elsewhere [7,8].

Figure 2 shows two sets of spectra, the upper one for CH_3F and the lower one for CHF_3. The top spectrum in each set was recorded above the C 1s threshold and thus shows the normal Auger spectrum. The bottom spectrum in each set was recorded below the C 1s pre-edge structure and thus shows the non-resonant photoelectron spectrum. The middle spectra are the difference spectra (i.e., the off resonance contribution subtracted from the on-resonance spectra) recorded at the C 1s → 3pe and σ^*a_1 resonances for CH_3F and at
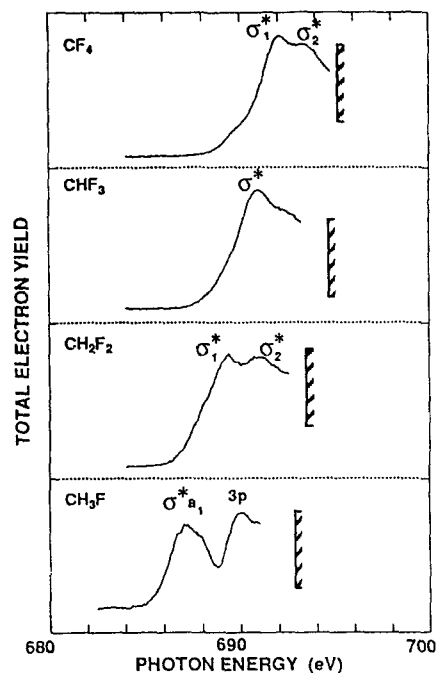
the 3pe and σ^*e resonances for CHF_3.

In these difference spectra, we can see strong satellite bands whose profiles are similar to the normal Auger bands (i.e., Spectator Auger bands) and the resonance enhanced components of the main photolines (i.e., the participant Auger bands). The participant-to-total intensity ratios are ∼ 15 % for C 1s → σ^* and ∼ 5 % for C 1s → 3pe for both CH_3F and CHF_3, suggesting that the electron excited in the valence-like orbital (σ^*) interacts with valence electrons more effectively than the Rydberg electron (3pe) does.

The selectivities can be seen in the enhancement of the photoelectrons for each molecule. When the C 1s electron of CH_3F is excited to the σ^*a_1 orbital, the enhancement occurs for the photoelectron bands P2 (overlap of $1e$ and $5a_1$) and P3 ($4a_1$), whereas P1 ($2e$) and P2 are enhanced at the C 1s → e' excitation. This suggests the participant process is more likely when the valence and excited electron orbitals have similar symmetries.
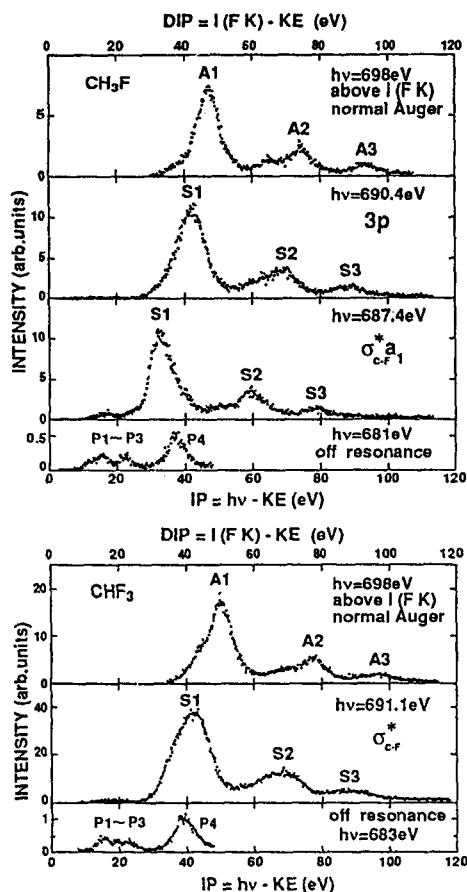
Figure 4. Electron spectra of CH$_3$F and CHF$_3$ recorded near the F 1s threshold.

these four molecules. The spectra are diffuse and no Rydberg series can be identified. This behavior is in sharp contrast to the behavior at the C 1s excitations. The excitation to the valence-like C-F antibonding orbitals is located in the Rydberg excitation region. This prevented us from assigning the observed structures unambiguously with the help of ab $initio$ SCF calculations. The exception is the F 1s $\rightarrow$ σ^*a_1 excitation of CH$_3$F, which is located below the Rydberg excitation region.

Figure 4 shows electron spectra of CH$_3$F and CHF$_3$ recorded near the F 1s edge. The normal Auger spectra (top ones) of both molecules consist of three broad bands, A1, A2, and A3, which correspond to the Auger final states with two outer-valence (F 2p-like) holes, with one outer-valence hole and one inner-valence (F 2s-like) hole, and with two inner-valence holes, respectively: the Auger transitions are $atomic$ like. In the resonance electron emissions, the spectator bands S1, S2, and S3, which are analogous to the A1, A2, and A3 normal Auger bands, are much more dominant than the participant Auger bands P1 to P3.

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When the C 1s electron of CHF$_3$ is excited, the P2 band (overlap of 3e and 5a_1) which has mostly C-F bonding character is significantly enhanced while the P1 band (overlap of 6a_1, 1a_2, 5e, and 4e) which has mostly F 2p lone pair character is not.

In the electron spectra of CH$_2$F$_2$, CHF$_3$, and CF$_4$, we have observed peaks which cannot 'be ascribed to either participant or spectator Auger decay (e.g., peak F in Fig. 2). The kinetic energies of the peaks are almost the same for all three molecules and thus we tentatively assign these to electron emission from the fragment (CF or C).

Figure 3 shows the total electron yield spectra of CH$_3$F, CH$_2$F$_2$, CHF$_3$, and CF$_4$ near the F 1s threshold. The F 1s chemical shifts are similar for

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