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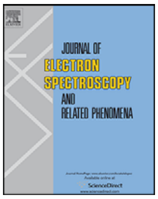

Photoabsorption spectra of CF_3I and thermally dissociated CF_3I near the C 1s, I 3d and F 1s ionisation thresholds

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ABSTRACT

We report soft X-ray total ion yield and angular-resolved ion yield spectra of CF_3I in the C 1s, I 3d and F 1s ionisation regions, and tentatively assign the observed electronic states. Anisotropy in ion yield is observed only for the C 1s → σ^*_{C-I} transition, indicating that the dipole moment for this transition is parallel to the C_{3v}. The effusive source of CF_3I is heated to 800 K to produce a mixture of CF_3 and I, and the resulting spectra are compared to those recorded at room temperature.

1. Introduction

Many investigations have previously been carried out on the electronic structure of trifluoromethyl iodide, CF_3I. Much information has been obtained, particularly concerning the outer valence states. For example, the valence shell photoelectron [1], electron energy loss [2,3] and VUV photoabsorption [4,5] spectra of CF_3I have been reported. The outer valence shell molecular orbital (MO) configuration of CF_3I in its X^1A_1 electronic ground state can be expressed (in C_{3v} symmetry) as

$$\ldots(4a_1)^2(5a_1)^2(3e)^4(6a_1)^2(4e)^4(5e)^4(1a_2)^2(7a_1)^2(6e)^4.$$

In the valence shell photoelectron spectra of [1], it is identified that the outermost MO in the ground state is essentially a p lone pair located on the I atom. The second highest occupied MO has σ_{C-F} bonding character while the C–F bonding orbitals and the fluorine lone pairs are much more strongly bonded. In the study of EELS and VUV photoabsorption spectra [2–5], a broad band is observed in the low energy region. This band can be assigned to the excitation of an electron from the I atom lone pair to an anti-bonding orbital along the C–I bond (n → σ^*), implying that CF_3I has a weak C–I bond. The broad band is enhanced in the low-energy, high-scattering angle EELS spectra [3,4]. Despite the existence of spectroscopic data in the valence shell region, the inner shell excitation region, where the MO model is expected to breakdown, is less well understood.

CF_3I is of interest as a potential fluorocarbon replacement in plasma-processing applications since its weak C–I bond makes it an efficient source of CF_3 radicals. The global warming potential (GWP) of CF_3I is estimated to be the same as that of carbon dioxide, indicating that CF_3I has less of a greenhouse effect than the main feed gases used by the plasma etching industry (e.g. CF_4; GWP = 6500, C_4F_6; GWP = 290). Recent study has shown that the concentration of CF_x radicals has significant effect on the behaviour of fluorocarbon plasmas [6]. To further understand these processes it is important to have knowledge of the interaction of CF_3 with other particles and radiation. However, no experimental data is available for inner shell ionisation of the CF_3 radical by soft X-ray radiation or electron impact. The main reason for the paucity of experimental data is the difficulty in producing sufficient number of radicals to study under controlled conditions. Here we use the thermal dissociation of CF_3I as an efficient source of CF_3 radicals. It has previously been reported that CF_3I completely decomposes at temperatures above 700 K [7,8].

To our knowledge no study has yet been reported of photoabsorption in the C and F K-shell excitation regions for either CF_3 or CF_3I. In this study we report total ion yield (TIY) and

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angle-resolved ion yield (ARIY) spectra in the vicinity of the C 1s (~290 eV), I 3d (~620 eV) and F 1s (~695 eV) thresholds for both pure CF_3I and a sample heated to 800 K. Heating of the sample results in complete thermal dissociation into CF_3 radicals and I atoms, as confirmed by residual gas analysis. Electronic transitions of the inner shell electron, observed in the photoabsorption spectrum recorded by scanning the exciting soft X-ray energy, give information about the unoccupied MOs such as transition energies, transition probabilities, and symmetry, and have analogous features among different molecules which contain the same element. Thus, we attempt to assign the photoabsorption peaks observed for CF_3I by comparison with those for CF_4, the photoabsorption spectra of which in the C 1s and F 1s edge regions have been well studied. As such, the present data supply basic data for understanding the soft X-ray photochemistry of the CF_3I molecule.

2. Experiment

The experiments were carried out at the c-branch of SPring-8's BL27SU [9], which makes use of a figure-8 undulator [10] and a varied-linespacing grating monochromator [11] to provide high-resolution soft X-rays polarized linearly in either the vertical or horizontal direction. Two identical micro-sphere plate detectors were oriented in the vertical and horizontal directions facing the interaction region between the incident photon beam and an effusive gas jet. The acceptance angle of each detector was approximately ±9°, and a potential of +3 V was applied to a mesh in front of each detector to ensure that only energetic fragments were detected [12,13]. Spectra were recorded as a function of photon energy using both horizontal and vertical polarisation of the incident radiation, enabling the relative detection efficiencies of the two detectors to be compensated for. A further detector positioned upstream of the ARIY detectors allowed for the simultaneous recording of TIY spectra. Incident photon flux was recorded by monitoring the drain current on the final refocusing mirror of the beamline and at a gold plate positioned downstream of the gas sample. In the C K-shell excitation region, however, measurements of the photocurrent suffer from carbon contamination on the surface of the optical components. This was corrected for by recording Ar 2p photoelectron spectra and comparing cross-section and angular distribution with their literature values in the photon energy region of interest [14]. The photoelectron spectra were recorded using a high-resolution hemispherical electron-energy analyzer (Gammadata Scienta SES-2002) fitted with a gas cell. The photoelectron spectra also provided a calibration of the incident photon energy, again by comparison to published data [15].

The pressure behind the gas nozzle was ~0.7 kPa during the measurements. The resolving power of the monochromator was set to 5000 for both the C 1s excitation region ($\Delta h\nu \sim 60$ meV) and the F 1s excitation region ($\Delta h\nu \sim 130$ meV).

The CF_3 radical was produced using a resistively heated molecular beam source [16–18]. It has previously been reported that the CF_3I molecule begins to dissociate into a CF_3 radical and an I atom at temperatures of ~700 K [7,8]. TIY spectra were recorded for the parent CF_3I molecule at room temperature (300 K) as well as for dissociated fragments (predominantly CF_3 and I) mixed with the residual CF_3I at a temperature of 800 K. In each spectra a baseline comprising contributions from valence ionisation by second-order radiation (assumed to be constant) was first subtracted. All ion-yield spectra were then normalized to acquisition time, gas pressure, and photon flux.

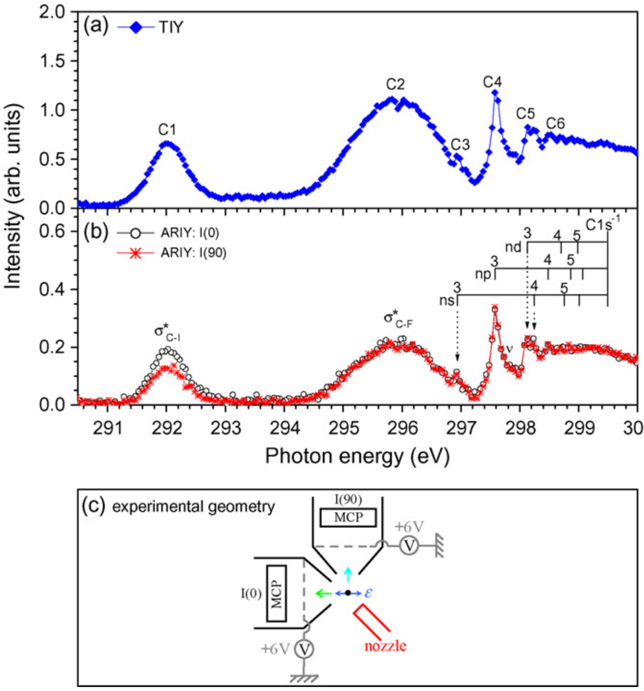

Fig. 1. (a) TIY spectrum near the C K-edge of CF_3I. (b) ARIY spectra, I(0) and I(90), detected in the directions parallel and perpendicular to the electric vector ϵ of the incident light, respectively. (c) Schematic illustration of retarding field ion analyzers.

3. Results and discussion

Fig. 1 shows the TIY and ARIY spectra recorded in the vicinity of the C 1s ionisation threshold. Two broad structures and several sharp structures are observed. The broad features labelled "C1" and "C2" at 292.0 eV and 295.9 eV are assigned to the excitation of the C 1s electron to σ^* anti-bonding orbitals. Considering the dissociation energies of the C–I (2.39 eV) and C–F (4.9 eV) bonds [19], the lower energy peak (C1) is assigned to excitation to the σ^*_{C-I} orbital. The ARIY spectra reveal an anisotropy in this transition, which is ascribed to the localization of the valence holes created as a result of the Auger decay of the C 1s core hole, itself polarized by excitation with linearly polarized light. This means that the transition dipole moment is parallel to the C_{3v} axis [20], and excitation does not lead to symmetry lowering. In contrast, the C 1s → σ^*_{C-F} transition (C2) is accompanied by several different C–F vibrations, resulting in a broader structure and no anisotropy observation in the ARIY spectra. This is due to the loose axial symmetry in this transition—the transition dipole is not parallel to the C_{3v}axis. The sharp structures (C3–C6) are assigned to Rydberg excitations, and assignments have been made using the Rydberg formula. Analysis of the n p series results in an IP = 299.5 eV and a quantum defect $\delta = 0.33$. With these assignments, the quantum defects δ of n s and n d series are 0.69 and −0.16, respectively. The peaks due to excitation of the 3p Rydberg states show shoulders on the high-energy side, most likely due to vibrational excitation with an energy spacing of ~300 meV.

Fig. 2 shows the TIY and ARIY spectra recorded in the vicinity of the I 3d and F 1s ionisation thresholds. Comparing with the total electron yield spectra of CF_4 or CHF_3 [20,21], the structure just below the F K-edge near 692 eV (peak F8) is attributed to the F 1s → σ^*_{C-F}transition. The observed anisotropy of this state is similar to that observed in the ARIY spectra of CF_4 [20], but no quantitative study has been made. Considering the energy separations between the C 1s → σ^*_{C-I} and σ^*_{C-F} transitions of around 5 eV, the structures at 620 eV (F1) and 625 eV (F2) are assigned to I $3d_{5/2}$ transitions