

## Assignment of the C K-Shell Photoabsorption Spectrum of CF<sub>3</sub>CN Molecule

Kazumasa Okada,\* Shuichiro Tanimoto, Toshio Ibuki,<sup>†</sup> Ko Saito, and Tatsuo Gejo<sup>††</sup>

*Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526*

<sup>†</sup>*Kyoto University of Education, Fushimi-ku, Kyoto 612-8522*

<sup>††</sup>*Institute for Molecular Science, Myodaiji, Okazaki 444-8585*

(Received July 23, 2001; CL-010684)

Assignment of the total C photoabsorption spectrum of CF<sub>3</sub>CN in the K-shell region has been established with the help of an angle-resolved photofragment ion spectroscopy. The anisotropy parameters for the energetic CF<sub>3</sub><sup>+</sup> and CN<sup>+</sup> fragments were evaluated at the selected photon energies. The linear C–C≡N skeleton basically held in this region since the strongly negative anisotropy parameters were obtained at the  $\pi_{\text{CN}}^* \leftarrow \text{C}_\text{F}(1s)$  transition.

Inner-shell excitation spectra of molecules in the regions of the C, N, O, and F K-shell excitations contain a variety of pronounced resonances.<sup>1</sup> Extensive studies have been performed so far to obtain information about the electronic structures of the inner-shell excited states of molecules. The assignment of features observed in the spectrum is, however, sometimes a difficult task because transitions from, for example, carbon atoms with different chemical environments occur at the different excitation energies and lead to the formation of complicated peaks in the spectrum. Angle-resolved ion yield spectroscopy has been developed and applied to K-shell excited diatomic and triatomic molecules,<sup>2–7</sup> showing that this technique is a powerful means to get information about symmetries of the K-shell excited states.

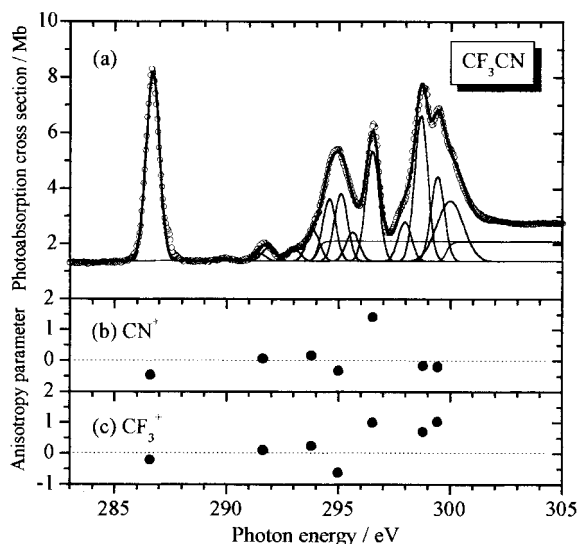
Trifluoroacetonitrile (CF<sub>3</sub>CN) is one of the intriguing molecules in two respects. Firstly, one can selectively excite a specific atom (F, N, or either C). Fluorine is the most electronegative atom and induces the largest chemical shift around it in a molecule. Secondly, we can investigate the fragmentation dynamics of the inner-shell excited molecule noticing the linearity of the C–C≡N skeleton. Whether anisotropic fragmentation can be observed in the polyatomic molecule is our concern here. In our previous study,<sup>8</sup> a strong anisotropy was observed for the energetic CF<sub>3</sub><sup>+</sup>, CF<sub>2</sub><sup>+</sup>, and CN<sup>+</sup> fragment ions at the  $\pi_{\text{CN}}^* \leftarrow \text{N}(1s)$  resonance excitation. That is, the  $\Pi$ – $\Sigma$  symmetry transition basically holds. In the present study we extend the result to the assignment of the C K-shell photoabsorption spectrum with the help of the angle-resolved time-of-flight (TOF) mass spectral data acquired at the selected photon energies.

The experiments were performed on the beamline BL8B1 at the UVSOR facility of the Institute for Molecular Science.<sup>9</sup> Photoabsorption spectrum was observed at room temperature in the C K-shell region with the energy resolution  $E/\Delta E \sim 2000$ .<sup>9</sup> An ion chamber with two 10-cm long electrodes was used. The photon beam entered through an Al thin filter. The ion current was fed to a picoammeter and stored in a personal computer, together with the sample pressure of CF<sub>3</sub>CN gas monitored with a capacitance manometer. The photon energy was calibrated using the  $\pi^*$  resonance transition of CO at 287.3 eV.<sup>10</sup>

The TOF mass spectra were also measured at several photon energies including the prominent resonance peaks observed. An energy resolution of about 1 eV was employed for the measurement. The sample gas was introduced into the main experimental

chamber as an effusive molecular beam through a gas nozzle which is mounted orthogonal to both the photon beam axis and the TOF mass spectrometer tube.<sup>11</sup> An Al thin filter was inserted upstream in order to suppress the scattered stray light. The pressures in the chamber during the measurements were kept at  $1 \times 10^{-3}$  Pa. The spectrometer was operated under the Wiley–McLaren space-focusing conditions<sup>12</sup> with an extraction field of  $\sim 250$  V/cm in the present study. The TOF mass spectra were acquired at 0° and 90° angles with respect to the linearly polarized electric vector of the incident photon. In these spectra the contribution of background originating from the ionization of valence electrons was subtracted by the measurement of the spectra at around 283 eV. The sample gas for the present study was purchased from SynQuest Laboratories, Inc. and was used without further purification.

The upper panel of Figure 1 shows the photoabsorption spectrum of CF<sub>3</sub>CN in the C K-shell excitation region. The most intense peak at 286.7 eV is assigned to the  $\pi_{\text{CN}}^* \leftarrow \text{C}_\text{N}(1s)$  transition by analogy with the corresponding spectrum of acetonitrile,<sup>13</sup> where the C<sub>N</sub>(1s) denotes the 1s electron of carbon atom of the C≡N group (the C<sub>F</sub>(1s) denotes that of CF<sub>3</sub> group). A small hump at 289.9 eV can be assigned to the promotion into the 3s Rydberg state. The spectrum in the photon energy region  $\geq 291$  eV is, however, composed of a number of transitions. In order to extract the peak positions of the overlapped and/or embedded states, we have carried out a least-squares peak fitting for the entire photoabsorption



**Figure 1.** (a) Photoabsorption spectrum of CF<sub>3</sub>CN in the C K-shell excitation region. The open circles are the experimental data and the thin solid curves are the individual transitions obtained by a least-squares fitting. The thick curve is the sum of the thin curves. Peak assignments are given in Table 1. (b) Anisotropy parameter  $\beta$  of the energetic CN<sup>+</sup> fragment ions with kinetic energies  $\geq 2.96$  eV. (c) Anisotropy parameter  $\beta$  of the energetic CF<sub>3</sub><sup>+</sup> fragment ions with kinetic energies  $\geq 2.37$  eV.

spectrum, assuming the peaks having the same FWHM. The result is also shown in Figure 1. The further assignment will be much easier when one obtains information about the symmetry character of each peak in the spectrum. We now focus on the analysis and results of the angle-resolved photofragment ion spectroscopy.

The angular distribution of fragment ions is expressed by the following equation on which the angle-resolved photofragment ion spectroscopy is based:<sup>14</sup>

$$d\sigma/d\Omega = (\sigma_t/4\pi) \cdot [1 + (\beta/2)(3\cos^2\theta - 1)], \quad (1)$$

where  $\sigma$  is the photoabsorption cross section,  $\sigma_t$  is the total photoabsorption cross section,  $\theta$  is the angle between the direction of light polarization and the velocity vector of the fragment ion, and  $\beta$  is the anisotropy parameter. In the present analysis the TOF mass spectral profiles of  $\text{CN}^+$  and  $\text{CF}_3^+$  ions observed at the  $0^\circ$  and  $90^\circ$  angles were used to obtain the anisotropy parameters. We took only the energetic ions with kinetic energies  $\geq 2.96$  and  $2.37$  eV for the  $\text{CN}^+$  and  $\text{CF}_3^+$  ions, respectively, into consideration because slow ions are ejected almost isotropically due to the long lifetimes.<sup>15</sup> The energetic ions showed two wings in the lower- and higher-mass regions in the TOF spectrum, just as observed in the previous paper.<sup>8</sup>

The profiles of  $\text{CN}^+$  and  $\text{CF}_3^+$  peaks were reproduced by the fitting method developed by Saito and Suzuki.<sup>16</sup> The resultant anisotropy parameter  $\beta$  values are shown in the lower panels of Figure 1 as a function of the photon energy. At the  $\pi_{\text{CN}}^* \leftarrow \text{C}_\text{N}(1s)$  resonance transition the  $\beta$  values for  $\text{CN}^+$  and  $\text{CF}_3^+$  ions were found to be  $-0.46$  and  $-0.21$ , respectively, which support our assumption that the linear  $\text{C}-\text{C}\equiv\text{N}$  skeleton is basically preserved in the C K-shell excitation region as well. This finding allows us to make assignment of the photoabsorption spectrum further, based on the anisotropic distributions of the energetic fragment ions. That is, one can assign a  $\Pi-\Sigma$  symmetry transition to the peak with a negative  $\beta$  value, whereas a  $\Sigma-\Sigma$  symmetry transition can be assigned to the peak with a positive  $\beta$  value.<sup>17</sup>

The distinct anisotropic distribution of the energetic ion was found at 295.1 and 296.5 eV. The  $\beta$  value for  $\text{CF}_3^+$  at 295.1 eV is  $-0.62$ , while  $\beta = +1$  at 296.5 eV. Similar results were obtained for the  $\text{CN}^+$  ions. We thus assign these two peaks to the  $\pi_{\text{CN}}^* \leftarrow \text{C}_\text{F}(1s)$  and  $\sigma_{\text{CC}}^* \leftarrow \text{C}_\text{F}(1s)$  transitions, respectively. The weak peak components were assigned by referring to the published data for similar compounds.<sup>18</sup> The peaks around 299 eV are heavily overlapped, and thus the evaluation of the deduced  $\beta$  values is not simple. The  $\beta$  value of  $\text{CN}^+$  suggests that the formed  $\text{CN}^+$  is ejected into isotropic direction. The positive  $\beta$  value of  $\text{CF}_3^+$  supports that a  $\sigma^*$  level is embedded in this region. Table 1 summarizes the energies, term values, quantum defects, and proposed assignments.

The experimental ionization potentials have not been reported yet, except an estimated value of 294 eV for the  $\text{C}_\text{N}(1s)^{-1}$  threshold.<sup>18</sup> The present analysis yields 294.1 and 299.8 eV for  $\text{C}_\text{N}(1s)^{-1}$  and  $\text{C}_\text{F}(1s)^{-1}$  thresholds, respectively. The latter threshold value agrees well with that for hexafluoro-2-butyne (299.9 eV).<sup>18</sup>

In summary, we have measured the total photoabsorption cross section of  $\text{CF}_3\text{CN}$  in the C K-shell excitation region. The features of the peaks have been assigned with the help of the data obtained by the angle-resolved photofragment ion spectroscopy, in which the anisotropy parameters for the  $\text{CF}_3^+$  and  $\text{CN}^+$  energetic fragment ions were evaluated at the selected photon energies. The analysis as to the fragmentation process is now in progress and the results will be presented elsewhere.<sup>19</sup>

**Table 1.** Energies, term values, quantum defects, and proposed assignment for  $\text{CF}_3\text{CN}$  in the C K-shell excitation region.

Energy / eV	Term value <sup>a</sup> / eV		Quantum defect		Proposed assignment	
	$\text{C}_\text{N}$	$\text{C}_\text{F}$	$\text{C}_\text{N}$	$\text{C}_\text{F}$	$\text{C}_\text{N}$	$\text{C}_\text{F}$
286.7	7.39				$\pi_{\text{CN}}^*$	
289.9	4.19		1.2		3s	
291.4	2.64		0.7		3p	
291.9	2.22				$\sigma_{\text{CC}}^*$	
293.0	1.09		0.5		4p	
293.9	0.22				$\text{Ryd}/\sigma_{\text{CF}}^*$	
294.1					IP	
294.6	-0.50	5.24			pseudo- $\pi_{\text{CF}}^*$	
295.1		4.72				$\pi_{\text{CN}}^*$
295.6		4.19		1.2		3s
296.5		3.32				$\sigma_{\text{CC}}^*$
298.0		1.87		0.3		3p
298.7		1.14		0.5		$4p/\sigma_{\text{CF}}^*$
299.4		0.40				pseudo- $\pi_{\text{CF}}^*$
299.8						IP
300.0	-5.9				double excitation	

<sup>a</sup>The  $\text{C}_\text{N}$  and  $\text{C}_\text{F}$  denote the carbon atoms of the  $\text{C}\equiv\text{N}$  and  $\text{CF}_3$  groups, respectively.

This work was supported by the Joint Studies Program of the Institute for Molecular Science and a Grant-in-Aid on Research for the Future 'Photoscience' from Japan Society for the Promotion of Science. The authors are grateful to the staff of UVSOR for stable operation of the storage ring and to Dr. H. Yoshida and Professor A. Hiraya for their valuable comments.

#### References and Notes

- J. Stöhr, "NEXAFS Spectroscopy," Springer, Berlin (1992).
- N. Saito and I. H. Suzuki, *Phys. Rev. Lett.*, **61**, 2740 (1988).
- K. Lee, D. Y. Kim, C. I. Ma, D. A. Lapiano-Smith, and D. M. Hanson, *J. Chem. Phys.*, **93**, 7936 (1990).
- N. Kosugi, *J. Electron Spectrosc. Relat. Phenom.*, **79**, 351 (1996) and references therein.
- J. Adachi, N. Kosugi, E. Shigemasa, and A. Yagishita, *J. Chem. Phys.*, **107**, 4919 (1997).
- P. Erman, A. Karawajcayk, E. Rachlew, M. Stankiewicz, and K. Yoshiki-Franzén, *Phys. Rev. A*, **56**, 2705 (1997).
- K. Okada, K. Ueda, T. Tokushima, Y. Senba, H. Yoshida, Y. Shimizu, M. Simon, H. Chiba, H. Okumura, Y. Tamenori, H. Ohashi, N. Saito, S. Nagaoka, I. H. Suzuki, E. Ishiguro, I. Koyano, T. Ibuki, and A. Hiraya, *Chem. Phys. Lett.*, **326**, 314 (2000).
- T. Ibuki, K. Okada, T. Gejo, and K. Saito, *Chem. Phys. Lett.*, **328**, 147 (2000).
- A. Hiraya, E. Nakamura, M. Hasumoto, T. Kinoshita, K. Sakai, E. Ishiguro, and M. Watanabe, *Rev. Sci. Instrum.*, **66**, 2104 (1995).
- A. P. Hitchcock and C. E. Brion, *J. Electron Spectrosc. Relat. Phenom.*, **18**, 1 (1980).
- T. Ibuki, K. Okada, K. Saito, T. Gejo, N. Saito, and I. H. Suzuki, *Nucl. Instr. Meth. A*, **467-468**, 1505 (2001).
- W. C. Wiley and I. H. McLaren, *Rev. Sci. Instrum.*, **26**, 1150 (1955).
- A. P. Hitchcock, M. Tronc, and A. Modelli, *J. Phys. Chem.*, **93**, 3068 (1989).
- R. N. Zare, *Mol. Photochem.*, **4**, 1 (1972).
- For example, see N. Saito, F. Heiser, O. Hemmers, K. Wieliczek, J. Viehhaus, and U. Becker, *Phys. Rev. A*, **54**, 2004 (1996).
- N. Saito and I. H. Suzuki, *Int. J. Mass Spectrom. Ion Processes*, **82**, 61 (1988).
- J. L. Dehmer and D. Dill, *Phys. Rev. A*, **18**, 164 (1978).
- M. B. Robin, I. Ishii, R. McLaren, and A. P. Hitchcock, *J. Electron Spectrosc. Relat. Phenom.*, **47**, 53 (1988).
- T. Ibuki, K. Okada, S. Tanimoto, K. Saito, and T. Gejo, to be published.