Inner shell excitation and dissociation of condensed formamide

4 AUTHORS, INCLUDING:

Ikeura-Sekiguchi Hiromi

National Institute of Advanced Industr…

52 PUBLICATIONS **466** CITATIONS

Yuji Baba

Japan Atomic Energy Agency

182 PUBLICATIONS **1,290** CITATIONS

ELSEVIER

applied
surface science

Inner shell excitation and dissociation of condensed formamide

Hiromi Ikeura-Sekiguchi[a,*], Tetsuhiro Sekiguchi[b], Yoshinori Kitajima[c], Yuji Baba[b]

[a]*Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan*
[b]*Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan*
[c]*High Energy Accelerator Research Organization, Oho, Tsukuba, Ibaraki 305-0801, Japan*

Abstract

Carbon and nitrogen K-shell excitation and dissociation of condensed formamide at 96 K were studied by near edge X-ray absorption fine structure (NEXAFS) recorded by total electron yield (TEY), total ion yield (TIY) and photon-stimulated desorption (PSD) yield of H^+ measurements. It was found that electronic transitions from the C 1s or the N 1s to the σ^* (C–H and/or N–H) enhanced ion yields of H^+ from the C–H and/or N–H functional groups. This selective dissociation indicates that the corresponding unoccupied molecular orbital has an antibonding character of the C–H and/or N–H. To investigate the molecular orientation of condensed formamide, incidence-angle-dependent TEY-NEXAFS spectra were measured. The CNO plane of the adsorbed formamide molecule is determined to be tilted away from the surface by an averaged angle of about $42°$.
© 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Inner shell spectroscopy has been applied to a basic subject to explore the unoccupied electronic structure of surface adsorbates [1]. Formamide adsorbates provide one of the most interesting examples for the N–H⋯O=C hydrogen bond that is a characteristic structural element in nucleic acids and proteins. For the sake of completely understanding the electronic spectroscopy of proteins, in particular, their circular dichroism (CD) spectroscopy which has been widely used for the study of protein conformation [2–4], knowledge of electronic excited states of the amide is essential. Because of the biochemical significance of the amide, valence-state excitation spectra and ultraviolet (UV) and vacuum-ultraviolet (VUV) photoabsorption spectra of formamide have been extensively studied both theoretically and experimentally for more than 30 years. The interpretation of the gas-phase valence-shell excitation spectrum has been summarized by Robin [5]. Valence excitation spectra, however, show relatively complicated features resulting from the various $\pi \Leftrightarrow \sigma$ valence and Rydberg excitations in addition to the $n \rightarrow \pi^*, \pi \rightarrow \pi^*$ and possibly $n \rightarrow \sigma^*$ excitations. On the other hand, core excitation spectra such as inner-shell electron energy loss spectroscopy (ISEELS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy can show simpler features, because core electrons can be selectively excited into the various valence orbitals or Rydberg states. In addition, NEXAFS spectra show variations in peak intensities at various angles of X-ray incidence between the direction of

* Corresponding author. Tel.: +81-298-54-5632;
fax: +81-298-54-5673.
E-mail address: hiromi@etl.go.jp (H. Ikeura-Sekiguchi).

propagation of incident synchrotron light and the surface plane. These differences result from excitation to final states of π or σ symmetry, each of which has different angular properties. NEXAFS spectroscopy, therefore, has the advantage of providing information on electronic structures of excited states.

Among total electron yield (TEY), total ion yield (TIY), photon-stimulated ion desorption (PSD) measurements and so on for NEXAFS, PSD is very sensitive to antibonding characters of unoccupied molecular orbitals [6–16]. Especially, H^+ PSD has been strongly enhanced at $C1s \rightarrow \sigma^*(C–H)$ resonance. In this work, to investigate the excited electronic structure of condensed formamide, H^+ PSD-NEXAFS spectra were measured near the carbon and the nitrogen K-edge. For a gas-phase formamide, ISEEL spectra and their interpretation have been reported by Ishii and Hitchcock [17]. Although many small organic molecules in gas phase have been analyzed with NEXAFS and ISEELS, only very few studies have been done on organic molecules in solid form. To our knowledge, the core excitation spectra of condensed formamide have not been reported previously. To investigate the molecular orientation of condensed formamide, incidence-angle-dependent TEY-NEXAFS spectra were also measured.

2. Experimental

The experiments were performed at the soft X-ray beam line 11A [18] at the Photon Factory. The energy width of the photon beam used was about 0.2 eV near the carbon K-edge. Desorbing ion yields were detected using a quadrupole mass spectrometer (ULVAC MSQ-400, QMS). A TIY spectrum was detected using a dual-microchannel plate (MCP). To obtain information on photoabsorption cross-sections, TEY spectra were measured by sample current. The ion and electron yield spectra have been normalized to the incident photon flux measured with an Au mesh. The SR was directed incident to the sample at an angle of about $5°$ from the surface level in the QMS and MCP detection. A typical value of acceptance angle is about $25°$ for the QMS. The MCP can accept about 80% of the solid angle in front of the sample. The Formamide (98.5%+, Junsei Chemical Co., Ltd.) was purified by several freeze-pump-thaw cycles before

introduction into an experimental chamber. A 30–50 l formamide was exposed to a sputtered Si(1 0 0) substrate at 96 K, which can produce a multilayer. The base pressure of the chamber was typically maintained at 3×10^{-8} Pa.

3. Results and discussion

H^+ ions exhibit the highest yield among the detected ions over all photon energies near the C and N K-edge. C^+, CH^+, NH^+, CHO^+, and CNO^+ ions are also observed. Although the amount of H^+ ions depends on the photon energy, it is roughly less than at least a half of the amount of total ions. H^+ ion yield spectra from the condensed $HCONH_2$ near the C K-edge and the N K-edge are shown in Fig. 1 and Fig. 2, along with each TEY curve. Resonant peak energies of the curves in the condensed formamide are similar to those in the gas phase near the C K-edge. On the other hand, resonant peak energies of the condensed formamide are different from those in the gas phase near the N K-edge. This result could be related to the N–H...O=C hydrogen bond. Resonant peaks in the TEY spectrum were assigned to transitions from the C 1s orbital to the $\pi^*(C=O)$ orbital at 288, the mixed 3s Rydberg /σ^*(HCN) orbital at 291, σ^*(C–N) orbital at 296.5, and the σ^*(C=O) at 301 eV by reference to the results of a gas-phase formamide
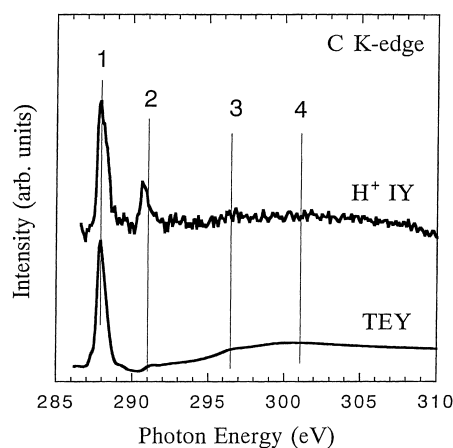

Fig. 1. Total electron yield and H^+ ion yield from condensed formamide at 96 K, at grazing photon incidence angle with respect to the surface, as a function of photon energy near the C K-edge.

Fig. 2. Total electron yield and H^+ ion yield from condensed formamide at 96 K, at grazing photon incidence angle with respect to the surface, as a function of photon energy near the N K-edge.
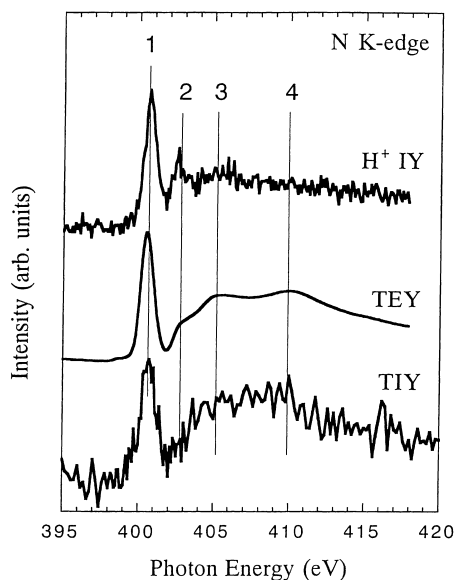
[17]. In Fig. 2, these were assigned to transitions from the N 1s orbital to the $\pi^*(C=O)$ orbital at 400.7, the mixed 3s Rydberg $/\sigma^*(HCN)$ orbital at 402.6, $\sigma^*(C–N)$ orbital at 405.2, and the $\sigma^*(C=O)$ at 410 eV. However, giving weight to the term values of N 1s $\rightarrow \sigma^*(C–N)$ orbital and N 1s $\rightarrow \sigma^*(C=O)$ orbital in gas-phase formamide [17], the third and fourth features (see Fig. 2) could also be assigned to N 1s $\rightarrow$ 3p Rydberg and N 1s $\rightarrow \sigma^*(C–N)$ orbital, respectively.

It is well known that the molecular structure of the solid [19,20] and the gas [21] phase formamide shows that all atoms within one molecule lie on a plane. Based on the amide resonance theory [22], the ionic $H_2N^+=C(H)O^-$ configuration resonantly stabilizes the C–N bond in planar formamide, which was supported by the interpretation of its chemical and physical properties [23,24]. It could, therefore, be expected that these spectra also have $\pi^*(C=N)$ features [25,26] if $H_2N^+=C(H)O^-$ configuration exists. Both K-edge spectra show the intense $\pi^*(C=O)$ features. However, the $\pi^*(C=N)$ features were not found in lower energy regions of $\pi^*(C=O)$ which can be estimated by the results of the other amide systems [25,26]. This finding suggests that the $H_2N^+=C(H)O^-$

configuration is not stable and that the planarity of formamide might be interpreted by another model. In fact, Wiberg et al. recently proposed a new resonance model [27–30].

As shown in Fig. 1 and Fig. 2, it was found that the desorption yields of the H^+ ions are enhanced at the second feature in both K-edges. The results are analogous to the previous results of the formic acid multilayer at 90 K [31]. In Fig. 2, the TIY did not show the enhanced yields at the second feature and is similar to the TEY. This indicates that the TIY consists of many other types of ions. Considering that selective excitation to an orbital localized at a bond induces desorption of a particular ion which is produced through the breaking of the specified bond [13], the $\sigma^*(HCN)$ orbital has an antibonding character of $\sigma^*(C–H)$ and/or $\sigma^*(N–H)$. Taking into account that ionic dissociation occurs selectively around the chosen atomic site where the core-electron excitation has taken place in adsorbed formic acid [21,22] (which is one of the series of substituted carbonyls (HCOX, X=OH), it is plausible that the enhanced H^+ yield originates from the antibonding character of the $\sigma^*(C–H)$ near the C K-edge and the $\sigma^*(N–H)$ near the N K-edge. However, to clarify the origin of H^+ ions caused by a rupture of C–H bond and/or N–H bond in both K-edges, further ion desorption study using two types of deuterated formamide, $DCONH_2$ and $HCOND_2$, is essential.

To investigate the molecular orientation of condensed formamide, N K-edge NEXAFS spectra at grazing and normal incidence were measured, shown in Fig. 3. It was found that the observed
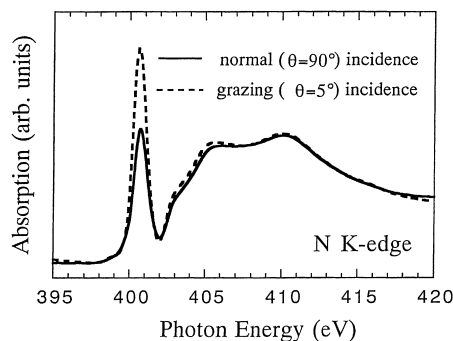

Fig. 3. Nitrogen K-edge NEXAFS spectra of condensed formamide at 96 K, at grazing and normal photon incidence angle with respect to the surface.

intensities in the π^*(C=O) features decrease from grazing to normal. The polarization dependence indicates that the adsorbed formamide molecules are oriented. The average angle between the plane of the formamide molecule and the surface was calculated from the peak intensity ratio at the two angles (I_5/I_{90}) of the π^*(C=O) resonance, using the formula reported by Stöhr [1]. Setting a polarization factor of $P = 0.995$ [18], it was determined that the CNO plane of the adsorbed formamide is tilted away from the surface by an average angle of about $42 \pm 4°$. This suggests that the condensed formamide is not amorphous under the present experimental condition. The obtained geometry was compared with the condensed formic acid in which the plane of formic acid molecule is tilted about $35°$ with respect to the surface [32]. It is considered that the difference in the geometry between the condensed formamide and the condensed formic acid is caused by the difference between the amino NH_2 and the hydroxyl OH functional groups. The amino group is expected to have a larger steric hindrance than the hydroxyl group.

4. Conclusions

Inner shell excitation and dissociation of condensed formamide were studied by NEXAFS spectroscopy using total electron, total ion and H^+ ion desorption yields. There are no π^*(C=N) features in the C and N K-edge NEXAFS spectra, although the existence of π^*(C=N) is expected based on the classic resonance model. It was found that electronic transitions from the C 1s or the N 1s to the second lowest unoccupied molecular orbital (the second LUMO) lead to enhanced ion yields of H^+ from the C–H and/or N–H functional groups. This indicates that the second LUMO has an antibonding character of σ^*(C–H) and/or σ^*(N–H). On the basis of the incidence-angle-dependence of NEXAFS peak intensities of the N1s $\rightarrow \pi^*$(C=O), it was determined that the CNO plane of the adsorbed formamide is tilted away from the surface by an average angle of about $42°$. The difference in the molecular orientation between the condensed formamide and the condensed formic acid is caused by the difference between the amino NH_2 and the hydroxyl OH functional groups.

References

[1] J. Stöhr, NEXAFS Spectroscopy, Springer, Berlin, 1992.
[2] J.T. Yang, C.-S.C. Wu, H.M. Martinez, Methods Enzymol.-Chem. 130 (1986) 208.
[3] I. Tinoco, Adv. Chem. Phys. 4 (1962) 113.
[4] R.W. Woody, I. Tinoco, J. Chem. Phys. 46 (1967) 4927.
[5] M.B. Robin, in: Higher Excited States of Polyatomic Molecules, Vol.2, Academic Press, New York, 1975, p. 122.
[6] R.A. Rosenberg, R.P. LaRoe, V. Rehn, J. Söhr, R. Jaeger, C.C. Park, Phys. Rev. B 28 (1983) 3026.
[7] R.A. Rosenberg, R.P. LaRoe, V. Rehn, I. Owen, G. Thronton, J. Vac. Sci. Technol. 4 (1986) 1451.
[8] D. Coulman, A. Puschmann, U. Höfer, H.-P. Steinrück, W. Feulner, D. Menzel, J. Chem. Phys. 93 (1990) 58.
[9] D. Menzel, in: A. Beswick (Ed.), Proceedings of AIP Conference on Synchrotron Radiation and Dynamic Phenomena, No.258, 1992, p.387.
[10] D. Menzel, G. Rocker, D. Coulman, P. Feulner, W. Wurth, Phys. Scr. 41 (1990) 588.
[11] D. Menzel, G. Rocker, H.P. Steinrück, D. Coulman, P.A. Heimann, W. Huber, P. Zebisch, D.R. Lloyd, J. Chem. Phys. 96 (1992) 1724.
[12] T. Sekiguchi, H. Ikeura, K. Tanaka, K. Obi, N. Ueno, K. Honma, J. Chem. Phys. 102 (1995) 1422.
[13] H.I. Sekiguchi, T. Sekiguchi, K. Tanaka, Phys. Rev. B 53 (1996) 12655.
[14] H.I. Sekiguchi, T. Sekiguchi, J. Phys. IV (Paris) 7 (1997) C2–499.
[15] A. Hoffman, G. Comtet, L. Hellner, G. Dujardin, M. Petravic, Appl. Phys. Lett. 73 (1998) 1152.
[16] A. Hoffman, M. Petravic, G. Comtet, A. Heurtel, L. Hellner, G. Dujardin, Phys. Rev. B 59 (1999) 3203.
[17] I. Ishii, A.P. Hitchcock, J. Chem. Phys. 87 (1987) 830.
[18] Y. Kitajima, K. Amemiya, Y. Yonamoto, T. Ohta, T. Kikuchi, T. Kosuge, A. Toyoshima, K. Ito, J. Synchrotron Radiat. 5 (1998) 729.
[19] J. Ladell, B. Post, Acta Crystallogr. 7 (1954) 559.
[20] E.D. Stevens, Acta Crystallogr. B 34 (1978) 544.
[21] A.H. Narten, S.I. Sandler, J. Chem. Phys. 71 (1974) 2069.
[22] L. Pauling, Nature of the Chemical Bond, 3rd Edition, Cornell University Press, Ithaca, 1960, p. 281.
[23] A.J. Bennet, Q.-P. Wang, H. Slebocka-Tilk, V. Somayaji, R.S. Brown, B.D. Santarsiero, J. Am. Chem. Soc. 112 (1990) 6383.
[24] S. Yamada, Angew. Chem. Int. Ed. Engl. 34 (1995) 1113.

[25] K. Oicni, E. Ito, K. Seki, T. Araki, S. Narioka, H. Ishii, T. Okajima, T. Yokoyama, T. Ohta, T. Inabe, Jpn. J. Appl. Phys. 32 (1993) 818.

[26] J.T. Francis, A.P. Hitchcock, J. Phys. Chem. 98 (1994) 3650.

[27] K.B. Wiberg, K.E. Laidig, J. Am. Chem. Soc. 109 (1987) 5395.

[28] K.B. Wiberg, C.M. Hadad, C.M. Breneman, K.E. Laidig, M.A. Murcko, J.J. LePage, Science 252 (1991) 1266.

[29] K.B. Wiberg, C.M. Breneman, J. Am. Chem. Soc. 114 (1992) 831.

[30] K.B. Wiberg, C.M. Hadad, P.R. Rablen, J. Cioslowski, J. Am. Chem. Soc. 114 (1992) 8644.

[31] H.I. Sekiguchi, T. Sekiguchi, J. Phys. IV (Paris) 7 (1997) C2–499.

[32] D.A. Outka, J. Stöhr, R.J. Madix, H.H. Rotermund, B. Hermsmeier, J. Solomon, Surf. Sci. 185 (1987) 53.