Theoretical study of the X-ray absorption spectra of small formic acid clusters

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Abstract

X-ray absorption spectra of small formic acid clusters, $(HCOOH)_n$, n=1-4, were examined theoretically within the framework of density functional theory. For monomer, assignment of the first peak around 532 eV was consistent with the experiment, whereas the second peak around 535 eV was assigned to a mixture of three bands, O1s (C=O) $\longrightarrow \sigma^*$(OH), O1s (OH) $\longrightarrow \pi^*$(OH), and O1s (OH) $\longrightarrow \sigma^*$(OH) excitations. For the dimer, relative intensities of the oscillator strengths of O1s (C=O) and O1s (OH) $\longrightarrow \sigma^*$(OH) excitations decrease due to strong hydrogen bond formation, whereas those of O1s (C=O) and O1s (OH) $\longrightarrow \pi^*$(C=O) excitations are insensitive to the dimerization.

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1 Introduction

Formic acid is of particular interest in its electronic and molecular structures and reactivity from both experimental and theoretical points of view [1,2], since it is one of the simplest model molecules for studying biological systems exhibiting organic acidic type bonding. Formic acid is known to form the most stable dimer with a complexation energy of ≈ 15 kcal mol^{-1} due to double-bridged strong OH $\cdots$ O hydrogen bonds (HBs) shown in Fig. 1. For larger clusters (n=3,4), Roy et al. have recently reported theoretical studies [3,4], where lowest-energy dimer unit(s) in C_s symmetry have been predicted for the stable clusters.

Recent progress in spectroscopic techniques in the soft X-ray region using synchrotron radiation has enabled us to examine in detail the electronic structures of molecules as well as the chemical reactions induced by inner-shell excitations [5–9]. Core electron excitation spectra of formic acid monomer have been reported by Ishii and Hitchcock [10] using inner shell electron energy loss spectroscopy (ISEELS) and by Prince et al. [11] using a high-resolution measurement of near edge X-ray absorption fine structure (NEXAFS) spectra. However, X-ray absorption (XA) spectra of formic acid clusters have never been observed. It is thus important to compare the XA spectra of free formic acid molecule with those of its clusters to explore the changes in the electronic structures upon cluster formation.

A treatment based on the density functional theory (DFT) [12] is now available to inner-shell excitations for analyses of XA spectra. This procedure is widely applied to relatively small molecules in the gas phase [12–15] as well as larger systems such as surface-adsorbed molecules using cluster models [16] and models of liquid water [17,18]. The present paper is a report of theoretical XA spectra of small formic acid clusters at the O K-edge within the DFT framework, by which we discuss the influence of the strong OH $\cdots$ O HB on the NEXAFS spectra.

2 Computational method

Geometry optimizations of formic acid and its clusters were carried out without any symmetry constraints using the Gaussian 98 program [19] at the MP2/cc-pVTZ level of approximation. Vibrational frequencies were calculated using the analytical second derivatives at the same level to confirm their stationary structures and correct the zero-point vibrational energies. Vibrational frequencies for trimers and tetramers were replaced with those of MP2/cc-pVDZ level to estimate thermochemical parameters because of the limitation of computer resources. Frequencies were scaled by multiplying 0.9784 on the MP2 calculations [20]. The basis set superposition error (BSSE) was corrected by the counterpoise method to estimate the stabilization energy for each cluster. Using these results, the thermal energy corrections were added to the total energy of the system at 298.15 K and 1 atm, with the principal isotope for each element.

The detailed computational procedure of the theoretical XA spectra has been described elsewhere [12–15]. In short, the XA spectra were generated by the transition potential (TP) method in combination with a double basis set technique [21]. In order to estimate the absolute excitation energies more accurately, relativistic and functional corrections were added to the excitation energy [14]. The relativistic effects on the IP of 0.33 eV for the O K-edge and functional correction of 0.83 eV for O1s (C=O) excitation and that of 0.68 eV for O1s (OH) excitation were added, where the latter values were determined by the difference between the experimental and computational values of the core-ionization energy of formic acid monomer in the gas phase [22].

The spectra were generated by a Gaussian convolution of the discrete lines by varying the broadenings to mimic the experimental spectra. For the region below 538 eV, the broadening [full width at half maximum (FWHM)] was set to 0.9 eV, and for the next 4 eV the FWHM was linearly increased up to 4.0 eV. The ionized center was described using the IGLO-III basis of Kutzelnigg et al. [23], while (6311/311/1) and (311/1) basis sets were used for the other heavy atoms and hydrogen atoms. The auxiliary basis sets were (5,2;5,2) for carbon and oxygen and (3,1;3,1) for hydrogen atoms. The gradient-corrected exchange (PD86) and correlation functionals (PD91) by Perdew and Wang were applied in the present study [24,25]. The calculations were performed using the StoBe-DeMon program [26]. Note that our procedures were intended to describe XA spectra up to the ionization threshold using the discrete basis sets, so that the spectra in the continuum region were not covered in the present study.

3 Results and discussion

3.1 Geometrical structures of formic acid clusters

Optimized structures for the most stable formic acid clusters, $(HCOOH)_n$, n=1-4, are shown in Fig. 1, and their structural parameters are listed in Table 1. The most stable structures of formic acid monomer (I) and its dimer

(II) are well-known [1], and the trimer and tetramer have also been studied theoretically by Roy et al. [3,4].

The structures obtained here are consistent with the previous theoretical studies. In the dimer, an eight-membered ring configuration (II) shown in Fig. 1 becomes the most stable structure, where each OH $\cdots$ O HB is almost linear due to the maximum of dipole-dipole interaction. The OH bond length, 1.00 Å, is longer than that of the monomer (0.97 Å). The HB length of OH $\cdots$ O is 1.65 Å, indicating that this structure has relatively strong HBs. A ring structure (III) is the most stable in the trimer, where the OH $\cdots$ O HB bends slightly from the OH axis and the OH bond is shorter than that in the dimer. Each of these HBs is weaker than that in the dimer (II), as exhibited on the bond length; the OH $\cdots$ O bond length is 1.72 Å in the trimer.

Such a single ring structure is not the most stable in the tetramer, where the structure (IV) composed of weakly bonded two-dimers (II) are more stable. The length of the OH bond and HB are both close to those of the stable dimer (II). Among many of such two-dimer configurations, the structure of the tetramer (IV) shown in Fig. 1 is the most stable and is also consistent with the structure reported by Roy et al.

3.2 XA spectra of formic acid clusters

The XA spectra calculated for the most stable clusters are shown in Fig. 2 and positions of the excitation peak for π^*(C=O) and σ^*(OH) along with IPs are listed in Table 2. As for the monomer, the calculated spectrum is consistent with the experimental spectra [10,11]. The first band at 532.4 eV is assigned to

O1s (C=O) $\longrightarrow$ π^*(C=O) excitation that corresponds to previous assignments by Ishii and Hitchcock [10] and Prince et al. [11]. The second band at 535.2 eV, presently assigned to the mixture of three transitions, O1s (C=O) $\longrightarrow$ σ^*(OH) and O1s (OH) $\longrightarrow$ π^*(C=O)/σ^*(OH) excitations, is different from the experimental assignments [10,11]. This band has previously been assigned to the mixture of two transitions, O1s (OH) $\longrightarrow$ π^*(C=O) and O1s (C=O) $\longrightarrow$ 3sa'(OH) excitation [10,11].

In the dimer, however, the first theoretical O1s (C=O) $\longrightarrow$ π^*(C=O) band is slightly shifted to a high-energy side from the monomer band, whereas the second band (assigned as O1s (OH) $\longrightarrow$ π^*(C=O) transition) is shifted to a lower-energy side (534.5 eV) from the monomer band. It should be noted that the transition to O1s (OH) $\longrightarrow$ σ^*(OH) is not involved in the second peak of the dimer. This transition is shifted to a high-energy side, 537.1 eV, and the intensity decreases due to the strong interaction by dimerization. The ionization potential (IP) of O1s (C=O) calculated for the dimer is slightly shifted to a higher energy compared with the monomer, whereas the IP of O1s (OH) for the dimer is shifted to a lower energy by ≈ 0.6 eV. These values are consistent with the core-electron binding energies (CEBEs) calculated by Aplincourt et al. [27]. The CEBE heavily depends on the electron density around the atom to be core-excited. The electron density around the oxygen atom of the hydroxyl group is perturbed more strongly than that of the carbonyl group by dimerization. We found that the term values are not so sensitive to the dimerization that all peaks involving the O1s (OH) excitation are shifted to lower energies.

In the trimer, the first peak assigned to O1s (C=O) $\longrightarrow$ π^*(C=O) excitation at 532.7 eV is located at a similar position to the dimer. The second peak at

534.7 eV that corresponds to O1s (OH) $\longrightarrow \pi^*$(C=O) excitation is slightly shifted to a higher energy position than the dimer, indicating that each HB weakened. The second peak is thus more sensitive to the formation of the HB than the first one.

In the tetramer, the calculated XA spectrum resembles that of the dimer except for the decreasing intensity of the band around 537 eV. This indicates that the spectral shape of the tetramer is mostly determined by that of the stable dimers and that the effect of weak HB (CH $\cdots$ O) between the two dimers is much less effective.

The influence of different configurations of the clusters on the XA spectra is also of interest. The XA spectra of two types of formic acid tetramers are shown in Fig. 3. One is the most stable planar structure (IV), which is also shown in Fig. 1, and the other is the structure with two stacked dimers. The Gibbs energy difference between these isomers, 2.03 kcal mol^{-1}, is inconsistent with the value (1.21 kcal mol^{-1}) reported by Roy et al.[4], probably because of the difference in the computational level of theory.

It is also notable that the interaction between the monomers in the stable dimers is obviously stronger than that between the dimers in the tetramers, although the calculation of the interaction energy for the tetramers is sensitive to the computational level of theory. Despite the difference in the orientations, the XA spectra of these isomers are very similar to each other. This implies that they depend only weakly on the orientation of the constituent dimers.

The structure of formic acid monomer itself does not change significantly by dimer formation, except that the OH bond is slightly elongated. To examine the spectral change caused by the dimerization, two model calculations were performed.

The first one is the effect of the lengthening of the OH bond. The shape of the XA spectra is found to be insensitive to this change (not shown), indicating that the change in the OH bond length itself is not important. The second model calculations are concerned with the relative orientations of the two formic acids in configuration (II) and how they are allowed to approach their equilibrium position; the HB distances are reduced by every 0.2 Å. The whole spectra are shown in Fig. 4 and the oscillator strengths for the π^*(C=O) and σ^*(OH) excitations are also shown in Fig. 5.

The two O1s (C=O/OH) $\longrightarrow \pi^*$(C=O) excitation peaks come close to each other (Fig. 5(a)). Two C=O and OH oxygen atoms in formic acid become equivalent to each other if the HB distance comes to the bond length of the hydroxyl group [27]. The excited π^*(C=O) orbital is actually insensitive by dimerization due to the out-of-plane character. The intensities of these π^*(C=O) excitation peaks are not appreciably changed due to the stable Frank-Condon density. Thus the peak shifts of π^*(C=O) excitations are mostly explained by the differences in the IPs (or CEBEs) for the two oxygen atoms in the dimer configuration.

On the other hand, the σ^*(OH) orbital is strongly perturbed by dimerization due to the in-plane character. Peak positions of σ^*(OH) excitation shift to higher energies upon dimerization because the orbital produces additional anti-bonding interaction between two formic acids, and the transition intensity almost disappears due to the significant decrease in the Frank-Condon density (Fig. 5(b)).

4 Summary

The structures and XA spectra for small sizes of formic acid clusters have been studied theoretically. Both transitions of O1s (C=O/OH) $\longrightarrow \sigma^*$(OH) disappear by dimerization, and the transitions O1s (C=O/OH) $\longrightarrow \pi^*$(C=O) are shifted closer to each other due to the strong HB interaction. The core electron excitation to the σ^*(OH) orbital, which expands along the HB, is strongly correlated with the strength of the HB. On the other hand, the excitation to the π^*(C=O) orbital is insensitive to the HB formation.

The XA spectra for the larger clusters (n=3,4) also show similar spectral features to those of stable dimers. This indicates that the strong OH $\cdots$ O hydrogen bond structures are also involved in these clusters. A comparison of the XA spectra with experimental ion yield spectra can be made in the forthcoming photoelectron-photoion coincident measurements on core-excited formic acid clusters.

5 Acknowledgement

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References

[1] S.Scheiner, Hydrogen bonding. A Theoretical Perspective, Oxford University Press, New York, 1997.

[2] C.F. Wilcox, S.H. Bauer, J. Chem. Phys. 107 (1997) 5794.

[3] A.K. Roy, A.J. Thakkar, Chem. Phys. Lett. 386 (2004) 162.

[4] A.K. Roy, A.J. Thakkar, Chem. Phys. Lett. 393 (2004) 347.

[5] J.Stöhr, NEXAFS Spectroscopy, Springer, Berlin, 1992.

[6] D.M. Hanson, Adv. Chem. Phys. 77 (1990) 1.

[7] R.N. Zare, Science 279 (1998) 1875.

[8] A.Nilsson, J. Electron Spectrosc. Relat. Phenom. 126 (2002) 3.

[9] K.Mase, M.Nagasono, S.Tanaka, T.Sekitani, S.Nagaoka, Fiz. Niz. Temp. 29 (2003) 321.

[10] I.Ishii, A.P. Hitchcock, J. Chem. Phys. 87 (1987) 830.

[11] K.C. Prince, R.Richter, M.deSimone, M.Alagia, M.Coreno, J. Phys. Chem. A 107 (2003) 1955.

[12] L.Triguero, L.G.M. Pettersson, H.Ågren, Phys. Rev. B 58 (1998) 8097.

[13] C.Kolczewski, R.Püttner, O.Plashkevych, H.Ågren, V.Staemmler, M.Martins, G.Snell, A.S. Schlachter, M.S. Anna, G.Kaindl, L.G.M. Pettersson, J. Chem. Phys. 115 (2001) 6426.

[14] O.Takahashi, L.G.M. Pettersson, J. Chem. Phys. 121 (2004) 10339.

[15] O.Takahashi, K.Saito, M.Mitani, H.Yoshida, F.Tahara, T.Sunami, K.Waki, Y.Senba, A.Hiraya, L.G.M. Pettersson, J. Electron Spectrosc. Relat. Phenom. 142 (2005) 113.

[16] M.Nyberg, M.Odelius, A.Nilsson, L.Pettersson, J. Chem. Phys. 119 (2003) 12577.

[17] M.Cavalleri, H.Ogasawara, L.G.M. Pettersson, A.Nilsson, Chem. Phys. Lett. 364 (2002) 363.

[18] P.Wernet, D.Nordlund, U.Bergmann, M.Cavalleri, M.Odelius, H.Ogasawara, L.A. Näslund, T.K. Hirsch, L.Ojamäe, P.Glatzel, L.G.M. Pettersson, A.Nilsson, Science 304 (2004) 995.

[19] M. J. Frisch, et al., Gaussian 98, revision A.4, 1998.

[20] J.B. Foresman, A.Frisch, Exploring Chemistry with Electronic Structure Methods, Second Ed., Gaussian Inc., 1993.

[21] H.Ågren, V.Carravetta, O.Vahtras, L.G.M. Pettersson, Theor. Chem. Acc. 97 (1997) 14.

[22] W.L. Jolly, K.D. Bomben, C.J. Eyermann, At. Data Nucl. Data Tables 31 (1984) 433.

[23] W.Kutzelnigg, U.Fleischer, M.Schindler, NMR-Basic Principles and Progress, Springer-Verlag, Heidelberg, Heidelberg, 1990.

[24] J.P. Perdew, Y.Wang, Phys. Rev. B 33 (1986) 8800.

[25] J.P. Perdew, Y.Wang, Phys. Rev. B 45 (1992) 13244.

[26] K.Hermann, L.G.M. Pettersson, M.E. Casida, C.Daul, A.Goursot, A.Koester, E.Proynov, A.St-Amant, D.R. Salahub, V.Carravetta, H.Duarte, N.Godbout, J.Guan, C.Jamorski, M.Leboeuf, V.Malkin, O.Malkina, M.Nyberg, L.Pedocchi, F.Sim, L.Triguero, A.Vela, Stobe-demon version 1.0.

[27] P.Aplincourt, C.Bureau, J.-L. Anthoine, D.P. Chong, J. Phys. Chem. A 105 (2001) 7364.

Table 1

Geometrical parameters for the lowest formic acid clusters, $(HCOOH)_n$, n=1-4

	R(OH)/Å	R(O ⋯ HO)/Å	Angle(O ⋯ HO)/deg
monomer	0.97		
dimer	1.00	1.65	179.5
trimer	0.99	1.72	165.9
tetramer	1.00,1.00	1.65, 2.51	178.9, 179.6

Table 2

Binding energies of core-electrons of O(1s) and spectral peak positions of π^*(C=O) and σ^*(OH) excitations for formic acid clusters, $(HCOOH)_n$, n=1-4

		IP	π^*(C=O)	σ^*(OH)
exp[a]	O1s (C=O)	538.95	531.86	
	O1s (OH)	540.65	534.89	535.36
monomer	O1s (C=O)	538.95[a]	532.4	535.0
	O1s (OH)	540.65[a]	535.2	535.2
dimer	O1s (C=O)	539.03	532.7	536.5
	O1s (OH)	540.03	534.5	537.1
trimer	O1s (C=O)	538.79	532.7	536.3
	O1s (OH)	539.99	534.7	537.3
tetramer	O1s (C=O)	538.91	532.7	536.4
	O1s (OH)	539.93	534.6	537.5

[a] All values are calibrated to the experimental IP of formic acid monomer.

Figure captions.

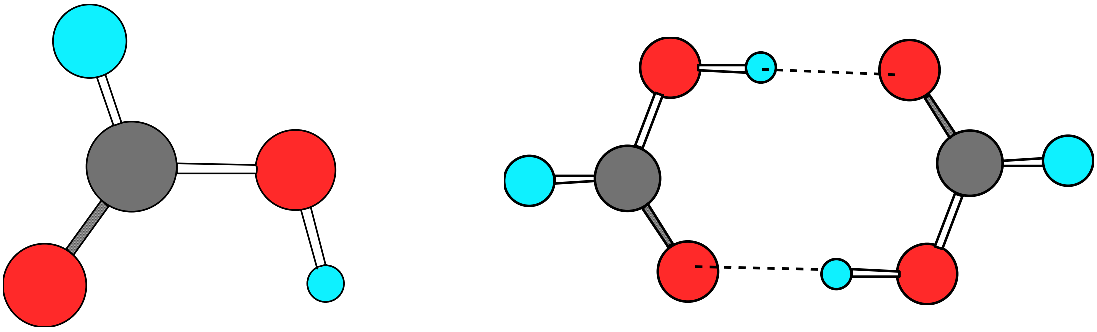
Fig. 1. The most stable structures optimized for formic acid clusters $(HCOOH)_n$, n=1-4.

Fig. 2. XA spectra of formic acid clusters. The most stable isomers (I) - (IV) are used for model calculations. Red and blue lines indicate calculated oscillator strengths from O1s (C=O) and O1s (OH) excitations, respectively. Binding energies of core-electrons of O1s $(C{=}O)^{-1}$ and O1s $(OH)^{-1}$ are also shown.

Fig. 3. XA spectra of two types of the formic acid tetramers. The most stable planar structure used in Fig. 2 and the most stable stacking structure are used for model calculations. These structures are also shown in the figure. Red and blue lines indicate calculated oscillator strengths from O1s (C=O) and O1s (OH) excitations, respectively.

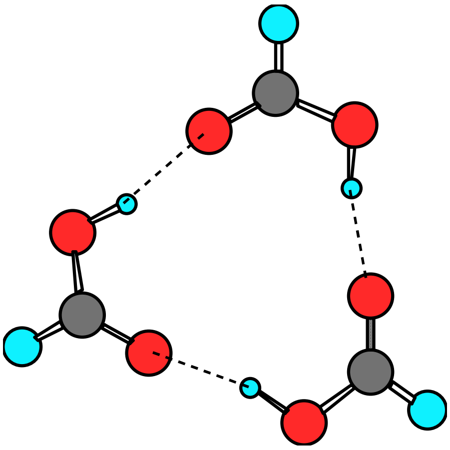
Fig. 4. Spectral change from dimer to monomer against the HB distance. Geometries for both formic acids were fixed. Red and blue lines indicate calculated oscillator strengths of O1s (C=O) and O1s (OH) core excitations, respectively.

Fig. 5. Variation of oscillator strengths for the core excitation to π^*(C=O) and σ^*(OH) against the HB length on dimerization of formic acid. The oscillator strengths are taken from Fig. 4.

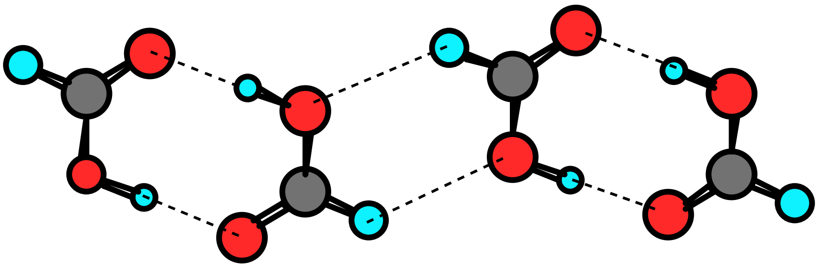


Monomer (I)

Dimer (II)



Trimer (III)



Tetramer (IV)

Fig. 1 Takahashi et al

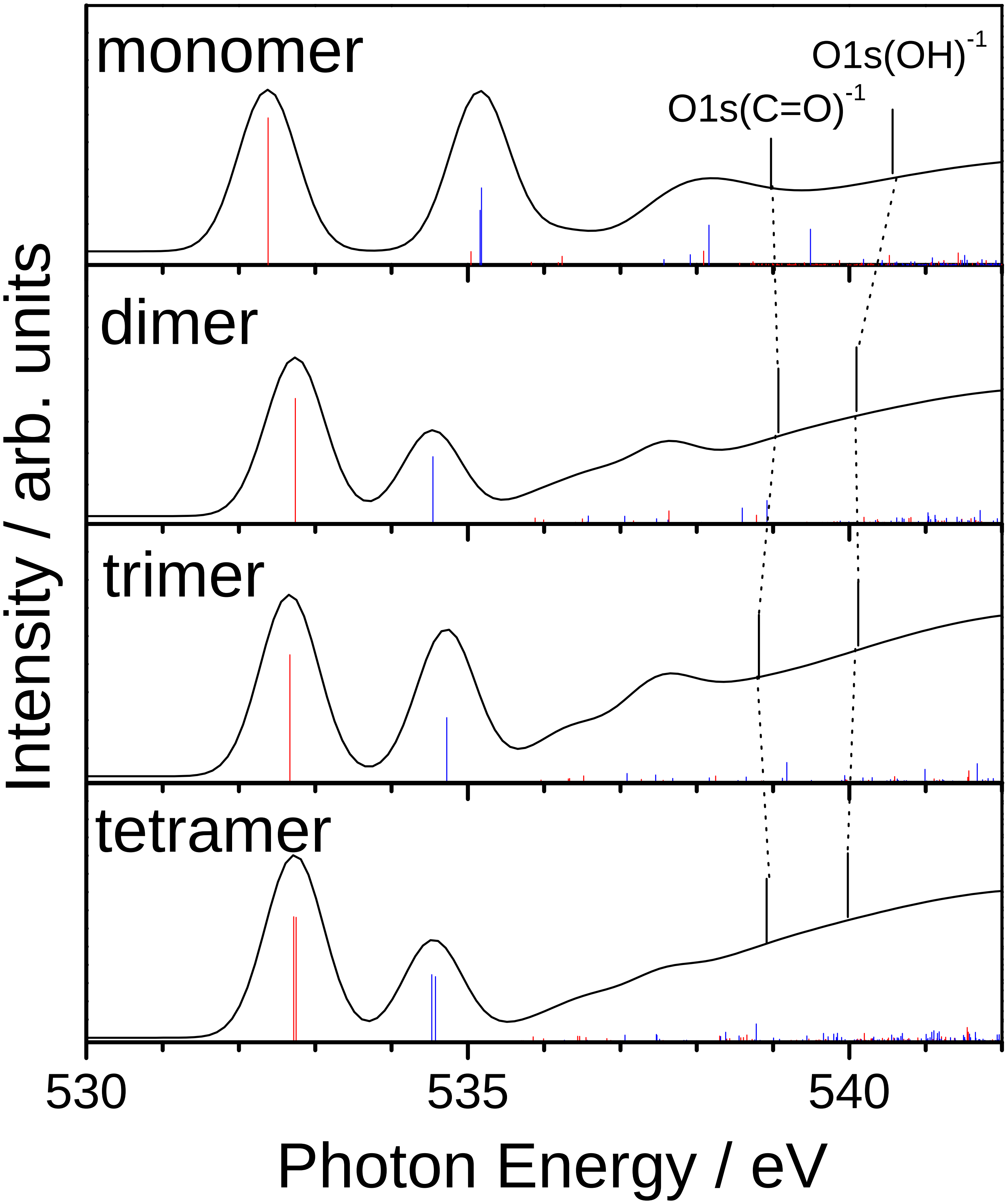
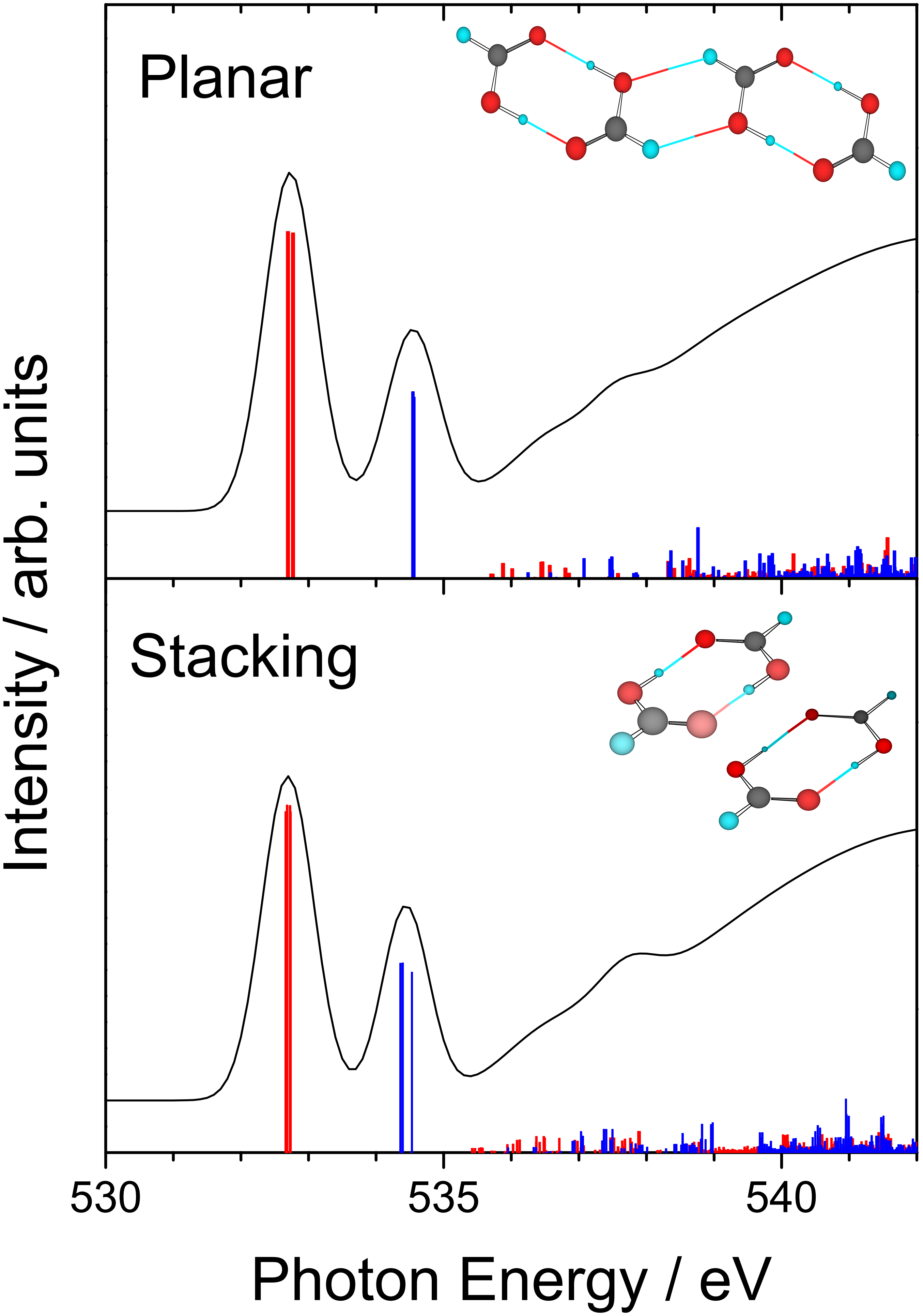


fig. 2 Takahashi et al.



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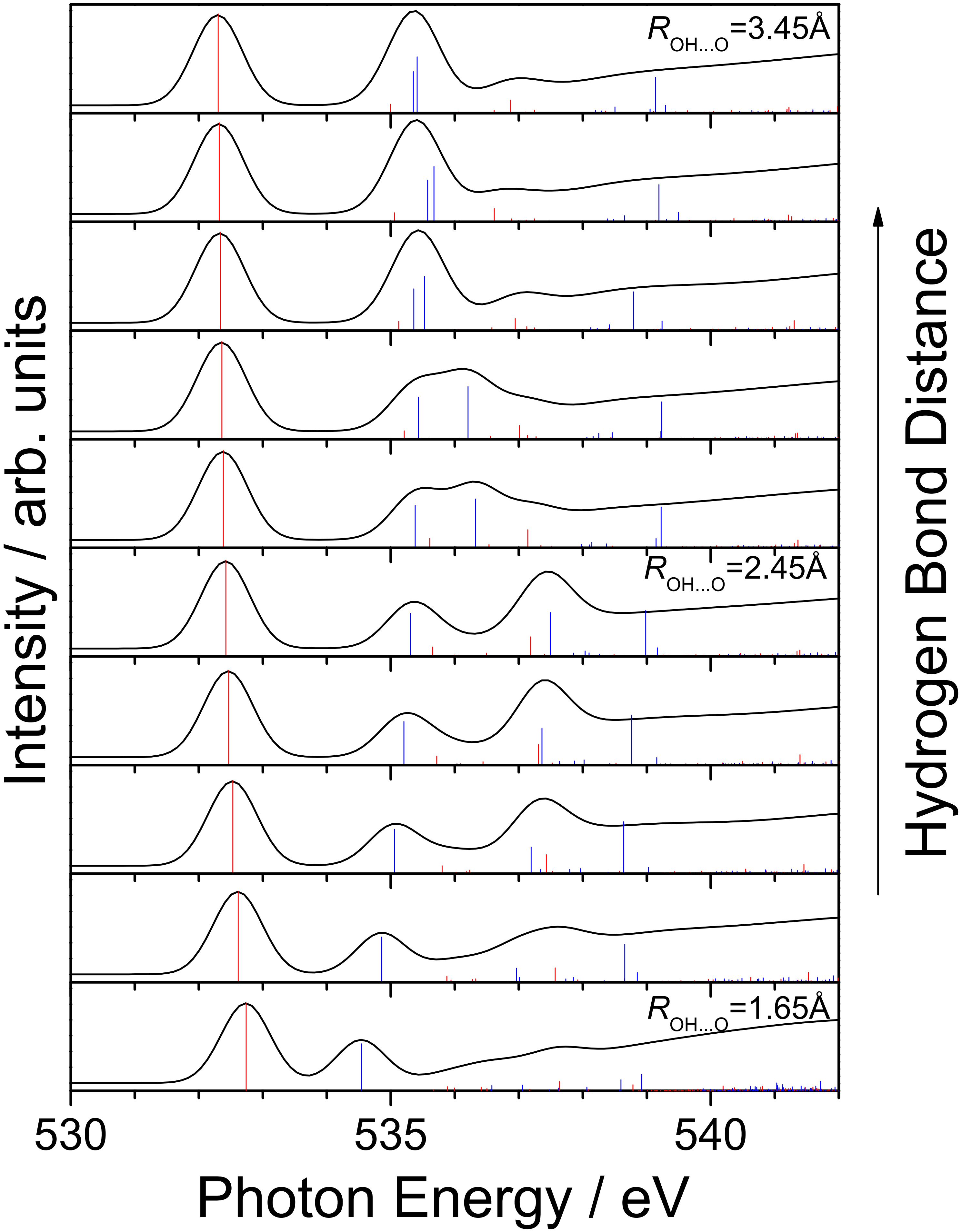

Fig. 4 Takahashi et al.

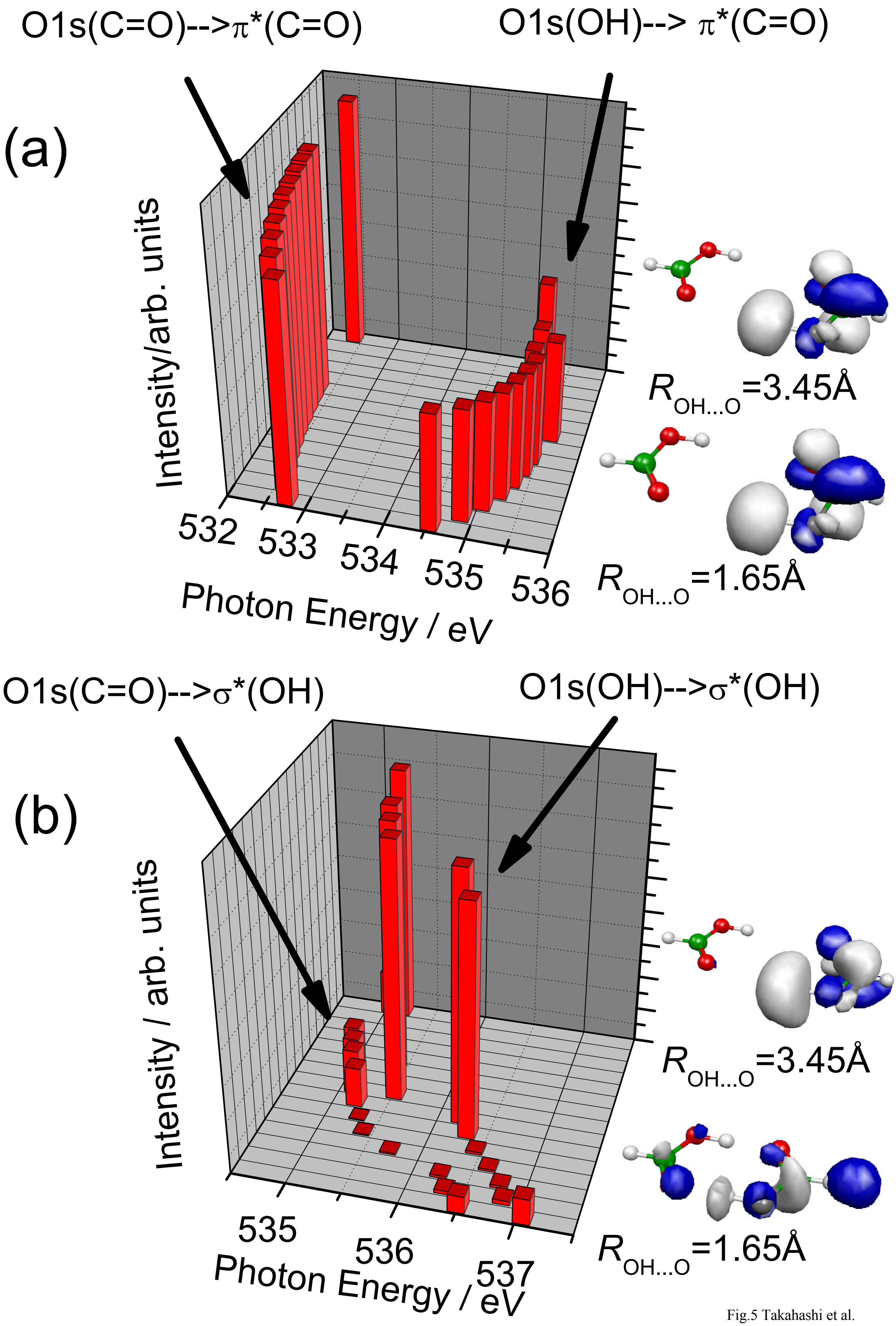

Fig.5 Takahashi et al.