

Studies of the X-ray Absorption Spectra of Some Methylcyano Esters

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Abstract

Density functional theory (DFT) has been applied to simulate core-excited photoabsorption spectra for some methylcyano esters within a transition potential (TP) framework. Our calculations for methylcyano formate at the N and O *K*-edges are consistent with previous experimental spectra. For methylcyano acetate the photoabsorption spectra at the N and O *K*-edges were reinvestigated experimentally. Contrary to the previous experiment, only one main peak was observed at the N *K*-edge and this peak was assigned to N(1s) $\rightarrow \pi^*$ excitation. This result was supported by our theoretical calculations. The general trends in the x-ray absorption spectra and the site-specific bond scission of methylcyano esters at the N and O *K*-edges are also discussed.

Key words: x-ray absorption spectra, density functional theory, methylcyano esters, core-excitation, site-selectivity

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1 Introduction

With the availability of synchrotron radiation sources investigation of chemical reactions using soft x-rays at the core-excitation level has become an active field in chemical physics. The core electrons are strongly localized at each atomic site and the core photoionization energies of a specific element furthermore show chemical shifts due to the chemical environment. This means that site-specific excitations and excitation-induced reactions can be expected [1–10]. Recently, chemical reactions of methylcyano formate and methylcyano acetate induced through site-specific core-excitation were reported by Ibuki *et al.*[5]. In that paper, an increase of the amount of N^+ ions was observed in the case of $\text{N}(1s) \rightarrow \pi^*$ excitation in methylcyano acetate and the relationship between the site-selectivity and molecular size was discussed. The mechanism of site-specific bond dissociation after Auger decay was confirmed theoretically in our previous papers[11,12] and the importance of the Auger decay process for the dissociation process has been underlined. In the previous paper the focus was on the Auger decay process to discuss the reaction mechanism, however the photoabsorption process should also be included in order to complete the analysis of the induced reactions of the methylcyano esters. The initial photoabsorption process is important to specify the energetics and the character of the excited state, and only this process can be controlled by changing the photon energy. Since the chemical reaction by core excitation proceeds through a multi-step process[10,13], we should discuss both the photoabsorption and Auger decay processes in conjunction to understand the reaction mechanism.

A further motivation of the present paper concerns the absorption spectra of methylcyano acetate at the N K -edge reported previously[5] which showed two main peaks assigned to $\text{N}(1s) \rightarrow \pi^*(\text{C}=\text{O})$ and $\text{N}(1s) \rightarrow \pi^*(\text{C}\equiv\text{N})$ transitions similar to the case of methylcyano formate. Our initial theoretical investigations, however, showed that the spectra of these two compounds should be different due to the differences in their π^* orbital characters; this difference should be reflected in the absorption spectra in contradiction to the reported experimental result. Furthermore, the interpretation of the O K -edge spectrum was not so clear. Having examined computationally a number of possible explanations for this discrepancy it was clear that a reexamination was also needed from the experimental side.

The recent development of theoretical approaches in the field of inner-shell excitations is remarkable. For relatively small molecules large-scale configuration interaction (CI) techniques have been developed to describe photoabsorption processes[14]. However, typical molecules that are of experimental interest in the field of site-selective chemistry via the core-excited state are too large for this procedure to be applied. In this case the static exchange (STEX)

approximation offers a good alternative technique to compute core-excited photoabsorption spectra and Hartree-Fock (HF)-STEX [15] as well as transition potential (TP) DFT-based [16] schemes have recently been developed and implemented.

In the present study, theoretical calculations of x-ray absorption (XA) spectra using the DFT-TP methodology are performed in order to examine the character of the excited states and to discuss the reactivity at the core-excited level for the methylcyano esters. Furthermore new experimental XA spectra for methylcyano acetate at both the N and O *K*-edges are reported.

2 Methods of Calculation

2.1 Geometry optimization of sample molecules

Geometries for the target molecules (methylcyano formate CH_3OCOCN (ester0) and methylcyano acetate $\text{CH}_3\text{OCOCH}_2\text{CN}$ (ester1)) were optimized using the Gaussian 98 program[17] at the MP2/cc-pVDZ level of approximation. Note that optimized geometries at the MP2/cc-pVDZ level are not significantly different from those using the DFT level and the small differences found do not affect the XA spectra. In the present paper, the target molecules of interest are characterized by the number of CH_2 groups between the $\text{C}=\text{O}$ and $\text{C}\equiv\text{N}$ groups. Although for each compound several different conformations can exist, we have confirmed through explicit calculations that this induces negligible differences in the XA spectra. This indicates that the character of the spectra is determined by the chemical environment near the core-excited atom for these species and that long-range effects are not important for the spectra. The all-trans conformer was thus used for the target molecules, and molecular structures of them are shown in Fig. 1.

2.2 X-ray absorption spectra

The DFT calculations for the XA spectra were performed at the gradient-corrected DFT level using the StoBe-DEMON program[18]. The theoretical XA spectra were generated by the transition potential (TP) method[19,20] in combination with a double basis set technique[15]. A detailed description of the method and implementation within the DFT framework can be found in the paper by Triguero *et al.*[16]. Briefly, the orbitals of the core-excited molecule were determined using a good quality molecular basis set with a half-occupied core-orbital at the ionization site. The orbitals for the excited

electron were then obtained by diagonalizing the Kohn-Sham matrix built using the optimized density in a basis set extended by a large set of diffuse basis functions (150–400 functions) centered on the excited atom. The obtained orbital energies and computed transition moments provide a representation of the excitation energies and associated intensities in the theoretical spectrum.

The TP calculation gives most of the relaxation effect upon core-ionization and provides a single set of orthogonal orbitals for the spectrum calculation. In order to determine the absolute energy position of the spectrum, Δ Kohn-Sham (Δ KS) calculations, *i.e.*, allowing full relaxation of the fully ionized core hole state, were performed to compute the relaxed ionization energy (IP). Relativistic corrections to the N and O *K*-edge IPs were +0.3 and +0.4 eV, respectively [21]. In the Δ KS-calculations the non-core-excited O atom was described by effective core potentials (ECP)[22]. This simplifies the definition of the core hole state, since the use of an ECP description eliminates the $1s$ level of the oxygen to which it is applied. This is especially useful for spectrum calculations of molecules with O atoms in several chemical environments.

The DFT-TP calculation of the spectrum corresponds to the STEX approach and thus neglects the relaxation effect on the molecular ion core upon adding the excited electron. This effect is the largest for the valence-like π^* excitations and, therefore, these states are computed with fully relaxed Δ KS calculations. The core-excited states were variationally determined with maintained orthogonality between the excited states through the following procedure: the first excited state is obtained by fixing the occupation of the core spin orbital to zero and placing the excited electron in the first π^* orbital. A full relaxation with this constraint leads to a state that is almost orthogonal to the ground state due to the $1s^{-1}$ configuration. The next state is then obtained by removing the variationally determined π^* orbital from the variational space and occupying the next level. This procedure gives a variational lower bound to the energy and guarantees the orthogonality between the excited states since all remaining orbitals now have to be orthogonal to the eliminated π^* level(s). The corresponding peaks in the energy-shifted TP spectrum have been shifted to include the additional relaxation effects obtained from the specific Δ KS excited state calculations.

In order to obtain an improved representation of relaxation effects in the inner orbitals, the ionized center was described by using the IGLO-III basis of Kutzelnigg *et al.*[23]. In the spectrum calculations a large [19s 19p 19d] diffuse even-tempered basis set centered on the ionization site was added; it is employed only in the last step of the calculation when the orbitals for the excitations have to be generated. The spectrum was generated through a Gaussian convolution of the discrete spectra with varying broadenings. For the region below the ionization threshold the broadening [full width at half maximum (FWHM)] was set to 0.3 eV, for the next 30 eV the FWHM was

linearly increased up to 4.5 eV and kept constant for the higher energies. The stability of the convoluted spectra with respect to the augmentation basis was investigated by extending the augmentation basis to include the excitation basis also on the nearest neighbors.

All DFT calculations were performed with the gradient-corrected Perdew exchange functional and the Perdew correlation functional[24].

3 Experimental methods

The experiment has been performed on the beamline BL-6 at HiSOR facility in Hiroshima University. A varied-line-spacing plane grating monochromator, which covers the energy range of 200-1200 eV with two gratings (G1:400-1200 eV and G2:200-600 eV), was installed at the beamline[25]. A resolving power of 6400 has been achieved at a photon energy of 400 eV[26]. A small chamber with an Al thin filter and a silicon photodiode was attached at the end of the beamline. Total photoabsorption cross sections at the N *K*-edge were acquired by using this chamber. A typical sample gas pressure was 300 mTorr. The Lambert-Beer law was applied to obtain the photoabsorption cross section. In case of the O *K*-edge, total electron yield was measured by an electron detector to remove the influence of residual water in the chamber. Sample gas was introduced through an effusive gas nozzle into a main chamber. Its axis was orthogonal to the axes of the incident light and the detection of electrons. The pressure in the main chamber was kept at about 5×10^{-6} Torr. The energy scales of the spectra were calibrated using some of the major peaks appearing in the spectrum of the N₂ molecule at the N *K*-edge[27] and the CO₂ molecule at the O *K*-edge [28]. Methylcyano acetate was purchased from Aldrich Co. Ltd. with a stated purity of 99 % or better. This sample is liquid at room temperature and atmospheric pressure. Therefore volatile impurities were removed from the sample through freeze and thaw cycles.

4 Results and discussion

First, we discuss the N *K*-edge XA spectrum for ester0 (Fig. 2(a)) with peak positions and proposed assignments given in Table 1(a). Two large peaks are obtained around 400 eV and these are consistent with the experiment. Based on the calculations they are assigned as mainly N(1s) \longrightarrow $\pi^*(\text{C}=\text{O}) + \pi^*(\text{C}\equiv\text{N})$ (out of plane) for the lower energy peak and N(1s) \longrightarrow $\pi^*(\text{C}\equiv\text{N})$ transitions for the other. This is in contradiction to the assignment made previously[5] which assigned these peaks to N(1s) \longrightarrow $\pi^*(\text{OO}')$ and $\pi^*(\text{CNOO}')$

states based on the character of the virtual MO's of the ground state. In general, the unoccupied orbital characters of the core excited state are affected by core hole screening that depends on which atom has a core hole. Thus, they are different from those obtained for the neutral ground state. As a result, an equivalent core model, *i.e.*, the Z+1 approximation, generates a better description of the orbitals available for excitation. Furthermore, since the excitation is at the N atom and the distance between the N and ether O atom is too long, the cross section for excitation across the molecule to the ether O atom should be expected to be small as is also obtained in our calculation. In general, the absorption intensity depends on the overlap between the initial and final state wave functions. Since our calculations include the core-hole state explicitly, these effects can be described correctly. In ester0, the π orbitals of C=O and C \equiv N are conjugated, resulting in a lowering of the energy level of the out of plane $\pi^*(\text{C}\equiv\text{N})$ through mixing with $\pi^*(\text{C}=\text{O})$. The lower peak around 404 eV consists of several states but is dominated by the N(1s) $\rightarrow \pi^*(\text{C}=\text{O}) + \pi^*(\text{C}\equiv\text{N})$ (out of plane) state. The broad bands with peak maxima around 410 eV and 423 eV were assigned to the double excitation and $\sigma^*(\text{C}\equiv\text{N})$, respectively[5]. The peak around 423 eV can be reproduced by our DFT calculation, but that around 410 eV can not be reproduced, because our procedure can not describe the multi-excitation state.

For the O *K*-edge, two different kinds of oxygen atoms are included: carbonyl oxygen and ether oxygen in this molecule. We thus need to combine spectra from these oxygens computed separately in order to generate the full spectrum. From another point of view, since the XA spectra for distinct atoms are computed separately it is easy to assign the character of each state. In Fig. 2(b), XA spectra from ether oxygen, carbonyl oxygen, and the summed spectra are shown in comparison with the experiment; peak positions and proposed assignments are given in Table 1(b). Computed oxygen spectra are consistent with the experiment similar to what was found for the N *K*-edge.

Next, the XA spectra for ester1 are discussed. In Fig. 3(a) the computed N *K*-edge XA spectra of ester1 is shown in comparison with the new experiment. Contrary to the previous experiment[5], our new experimental spectrum shows only one peak near 400 eV, which is assigned to N(1s) $\rightarrow \pi^*(\text{C}\equiv\text{N})$; this is consistent with our computed spectrum. Actually, in the large peak of this spectrum two transitions are included: N(1s) $\rightarrow \pi^*(\text{C}=\text{O})$ and $\pi^*(\text{C}\equiv\text{N})$. The energy difference between these states, however, is only 0.08 eV. Contrary to the case of ester0, since ester1 differs from ester0 through insertion of a CH₂ group between the C=O and C \equiv N groups, it is expected that the interaction between the unoccupied $\pi^*(\text{C}=\text{O})$ and $\pi^*(\text{C}\equiv\text{N})$ orbitals should become small. Since in the N *K*-edge XA spectrum the peak is dominated by the $\pi^*(\text{C}\equiv\text{N})$ orbital, the first peak is assigned as the $\pi^*(\text{C}\equiv\text{N})$ excited state of ester1. As in the case of ester0 at the N *K*-edge, we assign the broad bands with peak maxima around 412 eV and 425 eV to the double excitation and $\sigma^*(\text{C}\equiv\text{N})$,

respectively. In Fig. 3(b) we show the computed O K -edge XA spectrum of ester1 compared with our new experiment and the proposed peak assignments shown in Table 1(b). Similarly to what was found for ester0, the computed oxygen spectra are consistent with our experiment. The previous experiment may have been inadequate in terms of sample preparation.

Finally, the chemical reactions induced by core excitation for the methylcyano esters will be discussed. From the previous experiment[5], neither site-specific nor state-specific bond scission was observed for ester0 at the N and O K -edges. On the other hand, both site- and state-specificity were observed and discussed for ester1. Note that in the case of methylcyano esters, site-specific bond scission for a $C\equiv N$ triple bond is one of the specific reactions, and there are two contributions to the molecular size effect. One is the dependence on the length of the alkyl chain and the other is the conjugation of the $C=O$ and $C\equiv N$ groups; the former affects explicitly the Auger decay process, as we have shown in our previous papers[11,12]. The Auger decay probability depends on the valence orbital amplitudes near the excited atom. If the alkyl chain becomes long, then the characteristic valence orbitals are relatively localized and specific bond scission after Auger decay will be enhanced. This molecular size effect thus depends on the localizability of the valence orbital in the molecule. Especially, valence orbitals localized at the core hole site will be largely affected. A similar situation applies for unoccupied orbitals, i.e., the localizability of the unoccupied orbitals which include a valence character gets larger with increasing molecular size. Thus the effect of the site-specific excitation for small molecules will be weaker and, at the same time, the state-specificity will also be decreased. On the other hand, if there is π conjugation in the molecule, such as is the case for ester0, π orbitals can be delocalized and as a result, site-specific bond scission, for example, the $C\equiv N$ triple bond will disappear. The above discussion corresponds to the fact that no specific fragmentation pattern was observed for ester0 at neither the N nor the O K -edge even when the excitation energy was varied. For a system such as ester1 with one or more CH_2 groups inserted between the $C=O$ and $C\equiv N$ groups, a specific fragmentation pattern may be observed.

5 Conclusions

We have presented computed core excitation absorption spectra for some methylcyano esters using the DFT with TP method. For ester0, our calculations are consistent with the experimental spectra of Ibuki *et al.* for both the N and O K -edges, while for ester1 there is disagreement for both the N and O K -edge spectra. As a result from an experimental reinvestigation of ester1, the experimental spectrum is now consistent with our calculations both for the N and O K -edges. The original peak assignments of Ibuki *et*

al. for ester0 and ester1 were furthermore modified in the present work by calculating the core-excited state explicitly. In addition, the relationship between the site-specific bond scission and the molecular size was discussed. It should be noted that the fragmentation patterns of ions for these molecules, especially ester1 at the N *K*-edge, may be modified by reexamination using purified samples. Ibuki *et al.*[5], however, proposed a very important concept for the chemical reaction by core excitation, namely the molecular size effect on the site-specific fragmentation. The same concept has been proposed using a series of disilyl compounds by Nagaoka *et al.*[3].

In order to discuss the site-specific bond scission through core-excitation, it is necessary to consider the character of not only the unoccupied orbitals but also the occupied valence orbitals in the target molecule. The former is reflected by the XA spectrum, where the excitation energy can be controlled experimentally. On the other hand, the latter is reflected in the Auger decay and x-ray emission processes, but these processes are determined by the system and can not be controlled. In the alkyl chain, at least more than one CH₂ group is needed between the C=O and C≡N groups to avoid delocalization of the valence orbitals and the unoccupied-valence like orbitals for methylcyano esters. In this sense, the alkyl chain with the CH₂ groups is a good separator to eliminate an interference between the characteristic functional groups to avoid bond conjugation leading to delocalization. To realize the site-specific bond scission more efficiently, it is needed to explore the effect of specific functional groups or combinations of functional groups. In the present paper, the discussion is limited to the orbital character in the isolated molecule, because the target system is in the gas phase. In order to enhance the site-specificity and the state-specificity of chemical reactions induced by core-excitation in the condensed phase, the importance of the other processes has been pointed out[13]. Further investigations combining experiment with theory are required to resolve remaining issues related to site-specific bond scission induced by core-excitation.

6 Acknowledgment

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References

- [1] W. Eberhardt, T. K. Sham, R. Carr, S. Krummacher, M. Strongin, S. L. Weng, D. Wesner, *Phys. Rev. Lett.* 40 (1983) 1038.
- [2] D. M. Hanson, *Adv. Chem. Phys.* 77 (1990) 1.
- [3] S. Nagaoka, K. Mase, I. Koyano, *Trends Chem. Phys.* 6 (1997) 1.
- [4] T. Sekitani, E. Ikenaga, K. Fujii, K. Mase, N. Ueno, K. Tanaka, *J. Elec. Spectro. Related Phenomena* 101-103 (1999) 135.
- [5] T. Ibuki, K. Okada, K. Saito, T. Gejo, *J. Elec. Spectro. Related Phenomena* 107 (2000) 39.
- [6] E. Ikenaga, K. Kudara, K. Isari, S. A. Sardar, S. Wada, K. Mase, T. Sekitani, K. Tanaka, *J. Elec. Spectro. Related Phenomena* 114-116 (2001) 585.
- [7] E. O. Sako, Y. Kanameda, E. Ikenaga, M. Mitani, O. Takahashi, K. Saito, S. Iwata, S. Wada, T. Sekitani, K. Tanaka, *J. Elec. Spectro. Related Phenomena* 114-116 (2001) 591.
- [8] E. Ikenaga, K. Isari, K. Kudara, Y. Yasui, S. A. Sardar, S. Wada, T. Sekitani, K. Tanaka, K. Mase, S. Tanaka, *J. Chem. Phys.* 114 (2001) 2751.
- [9] P. Bennich, T. Wiell, O. Karis, M. Weinelt, N. Wassdahl, A. Nilsson, M. Nyberg, L. G. M. Pettersson, J. Stöhr, M. Samant, *Phys. Rev. B* 57 (1998) 9274.
- [10] K. Mase, M. Nagasono, S. Tanaka, T. Sekitani, S. Nagaoka, *Fiz. Niz. Temp.* 29 (2003) 321.
- [11] O. Takahashi, M. Mitani, M. Joyabu, K. Saito, S. Iwata, *J. Elec. Spectroscop. Relat. Phenom* 120 (2001) 137.
- [12] O. Takahashi, M. Joyabu, M. Mitani, K. Saito, S. Iwata, *J. Comp. Chem.* 24 (2003) 1329.
- [13] K. Tanaka, E. O. Sako, E. Ikenaga, K. Isari, S. A. Sardar, S. Wada, T. Sekitani, K. Mase, N. Ueno, *J. Elec. Spectroscop. Relat. Phenom* 119 (2001) 255.
- [14] N. Kosugi, *Theor. Chem. Acta* 72 (1987) 149.
- [15] H. Ågren, V. Carravetta, O. Vahtras, L. G. M. Pettersson, *Theor. Chem. Acc.* 97 (1997) 14.
- [16] L. Triguero, L. G. M. Pettersson, H. Ågren, *Phys. Rev. B* 58 (1998) 8097.
- [17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, J. R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman,

- J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wang., J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 98, revision A.4.
- [18] K. Hermann, L. G. M. Pettersson, M. E. Casida, C. Daul, A. Goursot, A. Koester, E. Proynov, A. St-Amant, D. R. Salahub, P. authors: H. Duarte, N. Godbout, J. Guan, C. Jamorski, M. Leboeuf, V. Malkin, O. Malkina, M. Nyberg, L. Pedocchi, F. Sim, L. Triguero, A. Vela, deMon-KS StoBe version 4.0.
- [19] J. C. Slater, *Adv. Quantum Chem.* 6 (1972) 1.
- [20] J. C. Slater, K. H. Johnson, *Phys. Rev. B* 5 (1972) 844.
- [21] L. Triguero, O. Plashkevych, L. G. M. Pettersson, H. Ågren, *J. Electron Spectrosc. Relat. Phenom.* 104 (1999) 195.
- [22] L. G. M. Pettersson, U. Wahlgren, O. Gropen, *J. Chem. Phys.* 86 (1987) 2176.
- [23] W. Kutzelnigg, U. Fleischer, M. Schindler, *NMR-Basic Principles and Progress*, Springer-Verlag, Heidelberg, 1990.
- [24] J. P. Perdew, *Phys. Rev. B* 33 (1988) 8822.
- [25] H. Yoshida, Y. Senba, T. Tokushima, Y. Mishima, A. Hiraya, *Nucl. Instrum. Methods in Phys. Res. A* 467-468 (2001) 589.
- [26] H. Yoshida, Y. Senba, T. Goya, Y. Azuma, M. Morita, A. Hiraya, to be published.
- [27] C. T. Chen, Y. Ma, F. Sette, *Phys. Rev. A* 40 (1989) 6737.
- [28] K. C. Prince, L. Avaldi, M. Coreno, R. Camilloni, M. de Simone, *J. Phys. B: At. Mol. Opt. Phys.* 32 (1999) 2551.

Table 1

Peak assignment of absorption spectra for each methylcyano ester compound.
(a) At the N *K*-edge.

molecule	DFT		Exp.	
	peak / eV	assignment	peak / eV	assignment
ester0	398.7	$\pi^*(\text{C}\equiv\text{N}, \text{ out of plane}) + \pi^*(\text{C}=\text{O})$	398.0 ^a	$\pi^*(\text{OO}')$
	399.4	$\pi^*(\text{C}\equiv\text{N})$	399.1 ^a	$\pi^*(\text{CNOO}')$
	403.6	Rydberg	402.9 ^a	3p
	406.8	Rydberg	404.1 ^a	4p
	406.9	IP	405.5 ^a	IP
			410 ^a	double excitation
	421	$\sigma^*(\text{C}\equiv\text{N})$	423 ^a	$\sigma^*(\text{C}\equiv\text{N})$
ester1	399.4	$\pi^*(\text{C}\equiv\text{N})$	399.9	
	403.1	Rydberg	402.2	
	406.1	IP		
			412	double excitation
	420-426	$\sigma^*(\text{C}\equiv\text{N})$	425	$\sigma^*(\text{C}\equiv\text{N})$

(b) At the O *K*-edge.

molecule	DFT			Exp.		
	peak / eV	assignment (C=O)	assignment (O-CH ₃)	peak / eV	assignment (C=O)	assignment (O-CH ₃)
ester0	531.8	$\pi^*(\text{C}\equiv\text{N}, \text{out of plane})$ $+\pi^*(\text{C}=\text{O})$		531.5 ^a	$\pi^*(\text{C}=\text{O})$	
	534.5		$\pi^*(\text{C}\equiv\text{N}, \text{out of plane})+\pi^*(\text{C}=\text{O})$	534.3 ^a	3p/ $\sigma^*(\text{C}-\text{O})$	$\pi^*(\text{C}=\text{O})$
	535.5	$\pi^*(\text{C}\equiv\text{N})$		536.9 ^a		$\sigma^*(\text{C}-\text{O})$
	539.4	IP		538.4 ^a	IP	
	540.4		Rydberg	539.7 ^a		Rydberg
	541.0		IP	540 ^a		IP
	ester1	532.4	$\pi^*(\text{C}=\text{O})$		532.1	
535.5			$\pi^*(\text{C}=\text{O})$	535.3		
537.1			Rydberg	537.1		
539.0		IP				
540.6			IP			
540.0		σ^*		541.5	σ^*	

^a From ref. 5.

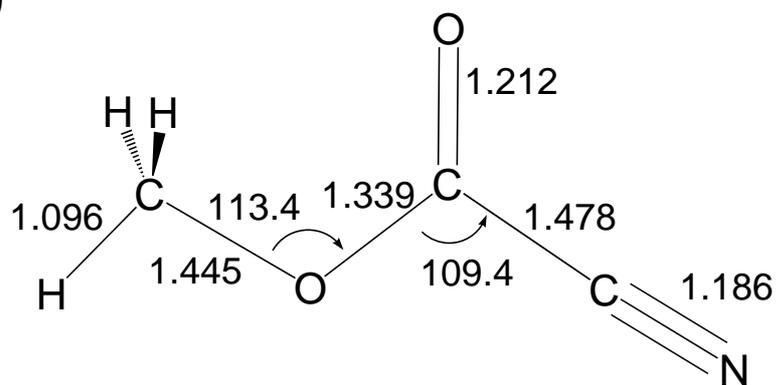
Figure captions.

Fig. 1. Optimized structures of the target molecules. (a)Methylcyano formate (ester0). (b)Methylcyano acetate (ester1).

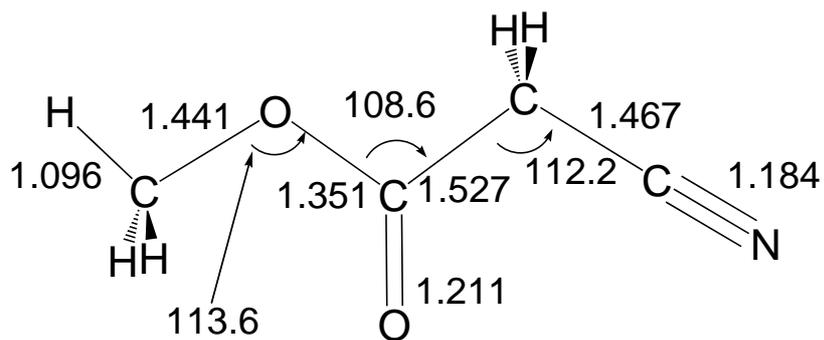
Fig. 2. A comparison of experimental and DFT computed absorption spectra for ester0 at (a) the N *K*-edge and (b) the O *K*-edge. Experimental spectra are referd to ref. [5]. The assignments of peaks and the ionized threshold are also shown in the DFT spectra with arrows.

Fig. 3. A comparison of experimental and DFT computed absorption spectra for ester1 at (a) the N *K*-edge and (b) the O *K*-edge. The assignments of peaks and the ionized threshold are also shown in the DFT spectra with arrows.

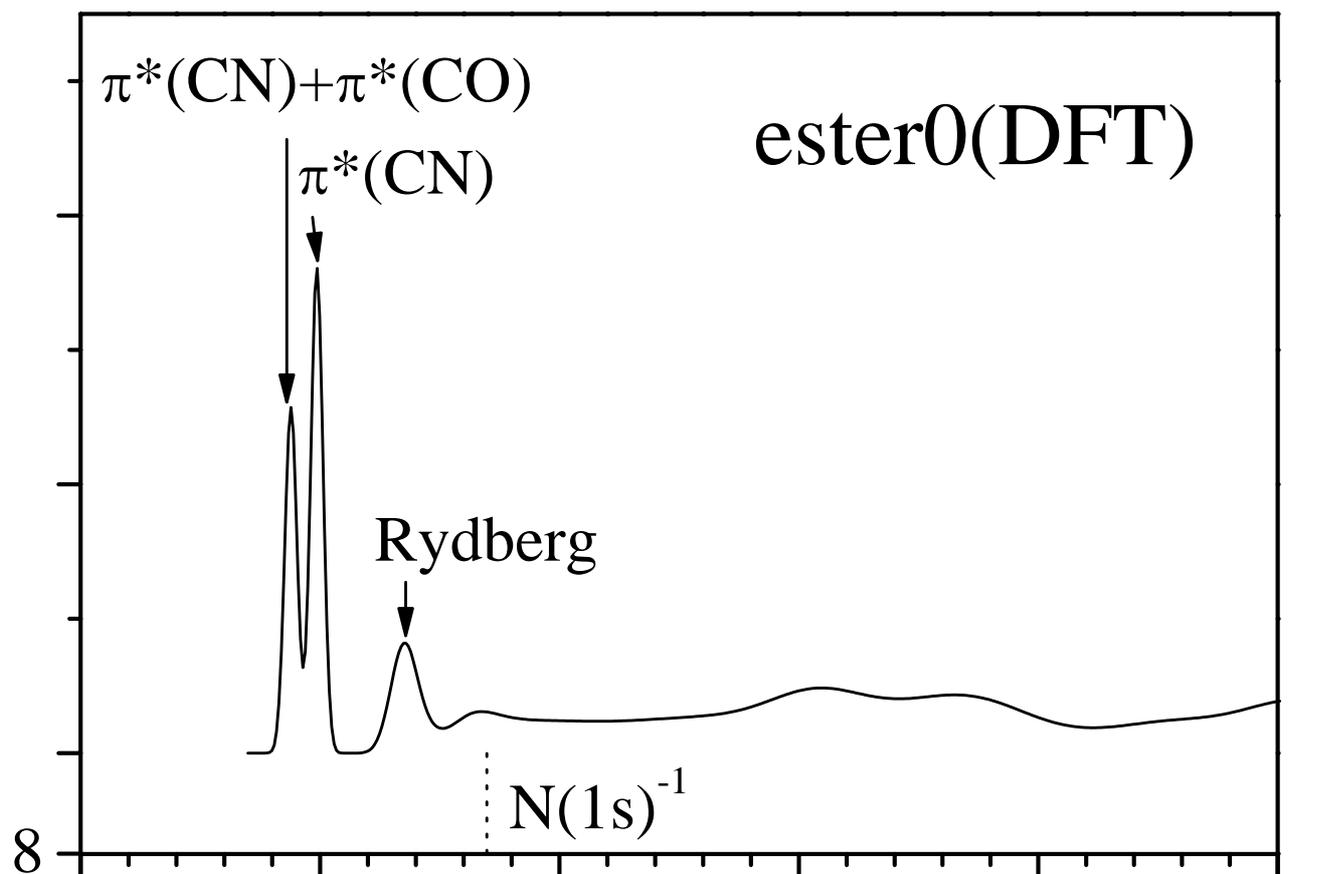
(a)



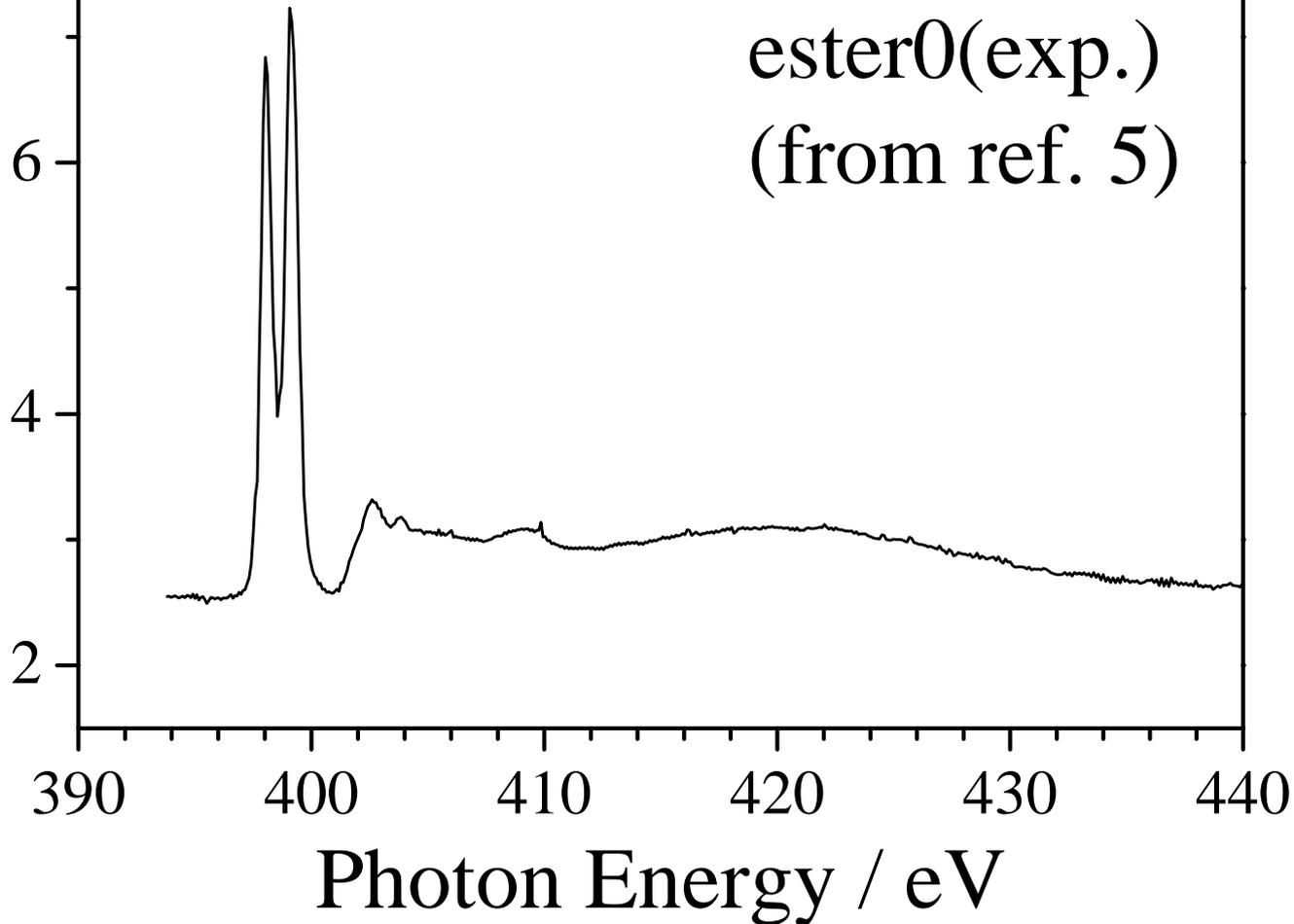
(b)



Absorption Cross Section / arb. units



Absorption Cross Section / Mb



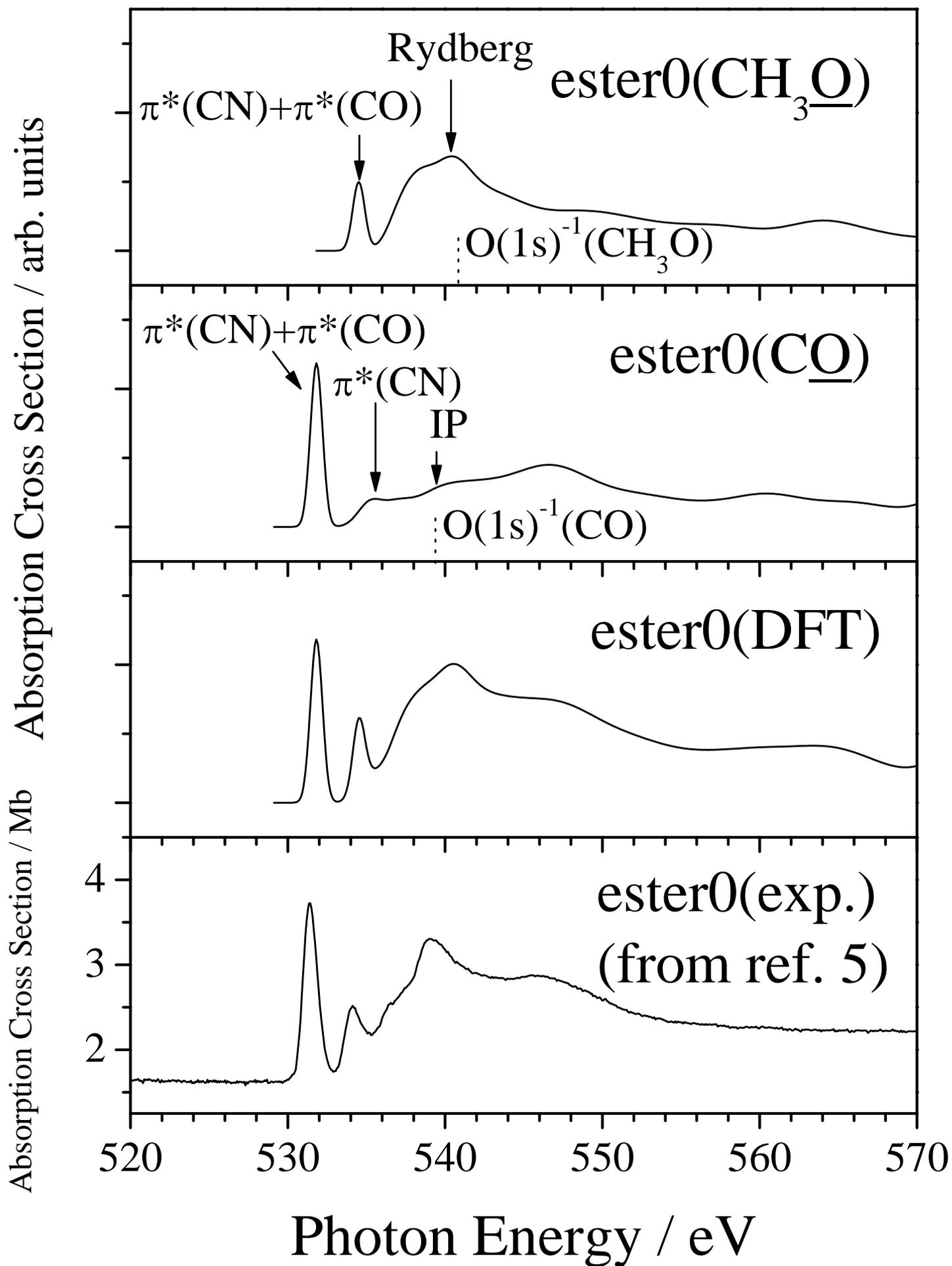


Fig.2(b) Takahashi et al.

Absorption Cross Section / arb. units

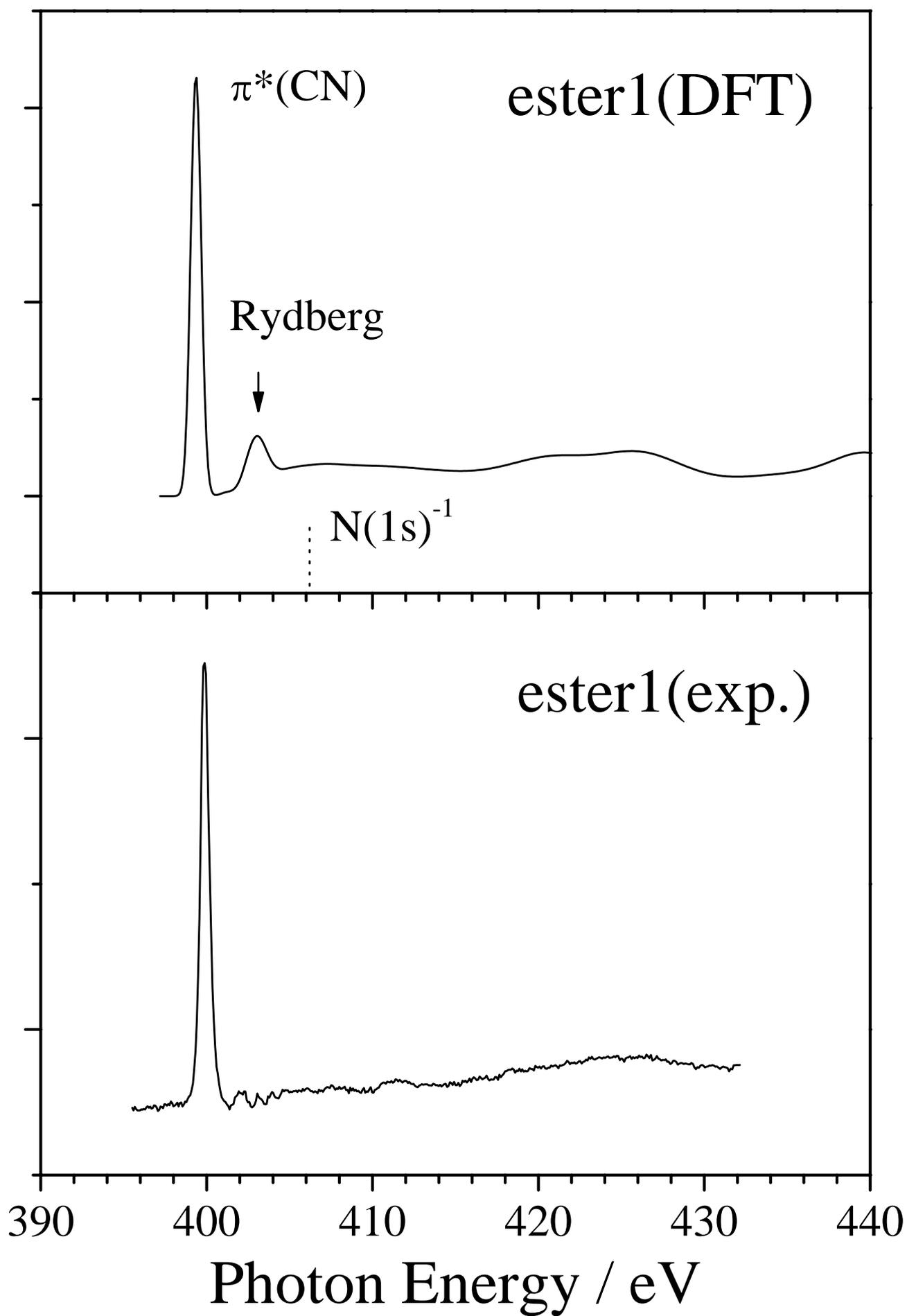


Fig.3(a) Takahashi et al.

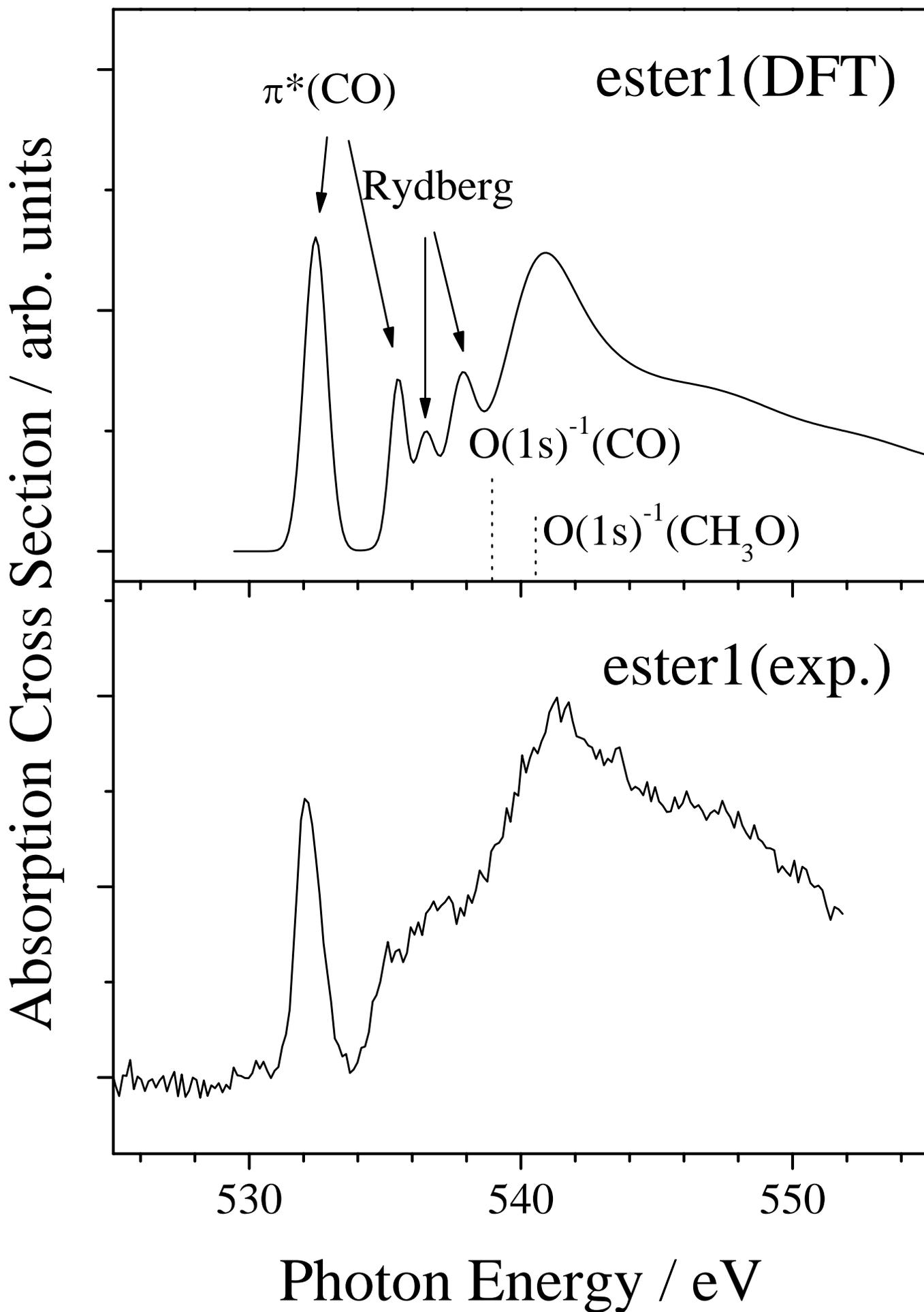


Fig 3(b) Takahashi et al.