J. Phys. Chem. A **2003,** *107,* 1955−1963

Near Edge X-ray Absorption Spectra of Some Small Polyatomic Molecules

Kevin C. Prince,*,†,‡ Robert Richter,† Monica de Simone,§ Michele Alagia,‡,§ and Marcello Coreno‡,∥

Sincrotrone Trieste, Strada Statale 14, km 163.5, in Area Science Park, I-34012 Basovizza (Trieste), Italy,
INFM-TASC, Laboratorio ELETTRA, I-34012 Basovizza (Trieste), Italy, and
Università di Roma III ed Unità INFM, Via della Vasca Navale 84, I-00146 Rome, Italy

Received: August 20, 2002; In Final Form: December 3, 2002

We report high resolution measurements of near edge X-ray absorption fine structure spectra (NEXAFS) at the carbon and oxygen K edges of the series of related organic molecules acetaldehyde, acetone, formic acid, methanol, dimethyl ether, and paraldehyde. The spectra are compared with previous measurements of these gases and formaldehyde and with theoretical calculations. Much more fine structure is resolved than previously, particularly at the carbon edge. The results are in good overall agreement with the theoretical predictions of Plashkevych et al. (*Chem. Phys.* **2000**, *260*, 11) that the methyl group spectrum is relatively independent of the functional groups to which it is bonded, as are the carbon and oxygen carbonyl group spectra. On the other hand, oxygen atoms in hydroxyl and ether groups are strongly influenced by neighboring atoms. All of the carbon edge spectra investigated show fine structure, and only in the case of acetone do the density of states and number of vibrational degrees of freedom begin to obscure fine detail. The term values of the strongest transitions to states of acetaldehyde and acetone at the C 1s and O 1s edges are in reasonable agreement with theoretical calculations. The splittings of the C $1s^{-1}$ 3p(CH_3) and 3p(CO) Rydberg states due to the low symmetry of the molecules are 0.6−0.7 and 0.38 eV for both molecules, in good agreement with theory. Absolute values of the photoabsorption cross-section, where available in the literature, show moderate to very poor agreement with measured values.

1. Introduction

The high-resolution inner shell spectra of diatomic molecules such as CO and O_2 have been studied extensively by X-ray absorption spectroscopy,[1,2] and although many polyatomic molecules have been studied by low-resolution electron energy loss spectra (EELS),[3] very little high-resolution work has been published.[4,5] The reason for this is partly that the larger number of initial and final states and vibrational degrees of freedom mask fine structure and partly limited resolution. One goal of the present study was to explore the electronic structure of a selection of more complicated molecules using high-resolution X-ray absorption and to test which factor limits the amount of information attainable. The family of molecules that was chosen consisted of small organic molecules containing oxygen with saturated and unsaturated C−O bonds and consisted of the simplest members of the series of alcohols, ethers, aldehydes, ketones, and carboxylic acids. They have symmetry C_{2v} (acetone and dimethyl ether, DME), C_s (methanol and formic acid), and C_{3v} or C_s (paraldehyde). Paraldehyde is a trimer of acetaldehyde consisting of saturated CO bonds in a buckled, six member ring, with a hydrogen and methyl group attached to each ring carbon atom.

In their early work, Hitchcock and Brion[3] reported the K edge spectra of formaldehyde, acetaldehyde, and acetone with resolution of 0.2−0.5 eV, resolving about 10 features at the carbon K edges and five or six at the oxygen K edges. The lowest lying feature was assigned to the π^* antibonding resonance associated with the C−O π bond, and the higher lying, broad resonances were assigned to the C−O and C−H σ^* antibonding resonances. The intermediate peaks were assigned to s, p, and d Rydberg states, and the quantum defects were reported. The valence-to-Rydberg np transitions were known to be split in the final state by the low symmetry of the molecules, and some splitting of the transitions from core-to-Rydberg states was observed. Hitchcock and Brion noted that the Rydberg transitions were stronger at the carbon than the oxygen edge and attributed this to the more localized nature of the O 1s orbital, which has less overlap with the diffuse final states. The results were also discussed in terms of the concept of additivity of spectra, in which spectra of larger molecules are approximated by sums of spectra of smaller ones. Later, Remmers et al.[4] carried out a NEXAFS study of formaldehyde with a complete Franck−Condon analysis for the π^* resonance. They revised a number of assignments, but despite their higher resolution, they did not observe vibrational structure at the oxygen K edge.

Methanol has been studied by Ishii and Hitchcock,[6,7] who reported the low-resolution EELS spectra of both methanol and formic acid by photoabsorption and ion yield spectroscopy,[8,9] and by Stolte et al.,[10] using negative ion spectroscopy. Ishii and Hitchcock discussed the results in terms of the chromophore concept, widely used in other areas of chemistry, in which each functional group has spectroscopic properties largely independent of other groups. This idea has been developed more recently by Plashkevych et al.[11] who carried out theoretical calculations on benzene substituted by the isoelectronic series $-CH_3$, $-NH_3$,

---

* To whom correspondence should be addressed. E-mail: Kevin.Prince@Elettra.Trieste.It.

† Sincrotrone Trieste.

‡ INFM- TASC.

§ Università di Roma III ed Unità INFM.

∥ Present address: CNR-Istituto di Metodologie Avanzate Inorganiche, Montelibretti (Rome), I-00016 Italy.

10.1021/jp0219045 CCC: $25.00

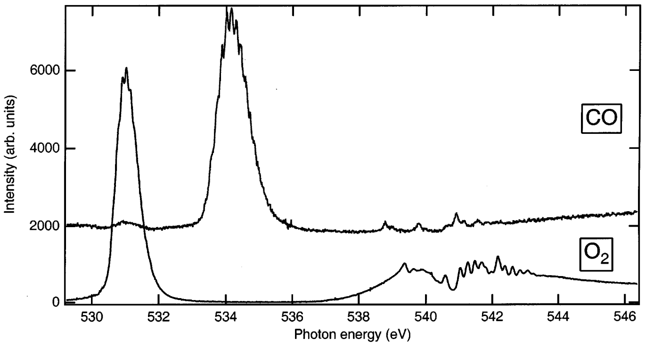

Figure 1. Simultaneous ion yield spectra of carbon monoxide (upper curve) and oxygen (lower curve) at the oxygen K edge. A small amount of oxygen is present in the CO spectrum.

−OH, and −F. They concluded that for 1s photoabsorption of the substituent, the relaxation (that is, the rearrangement of valence structure in the excited state) increases along this series. As a result, the methyl substituent has a spectrum substantially independent of how it is bonded, whereas the hydroxyl spectrum will depend on the neighboring bonds. For the chromophore or functional group model, these calculations predict that methyl groups (and possibly other carbon groups) will behave in a reproducible manner while the members further along the series will behave in a less uniform way. The concept has also been applied to a range of amino acids by Kaznacheyev et al.[12]

The EELS spectra of DME have been reported by Wight and Brion,[13] and other theoretical and experimental work relevant to this family of molecules has also been published.[14−23] So far, only the C 1s spectra of formaldehyde and methanol and the O 1s spectrum of formaldehyde have shown fine structure. We have previously given a brief description of some of the present results and discussed the applicability of the chromophore concept,[24] and here, we present a detailed analysis of the spectra.

2. Experimental Section

The measurements were performed on the Gas Phase Photoemission beamline[25] at the synchrotron radiation source Elettra, Trieste, Italy. Cross-sections were measured with a windowless, double absorption cell described elsewhere,[26] which permits the absolute cross-section to be derived from the ion currents and minimizes errors due to stray light, higher order light, and saturation effects.[27] The double cell method depends on achieving sufficient absorption for the currents in the two cells to be significantly different, so that the logarithm of the quotient of the currents reflects the change in cross-section. For paraldehyde, $(CH_3CHO)_3$, metal surfaces dissociated the gas to the monomer, so in this case the ion yield spectrum was measured using a time-of-flight, total ion yield spectrometer, with a gas inlet in polymer tubing.

At the carbon edge, the spectra were calibrated to the CO first vibrational level at 287.40 eV.[28] The calibration at the oxygen edge is discussed below.

3. Results

3.1. Calibration. Calibration of the energy scale at the oxygen edge is problematic for a number of reasons. Low-resolution EELS are available, which usually give good absolute values of energy, as well as ionization potentials from photoemission.

Several calibrations of photon energy at the oxygen K edge are available in the literature, and CO and O_2 data formed the basis of the calibration for the gases studied here. Figure 1 shows simultaneous ion yield spectra of CO and O_2 spectra taken in two adjacent chambers with this calibration, which gives very good relative energy scale reliability. We used the calibration of the energy of the maximum of the O $1s^{-1}$ π band of CO by Sodhi and Brion, 534.21(8) eV.[28] To obtain this point, the present vibrationally resolved spectra were fitted with a single Gaussian peak to simulate the low-resolution EELS spectra; the maxima are shifted by about 30 and 60 meV, respectively, for O_2 and CO with respect to the strongest vibrational peak.

Püttner et al.[2] calibrated their CO absorption spectrum against the O $1s^{-1}$ $3s\sigma$ state of NO. On this basis, they obtained the maximum absorption for the $\nu = 5$ state at 534.29 eV, as compared with the present value of 534.15 eV. For the $3s\sigma$ Rydberg state, we obtain an energy of 538.78 eV as compared with 538.91 eV; for $3d\pi$, we obtain an energy of 540.91 against 541.049 eV. Thus, our scales differ by an offset of about 150 meV.

We also compared the data to published spectra of O_2. On the vibrationally resolved spectra, the difference in energy between the strongest CO ($\nu = 5$) and O_2 ($\nu = 4$) vibrational peaks is 3.11 ± 0.01 eV. With the present calibration, we obtain the maximum of the π resonance of O_2 at 531.06 eV, as compared with the value of Hitchcock and Brion[29] of 530.8 eV. Saitoh et al.[30] obtained an energy of 530.521 ± 0.01 eV based on a calibration at 541.80 eV, in the Rydberg states of oxygen. The difference of 0.5 eV clearly indicates that strong disagreements exist.

In the Rydberg states, the energy of the first sharp peak, $3s\sigma_g$, is 539.37 eV, as compared with values of 539.05[31] and 538.97,[30] a difference of 0.4 eV. Because the present data set does not contain photoemission data, we are unable to resolve these contradictions and note simply that our primary calibration is based on the EELS data of Sodhi and Brion.[28]

3.2. Oxygen K Edge Spectra. We have shown previously that the O $1s^{-1}$ π resonance of formaldehyde supports vibrational fine structure.[24] The spectra of acetaldehyde, acetone, and formic acid, Figure 2, do not show this fine structure at the O $1s^{-1}$ π resonance, but the widths of the peak envelopes are similar, 0.9 ± 0.05 eV for the first two and slightly broader, 1.1 eV, for formic acid. We conclude that the lack of vibrational structure is not due to larger lifetimes (expected to vary little between such similar molecules) or to the excited state being dissociative (because the total width is the same). Rather, the absence of fine structure is due to the additional modes excited for the larger molecules, and furthermore, we conclude that the oxygen $1s^{-1}$ π^* core excited state of the carbonyl group is bound in aldehydes and ketones (and probably also carboxylic acids like formic acid), although a vibrational progression can be resolved only in formaldehyde.

The assignments are indicated in Table 1 and Figure 2 and are based on the calculations of Yang et al.[18] for acetaldehyde and acetone, which in turn generally supported the assignments of Hitchcock and co-workers[3]. The assignment of formic acid also follows previous work[7] and in addition to the strongest peaks, we observe a feature assigned to the 4s Rydberg state, with three vibrationally resolved peaks.

Acetone and acetaldehyde have peak cross-sections (measured with respect to the underlying continuum) of 3.6 Mb, while that of formic acid is 3.5 Mb. Calculated oscillator strengths have been published for acetone, acetaldehyde, and several related molecules[18] but not to our knowledge for formic acid. In agreement with the present results, the reported calculations predict that the peak cross-section changes little as a function

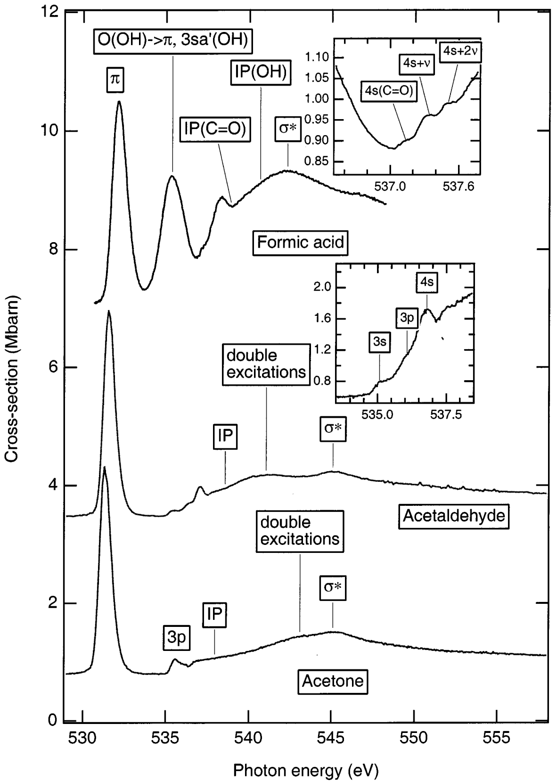

Figure 2. Oxygen K edge photoabsorption cross-section of formic acid, acetaldehyde, and acetone. The insets show regions with fine structure.

of the molecular structure. The theoretical peak cross-section is about 2 Mb, considerably lower than the present value.

The spectra of methanol and DME, Figure 3, do not show any new features with respect to previous measurements. Formic acid, methanol, and DME contain saturated C−O bonds, which show O 1s^{-1} 3s resonances of width 1.6, 1.0, and 1.2 eV, respectively. The significantly stronger broadening of formic acid suggests that the state is dissociative or, as previously pointed out, that it overlaps additional structure.[6,7] The spectrum of methanol shows four clear peaks at threshold, which have been identified previously.[8,9,24] In the formic acid spectrum, there is no sign of structure due to OH vibrations (457 meV in the ground state).

3.3. Carbon K Edge Spectra. The C 1s spectra of methanol and DME show rich structure, Figures 4 and 5, with about 20 states resolved for each gas. The spectrum of methanol resembles the lower resolution total ion yield spectrum of Hempelmann et al.[8] but not the absorption spectrum of Andersen et al.,[9] which was also reported in ref 8. Evidently, the latter spectrum was not well-normalized to incident flux to remove distortion by carbon absorption on the optics.

Both the methanol and the DME spectra strongly resemble the spectrum of methane,[32] with broader peaks and some shifts in relative energies and changes in intensities: this similarity is the starting point for the interpretation of the spectrum. The reduction in symmetry from T_d (methane) to C_s (methanol) and C_{2v} (DME) for these molecules is evidently a minor perturbation. The p symmetry states in principle split into three substates, $2a' + a''$ (C_s) or $a + b_1 + b_2$ (C_{2v}), but in the case of formaldehyde (C_{2v}), for instance, only two split substates were resolved[4,18] both theoretically and experimentally. For the occupied states, the valence states are sometimes discussed as the pseudo-π states, implying an effective local symmetry for the methyl group of C_{3v}, splitting p states into a and e states or σ and pseudo-π. We use this notation below, and on this basis, we obtain the assignment given in Table 2.

TABLE 1: Energies, Term Values, Assignment of States, and Quantum Defects at the O 1s Edge of Acetaldehyde, Acetone, Formic Acid, DME, and Methanol

no.	energy	term	assignment	quantum defect
acetaldehyde				
1	531.53	7.05	π^*	0.61
2	535.42	3.43	3sa′	1.01
3	536.32	2.57	3p	0.7
4	537.05	1.74	4s	1.2
IP	538.58 ± 0.06[33]			
5	541.0 ± 0.3		double excitations	
6	545.2 ± 0.3		σ^*	
acetone				
1	531.38	6.52	π^*	0.56
2	535.60	2.30	3p	0.57
3	536.94	1.16	4p	0.57
4	537.6	0.3	higher Rydberg states	
IP	537.90[35]			
5	543.1 ± 0.4		double excitations	
6	545.1 ± 0.3		σ^*	
formic acid				
1	532.17	6.78	O(CO)$\rightarrow\pi^*$	0.58
2	535.37	5.28	O(OH)$\rightarrow\pi^*$, 3sa′(OH)	1.4
3	537.16	1.79	4s(C=O)	1.24
4	537.34	1.61	4s + ν_3(C=O stretch)	
5	537.54	1.41	4s + 2ν_3(C=O stretch)	
6	538.37	2.28	3p(OH)	0.55
IP (C=O)	538.95 ± 0.05[33]			
IP (OH)	540.65 ± 0.05[33]			
7	542.3 ± 0.2		σ^*(C−O)	
DME				
1	535.56	3.0	3sa	0.87
IP	538.6[33]			
2	538.7		σ^*(C−O)	
methanol				
1	534.12	5.0	3sa′	1.35
2	535.83	3.3	3pa″	0.80
3	536.32	2.8	4p	0.71
4	537.10	2.0	4s	1.39
5	538.00	1.1	σ^*	
IP	539.1[33]			

For methanol, the first state is 3sa′, at an energy of 297.98 eV in good agreement with ref 8 and we assign the first two vibrations to methyl deformation and stretch modes, respectively, and the higher states to combination modes. The strongest state is 3pa′, and it corresponds to the 3p state in methane. The oscillator strength integrated over an interval of 0.5 eV across the main peak is about 0.021 electrons, as compared with 0.028 electrons for methane. Assuming that oscillator strength is roughly conserved between the methane and the methyl group, any split off state is expected to be about three times weaker.

A shoulder at about 180 meV higher energy is assigned to either the CO stretch, the methyl deformation mode (frequencies of 180−183 meV in the ground state), or possibly the OH bend mode (167 meV in the gs). Within the equivalent core approximation (ECA) (see below), the carbon atom becomes like a nitrogen atom in the excited state. The frequencies of NO stretch modes are in the range 150−200 meV, which is similar to the present value.

On the basis of the methane spectrum,[32] we assign the peak at 289.85 to 4sa′ + 3pσ′. These states can mix as they have the same symmetry, and a calculation with population analysis is needed to decide the orbital makeup. The 3pσ′−π splitting is thus 0.41 eV, similar to the value expected for the methyl group in acetaldehyde and acetone.[18] The structure at 290.27−290.34

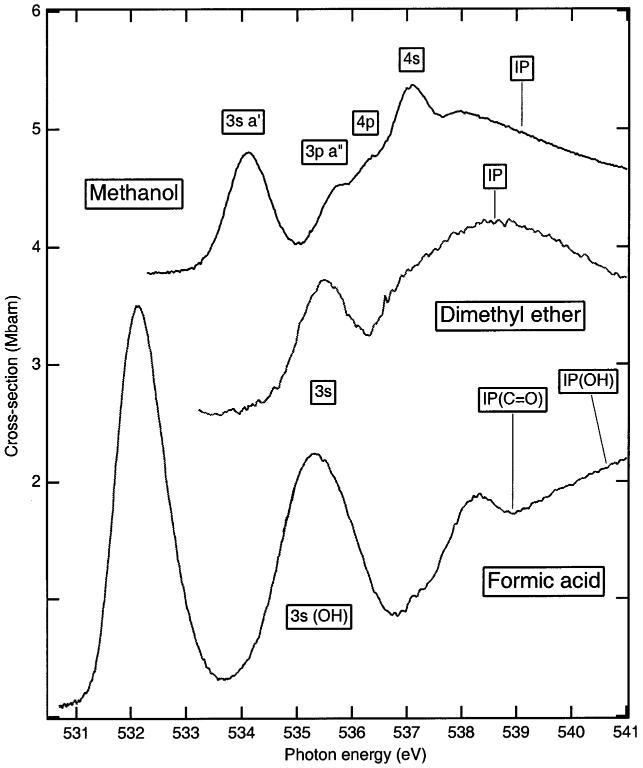

Figure 3. Oxygen K edge photoabsorption cross-sections of methanol, DME, and formic acid.

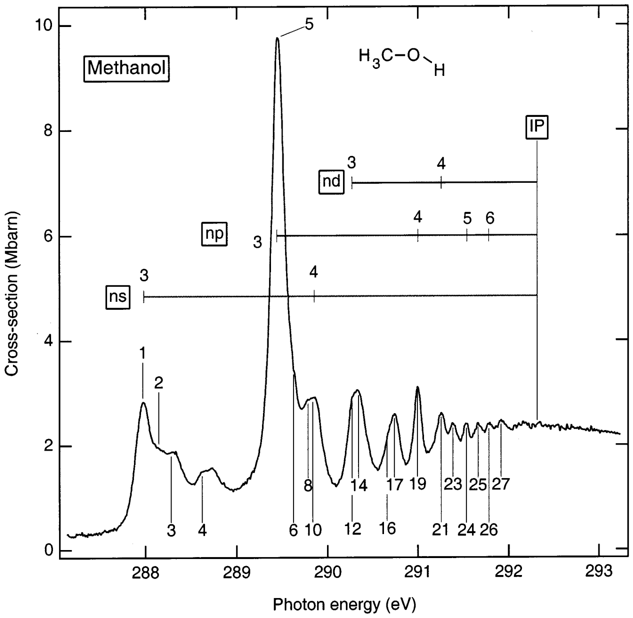

Figure 4. Carbon K edge photoabsorption cross-section of methanol. The labels of the states refer to the numbering in Table 2.

eV appears to be a doublet and is assigned to 3d, although another state may be present, which may be a second, symmetry split 3d state, labeled 3d′. This peak was assigned to 3pa′ by Hempelmann et al.[8] These states may indeed be mixed, but the presence of a similar feature in methane favors the assignment of at least one component to mainly 3d character. There is a rather strong peak at 290.74, which is tentatively assigned to the 3de state, as a similar but weaker feature occurs for methane. This is dipole forbidden and vibronically allowed under the T_d symmetry of methane and allowed here; we label it 3de, implying a t_2−e splitting of 0.39 eV.

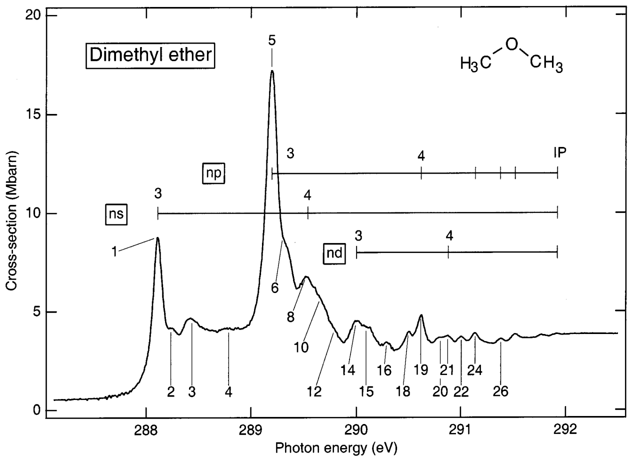

Figure 5. Carbon K edge photoabsorption cross-section of DME. The labels of the states refer to the numbering in Table 2.

TABLE 2: Term Values and Assignments for C 1s States of Methanol and DME and Peaks Assigned to Methyl Excitations of Acetaldehyde[a]

state no.	assignment (methane/other molecules)	methane	methanol	DME	acetaldehyde
1	3s		4.34	3.81	4.02
2	3s + ν_4/3s + ν	3.881	(0.17)	(0.13)	(0.15)
3	3s + ν_3	(0.191)	(0.30)	(0.33)	(0.36)
4	3s + ν_1 + ν_3, 3s + 2ν_3	3.323	(0.64)	(0.68)	
5	3p/3pσ', 3pπ	2.735	2.88	2.72	2.99
6	3p + ν_4/3p + CO stretch	(0.181)	(0.18)	(0.15)	(0.16)
7	4s + ν_3	2.466			
8	3p + ν_2 + ν_4, 3p + 2ν_4	(0.335)	(0.33)	(0.33)	
9	3p + ν_1	(0.410)			
10	/4sa′ + 3pσ', 3pσ'		2.47	2.26	2.30
11	3p + ν_3 + ν_4	(0.510)			
12	3d t_2, 3d e + ν_3/3d, and 3d′	2.04	2.05	2.13	
13	/4s				2.09
14	3p + 2ν_1, 3d e + ν_3 + ν_4/3d′	1.89	1.98	1.92	
15	−/3pσ			1.83	
16	?/3de	1.60	1.66	1.63	
17	3d t_2 + ν_1, 3d e + ν_1/?	1.52	1.58		
18	?/?			1.42	1.48
19	4p	1.27	1.32	1.30	
20	−/5(p + d)π(CH_3) and 3sσ(CO)			1.11	1.10
21	4d	1.06	1.06	1.04	
22	4p + ν			(0.19)	
23	4p + ν_1	(0.40)	(0.39)		
24	5p	0.745	0.78	0.78	
25	5d/?	0.658	0.66		
26	6p	0.47	0.54	0.54	
27	7p	0.349	0.40		
28	IP	290.735	292.32	291.92	291.35

[a] Methane[32] is also given for comparison. Term values (in eV) are given except where the state is assigned to a vibrational excitation. In this case, the vibrational quantum is given in brackets. Vibronic states of methane are indicated by ν: ν_1, symmetric stretch; ν_2, e-symmetry deformation; ν_3, t2 symmetry stretch; ν_4, t2 symmetry deformation. For the other molecules, the vibrations are those derived from the above. No subscript indicates an unidentified vibration.

Following ref 8, we assign the maximum at 291.0 eV to the 4p state (believed to have a small molecular field splitting) and identify higher np states as well. From the np series, we have extracted an IP of 292.32 eV, in very good agreement with Hempelmann et al. but lower than values derived from photoemission,[33] 292.4−292.8 eV. With our value of the IP, we calculated the quantum defect of the ns and nd series: 1.24 for 3sa′ and 4sa′, 0.41 for 3da′ and 4da′, and an average of 0.82 for the np series.

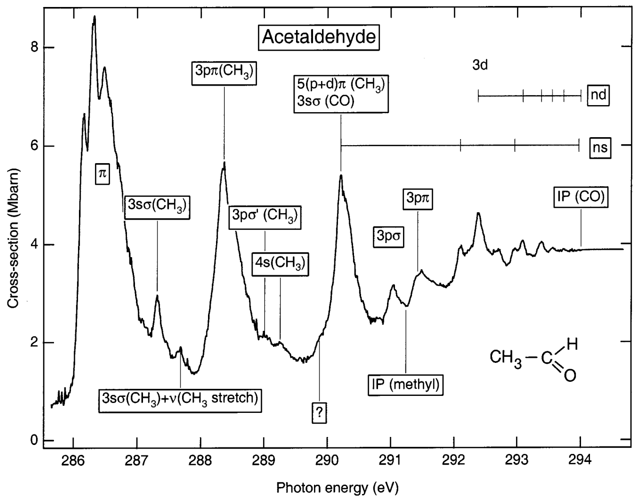

Figure 6. Carbon K edge photoabsorption cross-section of acetaldehyde.

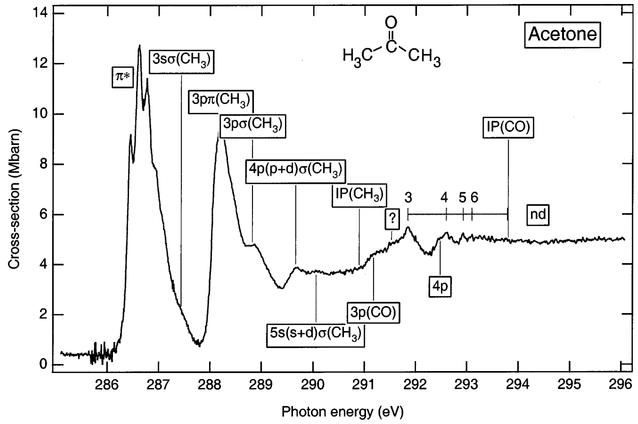

Figure 7. Carbon K edge photoabsorption cross-section of acetone.

The assignment of states for DME followed a similar procedure, and extrapolation of the np Rydberg states gives an IP of 291.92 ± 0.1 eV, again a little lower than the published values of 292.17−292.55 eV[33] and an average quantum defect of 0.74 for the np states. As Table 2 shows, the spectral features are very similar to methanol and methane.

The C 1s spectrum of acetaldehyde (Figure 6) consists of excitations of both the methyl and the carbonyl carbon 1s levels, and from the above considerations, the methyl carbon 1s states are expected to be similar to those of methane and methanol: the methyl group is bonded to another carbon atom instead of a hydrogen or oxygen atom. On this basis, the states identified as C 1s (methyl) excitations are included in Table 2; the similarity is evident, although less states are observed than for the other two gases. The assignment of the lower states takes into account the calculations of Yang et al.[18] and the resonant Auger spectra of Thompson et al.[17] For the higher states converging to the CO threshold, a Rydberg series of regularly decreasing intensity can be discerned (Table 3). A quantum defect analysis gives an IP of 293.97 eV, in good agreement with the literature value of 294.0 and a quantum defect of 0.10. We tentatively assign the series to nd states, but in any case, the extrapolation allows us to extract a good value for the carbonyl C 1s IP. Given the good agreement with the literature, we can also be confident that the methyl carbon IP is precise.

TABLE 3: Term Values and Assignments for Acetaldehyde at the Carbon K Edge[a]

state no.	energy (eV)	term (CO/CH$_3$)	assignment	quantum defect
1	286.17	7.83 (CO)	C(CO)→π*	0.68
2	(0.15)		π* + ν(CO stretch)	
3	(0.310)		π* + 2ν(CO stretch)	
4	(0.43)		π* + 3ν(CO stretch)	
5	(0.55)			
6	287.33	4.02 (CH$_3$)	3sσ(CH$_3$)	1.16
7	(0.15)		3sσ + ν(C−C stretch)	
8	(0.361)		3sσ + ν(CH$_3$ stretch)	
9	288.36	2.99 (CH$_3$)	3pπ(CH$_3$)	0.87
10	(0.16)		3p + ν(C−C stretch)	
11	289.05	2.30 (CH$_3$)	3pσ(CH$_3$)	1.57
12	289.26	2.09 (CH$_3$)	4s(CH$_3$)	1.45
13	289.87	1.48 (CH$_3$)	?(CH$_3$)	0.97
14	290.21	1.14 (CH$_3$)	5(p + d)π(CH$_3$)	0.55
		3.79 (CO)	3sσ(CO)	1.10
15	(0.145)		3sσ(CO) + ν	
16	291.02	2.98 (CO)	3pσ(CO)	0.87
17	(0.110)		3pσ + ν(CH$_3$ rock, CH bend)	
IP (methyl)	291.35			
18	291.4	2.60	3pπ(CO)	0.71
19	(0.08)			
20	291.62	2.38	?	
21	292.10	1.9	4sσ(CO)	1.33
22	(0.14)		4sσ(CO) + ν	
23	292.38	1.62	3d(CO)	0.10
24	292.67	1.33	4p(CO)	0.80
25	292.96	1.04	5sσ(CO)	1.39
26	293.09	0.91	4d(CO)	0.13
27	293.38	0.62	5d(CO)	0.3
28	293.55	0.45	6d(CO)	0.5
29	293.73	0.27	7d(CO) + higher Rydberg states	
IP (carbonyl)	294.0			

[a] Term values (in eV) are given except where the state is assigned to a vibrational excitation. In this case, the vibrational quantum is given in brackets.

The acetone spectrum, Figure 7, is assigned with reference to the spectrum of acetaldehyde and the calculations of Yang et al.[18] The most notable difference is the nonappearance of the 5(p + d)π (CH$_3$)/3sσ(CO) peak, which was one of the strongest peaks in the acetaldehyde spectrum but has practically disappeared from the acetone spectrum. (The principle quantum number is determined by the quantum defect calculated from the term value; the atomic character is determined from an analysis of the atomic orbitals contributing to the molecular orbital.) The calculations do predict a large change in spectral intensities, but they actually predict that the 3pπ peak is strongly attenuated while the 4p state is enhanced. Thus, it seems that the calculations are more reliable for the energy ordering of the states and overall behavior than for intensity. The acetone spectrum is much less structured than that of the previous molecules, and it seems that at this size of molecule, the number of electronic and vibrational degrees of freedom starts to diminish the level of detail that can be distinguished experimentally. The 3s(CH$_3$) state is almost degenerate with the π* state and visible only as a small shoulder. The assignment of both methyl and carbonyl states is given in Table 4.

At energies close to the carbonyl C threshold, a series of states of continuously decreasing intensity can again be discerned. A quantum defect analysis yields an IP of 293.50 eV, 0.3 eV lower than the literature value of 293.8 ± 0.09 eV.[33] The quantum defect is 0.13, and we label these states as nd as above. From this IP for the carbonyl C 1s, we have fixed the methyl C 1s at a value of 2.60 eV lower, the difference in the XPS binding energy. The corresponding terms and quantum defects are given in Table 4.

TABLE 4: Term Values and Assignments for Acetone at the Carbon K Edge[a]

state no.	energy (eV)	term (CO) (CH_3)	assignment	quantum defect
1	286.44	7.06 (CO)	C(CO)→π^*	0.62
2	(0.170)		$\pi^* + \nu$(CO stretch)	
3	(0.330)		$\pi^* + 2\nu$(CO stretch)	
4	(0.470)		$\pi^* + 3\nu$(CO stretch)	
5	(0.660)		$\pi^* + \nu$	
6	287.44	3.47 (CH_3)	3sσ(CH_3)	1.02
7	288.21	2.70 (CH_3)	3pπ(CH_3)	0.76
8	288.83	2.08 (CH_3)	3pσ(CH_3)	0.44
9	289.66	1.25 (CH_3)	4p(p + d)σ(CH_3)	0.70
10	290.05	0.86 (CH_3)	5s(s + d)σ(CH_3)	1.02
11	291.18	2.32 (CO)	3p(CO)	0.58
IP(CH_3)	290.90			
12	291.53	1.97		
13	291.85	1.65	3d(CO)	0.13
14	292.45	1.05	4p(CO)	0.40
15	292.60	0.90	4d(CO)	0.11
16	292.93	0.57	5d(CO)	0.11
17	293.10	0.40	6d(CO)	0.17
IP(CO)	293.50			

[a] Term values (in eV) are given except where the state is assigned to a vibrational excitation. In this case, the vibrational quantum is given in brackets.

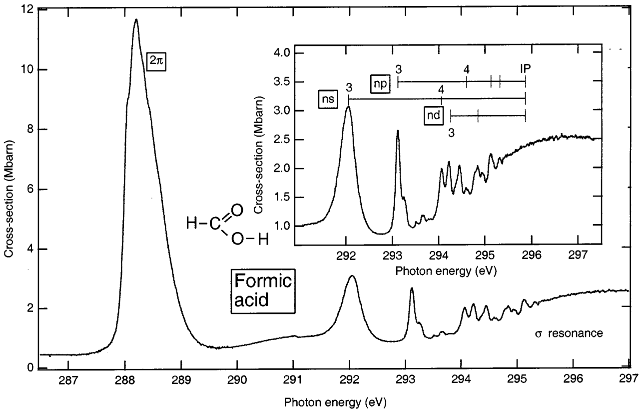

Figure 8. Carbon K edge photoabsorption cross-section of formic acid. The inset shows details of the Rydberg region and assignments.

The formic acid spectrum in Figure 8 shows a π^* resonance in which vibrational structure is partially resolved. This indicates that the C 1s π^* excited carbonyl group of a carboxylic acid is bound and the vibrational quantum of 146 meV is assigned tentatively to the C=O stretching mode. The assignment of the Rydberg states is straightforward, Table 5, and the extrapolation of the np series gives an IP of 295.87 eV (literature value 295.80 eV[33]). The Rydberg states are much less intense than for the other molecules.

The total ion yield spectrum of paraldehyde, the trimer of acetaldehyde, was measured at the carbon edge, Figure 9, and assigned as shown in Table 6. The IP does not appear to be available in the literature, so energies rather than term values are given. The first part of the spectrum resembles methanol and DME, and the two prominent peaks are assigned to the methyl 3s and 3p states, respectively. The 3s−3p splitting is similar to that of methane and less than that of methanol, indicating an influence of the bonding of the methyl group to a carbon, hydrogen, or oxygen atom. The other large peak is assigned to the 3p Rydberg state of the ring carbon; it is shifted to higher energy because it is bonded to two electronegative oxygen atoms, as well as to a methyl group and a hydrogen atom.

TABLE 5: Term Values and Assignments for Formic Acid at the Carbon K Edge[a]

state no.	energy (eV)	term	assignment	quantum defect
1	288.05	7.82	C(CO)→π^*	0.68
2	(0.15)		$\pi^* + \nu$(C=O stretch)	
3	(0.36)		$\pi^* + 2\nu$(C=O stretch)	
4	292.05	3.82	3s	1.11
5	293.12	2.75	3pa′	0.77
6	(0.130)		3p + ν	
7	293.55	2.22	3pa″	0.52
8	(0.09)		3pa″ + ν	
9	294.06	1.80	4s	1.25
10	294.22	1.65	3d	0.13
11	294.37	1.50	?	0.17/1.17
12	294.45	1.42	4p	0.77
13	294.60	1.27	?	0.73
14	294.85	1.02	?	0.35
15	294.94	0.93	4d	0.18
16	295.13	0.74	5p	0.77
17	295.32	0.55	6p	0.77
IP	295.87 ± 0.05			

[a] Term values (in eV) are given except where the state is assigned to a vibrational excitation. In this case, the vibrational quantum is given in brackets.

4. Discussion

For the O $1s^{-1}$ π^* states of the series formaldehyde, acetaldehyde, and acetone, the term values are 8.83, 7.05, and 6.52 eV, respectively, while the 3p Rydberg states have terms of 2.94, 2.57, and 2.30 eV. The trend of reduced energy with increasing size of the molecules is attributed to relaxation (which screens both the core hole and the excited electron), as well as delocalization of the excited electron. Formic acid has a value of 6.78 eV for the O $1s^{-1}$ π^* state, which is lower than formaldehyde due to the electronegative OH ligand.

For both acetaldehyde and acetone, the assignments of the other states follow Yang et al.,[18] who confirmed the original assignments of Hitchcock and Brion[3]. In the case of formic acid, we observe the three broad peaks previously reported by Ishii and Hitchcock[6,7] and assigned to O $1s^{-1}$ (C=O) π^*, O $1s^{-1}$ (OH) π^*, and overlapping O $1s^{-1}$ (C=O) Rydberg plus O $1s^{-1}$ (OH) σ transitions. The second peak is noticeably broader than the first and other π peaks, which is why it was suggested that it also contains intensity due to O $1s^{-1}$ (OH) 3σ transitions. The quantum defect for the latter is 1.4, similar to the value for methanol below. In addition, between the second and the third broad peaks, we observe three very weak peaks, with a vibrational spacing of about 180−200 meV and an effective quantum number of 2.76, assuming it is O $1s^{-1}$ (C=O) derived. The association with the carbonyl oxygen is supported by the fact that the vibrational spacing is just a little lower than the ground state C=O vibration of formic acid (220 meV) but rather different from the OH stretch (443 meV) and bend (152 meV.) We therefore assign these weak features to the O $1s^{-1}$ (C=O) 4σ transition, with a quantum defect of 1.24. The similarity of the vibrational quantum to the ground state value suggests that this has substantially pure Rydberg character, with little or no antibonding component.

In methanol, no vibrational structure is observed on the O $1s^{-1}$ 3s resonance, although the ground state OH stretch has a frequency of 457 meV, which would be easily observable even if considerably softened in the excited state. Similarly, no fine structure is observed on the O $1s^{-1}$ 3s(OH) resonance of formic acid. This suggests that in both cases the excited states are not bound and possibly undergo ultrafast dissociation, as occurs for water.[34] With the present larger molecules, scission may not

TABLE 6: Assignments for Paraldehyde at the Carbon K Edge[a]

state no.	energy (eV)	assignment	state no.	energy (eV)	assignment
1	287.06	3sa(CH_3)	8	289.36	3d
2	(0.14)	3sa + ν	9	289.87	?
3	(0.32)	3sa + ν	10	290.21	3p(CHO)
4	287.78	?	11	290.86	?
5	288.05	3p(CH_3)	12	291.08	?
6	(0.88)	3p + ν	13	291.65	?
7	288.8	4s	14	292.44	σ resonance

[a] Energies (in eV) are given except where the state is assigned to a vibrational excitation. In this case, the vibrational quantum is given in brackets.

only occur for the OH bond but also for the C−O bond. The two highest occupied orbitals have nonbonding oxygen character, while the third to fifth states have σ(CO), π(CH_3), and σ(OH) character, respectively. It is therefore reasonable to expect that the first empty orbital will have substantial CO antibonding character, favoring breaking of this bond. We return to this discussion below in the light of the ECA.

One would expect the O 1s spectrum of methanol and DME to be similar, but this is not found to be true experimentally: the methanol spectrum is richer, with several broad Rydberg states, whereas DME shows only one, together with a σ resonance. This may be a steric effect, with the surrounding methyl groups of the oxygen atom broadening the Rydberg states. In any case, the difference in the spectra is qualitatively consistent with the predictions of Plashkevych et al.[11] that the hydroxyl group shows extensive relaxation of the valence structure on core excitation. This interpretation is extended by the present work to include an oxygen atom in an ether.

For methanol and DME at the carbon edge, Figures 4 and 5 as noted above, the spectra are generally similar regarding the position of the main states. The 3s Rydberg state is dipole forbidden in methane but is observed due to vibronic coupling, while in methanol and DME it is allowed and correspondingly stronger with respect to the 3p state. There is a series of only partially resolved vibrational states between the 3s and the 3p states, and the peaks are broader in methanol than in methane or DME. This is unlikely to be due to unresolved vibrational structure as the lowest gs mode has an energy of 128 meV, and even if this is reduced in the excited state, it should be possible to resolve the first state, which has a Lorentzian width of about 100−110 meV. Rather, this could be due to dissociation by scission of a C−H, C−O, or O−H bond, leading to lifetime broadening. Because the potential energy surface is complex and multidimensional, it is difficult to give a precise interpretation. Vibrational structure is supported in an energy interval of over 1 eV above the first transition, but the potential may be bound along some coordinates and unbound along others (as in a saddle point in two dimensions.)

The vibrations that are observed are at about 170 and 302 meV and assigned to CH_3 deformation (180 and 183 in the gs) and CH_3 stretch (352 and 372 meV in the gs), respectively, indicating a moderate weakening of the CH bonds and bound potentials along these coordinates. The 3p state is also broadened but shows a clear shoulder at 330 meV, again assigned to the CH_3 stretch mode. As in the case of methane, there is a difference in the vibrational frequencies between the 3s (300 meV) and 3p (330 meV) states, due to the antibonding character of the former.

With regard to the energies of acetaldehyde and acetone, in Table 7, we compare the predictions of Yang et al.[18] with the present results. The π^* resonance is at lower experimental energies than predicted for reasons discussed by these authors. All experimental terms for acetaldehyde are shifted to higher energy, mostly by about 0.3−0.5 eV, suggesting an overall tendency toward relaxation in the final state, but otherwise, the agreement is good. The agreement for acetone is rather better, with one state not located (probably because the vibrational structure obscures detail) and a maximum discrepancy of 0.26 eV. The σ−π splitting of the Rydberg states is about 0.6−0.7 eV for 3p(CH_3) and 0.38 eV for 3p(CO) states.

TABLE 7: Comparison of Theoretical[18] and Experimental Terms for Acetaldehyde and Acetone

state	theoretical term[18]	experimental term value
	acetaldehyde	
π^*	5.86	7.83
3sσ(CH_3)	3.46	4.02
3pπ(CH_3)	2.61	2.99
3pσ(CH_3)	2.19	2.30
4s(CH_3)	1.65	2.09
5p(CH_3)	0.69	1.14
3sσ(CO)	3.19	3.79
3pσ(CO)	2.45	2.98
3pπ(CO)	2.17	2.60
	acetone	
π^*	5.02	7.06
3sσ(CH_3)	3.34	3.47
3pπ(CH_3)	2.66	2.70
3pσ(CH_3)	2.32	2.08
3pσ(CH_3)	1.66	
4p(CH_3)	0.99	1.25
5s(CH_3)	0.65	0.86

The $Z + 1$ approximation or ECA provides some guidance for assigning vibrational frequencies and structures, but the relevant equivalent core molecules have not been characterized and most are likely to be unstable. The equivalent core atom of oxygen is fluorine while that of carbon is nitrogen. Thus, for oxygen 1s excitation to the lowest unoccupied molecular orbital of methanol and DME, the equivalent molecules are methyl hydrogen fluoride and dimethyl fluoride: both contain a fluorine atom with two bonds and so they are likely to dissociate, in the first case to HF and a methyl radical or methyl fluoride and a hydrogen atom, and in the second case to a methyl radical and methyl fluoride. For the former, the hydrogen atom is light and has a higher vibrational frequency so this kinetic factor favors the expulsion of a hydrogen atom. On the other hand, the energy of the system is minimized by the scission of the C−O bond, so this thermodynamic factor favors this alternative pathway. A similar argument applies to the acid hydrogen of formic acid, namely, that O $1s^{-1}$ (OH) σ excitation may lead to the formation of a formyl radical and HF or formyl fluoride and a hydrogen atom. Again, the kinetically favored route is by expulsion of a hydrogen atom, but thermodynamics favors C−OH bond breaking.

Excitation of the carbonyl oxygen $1s^{-1}$ π resonance of the unsaturated molecules (formaldehyde, acetaldehyde, acetone, and formic acid) produces equivalent core molecules in which the carbonyl carbon has only three bonds instead of four. This is less likely to produce immediate dissociation: indeed, we have shown that the O $1s^{-1}$ π resonance of formaldehyde is bound, as it supports vibrational structure. This equivalent core argument supports our view that the π resonances of all aldehydes and ketones are bound, although vibrational structure cannot usually be resolved because too many modes are excited.

The cross-sections can be compared with published values. For the carbon K edge, Ishii and Hitchcock[6,7] measured peak

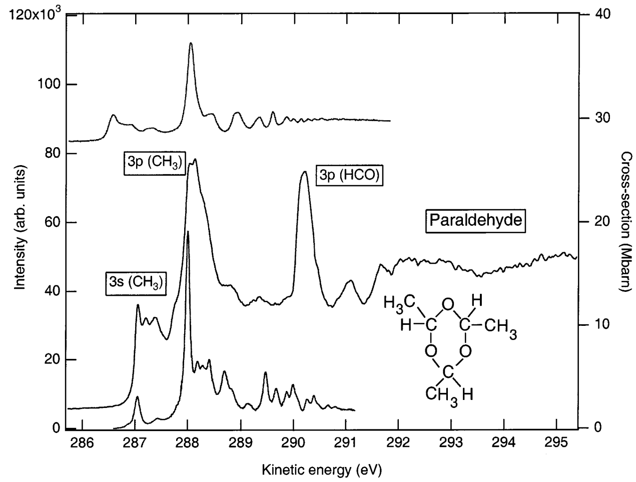

Figure 9. Center curve: paraldehyde total ion yield spectrum at the carbon K edge (left axis). Lower and upper curves: methane and methanol cross-sections, respectively (right scale). The methanol curve has been shifted 1.4 eV to align the strongest peak (methyl 3pσ states).

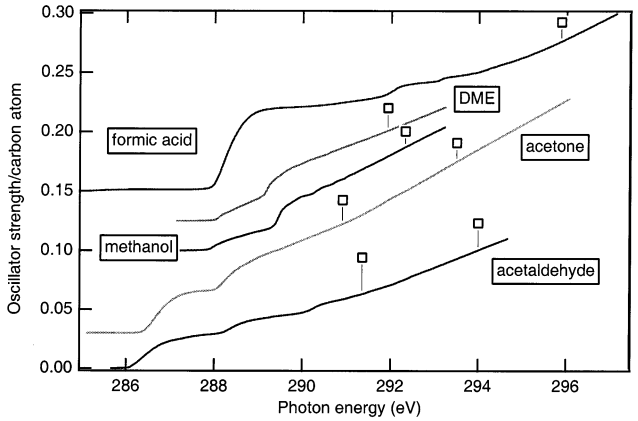

Figure 10. Integrated oscillator strengths per carbon atom. The curves other than acetaldehyde have been offset for clarity. Thresholds are marked by bars.

cross-sections of 9.9 Mb on the π* resonance of formic acid, a little lower than the present values, and about 2.6 Mb for the strongest feature (3p state) of methanol, as compared with 9.5 Mb in the present case. While part of the difference may be due to lower resolution, this is still a very substantial difference. At the oxygen edge, the values are 2.5 (formic acid) and 0.8 (methanol) as compared with 3.5 and 1.0 Mb in the present measurements. We conclude that there are rather large discrepancies in some cases between EELS-based and direct measurements of the cross-sections.

We can also compare the integrated oscillator strengths of these molecules near threshold, Figure 10. In this case, the absolute cross-section (after subtracting the continuum background) has been converted to differential oscillator strength, integrated and normalized to the number of carbon atoms in each molecule. Because there are carbonyl and methyl carbon atoms present, this would be expected to give a rather scattered plot unless the integrated cross-sections are similar. In fact, they are similar, and oscillator strengths per carbon atom at the (second) threshold (where two are present) are 0.09−0.10 for all molecules except formic acid, where the value is 0.126. Although the acetone molecule has a higher peak cross-section on the π* resonance, the integral per carbon atom at higher energy is very similar to that of acetaldehyde. This suggests an intensity borrowing process; indeed, the intensity also seems to be "repaid" around threshold; that is, there is a corresponding reduction of the Rydberg intensity that compensates the higher π* absorption. In terms of orbital parentage, intensity borrowing translates as the mixing of wave functions. This suggests a rule of thumb that for carbon-based functional groups of the types studied here, the integrated oscillator strength is about 0.1 or slightly larger for carboxylic groups.

The forms of the curves of methanol and DME are very similar, confirming once again that the functional group model works well. On the other hand, in formic acid, the oscillator strength is much more strongly concentrated in the π* resonance, with weak higher Rydberg states but with an even higher integral oscillator strength.

While the π resonance seems to have constant oscillator strength at the oxygen edge, the behavior appears to be different at the carbon edge for acetaldehyde and acetone. The acetone resonance is about 50% stronger than that of acetaldehyde, possibly indicating that the π* state is more localized than in acetone. This result is not consistent with calculations,[18] which predict that the resonances in the two molecules should have approximately equal oscillator strength.

5. Conclusions

The oxygen 1s^{-1} π excited carbonyl group is bound, as evidenced by the observation of vibrational structure in formaldehyde, and the similar width of the resonance for the larger molecules. However, they do not usually show fine structure due to the large number of vibrational degrees of freedom. We conclude that the chromophore model is usually a reasonable approximation for predicting electronic core absorption spectra of carbon groups, while at the vibrational level, it can be either an accurate or a poor approximation. For oxygen-containing groups, the spectra depend on neighboring atoms, in agreement with the theoretical predictions of Plashkevych et al.,[11] so that a chromophore model is not appropriate.

The effects of symmetry lowering on the methyl group have been explored by comparing methane with the series of lower symmetry molecules studied here. The most obvious effect is on the 3p Rydberg state, where splittings of 0.6−0.7 eV are observed. The carbonyl groups show splittings of 0.38 (acetaldehyde) and 0.53 (formic acid) eV.

Acknowledgment. We thank Luca Romanzin for technical assistance and all of our colleagues at Elettra for their help and encouragement. We also thank V&F Analyse und Messtechnik GmbH (Absam, Austria) for the donation of detectors.

References and Notes

(1) Coreno, M.; de Simone, M.; Prince, K. C.; Richter, R.; Vondracek, M.; Avaldi, L.; Camilloni, R. *Chem. Phys. Lett.* **1999**, *306*, 269.

(2) Püttner, R.; Dominguez, I.; Morgan, T. J.; Cisneros, C.; Fink, R. F.; Rotenberg, E.; Warwick, T.; Domke, M.; Kaindl, G.; Schlachter, A. *Phys. Rev. A* **1999**, *59*, 3415.

(3) Hitchcock, A. P.; Brion, C. E. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 231.

(4) Remmers, G.; Domke, M.; Puschmann, A.; Mandel, T.; Xue, C.; Kaindl, G.; Hudson, E.; Shirley, D. A. *Phys. Rev. A* **1992**, *46*, 3935.

(5) Prince, K. C.; Avaldi, L.; Coreno, M.; Camilloni, R.; de Simone, M. *J. Phys. B: At. Mol. Opt. Phys.* **1999**, *32*, 2551.

(6) Ishii, I.; Hitchcock, A. P. *J. Electron Spectrosc. Relat. Phenom.* **1988**, *46*, 55.

(7) Ishii, I.; Hitchcock, A. P. *J. Chem. Phys.* **1987**, *87*, 830.

(8) Hempelmann, A.; Piancastelli, M. N.; Heiser, F.; Gessner, O.; Rüdel, A.; Becker, U. *J. Phys. B: At. Mol. Opt. Phys.* **1999**, *32*, 2677.

(9) Andersen, J. N.; Johansson, U.; Nyholm, R.; Sorenson, S. L.; Wiklund, M. *MaxLab Ann. Rep.* **1997**, 180.

(10) Stolte, W. C.; Öhrwall, G.; Sant'Anna, M. M.; Dominguez Lopez, I.; Dang, L. T. N.; Piancastelli, M. N.; Lindle, d. W. *J. Phys. B: At. Mol. Opt. Phys*. **2002**, *35*, L253.

(11) Plashkevych, O.; Privalov, T.; Ågren, H.; Carravetta, V.; Ruud, K. *Chem. Phys.* **2000**, *260*, 11.

(12) Kaznacheyev, K.; Osanna, A.; Jacobsen, C.; Plashkevych, O.; Vahtras, O.; Ågren, H.; Carravetta, V. *J. Phys. Chem. A* **2002**, *106*, 3153.

(13) Wight, G. R.; Brion, C. E. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *4*, 25.

(14) Yang, B. X.; Kirz, J.; Sham, T. K. *Phys. Rev. A* **1987**, *36*, 4298.

(15) Eberhardt, W.; Sham, T. K.; Carr, R.; Krummacher, S.; Strongin, M.; Weng, S. L.; Wesner, D. *Phys. Rev. Lett.* **1983**, *50*, 1038.

(16) Rossi, A. R.; Davidson, E. R. *J. Phys. Chem*. **1992**, *96*, 10682.

(17) (a) Thompson, D. B.; Ji, D.; Chen, S. Y.; Hanson, D. M. *J. Phys. B: At. Mol. Opt. Phys.* **1999**, *32*, 5711. (b) Thompson, D. B.; Ji, D.; Lee, K. D.; Ma, C. I.; Hanson, D. M. *J. Phys. B: At. Mol. Opt. Phys.* **1999**, *32*, 2649.

(18) Yang, L.; Ågren, H.; Carravetta, V.; Petterson, L. G. M. *Phys. Scr*. **1996**, *54*, 614.

(19) Trofimov, A. B.; Moskovskaya, T. E.; Gromov, E. V.; Köppel, H.; Schirmer, J. *Phys. Rev. A* **2001**, *64*, 22504.

(20) Schirmer, J.; Barth, V.; Tarantelli, F. *Chem. Phys.* **1988**, *122*, 9.

(21) Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1995**, *102*, 6735.

(22) Fronzoni, G.; Stener, M.; Lisini, A.; Decleva, P. *Chem. Phys*. **1996**, *210*, 447.

(23) Sette, F.; Stöhr, J.; Hitchcock, A. P. *J. Chem. Phys.* **1984**, *81*, 4906.

(24) Prince, K. C.; Richter, R.; de Simone, M.; Coreno, M. *Surf. Rev. Lett*. **2002**, *9*, 159.

(25) Prince, K. C.; Blyth, R. R.; Delaunay, R.; Zitnik, M.; Krempasky, J.; Slezak, J.; Camilloni, R.; Avaldi, L.; Coreno, M.; Stefani, G.; Furlani, C.; de Simone, M.; Stranges, S. *J. Synchrotron Radiat.* **1998**, *5*, 565.

(26) Fronzoni, G.; Coreno, M. M.; de Simone, M.; Franceschi, P.; Furlani, C.; Furlan, S.; Prince, K. C.; Stener, M.; Decleva, P. *J. Chem. Phys. A*, submitted for publication.

(27) Samson, J. A. R.; He, Z. X.; Haddad, G. N. *J. Phys. B: At. Mol. Opt. Phys*. **1994**, *27*, 887.

(28) Sodhi, R. N. S.; Brion, C. E. *J. Electron Spectrosc. Relat. Phenom.* **1984**, *34*, 363.

(29) Hitchcock, A. P.; Brion, C. E. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 1.

(30) Saitoh, Y.; Kimura, H.; Suzuki, Y.; Nakatani, T.; Matsushita, T.; Muro, T.; Miyahara, T.; Fujisawa, M.; Soda, K.; Ueda, S.; Harada, H.; Kotsugi, M.; Sekiyama, A.; Suga, S. *Rev. Sci. Instrum.* **2000**, *71*, 3254.

(31) Ma, Y.; Chen, C. T.; Meigs, G.; Randall, K.; Sette, F. *Phys. Rev. A* **1991**, *44*, 1848.

(32) de Simone, M.; Coreno, M.; Alagia, M.; Richter, R.; Prince, K. C. *J. Phys. B: At. Mol. Opt. Phys.* **2002**, *35*, 61.

(33) Jolly, W. L.; Bomben, K. D.; Eyerman, C. J. *At. Data Nucl. Tables* **1984**, *31*, 433.

(34) Hjelte, I.; Piancastelli, M. N.; Fink, R. F.; Björneholm, O.; Bässler, M.; Feifel, R.; Giertz, A.; Wang, H.; Wiesner, K.; Ausmees, A.; Miron, C.; Sorenzen, S. L.; Svensson, S. *Chem. Phys. Lett*. **2001**, *334*, 151.

(35) Situmeang, R.; Thomas, T. D. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *98*−*99*, 105.