Effects of relaxation and hyperconjugation on shake-up transitions in X-ray excited photoelectron spectra of some small carbonyl compounds

by

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Abstract

The C1s and O1s core shake-up and HeII excited valence photoelectron spectra of formaldehyde, acetaldehyde and acetone have been studied experimentally and by INDO/CI calculations. It is found that the presence of the π type orbitals on the CH_3 groups of acetaldehyde and acetone is responsible for the large differences found in the core shake-up spectra between these molecules and formaldehyde. Due to the redistribution of charge in the oxygen acetaldehyde and acetone core ionised systems, the energy ordering between the C=O π orbital and the CH_3 $1b_1$ π type orbital is reversed, compared to the neutral molecules. The ionization from the $6a_1$ σ(C-O) orbital in acetone gives rise to a clearly observable vibrational progression whereas the corresponding orbital in formaldehyde is structureless. This indicates a substantial stabilization of the bonds due to the methyl substitution.

INTRODUCTION

The ability to resolve shake-up structures in core-ionized photoelectron spectroscopy has led to the opening of a new field of research, where molecular properties are related to observed satellite structure in spectra. Considerable effort has been made in assigning these structures in terms of transitions between well defined molecular orbitals. However, when a molecule is core-ionized to form a molecular cation, the rearrangement of the electronic structure leads to a different valence orbital structure in the final state. Therefore the analysis of shake-up spectra in terms of initial state orbitals may become less significant. In order to study this effect further, we have selected a series of three simple carbonyl compounds, namely formaldehyde, acetaldehyde and acetone, for which the C1s and O1s shake-up spectra have been recorded.

The three molecules represent a series of related systems where the hydrogen atoms of formaldehyde are substituted with one methyl group in acetaldehyde and two methyl groups in acetone. The valence orbitals on the methyl groups can be described as sp^3-hybridized into four σ-bonds. Due to the possibility of hyperconjugation, an interaction between some of these orbitals and the out-of-plane π-orbital localised on the carbonyl (C=O) group can take place. Thus, in acetaldehyde two π-type orbitals with mixed methyl-carbonyl character can be formed. For the same reason, three π-type orbitals can be formed in the acetone molecule.

It is well known that π–π^* transitions give rise to strong satellite lines in core level photoelectron spectra. It could therefore be expected that also π-type orbitals partly originating from methyl groups give rise to similar well-defined lines in spectra. The three molecules in the present study are obviously very well suited for such an investigation. Formaldehyde shake-up has already been extensively studied by both experimental and theoretical methods [1, 2] and assignments have been made of the lower lying shake-up structures. In the present investigation these results are considered in the interpretation of the acetaldehyde and acetone spectra.

The core level photoelectron spectra were excited using high intensity monochromatised X-rays. The shake-up transitions occur amongst the valence orbitals. In order to get a more detailed understanding of these orbitals, particularly with regard to the hyperconjugation effect, we have also carried out high resolution photoelectron spectroscopy studies using HeII excitation.

EXPERIMENTAL DETAILS

The X-ray excited photoelectron spectra were recorded on a high resolution gas phase instrument. A high intensity monochromatized AlK_α ($h\nu = 1487$ eV) excitation source was used for excitation of the spectra. For these spectra only a relative energy scale, giving the shake-up energy, was determined. The UV-excited spectra were recorded on a second spectrometer, which has been optimized for high resolution gas phase studies in the ultraviolet range [3]. A high intensity microwave ECR source was used to produce the exciting radiation for the HeII spectra presented in this investigation. This source has been described in detail in ref. [4]. Spectra were recorded in an energy range covering binding energies up to about 26 eV. The spectra of formaldehyde and acetaldehyde were calibrated against the Ar $3p_{1/2, 3/2}$ lines, which were recorded simultaneously with the sample spectra by using a gas mixture of the sample gas and argon in the gas cell. The acetone spectrum was calibrated against the Ne 2p lines.

The acetaldehyde and acetone samples were commercially obtained and of >99.5% purity. The formaldehyde was commercially obtained in the form of crystalline paraformaldehyde ($OH(H_2CO)H$). To produce pure formaldehyde in the gas phase the sample was heated under vacuum conditions in the spectrometer where the water was allowed to be pumped off. The purity was assessed by running a number of consecutive spectra and noting the relative intensities of the lines.

COMPUTATIONAL METHOD

The wavefunctions and energies were calculated from the INDO/CI program package of Zerner and co-workers [5-7]. The program package has a selection of parametrisations and in this study we have used both the Mataga-Nishimoto [8] and Ohno-Klopman [9] parametrizations for the gamma integrals. For completeness, calculations were also done using INDO/2 theoretical gamma integrals, although these are primarily used in ground state calculations, e.g. geometry optimizations, rather than for spectroscopic calculations involving excited states. The equivalent core approximation is used to describe the core-ionised species. In all calculations, a single determinant description was used for the initial (unionised) state of the system. The excitations considered in the configuration interaction (CI) calculations included, in all cases, the full set of single excitations, $\sigma \rightarrow \sigma^*$ as well as $\pi \rightarrow \pi^*$. However, due to program limitations on the total number of symmetry adapted configurations to slightly more than 200, not all double excitations could be included. The number of double excitations depended on the size of the molecule but was in all cases in the order of 100.

The intensities of the shake-up satellites in the core photoelectron spectra were calculated from the SHAKEINT program package [1] which is based on the sudden approximation [10,11]. In this approximation the allowed transitions are restricted to orbitals of the same symmetry. The use of the equivalent core approximation limits the final states gaining intensity to those of singlet coupled valence parentage. In this approximation it is assumed that there is no significant mixing between states of singlet and triplet parentage. Further details of the method used can be found in references [1,12,13].

RESULTS

HeII photoelectrons spectra

The HeII excited photoelectron spectrum of the formaldehyde molecule is shown in Fig. 1. Five bands are observed due to ionization from the orbitals belonging to the ground state electron configuration (C_{2v} symmetry)

$$[....]\ 4a_1^2\ 1b_2^2\ 5a_1^2\ 1b_1^2\ 2b_2^2$$

The ionization energies are given in Table I, along with the calculated orbital energies obtained for formaldehyde. The assignments given in the figure correspond to the results obtained by the calculations and are the same as obtained in previous studies [14]. The $2b_2$ orbital has essentially σ lone-pair character and is localised on the oxygen, while the $1b_1(\pi)$ and $5a_1(\sigma)$ orbitals correspond to the split components of the doubly degenerate 1π orbital in the CO molecule.The σ component acquires higher binding energy due to a bonding interaction with the hydrogen atoms. The innermost band due to ionization from the $4a_1$ orbital is very broad (FWHM > 1 eV) and shows no vibrational fine structure. This suggests that the cationic state is strongly repulsive or that the Franck-Condon region falls on a steeply sloping part of the potential surface. In the case of acetaldehyde the corresponding 6a' orbital is found at a slightly lower binding energy (19.4 eV), where it gives rise to a narrower band which also shows some indication of weak fine structure. In the case of acetone, the band ($6a_1$) is found at even lower binding energy (18 eV) and displays a clear vibrational progression in the lower energy part of the band. Thus, this inner valence orbital, which is primarily associated with the C2s atomic orbital in the carbonyl group, becomes gradually destabilized with respect to the binding energy when methyl substituents are added. At the same time the chemical bond appears to be strengthened, as suggested by the vibrational structure. This could indicate that there exist repulsive correlation states in the inner valence region of all three molecules, which interact strongly with the single hole states and cause predissociation in this energy region.

The HeII excited spectrum of acetaldehyde is shown in Fig. 2. The electron binding energies are summarised in Table 2 together with the calculated counterparts using Koopmans' theorem. From the calculations and qualitative arguments we expect to observe eight bands in the valence electron spectrum corresponding to the neutral ground state configuration (in C_s symmetry)

$$[....]\ (5a')^2\ (6a')^2\ (7a')^2\ (8a')^2\ (1a'')^2\ (9a')^2\ (2a'')^2\ (10a')^2$$

Two of the additional valence orbitals, as compared to formaldehyde, are related to the C(2p)-H(1s) bonds of the methyl group and the third to the methyl C2s orbital. Since only seven bands can be clearly observed there is obviously some overlap in the spectrum. Due to its comparatively high intensity and large width we therefore associate the fourth band with the ionization from two orbitals. The assignments suggested from the calculations are given in the figure and in Table 2. They agree with previous results [14]. As can be seen, in the inner valence region a second band is added compared to formaldehyde. This reflects the addition of the new C2s orbital.

Fig. 3 shows the spectrum recorded for acetone. The measured adiabatic and vertical electron binding energies are collected in Table 3 and are given along with the calculated Koopman's energies. The assignments given in C_{2v} symmetry in the figure correspond to the ordering obtained in the calculations and in previous studies [14]. In this case there are six more valence orbitals than in formaldehyde. The overlap between the bands is substantial in the range between 13 eV and 17 eV (cf Fig. 3). Therefore, the electron binding energies for some of the orbitals are less well determined for acetone than for the other two molecules, particularly the $7a_1$ and $3b_2$ orbitals. Two bands are now seen in the energy range around 24 eV. They correspond to ionization from the $2b_2$ and $5a_1$ orbitals, in increasing binding energy order, and are primarily related to the C2s orbitals of the two methyl groups. The energy splitting between these to bands is small, only 1.4 eV, in comparison with the energy difference to the third C2s type orbital related to the C=O carbon, which is about 6 eV, reflecting the small overlap between the C2s orbitals localized on the two methyl groups.

As can be seen from Figs. 1, 2 and 3, the spectra show extensive vibrational structure in some of the photoelectron bands. This structure will be discussed in detail elsewhere in connection with Franck-Condon analyses carried out to determine structure parameters of the ionic states [15].

The O1s shake-up spectra

The experimental O1s shake-up spectra of formaldehyde, acetaldehyde and acetone are presented in figures 4,5 and 6, respectively, with the convoluted theoretical INDO/CI spectra obtained from the Mataga-Nishimoto parametrisation inserted for comparison. As can be seen, the shake-up region of formaldehyde shows one intense line at 12.2 eV, followed by some weaker features and an extensive shake-off continuum. In the cases of acetaldehyde and acetone the general structures are the same as for formaldehyde except for the presence of a new line appearing at 7.5 eV in acetaldehyde and at 8.4 eV in acetone. The counterparts to the line at 12.2 eV in formaldehyde are rather observed at 12.9 eV and 13.4 eV for acetaldehyde and acetone, respectively, as suggested from both the line shapes and intensities.

The experimental binding energies and relative intensities for the O1s shake-up spectra are summarised in Tables 4-9 along with the calculated INDO-CI shake-up energies and intensities. The following three different sets of parameters were considered in the calculations: a) Mataga-Nishimoto integrals b) Ohno-Klopman integrals and c) theoretical INDO/2 gamma integrals. The results for Mataga-Nishimoto parameterisation for formaldehyde are taken from reference [1]. In the tables the calculated energies and intensities are given for each set of parameters before and after the inclusion of configuration interaction (CI). In most of the proceeding discussion emphasis is placed on the results obtained from the Mataga-Nishimoto integral parameterisation, which is found to give the best overall results.

The C1s shake-up spectra

The experimental C1s shake-up spectra are shown in Figs. 7,8 and 9 and are summarised in Tables 10-15 together with the calculated INDO/CI results. The shake-up spectrum of formaldehyde has previously been presented and discussed in some detail in ref. [1], bud is included as Fig.7 for comparison. The present spectrum displays a larger energy range, showing the double ionization continuum, which appears to show a very broad resonance at about 45 eV shake-up energy. It should be noted that the background level in all the spectra can be deduced from the intensity at the high kinetic energy limit and that this low spectrometer background, for the kinetic energies obtained in XPS, is constant over the studied energy range.

In all the C1s shake-up spectra a small but distinct peak shows up at about 5 eV shake-up energy. In the previous report [1] this structure was assigned to a state localized of triplet parentage to the carbonyl group. This peak is not simulated in the calculations since only singlet parent coupled states are considered.

At about 10 eV from the carbonyl C1s main line a strong line is observed which dominates the low energy shake-up region in all three spectra. This line is associated with the $\pi-\pi^*$ shake-up transition in the carbonyl group.

DISCUSSION

The assignments of the HeII-excited spectra suggested above on the basis of the INDO calculations can be partly made also on qualitative or semi-quantitative grounds. This will be discussed in the following, while the last part of the discussion will deal with the shake-up spectra. For the discussion of the shake-up structure it is necessary to have some knowledge about the valence electron structure in the core-ionised systems, in addition to the ground state or valence ionised systems. In particular, the π-orbitals are known to give rise to strong satellite bands and are therefore of special interest in this context. For this reason we give in Table 16 the coefficients of the oxygen and carbon 2p(π)-functions in the expansion of the π-orbitals obtained in the INDO/CI calculations for both the neutral and core ionised states.

HeII-excited spectra

In the case of acetaldehyde, where one of the hydrogen atoms of formaldehyde is replaced by a methyl group, an additional out of plane π–type orbital is present, which is mixed with the C=O π-orbital via hyperconjugation. From earlier studies it is known that the orbitals associated with the methyl group have binding energies that lie in the energy range between 14 and 15 eV. A more accurate value of 14.3 eV has been suggested in studies using a sum rule applied to the binding energies of atomic or molecular subunits to predict the energies of the composite molecule [17]. Fig.10 shows the energies of the two subunits H_2CO and CH_4 along with the binding energies of the composite molecules acetaldehyde and acetone of the present study. From the UV photoelectron spectrum of acetaldehyde, illustrated in Fig.2, it can be seen that the in-plane σ-type component of the "methyl orbitals" remains essentially unshifted at 14.2 eV, although a slightly increased binding energy would have been expected due to an inductive shift in the initial state. However, this effect is out weighted by the interaction of the close lying 8a' orbital due to anti-bonding character of the overlapping basis orbitals, as seen from the INDO orbital expansion coefficients. In contrast, the out-of-plane component, 1a", is significantly shifted towards higher binding energy (15.4 eV). This shift can be associated with an interaction via hyperconjugation with the C=O π type orbital, 2a", which in turn is shifted from 14.4 eV in formaldehyde to the lower binding energy 13.1 eV in acetaldehyde. Hence a total splitting of 2.3 eV between the π-type orbitals is obtained. If we assume that this splitting essentially is due to the hyperconjugation, with only a small influence from induction, the resonance integral β describing the interaction is approximately 1 eV. This assumption is justified by the fact that the electron donating ability of the CH_3 group is only slightly higher than for the hydrogen atom.

It is also seen from the calculations that the gradual shift in energy of the highest occupied orbital, the oxygen lone pair, upon methyl substitution is primarily due to the anti-bonding character of the overlap with the orbitals of the carbon atoms, and the fact that the oxygen contribution to the highest molecular orbital is gradually diminished when methyl groups are added.

As discussed above, the addition of a second methyl group to form acetone leads to the formation of a third out of plane bonding, π, and antibonding, π^*, pair of orbitals. In the C2v symmetry of the molecule, the π-type orbitals acquire a_2 and b_1 symmetry (cf Fig. 10). These orbitals are observed at 14.5 eV ($1a_2$) and 15.6 eV ($1b_1$) binding energy, respectively (cf Table 3). As in the case of acetaldehyde, the CH_3 $1b_1(\pi)$ orbital interacts with the C=O $2b_1(\pi)$ orbital via hyperconjugation. The splitting between these orbitals is 3.2 eV, which is about 1 eV larger than for acetaldehyde. This increase reflects the influence on the electronic structure around 14-15 eV by the additional methyl group.

O1s shake-up spectra.

In formaldehyde, the $1b_1(\pi)$ orbital is localised completely on the C=O unit. The INDO/CI calculations clearly show that the strong O1s shake-up line at 12.2 eV corresponds essentially to the $1b_1(\pi) \rightarrow 2b_1(\pi^*)$ transition (see Table 4), which agrees with the general observation that $\pi \rightarrow \pi^*$ shake-up transitions in core level photoelectron spectra tend to give rise to well defined satellite lines. Table 5 gives the expansion coefficients for the various shake-up transitions for the three parametrisations used. As can be seen from this table, the $1b_1(\pi) \rightarrow 2b_1(\pi^*)$ transition accounts almost completely for the observed peak. This assignment is in agreement with the result obtained by Basch [16] from earlier *ab initio* calculations. The results using Mataga-Nishimoto and Ohno-Klopman parametrisation are approximately equivalent, whereas the wavefunction obtained with theoretical gamma integrals gives too large shake-up intensity.The calculated shake-up energy using all parameterisations is 2.2-2.6 eV too low (cf Table 10). As discussed in ref. 1, one reason for this is the neglect of the interaction with doublet arising from a triplet-coupled valence excitation, which would fall at a lower energy and push the singlet coupled, stronger peak, to higher energy.

The results presented in Table 16 show that the $1b_1(\pi)$ and $2b_1(\pi^*)$ orbitals of formaldehyde undergo an important change upon the creation of the O1s hole. In the former orbital the electronic charge becomes much more strongly localised on the oxygen atom, while in the latter the opposite transfer of charge occurs. This implies that the $1b_1(\pi)$ electron binding energy increases significantly, due to the higher binding energy of O2p than C2p, while the $2b_1(\pi^*)$ energy decreases. Consequently, the shake-up energy will be much larger in the core ionised system than would be expected from a consideration of the neutral ground state properties.

At energies above 12.2 eV at least two more transitions are predicted to gain a small intensity in the formaldehyde spectrum. These transitions more than likely contribute to the weaker structures lying at higher binding energies. However, the type of limited basis set calculations carried out in the present study do not account for transitions to Rydberg states, which are also expected to contribute to the spectrum in this energy region and, therefore, a more detailed assignment of this energy region can not be performed.

In the experimental shake-up spectrum of acetaldehyde the presence of the new π-type orbital formed by the methyl group in addition to the C=O π orbital is reflected by the appearance of a second strong peak at 7.5 eV. The two strong shake-up lines have an energy separation of 5.3 eV, which is about twice as large as the splitting observed in the valence PES. However, this splitting does not represent the splitting in the ground state or in the valence photoelectron spectrum. As can be seen from Table 16, it is the peak at 12.9 eV that mainly corresponds to the transition from the C=O π orbital, while the peak at 7.5 eV should be associated with the new π-orbital associated with the methyl group. This would also be expected from the point of view that the hyperconjugation between the two π-type orbitals is not extremely large in the O1s ionized molecule, since the core ionized oxygen atom is chemically equivalent with a fluorine atom, which would normally engage very weakly in π-bonding. The shake-up energy should therefore be similar to that of formaldehyde. This interpretation also agrees with the shape of the lines in the experimental spectrum, since it is obviously the very broad line at the higher binding energy that bears some resemblance to the strong shake-up line in the spectrum of formaldehyde. The width of the line is due to the large change in equilibrium bond distance for the shake-up state when compared to the neutral ground state. The carbonyl π - π^* shake-up transition probably leads to a dissociative final state.

As for formaldehyde, the large shake-up energy of the C=O π orbital of acetaldehyde is related to a redistribution of the charge upon the creation of the core hole. As can be seen from Table 16, the 1π orbital has acquired very pronounced oxygen 2p character, which leads to an increase in the binding energy. The large effect of an oxygen 2p orbital on the binding energy of π-orbitals has been amply demonstrated in the literature. Comparing, for example, the energy of the $1b_1(\pi)$ orbital in pyrrol with that of furan, it is seen that the binding energy of the latter, with a substantial contribution from O2p, is about 16 eV whereas the former is only about 13 eV [18]. For the O1s core ionised system, where a fluorine 2p orbital should be considered rather than the oxygen 2p, according to the equivalent core approximation, an even larger influence on the binding energy could be envisioned. The composition of the ground state methyl π-type orbital, on the other hand, is essentially unchanged by the core hole. However, its character as a bonding orbital in the neutral system is changed to weakly antibonding in the core ionised system. This is due to the hyperconjugation, which now stabilises the C=O π orbital and destabilises the methyl π-type orbital. Therefore, the latter acquires a smaller binding energy in the final state, with the consequence that the shake-up energy is much lower than for the C=O π orbital.

The assignment of the more intense of the shake-up lines in acetaldehyde to the same $\pi \rightarrow \pi^*$ transition as in the case of formaldehyde has been suggested previously [2]. In this earlier publication the origin of the lower energy peak was uncertain and it was associated with a transition of triplet parentage, although from intensity considerations this assignment was questionable. As pointed out above, the present study clearly shows that this peak should be associated with the new π-type orbital formed from the methyl group. Although the strong shake-up peaks are dominated by the $\pi \rightarrow \pi^*$ transitions, the higher, more intense, peak also acquires some contributions from $\sigma \rightarrow \sigma^*$ transitions. In both the Mataga-Nishimoto and Ohno-Klopman calculations, a second, weaker, peak is predicted within 0.5 eV of the $1\pi \rightarrow 3\pi^*$ peak, with dominant $10\sigma \rightarrow 11\sigma^*$ character, although it is placed below the stronger peak in the first case and above it in the second. Since the mixing with the $1\pi \rightarrow 3\pi^*$ transition apparently is strong (cf Table 7), final state correlation is found to be important.

It should also be noticed that the hyperconjugation leads to a second π^* orbital in acetaldehyde, at higher energy, associated primarily with the methyl group. In principle, shake-up transitions to this orbital are possible, but the calculations yield very low intensity in these cases. The transition to this orbital leads to a small charge transfer in the system, explaining the weak intensity.

In the shake-up spectrum of acetone, owing to the C_{2v} symmetry of this molecule, the additional orbital is of a_2 symmetry and therefore the transition from this orbital to the unoccupied $3b_1(\pi^*)$ orbital is monopole forbidden. An antibonding $2a_2(\pi^*)$ orbital is also present, but the INDO/CI calculations indicate that the intensity of the corresponding shake-up transition is very low, as was found for the transition to the uppermost π^* orbital in acetaldehyde. Thus, as in the case of acetaldehyde, two shake-up transitions to the $3b_1(\pi^*)$ are expected to acquire high intensity, which is also observed. The splitting between these shake-up lines, which are very similar in shape to those of acetaldehyde, is 5.0 eV.

As in the case of acetaldehyde, the splitting is larger than in the valence PES and the energy ordering of the orbitals is reversed, due to the dramatic effect on the orbital structure upon the creation of the oxygen core hole (cf Table 16). From the calculations, the lower shake-up structure is assigned to arise almost completely from the $2b_1(CH_3\pi) \rightarrow 3b_1(\pi^*)$ transition, cf Tables 8 and 9. The origin of the second intense structure in Fig.6 is a little more complicated than in the case of acetaldehyde. In fact, from the present calculations it appears that this structure is made up of a number of transitions. In the CI calculation the three transitions $4b_2(\sigma) \rightarrow 5b_2(\sigma^*)$, $1b_1(\pi) \rightarrow 3b_1(\pi^*)$ and $9a_1(\sigma) \rightarrow 10a_1(\sigma^*)$ are found to be heavily mixed. When using the Mataga-Nishimoto parametrization the first of these transitions was calculated to lie at approximately 12.63 eV and the third at 13.00 eV, while the second transition is heavily mixed into the other two states. When Ohno-Klopman parametrization was used, the transition assigned to the first state remains the same, $2b_1(\pi) \rightarrow 3b_1(\pi^*)$, but now the $1b_1(\pi) \rightarrow 3b_1(\pi^*)$ transition is rather unambiguously assigned to a structure at approximately at 12.83 eV, although with an intensity of only 1.2%. Two heavily mixed $\sigma \rightarrow \sigma^*$ transitions are also calculated to lie close to this transition with energies of 12.83 and 14.32 eV, the strongest of these, the $9a_1(\sigma) \rightarrow 10a_1(\sigma^*)$, having an intensity of 1.5%.

Another difference between the shake-up spectra of acetaldehyde and acetone is that the splitting between the two strong peaks is smaller in the latter molecule. This could be connected to the difference in the final state hyperconjugation between the $1b_1$(C=O π) and $2b_1$(CH_3 π) orbitals, which is much larger for acetaldehyde than for acetone (cf Table 16).

C1s Shake-up Spectra

The C1s shake-up spectrum of formaldehyde has been thoroughly discussed in our earlier paper [1]. From Table 16 an important difference between O1s and C1s shake-up spectra can be observed. In the case of C1s ionisation in formaldehyde the O2p and C2p contributions to the $1b_1(\pi)$ and $2b_1(\pi^*)$ orbitals are nearly the same. This is in great contrast to O1s ionization, where the $1b_1(\pi)$ orbital is has a large O2p character and the $2b_1(\pi^*)$ orbital has a strong C2s character. As was pointed out in the discussion of the O1s shake-up spectra above, this implies that the $1b_1(\pi)$ orbital is destabilised and the $2b_1(\pi^*)$ orbital is stabilised. Therefore we get a smaller shake-up energy for the $1b_1(\pi) \rightarrow 2b_1(\pi^*)$ transition in the case of C1s ionisation, cf Tables 4 and 10. This is also in agreement with the results reported in ref. [19] in the case of the shake-up spectra in the CO molecule.

As can be seen from Table 16 the swapping of the methyl and carbonyl π orbitals observed for O1s ionization in acetaldehyde and acetone is not so significant in the case of C1s ionization. However, the same pattern is reproduced, i.e. the 1π (CH_3) orbital gets a larger carbonyl character in the C1s ionized system whereas the and the 2π(CO) orbital gets a CH_3 character. Thus, the stabilization of the 1π orbital and the destabilization of the 2π orbital is less marked for C1s than for O1s ionization. Furthermore, the $3\pi^*$ orbital is little influenced by the ionization. Therefore, we expect generally smaller shake-up energies and also a smaller splitting between the two $\pi - \pi^*$ transitions in the C1s case. This is also observed in our experimental spectra, c.f. Figs. 7-9 and Tables 10,12,14. It should, however, be noted that the peak with the higher shake-up energy, according to the calculations, also contains contributions from σ–σ transitions.

CONCLUSIONS

The O1s, C1s core shake-up and HeII excited valence photoelectron spectra of formaldehyde, acetaldehyde and acetone have been recorded. Assignments of the spectra have been made from INDO/CI calculations. It is found that the addition of the CH_3 π type orbitals in acetaldehyde and acetone, in the case of acetone $1b_1(\pi)$, is primarily responsible for the appearance of a second intense shake-up peak compared with the spectrum of formaldehyde. The new shake-up peak occurs at a lower excitation energy than that associated with the $\pi(C=O) \rightarrow \pi^*$ transition, which is due to an energy reversal between the two π-type orbitals in the oxygen core-ionised systems, due to a large charge redistribution as compared to the neutral system. The CI calculations show that, although the $\pi(C=O) \rightarrow \pi^*$ shake-up transition dominates in the formation of the more intense peak at the higher binding energy, $\sigma \rightarrow \sigma^*$ transitions also contribute substantially to this peak, that is, electron correlation is important for a quantitative description of the shake-up structure.

The ionization from the $6a_1$ σ(C-O) orbital in acetone is found to give rise to a clearly observable vibrational progression, whereas the corresponding band in formaldehyde is structureless. The corresponding band in acetaldehyde, lying at an energy between those of the other two molecules, shows only weak indications of fine structure.Thus, this inner valence orbital becomes gradually destabilized with respect to the binding energy when methyl substituents are added. At the same time the chemical bond appears to be strengthened which may reflect the existence of repulsive correlation states in the inner valence region of all three molecules, which interact strongly with the single hole states and cause predissociation in this energy region.

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Table 1. *Experimental electron binding energies, calculated INDO orbital energies using Mataga-Nishimoto parametrisation, and assignments of the outer valence region of formaldehyde. The vertical binding energies correspond to the maximum intensity of the band.*

Formaldehyde

Electron binding energy (eV)		INDO orbital energy (eV)	Assignment
Vertical	Adiabatic		
10.885	10.885	10.77	$2b_2^{-1}$ ($^2B_2$)
14.41	13.97	13.36	$1b_1^{-1}$ ($^2B_1$)
15.99	15.83	16.32	$5a_1^{-1}$ ($^2A_1$)
16.9	16.23	19.20	$1b_2^{-1}$ ($^2B_2$)
21.2			$4a_1^{-1}$ ($^2A_1$)

Table 2. *Experimental electron binding energies, calculated INDO orbital energies using Mataga-Nishimoto parametrisation, and assignments of the outer valence region of acetaldehyde. The vertical binding energies correspond to the maximum intensity of the band.*

Acetaldehyde

Electron binding energy (eV)		INDO orbital energy (eV)	Assignment
Vertical	Adiabatic		
10.231	10.2431	10.44	10a'
13.12	12.63	12.65	2a''
14.2		15.01	9a'
15.4		16.64	1a''
15.8		17.36	8a'
16.5		19.06	7a'
19.4		23.6	6a'
24.4			5a'

Table 3. Experimental electron binding energies, calculated INDO orbital energies using Mataga-Nishimoto parametrisation, and assignments of the outer valence region of acetone. The vertical binding energies correspond to the maximum intensity of the band.

Acetone

Electron binding energy (eV)		INDO orbital energy (eV)	Assignment
Vertical	Adiabatic		
9.708	9.708	9.95	$5b_2$
12.4		12.04	$2b_1$
13.4		14.66	$4b_2$
14.0		14.74	$8a_1$
14.5		16.35	$1a_2$
15.6		18.02	$1b_1$
15.9		18.82	$7a_1$
16.4		18.98	$3b_2$
17.813	17.813		$6a_1$
23.0			$2b_2$
24.6			$5a_1$

Table 4. *Calculated INDO-CI results for the strongest O1s shake-up satellites in formaldehyde for a) Mataga-Nishimoto*, b) Ohno-Klopman and c) INDO/2 theoretical gamma integrals compared with experimental data from reference [2].*

Formaldehyde

	State	Before CI		After CI		Experimental [1]	
		Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)
a) [2]							
	1	0.00	100.0	0.00	100.0	0	100
	2	10.80	16.6	9.62	7.3	12.2	4.3
	3	14.70	1.6	14.45	0.7		
	4	17.64	1.1	17.81	1.1		
b)							
	1	0.00	100.0	0.00	100.0		
	2	10.12	11.9	9.41	5.9		
	3	14.35	1.5	14.29	1.2		
	4	18.06	1.0	17.97	1.0		
c)							
	1	0.00	100.0	0.00	100.0		
	2	12.56	29.2	10.01	10.8		
	3	18.39	2.1	17.11	0.7		
	4	21.57	1.3	20.51	1.2		

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[1] Taken from ref. [2].

[2] Taken from ref. [1].

Table 5. Energy and wavefunction for the strongest O1s calculated shake-up states in formaldehyde using a) Mataga-Nishimota, b) Ohno-Klopman and c) INDO/2 theoretical gamma integrals.

Formaldehyde

	State	Energy (eV)	Intensity (%)	C.I. Wavefunction
a)				
	1	0.00	100.0	$0.98515<0/0>+\ldots$
	2	9.62	7.3	$-0.94846<1b_1(\pi)\rightarrow 2b_1(\pi^*)>+\ldots$
	3	14.45	0.7	$0.89628<2b_2(\sigma)\rightarrow 3b_2(\sigma^*)>+0.14319<1b_2(\sigma)\rightarrow 3b_2(\sigma^*)>+\ldots$
	4	17.81	1.1	$-0.96175<5a_1(\sigma)\rightarrow 6a_1(\sigma^*)>+\ldots$
b)				
	1	0.0	100.0	$0.99125<0/0>+\ldots$
	2	9.41	5.9	$0.96043<1b_1(\pi)\rightarrow 2b_1(\pi^*)>+\ldots$
	3	14.29	1.2	$-0.96448<2b_2(\sigma)\rightarrow 3b_2(\sigma^*)>+\ldots$
	4	17.97	1.0	$0.96881<5a_1(\sigma)\rightarrow 6a_1(\sigma^*)>+\ldots$
c)				
	1	0.00	100.0	$-0.93512<0/0>+\ldots$
	2	10.01	10.8	$-0.93512<1b_1(\pi)\rightarrow 2b_1(\pi^*)>+\ldots$
	3	17.11	0.7	$-0.91427<2b_2(\sigma)\rightarrow 3b_2(\sigma^*)>+0.17576<1b_2(\sigma)\rightarrow 3b_2(\sigma^*)>-0.15525(7)+\ldots$
	4	20.51	1.2	$-0.92581<5a_1(\sigma)\rightarrow 6a_1(\sigma^*)>+\ldots$
		23.18		$0.85391<1b_2(\sigma)\rightarrow 3b_2(\sigma^*)>+0.22519<(1b_1(\pi)\rightarrow 2b_1(\pi^*))^2>+0.22340<4a_1(\sigma)\rightarrow 6a_1(\sigma^*)>+..$

Table 6. *Calculated INDO/CI results for the lowest* O_{1s} *shake-up satellites in acetaldehyde for a) Mataga-Nishimoto, b) Ohno-Klopman and c) INDO/2 theoretical gamma integrals, compared with experimental data from reference /2/.*

Acetaldehyde

	State Assignment	Before CI		After CI		Experimental [1]	
		Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)
a)							
	1	0.00	100.0	0.00	100.0		
	2	9.14	7.5	8.84	7.7	7.50	2.3
	3	11.14	<0.1	10.86	2.0		
	4	11.55	10.9	11.21	6.6	12.94	4.7
	5	12.03	0.2	11.91	0.7		
	6	13.52	0.8	13.50	0.4		
b)							
	1	0.00	100.0	0.00	100.0		
	2	9.39	6.6	9.01	8.5		
	3	11.06	7.2	10.87	2.9		
	4	11.53	<0.1	11.37	0.7		
	5	12.75	0.2	12.57	0.2		
	6	14.08	0.9	14.03	1.0		
		14.79	<0.1	14.72	0.2		
c)							
	1	0.00	100.0	0.00	100.0		
	2	11.50	8.9	10.72	16.0		
	3	13.42	24.0	12.74	10.1		
	4	15.67	0.2	15.51	0.8		
	5	17.57	0.2	17.44	0.3		

---

[1] Taken from reference [2]

Table 7. *Energy and wavefunction for the strongest O_{1s} calculated shake-up states in acetaldehyde using a) Mataga-Nishimoto b) Ohno-Klopman and c) INDO/2 theoretical gamma integrals.*

Acetaldehyde

State	Energy (eV)	Intensity (%)	C.I. Wavefunction
a)			
1	0.00	100.0	$0.99809\langle 0\vert 0\rangle+\ldots$
2	8.84	7.7	$0.98238\langle 2\pi\rightarrow 3\pi^*\rangle+\ldots$
3	10.86	2.0	$-0.88710\langle 10\sigma\rightarrow 11\sigma^*\rangle+0.41027\langle 1\pi\rightarrow 3\pi^*\rangle+\ldots$
4	11.21	6.6	$0.86995\langle 1\pi\rightarrow 3\pi^*\rangle+0.36757\langle 10\sigma\rightarrow 11\sigma^*\rangle+\ldots$
5	11.91	0.7	$-0.94307\langle 9\sigma\rightarrow 11\sigma^*\rangle+\ldots$
6	13.50	0.4	$0.92957\langle 10\sigma\rightarrow 12\sigma^*\rangle+\ldots$
b)			
1	0.00	100.0	$0.99890\langle 0\vert 0\rangle+\ldots$
2	9.01	8.5	$0.96255\langle 2\pi\rightarrow 3\pi^*\rangle+\ldots$
3	10.87	2.9	$-0.84430\langle 1\pi\rightarrow 3\pi^*\rangle-0.48954\langle 10\sigma\rightarrow 11\sigma^*\rangle+\ldots$
4	11.37	0.7	$0.82322\langle 10\sigma\rightarrow 11\sigma^*\rangle-0.46312\langle 1\pi\rightarrow 3\pi^*\rangle+\ldots$
5	12.57	0.2	$-0.94738\langle 9\sigma\rightarrow 11\sigma^*\rangle+\ldots$
6	14.03	1.0	$-0.90723\langle 10\sigma\rightarrow 12\sigma^*\rangle+\ldots$
7	14.72	0.2	$0.90757\langle 9\sigma\rightarrow 12\sigma^*\rangle+\ldots$
c)			
1	0.00	100.0	$-0.99822\langle 0\vert 0\rangle+\ldots$
2	10.72	16.0	$-0.92031\langle 2\pi\rightarrow 3\pi^*\rangle+0.32088\langle 1\pi\rightarrow 3\pi^*\rangle+\ldots$
3	12.74	10.1	$0.90312\langle 1\pi\rightarrow 3\pi^*\rangle+0.32675\langle 2\pi\rightarrow 3\pi^*\rangle+\ldots$
4	15.51	0.8	$0.74184\langle 10\sigma\rightarrow 11\sigma^*\rangle-0.40306\langle 10\sigma\rightarrow 12\sigma^*\rangle+\ldots$
5	17.44	0.3	$0.77844\langle 10\sigma\rightarrow 12\sigma^*\rangle+0.31708\langle 10\sigma\rightarrow 11\sigma^*\rangle+\ldots$

Table 8. Calculated INDO/CI results for the lowest O1s shake-up satellites in acetone for a) Mataga-Nishimoto, b) Ohno-Klopman, and c) INDO/2 theoretical gamma integrals compared with experimental data from reference [2].

Acetone

	State Assignment	Before CI		After CI		Experimental [1]	
		Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)
a)							
	1	0.00	100.0	0.00	100.0		
	2	9.85	14.7	9.85	14.2	8.39	2.3
	3	12.34	0.6	12.63	1.96		
	4	12.48	0.7	13.00	3.29	13.38	3.1
b)							
	1	0.00	100.0	0.00	100.0		
	2	9.81	12.2	9.61	12.4		
	3	12.81	2.3	12.83	1.2		
		13.83	0.7	13.43	0.1		
		14.08	0.7	14.32	1.5		
		17.19	0.1	17.33	0.2		
		18.27	0.7	18.32	1.3		
c)							
	1	0.00	100.0	0.00	100.0		
	2	12.72	28.9	11.73	24.3		
	3	15.16	12.7	14.35	1.1		
		17.84	1.1	16.75	0.1		
		18.59	0.3	17.96	1.1		

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[1] Taken from ref [2].

Table 9. Energy and wavefunction for the strongest O1s calculated shake-up states in acetone using a) Mataga-Nishimoto b) Ohno-Klopman and c) INDO/2 theoretical gamma integrals.

Acetone

State	Energy (eV)	Intensity (%)	C.I. Wavefunction
a)			
1	0.00	100.0	$-0.99726<0\vert 0>+\ldots$
2	9.85	14.2	$-0.98595<2b_1(\pi)\rightarrow 3b_1(\pi*)>+\ldots$
3	12.63	2.0	$-0.71671<4b_2(\sigma)\rightarrow 5b_2(\sigma*)>+0.63693<1b_1(\pi)\rightarrow 3b_1(\pi*)>+0.23097<9a_1(\sigma)\rightarrow 10a_1(\sigma*)>+\ldots$
4	13.00	3.3	$-0.69729<9a_1(\sigma)\rightarrow 10a_1(\sigma*)>+0.59802<1b_1(\pi)\rightarrow 3b_1(\pi*)>+0.27158<4b_2(\sigma)\rightarrow 5b_2(\sigma*)>+\ldots$
5	……		$0.62628<4b_2(\sigma)\rightarrow 5b_2(\sigma*)>+0.57773<9a_1(\sigma)\rightarrow 10a_1(\sigma*)>+0.45659<1b_1(\pi)\rightarrow 3b_1(\pi*)>+\ldots$
b)			
1	0.00	100.0	$-0.99837<0\vert 0>+\ldots$
2	9.61	12.4	$-0.97055<2b_1(\pi)\rightarrow 3b_1(\pi*)>+\ldots$
3	12.83	1.2	$-0.93950<1b_1(\pi)\rightarrow 3b_1(\pi*)>+\ldots$
4	13.43	0.1	$-0.71065<4b_2(\sigma)\rightarrow 5b_2(\sigma*)>-0.59238<9a_1(\sigma)\rightarrow 10a_1(\sigma*)>-0.30647<3b_2(\sigma)\rightarrow 5b_2(\sigma*)>+\ldots$
5	14.32	1.5	$0.68560<9a_1(\sigma)\rightarrow 10a_1(\sigma*)>-0.63124<4b_2(\sigma)\rightarrow 5b_2(\sigma*)>-0.24410<3b_2(\sigma)\rightarrow 5b_2(\sigma*)>+\ldots$
6	17.33	0.2	$0.65021<8a_1(\sigma)\rightarrow 11a_1(\sigma*)>-0.49330<2b_2(\sigma)\rightarrow 6b_2(\sigma*)>+0.30070<1b_1(\pi)\rightarrow 3b_1(\pi*)>+\ldots$
7	18.32	1.3	$0.96059<8a_1(\sigma)\rightarrow 10a_1(\sigma*)>+\ldots$
c)			
1	0.0	100.0	$-0.99476<0\vert 0>+\ldots$
2	11.73	24.3	$0.88464<2b_1(\pi)\rightarrow 3b_1(\pi*)>-0.38253<1b_1(\pi)\rightarrow 3b_1(\pi*)>+\ldots$
3	14.35	1.1	$0.86033<1b_1(\pi)\rightarrow 3b_1(\pi*)>+0.38094<2b_1(\pi)\rightarrow 3b_1(\pi*)>+\ldots$
4	16.75	0.1	$-0.72690<9a_1(\sigma)\rightarrow 10a_1(\sigma*)>-0.58168<4b_2(\sigma)\rightarrow 5b_2(\sigma*)>+\ldots$
5	19.96	1.1	$0.57424<4b_2(\sigma)\rightarrow 5b_2(\sigma*)>+0.53824<9a_1(\sigma)\rightarrow 10a_1(\sigma*)>-0.32573<9a_1(\sigma)\rightarrow 11a_1(\sigma*)>+\ldots$

Table 10. *Calculated INDO/CI results for the strongest C1s shake-up satellites in formaldehyde for a) Mataga-Nishimoto, b) Ohno-Klopman and c) INDO/2 theoretical gamma integrals, compared with experimental data.*

Formaldehyde

	State Assignment	Before CI		After CI		Experimental	
		Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)
a)[1]							
	1	0.00	100.0	0.00	100.0		
	2	9.79	8.4	10.23	5.3	10.7	3.4
	3	12.71	0.2	14.12	5.7	16.3	0.8
	4	21.91	4.8	22.10	1.1	19.91	1.5
	5	26.09	4.6	27.29	6.8	25.0	1.4
b)							
	1	0.00	100.0	0.00	100.0		
	2	8.82	8.8	9.21	9.5		
	3	12.68	0.2	13.53	4.0		
	4	21.03	5.4	20.82	2.7		
		25.00	0.8	25.16	3.4		
		25.57	5.0	25.40	1.7		
c)							
	1	0.00	100.0	0.00	100.0		
		11.06	12.2	10.38	0.7		
		16.10	4.4	12.08	1.7		
		12.81	0.4	15.19	5.9		
		18.64	0.5	17.49	2.4		
		22.59	6.3	22.66	1.5		
		26.74	7.5	28.28	12.2		
		22.45	0.4	29.19	2.9		

---

[1] Taken from reference [1]

Table 11. *Energy and wavefunction for the strongest C1s calculated shake-up states in formaldehyde using a) Mataga-Nishimoto b) Ohno-Klopman and c) INDO/2 theoretical gamma integrals.*

Formaldehyde

State	Energy (eV)	Intensity (%)	C.I. Wave Function
a)			
C_1			
1	0.00	100.0	$-0.9671<0\vert 0>+\ldots$
	6.90	0.2	$-0.9755<(2b_2(\sigma)\rightarrow 2b_1(\pi^*))^2> - 0.1434<1b_1(\pi)\rightarrow 2b_1(\pi^*),\ 2b_2(\sigma)\rightarrow 2b_1(\pi^*)> + \ldots$
2	10.23	5.3	$0.9469<1b_1(\pi)\rightarrow 2b_1(\pi^*)> - 0.1329<2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> + \ldots$
3	14.12	5.7	$0.9364<(1b_1(\pi)\rightarrow 2b_1(\pi^*))^2>+0.1244<7a_1(\sigma)\rightarrow 9a_1(\sigma^*),\ 1b_1(\pi)\rightarrow 9a_1(\sigma^*)> + \ldots$
4	22.10	1.1	$-0.5695<1b_2(\sigma)\rightarrow 3b_2(\sigma^*)>+0.5542<(2b_2(\sigma)\rightarrow 8a_1(\sigma^*))^2>+0.2892<1b_2(\sigma)\rightarrow 8a_1(\sigma^*),\ 2b_2(\sigma)\rightarrow 8a_1(\sigma^*)>-0.2270<1b_1(\pi)\rightarrow 8a_1(\sigma^*),\ 1b_1(\pi)\rightarrow 9a_1(\sigma^*)> + \ldots$
5	27.29	6.8	$-0.5622<6a_1(\sigma)\rightarrow 8a_1(\sigma^*)> + 0.3861<7a_1(\sigma)\rightarrow 9a_1(\sigma^*)> + 0.3390<7a_1(\sigma)\rightarrow 9a_1(\sigma^*),\ 1b_1(\pi)\rightarrow 8a_1(\sigma^*)> - 0.2932<1b_2(\sigma)\rightarrow 3b_2(\sigma^*)>+ \ldots$
b)			
C_1			
1	0.00	100.0	$-0.9791<0\vert 0>+\ldots$
	6.25	0.3	$0.9800<(2b_2(\sigma)\rightarrow 2b_1(\pi^*))^2> + \ldots$
2	9.21	9.5	$0.9569<1b_1(\pi)\rightarrow 2b_1(\pi^*)> + 0.1981<2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> + \ldots$
3	13.53	4.0	$0.9628<(1b_1(\pi)\rightarrow 2b_1(\pi^*))^2> - 0.1039<2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> + \ldots$
4	20.82	2.7	$-0.7120<1b_2(\sigma)\rightarrow 3b_2(\sigma^*)> - 0.4431<1b_1(\pi)\rightarrow 2b_1(\pi^*),\ 2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> - 0.2412<1b_1(\pi)\rightarrow 2b_1(\pi^*),\ 2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> + 0.2143<1b_2(\sigma)\rightarrow 8a_1(\sigma^*),\ 2b_2(\sigma)\rightarrow 8a_1(\sigma^*)>+ \ldots$
	25.16	3.4	$-0.7935<7a_1(\sigma)\rightarrow 9a_1(\sigma^*)> - 0.3463<6a_1(\sigma)\rightarrow 8a_1(\sigma^*)> -0.2313<7a_1(\sigma)\rightarrow 2b_1(\pi^*),\ 1b_1(\pi)\rightarrow 8a_1(\pi^*)> + \ldots$
5	25.40	1.7	$0.6604<6a_1(\sigma)\rightarrow 8a_1(\sigma^*)> -0.3728<7a_1(\sigma)\rightarrow 2b_1(\pi^*),\ 1b_1(\pi)\rightarrow 8a_1(\sigma^*)> + 0.3272<7a_1(\sigma)\rightarrow 9a_1(\sigma^*)> + \ldots$
c)			
C_1			
1	0.00	100.0	$0.9423<0\vert 0>+\ldots$
2	10.38	0.7	$0.8510<1b_1(\pi)\rightarrow 2b_1(\pi^*)> - 0.3463<(1b_1(\pi)\rightarrow 2b_1(\pi^*))^2> + 0.2603<7a_1(\sigma)\rightarrow 9a_1(\sigma^*)> + \ldots$
	12.08	1.7	$-0.8039<2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> + 0.3468<1b_1(\pi)\rightarrow 2b_1(\pi^*),\ 2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> + 0.3123<1b_1(\pi)\rightarrow 2b_1(\pi^*),\ 2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> -0.2151<1b_2(\sigma)\rightarrow 3b_2(\sigma^*)> + \ldots$
3	15.19	5.9	$0.7123<(1b_1(\pi)\rightarrow 2b_1(\pi^*))^2> - 0.4173<7a_1(\sigma)\rightarrow 8a_1(\sigma^*)> + 0.2503<1b_1(\pi)\rightarrow 2b_1(\pi^*)> + \ldots$
	17.49	2.4	$-0.6974<7a_1(\sigma)\rightarrow 8a_1(\sigma^*)> - 0.3439<(1b_1(\pi)\rightarrow 2b_1(\pi^*))^2> + 0.3087<7a_1(\sigma)\rightarrow 2b_1(\pi^*),\ 1b_1(\pi)\rightarrow 8a_1(\sigma^*)> - 0.2713<1b_1(\pi)\rightarrow 2b_1(\pi^*)> +\ldots$
4	22.66	1.5	$-0.7635<1b_2(\sigma)\rightarrow 3b_2(\sigma^*)> + 0.3272<2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> - 0.2715<6a_1(\sigma)\rightarrow 8a_1(\sigma^*)> +\ldots$
5	28.28	12.2	$-0.7283<6a_1(\sigma)\rightarrow 8a_1(\sigma^*)>+0.2474<7a_1(\sigma)\rightarrow 9a_1(\sigma^*)>-0.2060<1b_1(\pi)\rightarrow 2b_1(\pi^*),\ 2b_2(\sigma)\rightarrow 3b_2(\sigma^*)+\ldots$
	29.19	2.9	$0.5777<1b_1(\pi)\rightarrow 2b_1(\pi^*),\ 2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> + 0.3602<1b_2(\sigma)\rightarrow 3b_2(\sigma^*)> + 0.3505<(1b_1(\pi)\rightarrow 2b_1(\pi^*),\ 2b_2(\sigma)\rightarrow 3b_2(\sigma^*)> - 0.3022<7a_1(\sigma)\rightarrow 3b_2(\sigma^*),\ 2b_2(\sigma)\rightarrow 9a_1(\sigma^*)> +\ldots$

Table 12. Calculated INDO/CI results for the lowest C1s shake-up satellites in acetaldehyde for a) Mataga-Nishimoto, b) Ohno-Klopman, and c) INDO/2 theoretical gamma integrals, compared with experimental data.

Acetaldehyde

	State Assignment	Before CI		After CI		Experimental	
		Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)
a)							
C_1[1]							
	1	0.00	100.0	0.00	100.0		
		6.31	0.0	9.77	0.4		
	2	8.04	3.3	11.02	1.9		
		10.76	4.5	13.48	1.3		
	3	11.00	3.2	13.81	4.3	13.5	3.6
	4	13.33	0.0	15.72	3.8		
C_2							
	1	0.00	100.0	0.00	100.0		
		7.67	1.2	7.50	0.9		
		9.43	0.5	8.82	0.8		
	5	19.95	5.4	21.86	4.5	18.97	3.5
	6	23.25	0.0	22.81	2.3		
		23.25	0.0	23.27	2.0		
b)							
C_1[1]							
	1	0.00	100.0	0.00	100.0		
		6.31	0.0	9.30	0.7		
	2	7.92	3.3	10.67	5.0		
	3	10.80	4.4	13.28	3.3		
	4	14.12	0.0	15.35	1.7		
C_2							
	1	0.00	100.0	0.00	100.0		
		7.90	1.2	6.71	1.3		
		8.67	0.8	8.10	2.0		
		18.18	2.5	18.7	1.8		
	5	19.18	5.3	19.62	3.2		
c)							
C_1[1]							
	1	0.00	100.0	0.00	100.0		
		5.35	0.0	9.97	0.1		
		10.01	5.1	12.43	1.2		
	4	16.44	0.1	17.05	8.9		
	5	14.90	0.0	17.21	5.1		
C_2							
	1	0.00	100.0	0.00	100.0		
		10.98	1.0	7.90	0.4		
	3	10.90	0.9	10.21	4.0		
	4	13.70	0.0	16.39	6.5		
	5	23.19	2.4	22.65	3.6		

[1] A measured chemical shift of 2.62 eV has been added to the carbonyl carbon.

Table 13. Energy and wavefunction for the strongest C1s calculated shake-up states in acetaldehyde using a) Mataga-Nishimoto b) Ohno-Klopman and c) INDO/2 theoretical gamma integrals.

Acetaldehyde

State	Energy (eV)	Intensity (%)	C.I. Wavefunction
a)			
C_1[a]			
1	0.00	100.0	$0.9660<0\vert 0>+\ldots$
	9.79	0.4	$-0.9649<(11\sigma\to3\pi^*)^2>+0.2149<2\pi\to3\pi^*>+\ldots$
2	11.02	1.9	$0.6938<2\pi\to3\pi^*>-0.5828<11\sigma\to12\sigma^*>+\ldots$
	13.48	1.3	$-0.5802<1\pi\to3\pi^*>-0.5599<11\sigma\to13\sigma^*>+0.2392<2\pi\to3\pi^*>+0.3439<10\sigma\to13\sigma^*, 2\pi\to4\pi^*>+\ldots$
3	13.81	4.3	$-0.6714<1\pi\to3\pi^*> + 0.6090<11\sigma\to13\sigma^*> +\ldots$
4	15.72	3.8	$0.8597<(2\pi\to3\pi^*)^2> - 0.3942<1\pi\to3\pi^*, 2\pi\to3\pi^*> + \ldots$
C_2			
1	0.00	100.0	$-0.9942<0\vert 0>+\ldots$
	7.50	0.9	$0.9023<11\sigma\to12\sigma^*>-0.3261<11\sigma\to13\sigma^*>+\ldots$
	8.82	0.8	$0.8296<2\pi\to3\pi^*>-0.4768<11\sigma\to13\sigma^*>+ \ldots$
5	21.86	4.5	$-0.4561<1\pi\to4\pi^*>+0.4554<8\sigma\to14\sigma^*>+0.4359<8\sigma\to15\sigma^*>-0.3579<10\sigma\to16\sigma^*>+\ldots$
6	22.81	2.3	$0.6076<9\sigma\to3\pi^*, 10\sigma\to3\pi^*>+0.5301<10\sigma\to16\sigma^*>-0.2251<1\pi\to4\pi^*>+0.2077<8\sigma\to14\sigma^*>+\ldots$
	23.27	2.0	$0.6473<9\sigma\to3\pi^*, 10\sigma\to3\pi^*>-0.5364<10\sigma\to16\sigma^*>+0.2199<1\pi\to4\pi^*>-0.2113<8\sigma\to14\sigma^*>+\ldots$
b)			
C_1[a]			
1	0.00	100.0	$0.9800<0\vert 0>+\ldots$
	9.20	0.7	$-0.9630<(11\sigma\to3\pi^*)^2>+0.2292<2\pi\to3\pi^*>+\ldots$
2	10.67	5.0	$-0.9324<2\pi\to3\pi^*>+\ldots$
3	13.28	3.3	$-0.8554<1\pi\to3\pi^*>-0.2598<11\sigma\to13\sigma^*> + \ldots$
4	15.35	1.7	$0.8036<(2\pi\to3\pi^*)^2>+0.2084<1\pi\to3\pi^*>+ \ldots$
C_2			
1	0.00	100.0	$-0.9862<0\vert 0>+\ldots$
	6.71	1.3	$0.8461<11\sigma\to12\sigma^*>-0.4047<11\sigma\to13\sigma^*>+\ldots$
	8.10	2.0	$-0.8145<2\pi\to3\pi^*>+0.4576<11\sigma\to13\sigma^*>+\ldots$
	18.70	1.8	$0.9110<9\sigma\to14\sigma^*>+0.1813<10\sigma\to14\sigma^*>+ \ldots$
5	19.62	3.2	$0.7754<1\pi\to4\pi^*>+0.2268<8\sigma\to12\sigma^*>+ \ldots$
c)			
C_1[a]			
1	0.00	100.0	$-0.9311<0\vert 0>+\ldots$
	9.97	0.1	$-0.9826<(11\sigma\to3\pi^*)^2>+\ldots$
2	12.43	1.2	$-0.8510<2\pi\to3\pi^*>-0.1209<9\sigma\to12\sigma^*>+\ldots$
4	17.05	8.9	$0.5747<(2\pi\to3\pi^*)^2>+0.4646<11\sigma\to3\pi^*, 2\pi\to12\sigma^*>+\ldots$
5	17.21	5.1	$-0.5622<11\sigma\to3\pi^*, 2\pi\to12\sigma^*>-0.7074<11\sigma\to3\pi^*, 2\pi\to12\sigma^*>-0.4148<(2\pi\to3\pi^*)^2>+\ldots$
C_2			
1	0.00	100.0	$-0.9361<0\vert 0>+\ldots$
	7.90	0.4	$0.8198<11\sigma\to12\sigma^*>+0.2850<2\pi\to3\pi^*>+\ldots$
	10.21	4.0	$0.8148<2\pi\to3\pi^*>-0.2633<11\sigma\to12\sigma^*> +\ldots$
	16.39	6.5	$-0.8731<(2\pi\to3\pi^*)^2>+ 0.1901<(10\sigma\to3\pi^*)^2>+0.1503<10\sigma\to14\sigma^*>+\ldots$
5	22.65	3.6	$- 0.4198<1\pi\to4\pi^*>+0.4216<8\sigma\to14\sigma^*>-0.4086<8\sigma\to13\sigma^*> +$

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[a] A measured chemical shift of 2.62 eV has been added to the carbonyl carbon

Table 14. Calculated INDO/CI results for the strongest C1s shake-up satellites in acetone for a) Mataga-Nishimoto, b) Ohno-Klopman, and c) INDO/2 theoretical gamma integrals, compared with experimental data.

Acetone

	State Assignment	Before CI		After CI		Experimental	
		Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)	Energy (eV)	Intensity (%)
a) C_1[1]							
	1	0.00	100.0	0.00	100.0		
		0.00	0.0	10.19	1.0		
	2	7.99	3.7	11.10	5.8	10.44	1.8
	3	12.38	3.5	15.14	8.0	13.38	3.2
	4	18.06	0.0	21.43	2.3	18.68	3.9
C_2							
	1	0.00	100.0	0.00	100.0		
		8.81	14.7	8.81	0.6		
	5	24.44	0.0	22.60	9.1	26.47	2.9
b) C_1[1]							
	1	0.00	100.0	0.00	100.0		
		6.76	0.0	9.72	1.7		
	2	7.69	3.6	10.58	5.4		
	3	12.22	0.0	14.73	5.1		
		18.35	0.2	21.56	0.9		
C_2							
	1	0.00	100.0	0.00	100.0		
		8.27	0.5	8.26	0.5		
		8.91	0.9	8.99	0.6		
		19.32	0.4	19.11	1.0		
		20.23	4.8	20.32	2.2		
		20.41	4.2	20.73	5.9		
c) C_1[1]							
	1	0.00	100.0	0.00	100.0		
		9.93	5.0	13.61	7.0		
		12.45	0.1	16.93	13.8		
		25.62	1.9	29.24	3.2		
C_2							
	1	0.00	100.0	0.00	100.0		
		14.27	0.3	13.49	0.3		
		15.11	0.1	15.20	0.2		
		21.65	0.0	21.66	0.6		
		21.71	0.8	21.82	2.1		
		22.52	0.5	23.48	9.5		

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[1] A measured chemical shift of 2.59 eV has been added to the carbonyl carbon.

Table 15. Energy and wavefunction for the strongest C1s calculated shake-up states in acetone using a) Mataga-Nishimoto b) Ohno-Klopman and c) INDO/2 theoretical gamma integrals.

Acetone

State	Energy (eV)	Intensity (%)	C.I. wavefunction
a)			
C_1[1]			
1	0.00	100.0	$0.9651\langle 0\vert 0\rangle+\ldots$
	10.19	1.0	$0.9285\langle 2b_1(\pi)\rightarrow 3b_1(\pi^*),\ 4b_2(\sigma)\rightarrow 5b_2(\sigma^*)\rangle - 0.3249\langle 2b_1(\pi)\rightarrow 3b_1(\pi^*)\rangle + \ldots$
2	11.10	5.8	$-0.8843\langle 2b_1(\pi)\rightarrow 3b_1(\pi^*)\rangle + 0.3069\langle 2b_1(\pi)\rightarrow 3b_1(\pi^*),\ 4b_2(\sigma)\rightarrow 5b_2(\sigma^*)\rangle + \ldots$
3	15.14	8.0	$-\ 0.6819\langle (2b_1(\pi)\rightarrow 3b_1(\pi^*))^2\rangle+0.6814\langle 1b_1(\pi)\rightarrow 3b_1(\pi^*)\rangle + \ldots$
4	21.43	2.3	$-0.8478\langle 1a_2(\pi)\rightarrow 3b_1(\pi^*),\ 4b_2(\sigma)\rightarrow 12a_1(\sigma^*)\rangle - 0.4129\langle (1a_2(\pi)\rightarrow 3b_1(\pi^*))^2\rangle + \ldots$
C_2[2]			
	0.00	100.0	$-0.9974\langle 0\vert 0\rangle+\ldots$
	8.81	0.6	$-0.7977\langle 3\pi\rightarrow 4\pi^*\rangle - 0.5928\langle 9\sigma\rightarrow 11\sigma^*\rangle + \ldots$
5	22.60	9.1	$0.4975\langle 2\pi\rightarrow 4\pi^*,\ 7\sigma\rightarrow 10\sigma^*\rangle + 0.4586\langle 2\pi\rightarrow 4\pi^*,\ 8\sigma\rightarrow 10\sigma^*\rangle - 0.3172\langle 2\pi\rightarrow 4\pi^*,\ 8\sigma\rightarrow 13\sigma^*\rangle + \ldots$
b)			
C_1[1]			
	0.00	100.0	$-0.9793\langle 0\vert 0\rangle+\ldots$
	9.72	1.7	$0.8969\langle (4b_2(\sigma)\rightarrow 3b_1(\pi^*))^2\rangle- 0.4213\langle 2b_1(\pi)\rightarrow 3b_1(\pi^*)\rangle + \ldots$
2	10.58	5.4	$-0.8655\langle 2b_1(\pi)\rightarrow 3b_1(\pi^*)\rangle- 0.4128\langle (4b_2(\sigma)\rightarrow 3b_1(\pi^*))^2\rangle + \ldots$
3	14.73	5.1	$0.7299\langle (2b_1(\pi)\rightarrow 3b_1(\pi^*))^2\rangle+ 0.6075\langle 8a_1(\sigma)\rightarrow 11a_1(\sigma^*)\rangle + \ldots$
	21.56	0.9	$-0.5402\langle 1a_2(\pi)\rightarrow 2a_2(\pi^*)\rangle -0.3317\langle (1b_1(\pi)\rightarrow 3b_1(\pi^*))^2\rangle + 0.2799\langle 2b_1(\pi)\rightarrow 4b_1(\pi^*)\rangle + \ldots$
C_2[2]			
	0.00	100.0	$-0.9984\langle 0\vert 0\rangle+\ldots$
	8.26	0.5	$-0.9824\langle 3\pi\rightarrow 4\pi^*\rangle + \ldots$
	8.99	0.6	$-0.9877\langle 9\sigma\rightarrow 11\sigma^*\rangle + \ldots$
	19.11	1.0	$-0.8019\langle 6\sigma\rightarrow 12\sigma^*\rangle + 0.4444\langle 10\rangle + 0.3107\langle 5\rangle + \ldots$
	20.32	2.2	$0.9198\langle 1\pi\rightarrow 4\pi^*\rangle - 0.3181\langle 5\sigma\rightarrow 12\sigma^*\rangle - 0.1577\langle 6\sigma\rightarrow 12\sigma^*\rangle + \ldots$
	20.73	5.9	$0.8594\langle 5\sigma\rightarrow 12\sigma^*\rangle + 0.3623\langle 1\pi\rightarrow 4\pi^*\rangle + 0.3019\langle 6\sigma\rightarrow 12\sigma^*\rangle + \ldots$
c)			
C_1[1]			
1	0.00	100.0	$-0.9311\langle 0\vert 0\rangle+\ldots$
2	13.61	7.0	$-0.9350\langle 2b_1(\pi)\rightarrow 3b_1(\pi^*)\rangle - 0.1676\langle 8a_1(\sigma)\rightarrow 10a_1(\sigma^*)\rangle +\ldots$
3	16.93	13.8	$-0.8123\langle (2b_1(\pi)\rightarrow 3b_1(\pi^*))^2\rangle - 0.4031\langle 1b_1(\pi)\rightarrow 3b_1(\pi^*)\rangle +\ldots$
	29.43	3.2	$0.7170\langle 2b_2(\sigma)\rightarrow 5b_2(\sigma^*)\rangle + 0.3085\langle 4b_2(\sigma)\rightarrow 3b_1(\sigma^*),\ 2b_2(\sigma)\rightarrow 5b_2(\sigma^*)\rangle - 0.2952\langle 4b_2(\sigma)\rightarrow 5b_2(\sigma^*)\rangle + 0.2653\langle 3b_2(\sigma)\rightarrow 10a_1(\sigma^*),\ 4b_2(\sigma)\rightarrow 10a_1(\sigma^*)\rangle +\ldots$
C_2[2]			
1	0.00	100.0	$0.9965\langle 0\vert 0\rangle+\ldots$
	13.49	0.3	$-\ 0.5172\langle 3\pi\rightarrow 4\pi^*\rangle+0.7100\langle 9\sigma\rightarrow 11\sigma^*\rangle - 0.4128\langle 8\sigma\rightarrow 11\sigma^*\rangle + \ldots$
	15.20	0.2	$-0.8323\langle 8\sigma\rightarrow 11\sigma^*\rangle - 0.5083\langle 9\sigma\rightarrow 11\sigma^*\rangle + \ldots$
	21.66	0.6	$0.5655\langle 2\pi\rightarrow 6\pi^*\rangle - 0.3425\langle 7\sigma\rightarrow 12\sigma^*\rangle + 0.3032\langle 7\sigma\rightarrow 13\sigma^*\rangle - 0.2002\langle 1\pi\rightarrow 5\pi^*\rangle +\ldots$
	21.82	2.1	$-0.6252\langle 7\sigma\rightarrow 12\sigma^*\rangle - 0.5643\langle 2\pi\rightarrow 6\pi^*\rangle - 0.3873\langle 1\pi\rightarrow 5\pi^*\rangle + 0.2686\langle 7\sigma\rightarrow 13\sigma^*\rangle +\ldots$
	23.48	9.5	$0.5732\langle 7\sigma\rightarrow 12\sigma^*\rangle + 0.5492\langle 1\pi\rightarrow 5\pi^*\rangle + 0.4995\langle 6\sigma\rightarrow 12\sigma^*\rangle - 0.2447\langle 7\sigma\rightarrow 13\sigma^*\rangle +\ldots$

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[1] A measure chemical shift of 2.59 eV has been added to the carbonyl carbon.

[2] On ionisation of the methyl carbons C_{2V} symmetry is no longer preserved.

Table 16. Atomic orbital coefficients in the molecular p type orbitals obtained in the INDO/CI calculations using Mataga-Nishimoto parametrisation. Only the O2p and C2p basis orbitals are used for clarity. C2p(Me) symbolises the 2p on the methyl atom.

AO	MO					
Formaldehyde						
	$1b_1(\pi)$			$2b_1(\pi^*)$		
			C=O			C=O
	GS	$O1s^{-1}$	$C1s^{-1}$	GS	$O1s^{-1}$	$C1s^{-1}$
O2p	-0.81	0.93	0.69	-0.59	0.37	-0.72
C2p	-0.59	0.37	0.72	0.81	-0.93	0.69

Acetaldehyde												
	1π				2π				$3\pi^*$			
			C=O	CH_3			C=O	CH_3			C=O	CH_3
	GS	$O1s^{-1}$	$C1s^{-1}$	$C1s^{-1}$	GS	$O1s^{-1}$	$C1s^{-1}$	$C1s^{-1}$	GS	$O1s^{-1}$	$C1s^{-1}$	$C1s^{-1}$
O2p	0.19	-0.82	-0.39	0.09	0.80	0.46	0.60	-0.79	-0.56	-0.34	0.69	0.61
C2p	0.29	-0.30	-0.54	0.20	0.51	-0.04	0.46	-0.58	0.81	0.91	-0.70	-0.78
C2p(Me)	0.67	-0.40	-0.55	0.75	-0.21	-0.64	-0.46	0.14	-0.03	-0.11	0.07	0.03

Acetone												
	$1b_1(\pi)$				$2b_1(\pi)$				$3b_1(\pi^*)$			
			C=O	CH_3			C=O	CH_3			C=O	CH_3
	GS	$O1s^{-1}$	$C1s^{-1}$	$C1s^{-1}$	GS	$O1s^{-1}$	$C1s^{-1}$	$C1s^{-1}$	GS	$O1s^{-1}$	$C1s^{-1}$	$C1s^{-1}$
O2p	-0.19	0.60	-0.29	.....	0.81	0.74	0.68	.....	0.55	-0.31	0.67	.....
C2p	-0.34	0.41	-0.50	.....	0.47	0.05	0.48	.....	-0.81	0.90	-0.71	.....
C2p(Me)	-0.47	0.36	-0.43	.....	-0.15	-0.34	-0.26	.....	0.03	-0.10	0.07	.....
C2p(Me)	-0.47	0.36	-0.43	.....	-0.15	-0.34	-0.26	.....	0.03	-0.10	0.07	.....

FIGURES

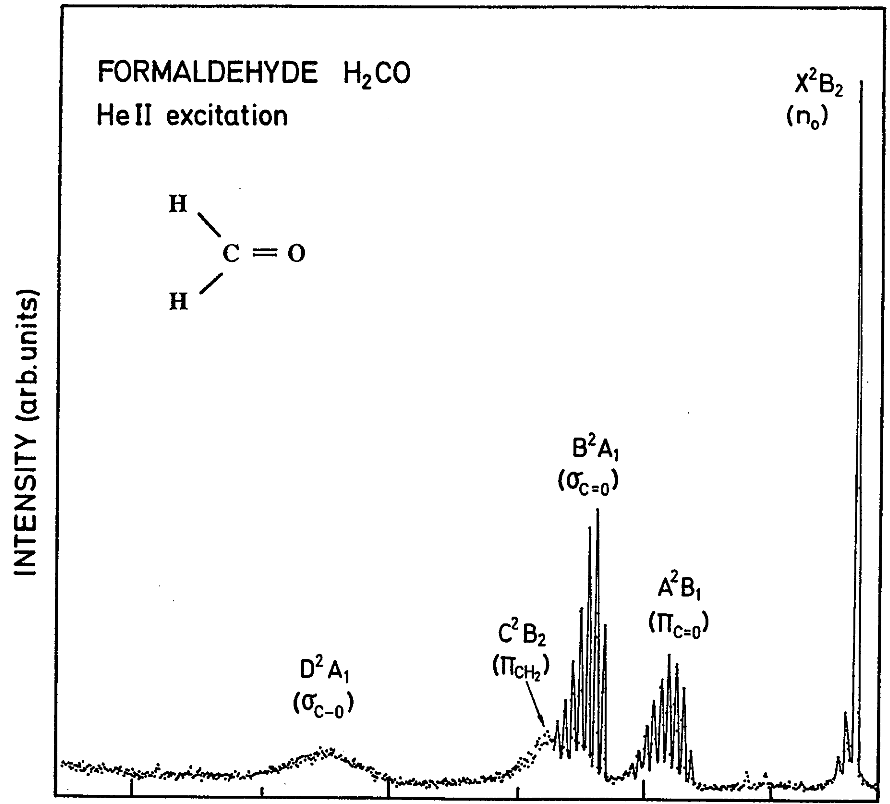

Fig.1 *The HeII excited photoelectron spectrum of formaldehyde between 10 and 26 eV.*

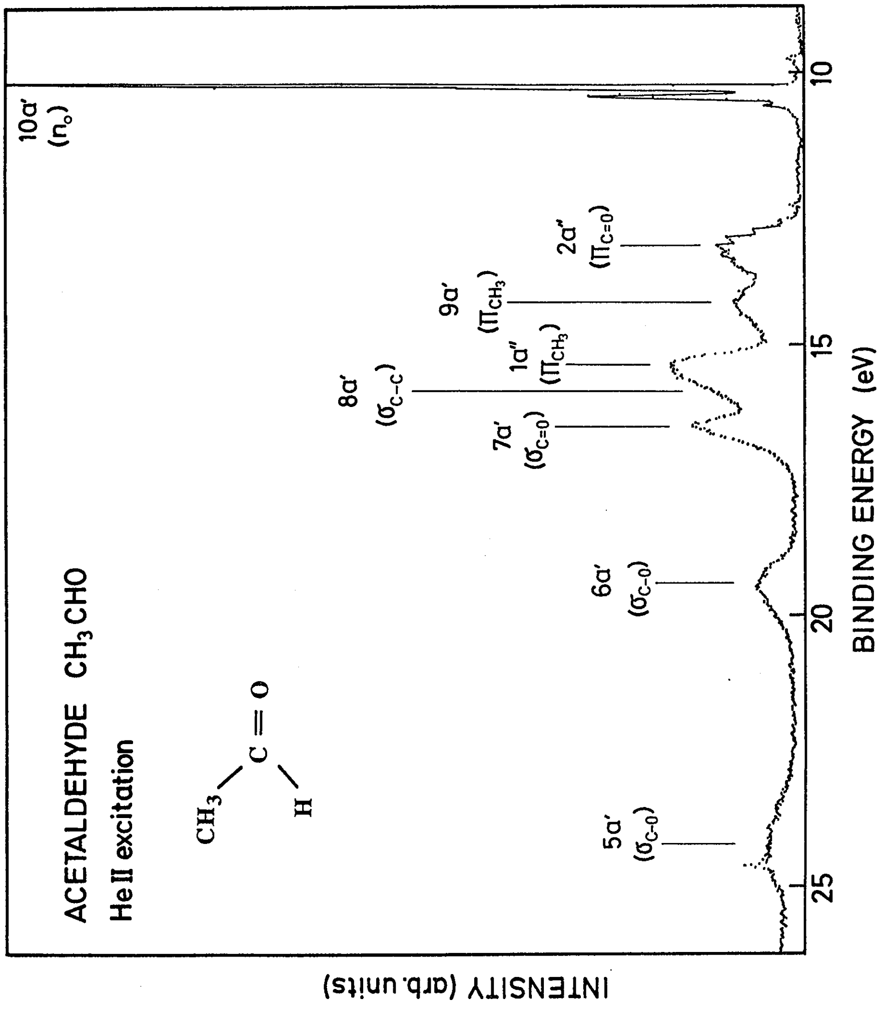

Fig.2 *The HeII excited photoelectron spectrum of acetaldehyde between 10 and 26 eV.*

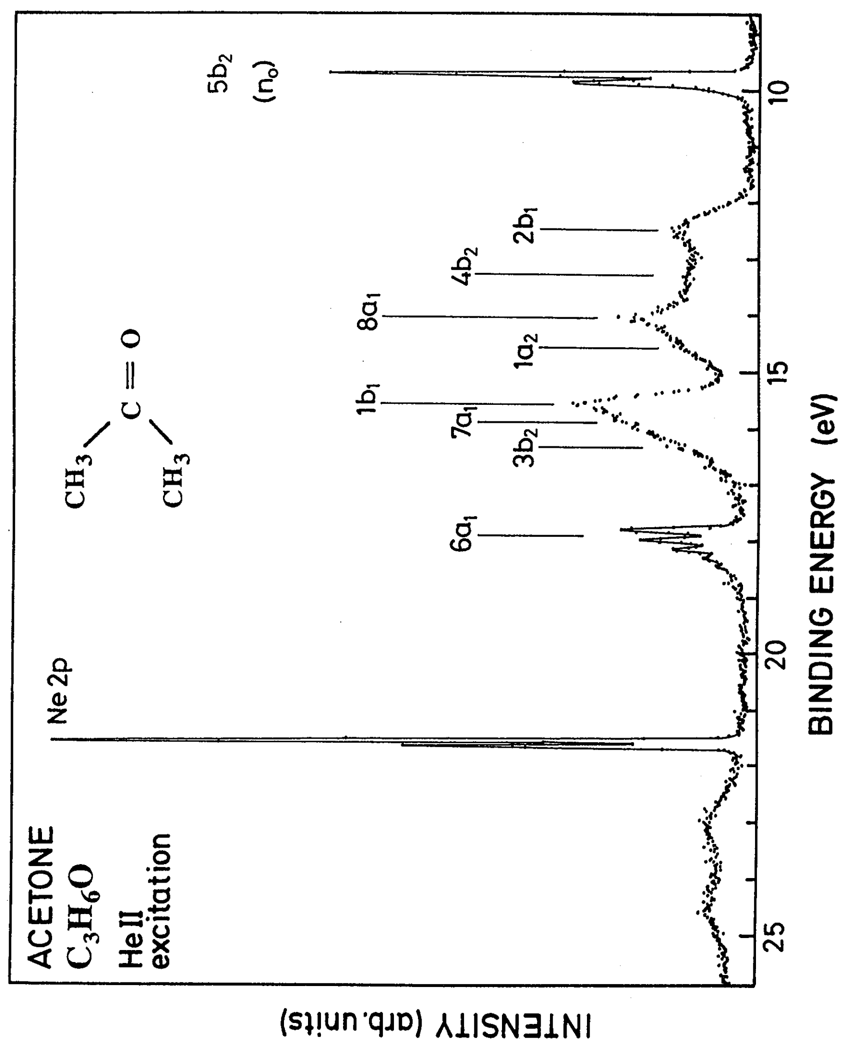

Fig.3 *The HeII excited photoelectron spectrum of acetone between 10 and 26 eV. The Ne2p lines are used for calibration.*

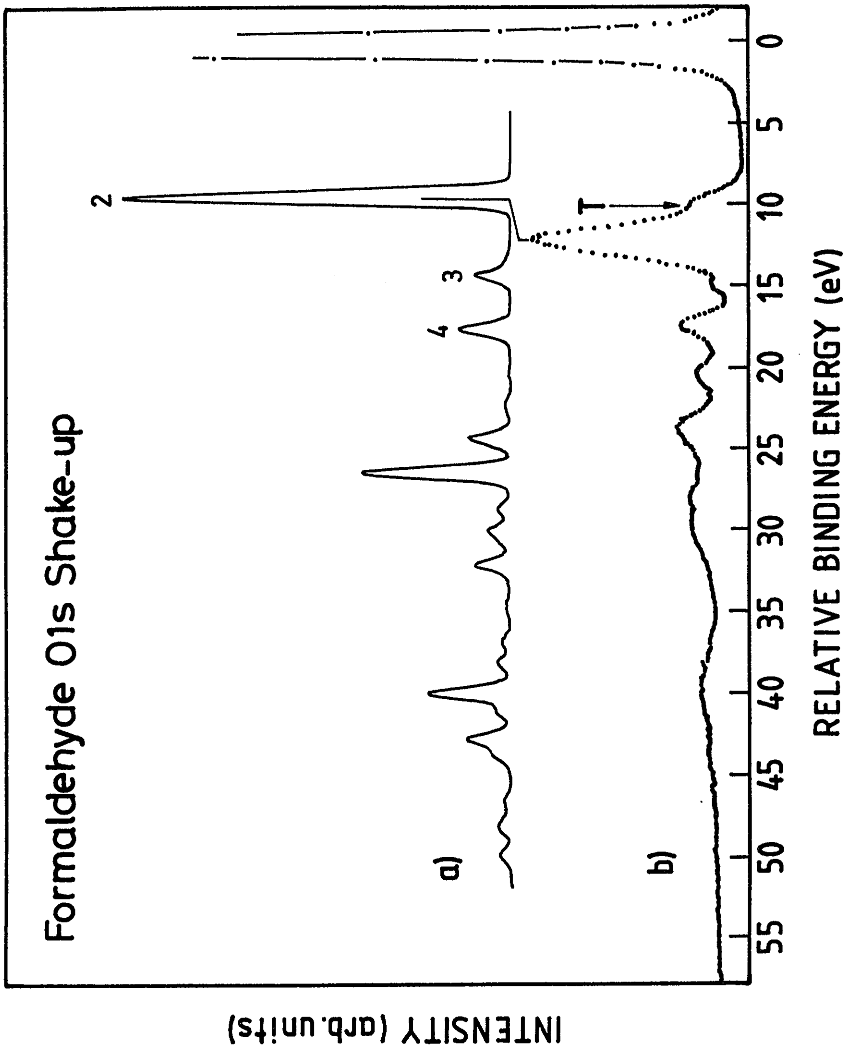

Fig.4 *a) The convoluted INDO/CI O1s shake-up spectrum of formaldehyde using Mataga-Nishimto parametrisation and b) The experimental shake-up spectrum excited by monochromatized Al Ka X-rays (hn = 1487 eV). The arrow marked with a T indicates a structure associated with a triplet coupled parent state of the ion.*

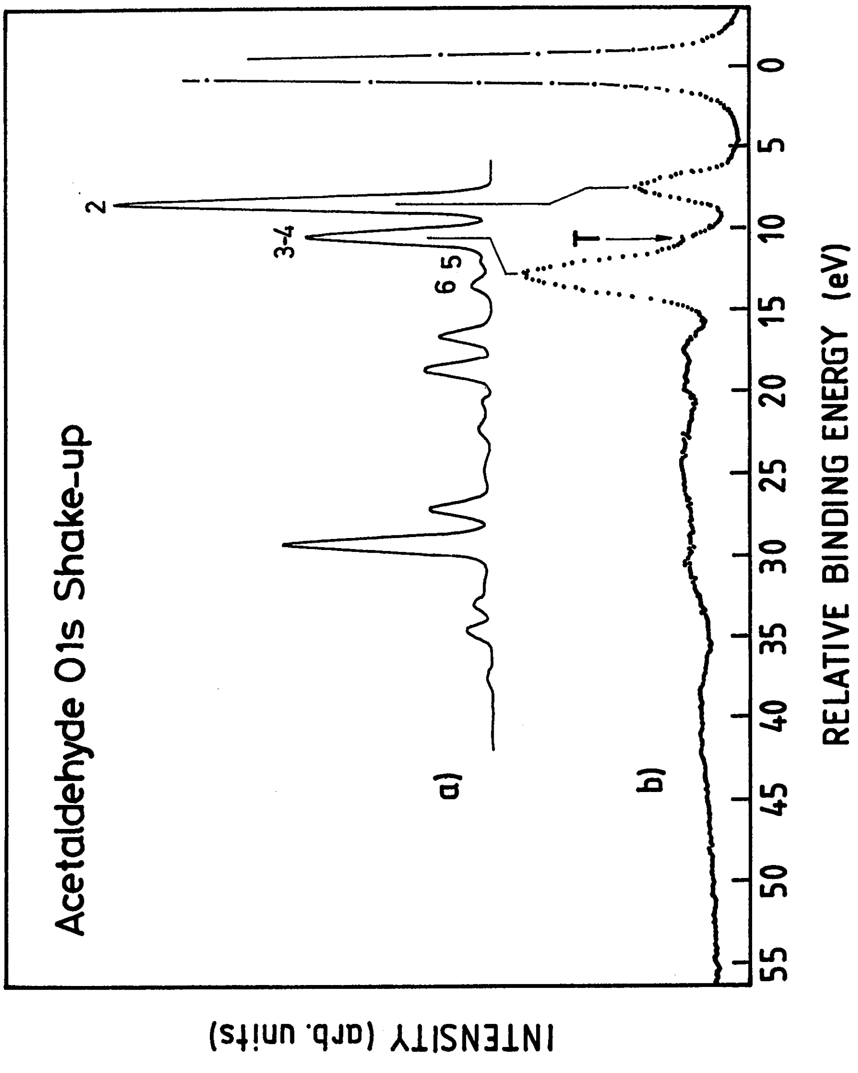

Fig.5 *a) The convoluted INDO/CI O1s shake-up spectrum of acetaldehyde using Mataga-Nishimto parametrisation and b) The experimental shake-up spectrum excited by monochromatized Al Ka X-rays (hn = 1487 eV). The arrow marked with a T indicates a structure associated with a triplet coupled parent state of the ion.*

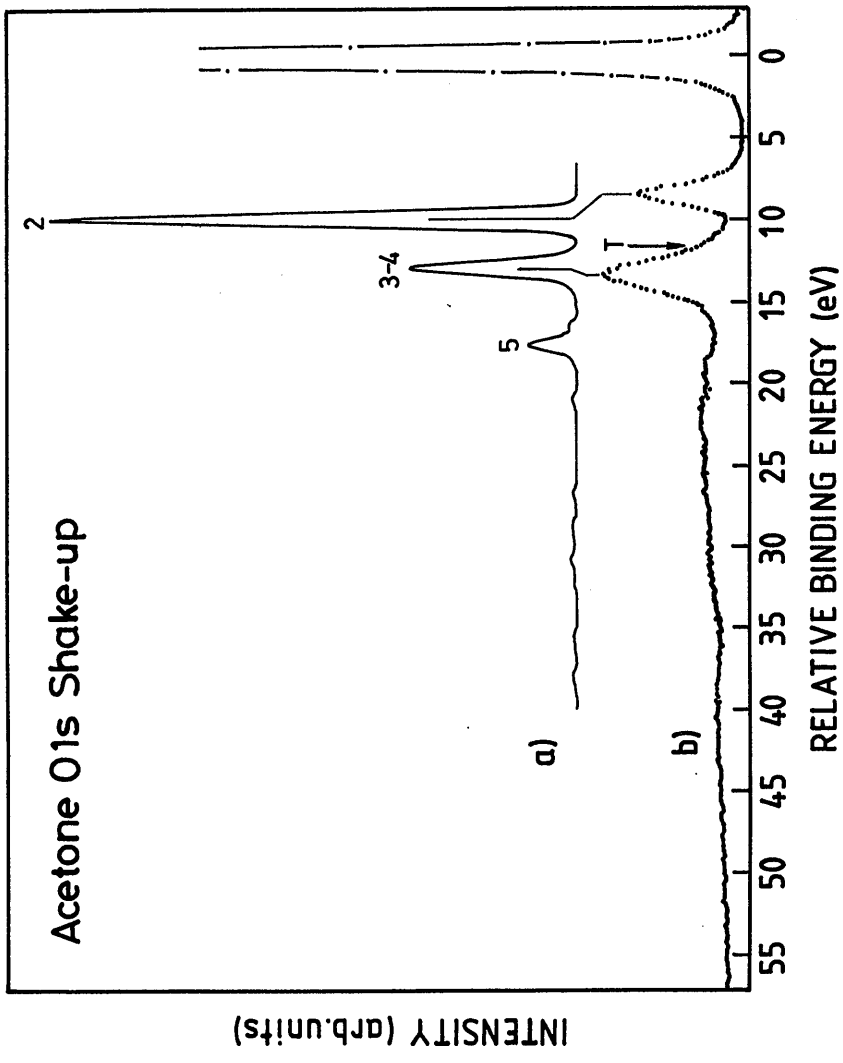

Fig.6 *a) The convoluted INDO/CI O1s shake-up spectrum of acetone using Mataga-Nishimto parametrisation and b) The experimental shake-up spectrum excited by monochromatized Al Ka X-rays (hn = 1487 eV). The arrow marked with a T indicates a structure associated with a triplet coupled parent state of the ion.*

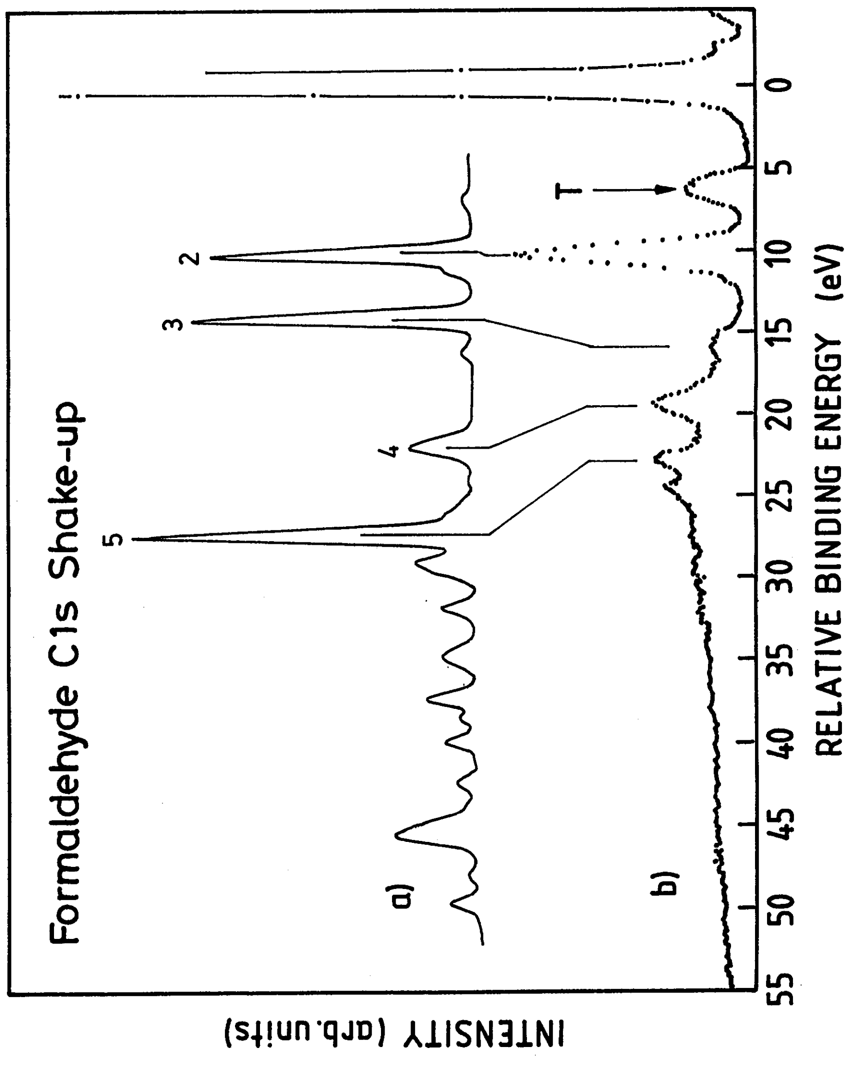

Fig.7 *a) The convoluted INDO/CI C1s shake-up spectrum of formaldehyde using Mataga-Nishimto parametrisation and b) The experimental shake-up spectrum excited by monochromatized Al Ka X-rays (hn = 1487 eV). The arrow marked with a T indicates a structure associated with a triplet coupled parent state of the ion.*

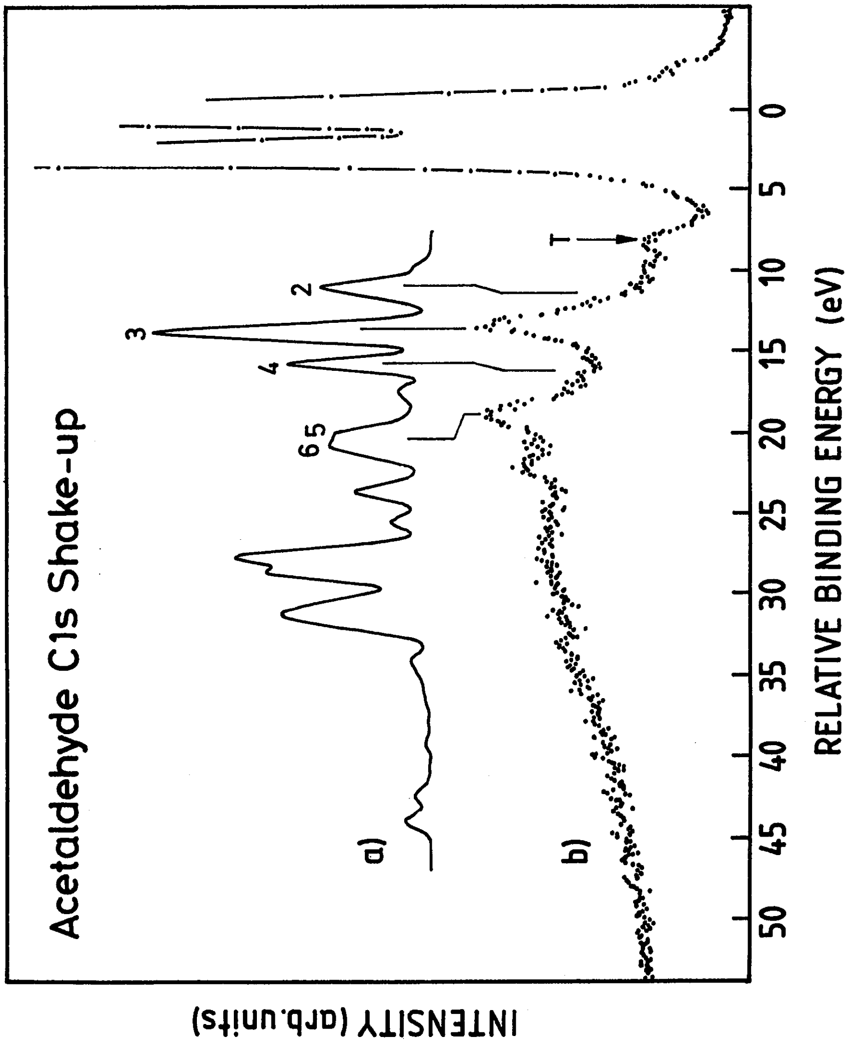

Fig.8 *a) The convoluted INDO/CI C1s shake-up spectrum of acetaldehyde using Mataga-Nishimto parametrisation and b) The experimental shake-up spectrum excited by monochromatized Al Ka X-rays (hn = 1487 eV). The arrow marked with a T indicates a structure associated with a triplet coupled parent state of the ion.*

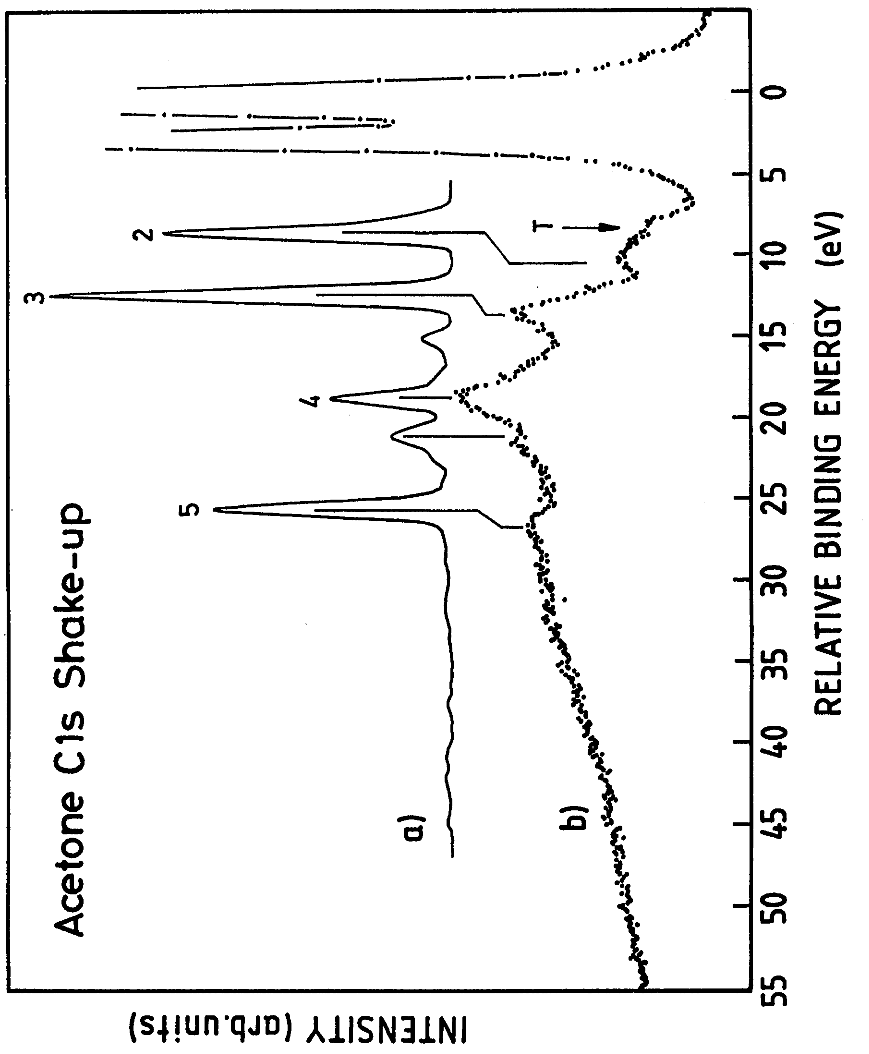

Fig.9 *a) The convoluted INDO/CI C1s shake-up spectrum of acetone using Mataga-Nishimto parametrisation and b) The experimental shake-up spectrum excited by monochromatized Al Ka X-rays (hn = 1487 eV). The arrow marked with a T indicates a structure associated with a triplet coupled parent state of the ion.*

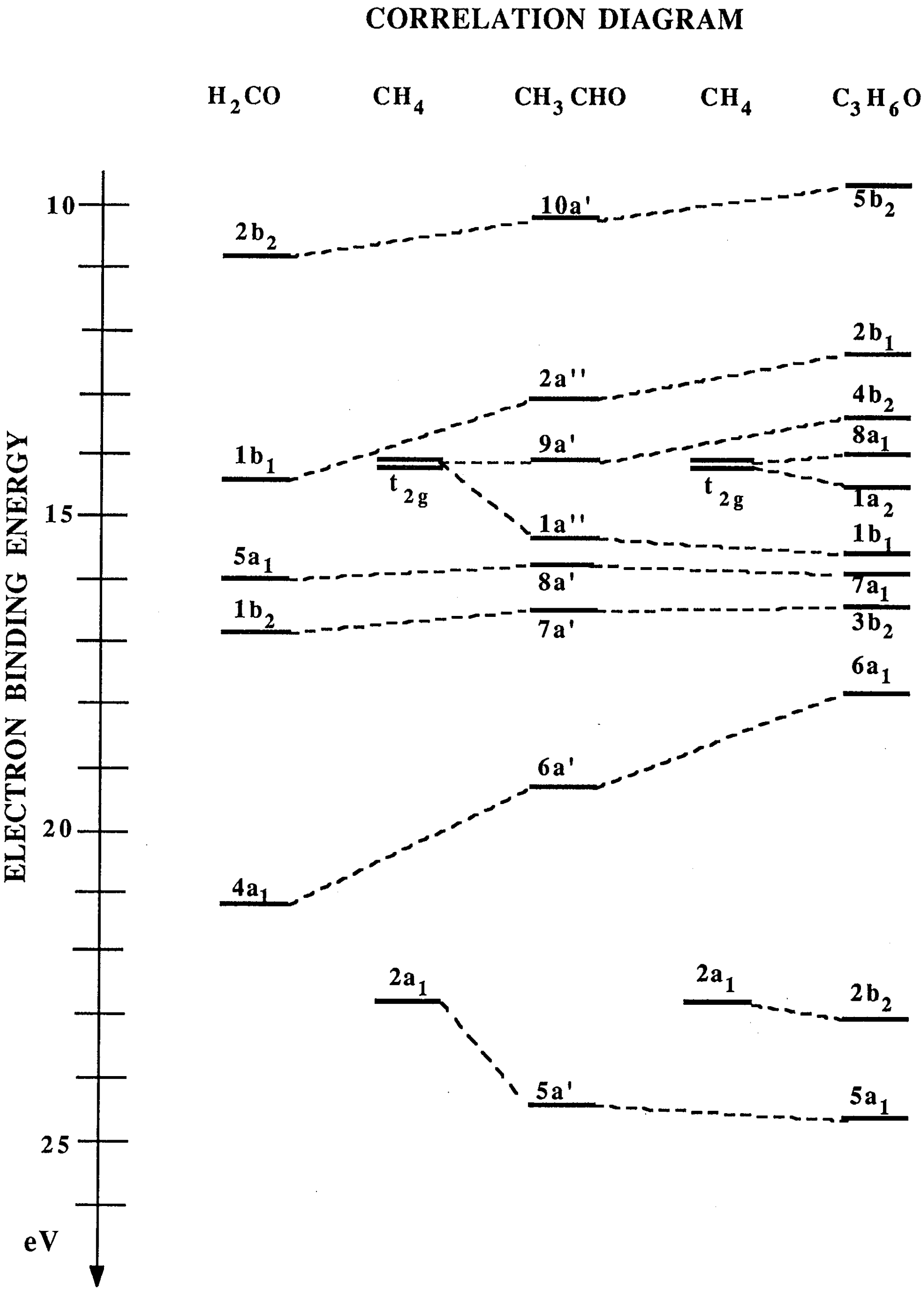

Fig.10 *Correlation diagram for the binding energies of the neutral molecules in the present study and methane /10/. The dotted lines connect orbitals with similar localization properties.*