A high resolution HeI excited photoelectron spectrum of the H_2CO molecule

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Abstract

The HeI excited photoelectron spectrum of the H_2CO molecule has been recorded with high resolution. Detailed studies have been carried out of the vibrational structure observed in the four photoelectron bands. The vibrational energies and intensities have been determined using a curve fitting procedure. In the outermost band corresponding to the X $^2B_2$ electronic state of H_2CO^+ a very extensive new vibrational structure is observed. It has been analysed primarily in terms of different vibrational progressions in the ν_3 mode excited in various combinations with the ν_1 and ν_2 modes. These vibrational states are not reached in direct photoelectron transitions but must be due to the presence of an intermediate state in the photoionisation process similarly to what has been found earlier for the CO molecule.

INTRODUCTION.

The formaldehyde molecule is of great interest in both physics and chemistry. It has therefore been studied extensively previously both experimentally and theoretically. Photoelectron spectra of the valence energy region have been obtained with different excitation sources including HeI and HeII radiation in the UV region [1-5], synchrotron radiation [6] and monochromatized X-rays [5].

The HeI excited photoelectron spectrum shows four bands, which all exhibit rich vibrational structure. Using the observed vibrational energies and intensities it is possible to carry out a Franck-Condon analysis to determine the equilibrium bond distances and to obtain information about the potential curves of the final ionic states. An analysis of this kind was performed recently [7] for the A^2B_1 state on the basis of previous results from UV photoelectron spectroscopy. The change in the CO bond length could be determined to be 0.12 - 0.13 Å. However, it was also concluded that for a more decisive determination of the CH bond length and the HCH bond angle more detailed experimental data are needed. Also, Green's function calculations incorporating many-body effects and involving vibrational excitations were performed previously [8].

The present study using HeI photoelectron spectroscopy has been carried out in order to obtain a well resolved spectrum, which gives additional information related to the electronic structure and which facilitates the determination of equilibrium geometries and potential curves of the outer valence states. During the recording of the spectra, new extensive weak vibrational progressions not expected in direct photoionisation, were observed. This structure seems to be due to the presence of an intermediate state in the photoionization process, since the relative intensities do not correspond to a regular Franck-Condon profile.

EXPERIMENTAL DETAILS.

The spectra presented in this paper were recorded using a high resolution electron spectrometer specially designed for gas phase studies in the VUV region [9]. The excitation source used was a high intensity microwave ECR lamp producing intensive and narrow resonance radiation in a gas discharge [10]. In the present study the HeI line at 21.218 eV was used. The formaldehyde sample was commercially obtained in the form of crystalline paraformaldehyde ($OH(H_2CO)H$). To produce pure formaldehyde in gas phase the sample was heated under vacuum conditions, using a thermo controlled oil bath. The oil bath was held at temperatures between 60 and 75 °C which produced gas pressures between 1.2 and 1.8 Torr.

Water is released in the depolymerization process of paraformaldehyde and tends to give rise to an intense spectrum unless it is removed. Therefore, before the recording of spectra, remaining water in the sample was boiled off by heating the sample above the boiling point for water. In an attempt to further reduce the water content, diphosphorpentoxide (P_2O_5) was added to dehydrate the gas. Recorded spectra of the gas obtained by this drying arrangement showed, however, a new broad structure between 11.8 to 13.0 eV. This structure can also be seen in the formaldehyde spectrum recorded by Kimura et al [3].

The spectra were calibrated against the Kr $4p_{1/2,\,3/2}$ lines, which were recorded simultaneously with the formaldehyde spectrum using a gas mixture in the gas cell. The resulting accuracy in the determination of line positions is better than 5 meV for well defined lines. The energies and relative intensities of the lines have been determined using a curve fitting method described in ref. [11].

RESULTS AND DISCUSSION.

The valence electron configuration of formaldehyde is

$4a_1^2\ 1b_2^2\ 5a_1^2\ 1b_1^2\ 2b_2^2$

The $4a_1$ orbital belongs to the inner valence region which is not included in the present study. However, it can be observed in the HeII excited spectrum, where it gives rise to a broad structureless band centred at 24.5 eV [4,5]. The photoelectron bands that correspond to ionization from the four outer valence orbitals are readily seen in the HeI-excited spectrum (cf Fig.1). The cationic states reached in the photoelectron transitions are given on top of the corresponding band in the figure. These assignments agree with the results of many-body calculations [8].

As in previous studies, all bands exhibit extensive vibrational structure. In order to discuss the details of this structure it is useful to consider the localisation properties of the molecular orbitals and make comparisons with the spectrum of the CO molecule. The $2b_2(\sigma)$ orbital, which is essentially non-bonding (oxygen lone-pair) and the $1b_1(\pi)$ orbital, which is C=O bonding, closely resemble the corresponding orbitals of the CO molecule. Accordingly, the photoelectron bands corresponding to these orbitals are very similar to the corresponding bands in the photoelectron spectrum of the CO molecule. However, the vibrational structure is much more complex in the case of formaldehyde due to the larger number of vibrational degrees of freedom. The $5a_1$ orbital corresponds to the in-plane component of the 1π orbital originating from the CO molecule, but is stabilized in energy with respect to the $1b_1$ orbital due to a significant interaction with the hydrogen atoms. Finally, the $1b_2$ orbital is essentially built up from C2p and an antisymmetric combination of H1s orbitals and is therefore primarily of CH_2 π character.

In the following, high resolution recordings of each photoelectron band will be presented separately with special emphasis on the vibrational structure. Three of the normal vibrations in the formaldehyde molecule are totally symmetric (a_1 representation) and these can become strongly excited in the photoelectron transitions if the final states maintain the C_{2v} symmetry. The three remaining modes are of b_1 (2 modes) and b_2 symmetry. The energies in the neutral ground state of the ν_1, ν_2 and ν_3 modes, which are of a_1 symmetry, are 345 meV, 213 meV and 186 meV, respectively [12].

The X $^2B_2$ state.

Removal of an electron from the $2b_2$ nonbonding orbital has only little influence on the bond lengths and angles. The spectrum therefore consists of a strong line corresponding to the adiabatic (0-0) transition at 10.885 eV, and only weak vibrational structure. Figure 2 shows a detailed recording of the band in the range of the 0-0 transition. Single quanta of the totally symmetric v_1, v_2 and v_3 vibrational modes are observed at 11.210, 11.088 and 11.035 eV, respectively, with intensities in the order of 5 % of the main peak. These excitations were well described in many-body calculations [8]. The vibrational energies (0-1 spacings) are only between 5 and 8% smaller than the corresponding values of the neutral ground state, which is in agreement with the lone-pair character of the $2b_2$ orbital.

In addition to these peaks a number of weaker lines can be seen at higher binding energies. A few similar lines, but more intense, were observed also in the synchrotron radiation photoelectron spectrum recorded with a photon energy of 14.55 eV [6]. These lines can be analysed in terms of vibrational progressions, the most prominent of which involve excitations of the v_3 mode. Simple progressions in the v_1, v_2 and v_3 modes are apparently weak in the beginning of the band. The highest intensity is observed for combination bands, in particular the v_1+nv_3 (n=0,1,2...) and the $v_1+v_2+nv_3$ progressions. However, while the former progression disappears at about 12.5 eV, the latter progression acquires much higher intensity at even higher binding energy. Various other combinations can be formed, and these excitations probably give rise to progressions of low intensity forming a background in this part of the spectrum.

The vibrational structure observed in Fig. 2 extends towards even higher binding energies. In Fig.3 a spectrum is shown which involves the energy region up to the first part of the $1b_1^{-1}$ band. As can be seen, a large number of vibrational excitations are present in the entire region with an intensity in the order of 0.5% or less of the main (0-0) peak. The vibrational assignments based upon those of Fig. 2 are indicated by the bar diagrams in Fig. 3. Table 1 summarizes the energies and relative intensities of the levels associated with this state. The line positions and the relative intensities were obtained by fitting gaussian curves to the spectra. Due to the substantial overlap between different lines the fitting is not very accurate for the lines of lowest intensity.

At binding energies higher than 12 eV three dominating progressions in the v_3 mode are observed. Except the v_1+nv_3 and $v_1+v_2+ nv_3$ progressions also the $2v_2+nv_3$ progression has acquired a comparatively high intensity in this region. Thus, it seems that in particular a quantum of the v_1 mode or two quanta of the $2v_2$ mode facilitates the population of highly excited vibrational states. As can be seen, the overall intensity goes through a minimum in the 12.0 eV energy range and increases again closer to the A state. Hence, the observed relative intensities in the progressions do not correspond to the Franck-Condon factors for direct photoelectron transitions from the neutral ground state. The components of the v_1+nv_3 progression can be followed from n=1 to n=18, although the first few components can only be inferred in Fig. 2. The progression has its maximum intensity late in the series, at n=16 and the even higher components expected above n=18 are apparently hidden under the intense peaks of the $1b_1$ band. The vibrational spacing is essentially constant in the band.

The $\nu_1+\nu_2+n\nu_3$ progression can be followed for the quantum numbers n=0...13. In this case the vibrational spacings decrease markedly with increasing quantum number, suggesting that excitations of the C=O stretching modes weaken the chemical bonding sufficiently for an anharmonicity to become apparent. The progression has an intensity maximum at n=9.

The $2\nu_2+n\nu_3$ progression can be observed for vibrational quantum numbers n=0...10 with more or less constant vibrational spacings. The intensity increases sharply from n=5 towards a maximum at n=8.

Three lines associated with water impurities are observed in the region between the main peaks in the X state and the A state (cf Fig. 2). These lines correspond to the adiabatic 0-0 transition at 12.615 eV, and the ν_1 and ν_2 vibrational excitations at 13.017 and 12.792 eV. Due to the presence of these peaks the identification of the vibrational structure related to formaldehyde is somewhat uncertain in this region of the spectrum. The water is released in the formaldehyde depolymerization process, as discussed above, and is difficult to remove entirely from the sample.

A very long bar diagram indicating a progression in the ν_3 mode that extends even into the A state is shown in the upper part of Fig. 3. This is inserted in order to show the constant spacings between the lines. For such a long progression extending over a range of more than 3 eV a decrease in the vibrational spacings would be expected due to some anharmonicity of the potential curve. Since this is not observed it seems more likely that the higher components are associated with combined excitations of the ν_3 mode and other vibrational modes. One likely candidate is $3\nu_2+n\nu_3$, which has approximately the same energy for n=0 as $n\nu_3$ with n=4. This progression could be expected to appear at high energies since $2\nu_2+n\nu_3$ shows an intensity maximum in the 12.5 eV range. Perhaps even more likely is the $2\nu_1+n\nu_3$ progression in view of the very high intensity of the $\nu_1+n\nu_3$ progression in 13.5 eV range. The n=0 component of the $2\nu_1+n\nu_3$ progression is expected to approximately coincide with the n=4 component of the $n\nu_3$ progression. Also, the n=3 component coincides with the n=7 component of the $n\nu_3$ series, where in fact a step in the progression can be inferred (cf Table 1).

Very weak structures can be observed close to the 0-0 transition. Two such features at 10.789 eV and 10.981 eV are included in Table 1 and can be clearly observed in Fig. 2. They are probably associated with hot band excitations.

Finally, it should be noticed that the extensive weak vibrational structure observed far outside the energy region where the direct photoionization is expected to give any appreciable intensity, appears to have a counterpart in the spectrum of the CO molecule. In that case the vibrational structure of the X $^2\Sigma^+$ state could be observed up to the vibrational level v=33 in the HeI excited spectrum [12,13]. The extensive excitations were associated with a non-direct population of the vibrational levels due to the influence of a broad intermediate electronic state, which could be a shape-resonance, in the photoionization process. Due to the similarity between the extended weak vibrational structure of present spectrum and that observed in the CO spectrum it may be proposed that it has a similar origin as that of CO. From the study of ref [6], which involves determination of the photoionization cross section as a function of photon energy, the presence of such an intermediate state may be inferred in the range between 20 and 22 eV. It should therefore be very interesting to perform detailed studies of the vibrational structure as function of photon energy in the energy range 20-25 eV.

The A $^2B_1$ state

As mentioned above, this state is reached by ionization from the bonding $1b_1$ π (C=O) orbital formed from the $2p_x$ (C) and $2p_x$ (O) atomic orbitals. Hence, the photoelectron band is expected to show strong excitations of the ν_2 C=O stretching mode. Two such progressions have been observed in previous experimental studies [1]. In the many-body calculations by Domcke and Cederbaum [8] it was shown that the second progression corresponds to ν_2 mode excited in combination with a single quantum of the ν_3 mode.

In the present study a long progression is observed, where the individual lines in general are composed of more than one component. Only the weak line at 13.968 eV is narrow and symmetric as expected for the line corresponding to the adiabatic (0-0) transition. As can be seen from Fig. 3, the second line (at 14.1 eV) in the present spectrum is asymmetric with a shoulder on the high binding energy side which indicates that it is composed of two overlapping lines. By using a curve fitting procedure the energies of the two components were found to be 14.100 eV and 14.126 eV, respectively. The spacings to the 0-0 line are thus 132 eV and 158 eV. Two vibrational progressions $n\nu_2$ and $n\nu_2+\nu_3$ can be readily identified out of these two excitations in accordance with refs [7,8]. At high energies a third progression in the ν_2 mode can be observed. It can probably be associated with the $n\nu_2+2\nu_3$ progression, which is expected to have an observable intensity. The progression can be followed back to the fifth peak of the band but not at even lower energies due to the low intensity of these components. The line positions and relative intensities obtained from a similar line fitting procedure as for the first band are given in Table 2.

As can be seen in Table 2, the vibrational spacings decrease with increasing vibrational quantum number n indicating a positive anharmonicity. Using a Morse potential curve fit a dissociaton energy of about 6 eV can be obtained for this state along the q_2 normal coordinate.

It should be noticed that the above assignment of the adiabatic transition to the line at 13.968 eV is at variance with earlier studies, which have associated this transition with the second line at 14.1 eV. However, as pointed out above, this second line in our spectrum consists of two components, both acquiring a rather high intensity (cf Table 2). This would not be expected for the line corresponding to the adiabatic transition unless very strong hot band excitations were present. Such an assumption seems unreasonable for the present state. One difficulty with the present assignment is that the 0-ν_2 spacing is only 132 meV, while at higher energies the spacing is in the order of 140-150 meV. Since obviously the ν_2 and ν_3 modes have nearly the same energy when excited in single quanta, the low energy spacing of the ν_2 mode could be explained by a shift due to a Fermi resonance occurring between these two modes which have the same symmetry.

Additional very weak structure observed in the band can be associated with vibrational excitations in the X state. A progression with energy spacings corresponding to excitations of the ν_3 mode is indicated in Fig. 5.

The B $^2A_1$ state

This state is created by ionization from the ($5a_1$) σ (C=O) bonding orbital. As for the A state, the ν_2 vibrational mode is thus expected to be strongly excited. However, the $5a_1$ orbital is much more complex than $1b_1$ since it is formed from the carbon sp^2 hybrid (2s(C), $2p_x$(C) and $2p_y$(C) orbitals) and the oxygen sp hybrid (2s(O) and $2p_z$(O) orbitals). Thus, the vibrational structure could be expected to be more complex than in the $1b_1$ band. As can be seen from Fig 6., which shows a detailed recording of the energy region between 15.5 and 18.5 eV, the vibrational structure is in fact simpler than of the $^2B_1$ state. In Table 3 we give the energies and relative intensities of the vibrational states.

The adiabatic (0-0) transition corresponds to the line observed at 15.837 eV, which is somewhat lower than the value given previously in ref [1]. As in earlier studies a vibrational progression in the ν_2 mode can be identified with a 0-1 spacing of 160 meV. The vibrational spacings converge slightly with increasing quantum number indicating a positive anharmonicity in the potential curve. From this anharmonicity a dissociation energy of about 4.8 eV can be calculated along the q_2 normal coordinate, using a Morse potential curve. The progression can be clearly observed to the level with quantum number n=6 and also the n=7 and 8 components may be inferred. The lines are symmetric and show no indication of overlapping structures that could imply the presence other vibrational excitations. Above the peak corresponding to n=6 the structure gets complex and diffuse with several overlapping bands due to the overlap with the excitations associated with the C state. The width of the peaks in the series increase from ca 16 meV in the beginning of the band to about 21 meV at higher energies, which may be indicative of a decrease in the lifetime of the ion towards higher vibrational levels. Alternatively, this increase in linewidth may reflect the presence of other vibrational excitations coinciding with the lines of the ν_2 progression. The many-body calculations presented in ref. [8] suggest that such contributions may be present in the spectrum due to a weak excitation of the ν_3 mode.

The C $^2B_2$ state

The C $^2B_2$ state corresponds to ionization from the ($1b_2$) orbital. This orbital is formed from the carbon sp^2 hybrid (2s(C), $2p_x$(C) and $2p_y$(C) orbitals) and the 1s(H) and is primarily a σ (CH) bonding orbital. Energies and relative intensities of some of the well resolved vibrational components observed in the present study are given in Table 4.

The adiabatic transition can be identified as corresponding to the weak peak at 16.241 eV (cf Fig. 6), since there is obviously no line at even lower energy that can be associated with this transition. This confirms the result obtained in ref [1]. A strong vibrational progression can be observed with a 0-1 spacing of 175 meV. This probably reflects excitations of the ν_3 mode, which was found to be strongly coupled to this ionization in ref [8]. The reduction in the vibrational energy from the value in the neutral ground state is very small, only 6%, considering the fact that the energy difference between the adiabatic and vertical binding energies is at least in the order of one vibrational quantum. The progression can be followed up to v=3 or v=4 where the intensity of the components apparently starts to decrease significantly. As can be seen from Fig.6 the energies of the v=2 and v=3 states are similar to the energies of high vibrational levels of the $^2A_1$ state so the lines at 16.583 and 16.794 eV are obviously composed of more than one component. At higher energies the vibrational structure gets even more complex. However, one progression with the same spacings as observed in the low binding energy part of the band can be inferred, as indicated in the figure. It is not possible to unambiguously identify the components at lower energies, due to the overlap with the intense lines of the $^2A_1$ state in this region. The interpretation of the progression is therefore uncertain but it might correspond to $\nu_1 + n\nu_3$, which was predicted to have a rather high intensity in the many-body calculations [8]. By extrapolating the observed structure towards lower energy, the vibrational energy of the ν_1 mode can be estimated to be 220 meV. An even weaker series with the same spacings can be seen which can be associated with the $2\nu_1 + n\nu_3$ progression. It should also be noticed that in the range of strong overlap between the B and C states between 16.5 and 18 eV excitations of the antisymmetric ν_6 mode could be expected due to vibronic interaction. This could explain partly the complex structure in the spectrum, in particular since the ν_6 mode has a low energy (145 meV in the neutral ground state [12]).

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TABLES

Table 1. Energies, relative intensities and assignments of the lines in the X-state.

[a] The relative intensities are referred to the 0-0 peak in the X-state.

Energy (eV)	Relative Intensity [a]	Width (meV) (FWHM)	Assignment
10.789	-	-	v_6 1-0
10.885	100	45	0-0
10.981	-	-	v_6
11.035	4.6	47	v_3
11.088	5.6	45	v_2
11.136	-	-	$v_3 + v_6$
11.152	-	-	-
11.200	-	-	$2\ v_3$
11.210	2.4	47	v_1
11.289	0.018	-	$2\ v_2$
11.355	0.075	35	$v_1 + v_3$
11.356	-	-	$3\ v_3$
11.413	0.16	38	$v_1 + v_2$
11.436	0.018	-	$2\ v_2 + v_3$
11.500	0.055	35	$v_1 + 2\ v_3$
11.510	-	-	$4\ v_3$
11.568	0.094	38	$v_1 + v_2 + v_3$
11.584	0.018	-	$2\ v_2 + 2\ v_3$
11.640	0.021	33	$v_1 + 3\ v_3$
11.664	-	-	$5\ v_3$
11.719	0.087	38	$v_1 + v_2 + 2\ v_3$
11.750	0.043	33	$2\ v_2 + 3\ v_3$
11.784	0.018	-	$v_1 + 4\ v_3$
11.816	-	-	$6\ v_3$
11.877	0.094	42	$v_1 + v_2 + 3\ v_3$
11.913	0.040	33	$2\ v_2 + 4\ v_3$
11.927	0.018	-	$v_1 + 5\ v_3$
11.982	-	-	$7\ v_3$
12.029	0.087	42	$v_1 + v_2 + 4\ v_3$
12.075	0.040	33	$2\ v_2 + 5\ v_3$
12.086	0.018	-	$v_1 + 6\ v_3$
12.135	-	-	$8\ v_3$
12.175	0.063	38	$v_1 + v_2 + 5\ v_3$
12.228	0.17	38	$2\ v_2 + 6\ v_3$
12.260	0.028	-	$v_1 + 7\ v_3$
12.285	-	-	$9\ v_3$
12.319	0.037	33	$v_1 + v_2 + 6\ v_3$
12.386	0.38	45	$2\ v_2 + 7\ v_3$
12.415	0.049	-	$v_1 + 8\ v_3$
12.432	-	-	$10\ v_3$

Table 1. *Continued.*

Energy (eV)	**Relative Intensity** [a]	**Width (meV) (FWHM)**	**Assignment**
12.458	0.018	-	$v_1 + v_2 + 7\ v_3$
12.537	0.36	38	$2\ v_2 + 8\ v_3$
12.566	0.053	-	$v_1 + 9\ v_3$
12.568	-	-	$11\ v_3$
12.603	0.018	-	$v_1 + v_2 + 8\ v_3$
12.682	0.42	38	$2\ v_2 + 9\ v_3$
12.707	-	-	$12\ v_3$
12.712	0.053	-	$v_1 + 10\ v_3$
12.753	0.018	-	$v_1 + v_2 + 9\ v_3$
12.831	0.33	38	$2\ v_2 + 10\ v_3$
12.857	-	-	$13\ v_3$
12.866	0.16	38	$v_1 + 11\ v_3$
12.910	0.018	-	$v_1 + v_2 + 10\ v_3$
12.974	0.17	33	$2\ v_2 + 11\ v_3$
13.005	-	-	$14\ v_3$
13.015	0.18	38	$v_1 + 12\ v_3$
13.119	0.091	33	$2\ v_2 + 12\ v_3$
13.150	-	-	$15\ v_3$
13.162	0.16	38	$v_1 + 13\ v_3$
13.225	0.040	28	$2\ v_2 + 13\ v_3$
13.292	-	-	$16\ v_3$
13.315	0.24	38	$v_1 + 14\ v_3$
13.380	0.078	45	$2\ v_2 + 14\ v_3$
13.444	-	-	$17\ v_3$
13.475	0.29	35	$v_1 + 15\ v_3$
13.521	0.059	33	$2\ v_2 + 15\ v_3$
13.599	-	-	$18\ v_3$
13.630	0.35	35	$v_1 + 16\ v_3$
13.668	0.075	33	$2\ v_2 + 16\ v_3$
13.749	-	-	$19\ v_3$
13.782	0.24	42	$v_1 + 17\ v_3$
13.898	-	-	$20\ v_3$
13.934	0.15	42	$v_1 + 18\ v_3$
14.046	-	-	$21\ v_3$
14.205	-	-	$22\ v_3$
14.350	-	-	$23\ v_3$
14.508	-	-	$24\ v_3$
14.660	-	-	$25\ v_3$
14.805	-	-	$26\ v_3$
14.953	-	-	$27\ v_3$
15.102	-	-	$28\ v_3$
15.250	-	-	$29\ v_3$
15.401	-	-	$30\ v_3$
15.544	-	-	$31\ v_3$

Table 2. *Energies, relative intensities and assignments of the lines in the A-state.*

[a] The relative intensities are referred to maximum band in the A-state (3 v2 band).

Energy (eV)	**Relative Intensity** [a]	**Width (meV) (FWHM)**	**Assignment**
13.968	6	38	0-0
14.100	28	38	v_2
14.126	13	35	v_3
14.255	74	38	$2\ v_2$
14.286	25	35	$v_3 + v_2$
14.406	100	38	$3\ v_2$
14.440	37	35	$v_3 + 2\ v_2$
14.554	96	38	$4\ v_2$
14.588	42	35	$v_3 + 3\ v_2$
14.623	13	38	$v_1 + 2\ v_2$
14.701	74	38	$5\ v_2$
14.736	37	35	$v_3 + 4\ v_2$
14.771	14	38	$v_1 + 3\ v_2$
14.845	52	38	$6\ v_2$
14.881	30	38	$v_3 + 5\ v_2$
14.919	14	42	$v_1 + 4\ v_2$
14.986	37	42	$7\ v_2$
15.024	22	42	$v_3 + 6\ v_2$
15.066	12	45	$v_1 + 5\ v_2$
15.124	27	45	$8\ v_2$
15.165	15	42	$v_3 + 7\ v_2$
15.208	11	47	$v_1 + 6\ v_2$
15.260	19	47	$9\ v_2$
15.303	11	45	$v_3 + 8\ v_2$
15.344	7	47	$v_1 + 7\ v_2$
15.393	14	52	$10\ v_2$
15.440	8	49	$v_3 + 9\ v_2$
15.493	7	57	$v_1 + 8\ v_2$
15.530	9	57	$11\ v_2$
15.580	8	52	$v_3 + 10\ v_2$
15.654	8	61	$12\ v_2$
15.711	7	59	$v_3 + 11\ v_2$

Table 3. *Energies, relative intensities and assignments of the lines in the B-state.*

[a] The relative intensities are referred to maximum band in the B-state (2 v_2 band).

Energy (eV)	**Relative Intensity** [a]	**Width (meV) (FWHM)**	**Assignment**
15.837	51	33	0-0
15.997	97	35	v_2
16.153	100	38	2 v_2
16.306	69	38	3 v_2
16.457	40	38	4 v_2
16.605	24	49	5 v_2
16.751	11	49	6 v_2

Table 4. *Energies, relative intensities and assignments of the lines in the C-state.*

[a] The relative intensities are referred to maximum band in the C-state (v_2 band).

Energy (eV)	**Relative Intensity** [a]	**Width (meV) (FWHM)**	**Assignment**
16.241	54	42	0-0
16.416	100	45	v_2
16.583	20	49	2 v_2
16.794	-	-	3 v_2

FIGURES

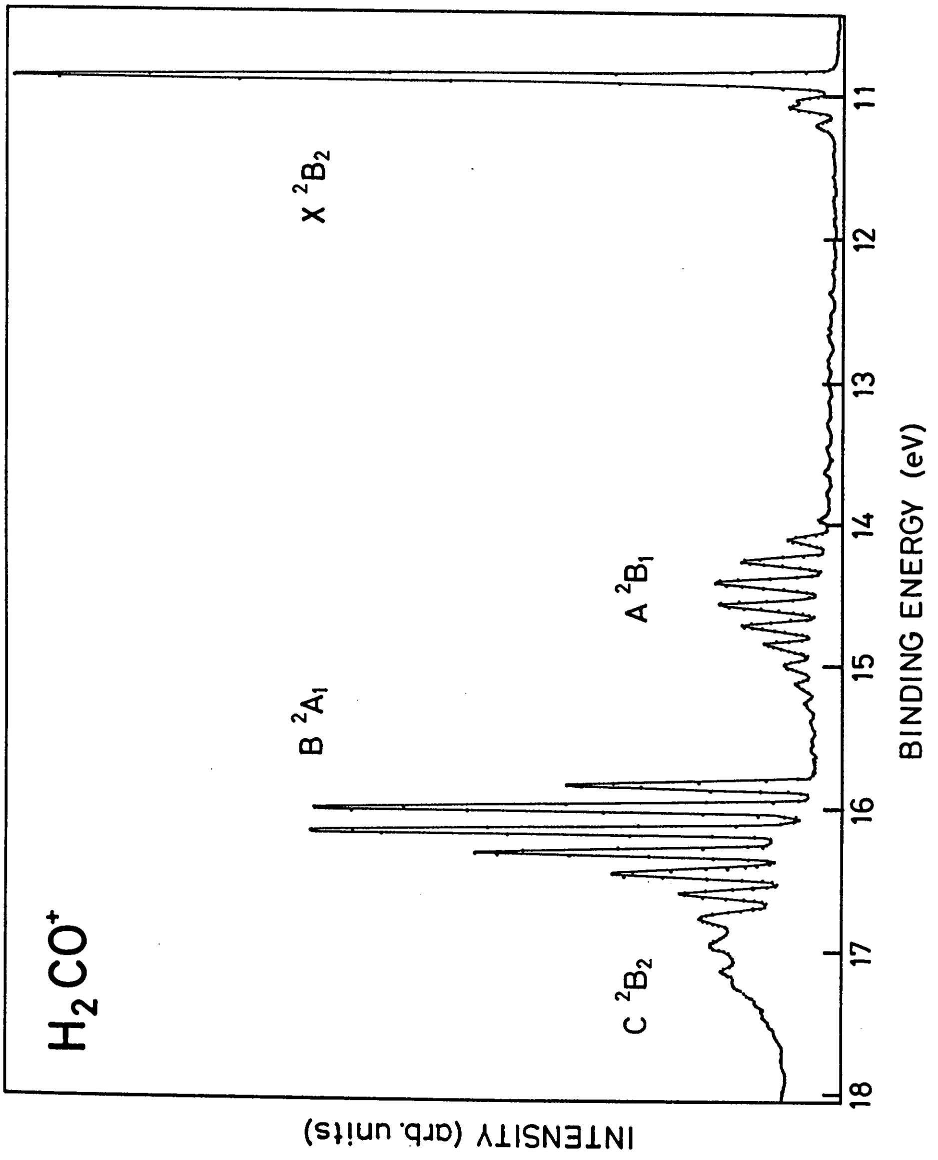

Fig.1. *The HeI excited photoelectron spectrum of the formaldehyde molecule. The final cationic states reached in the photoelectron transitions are given above each band.*

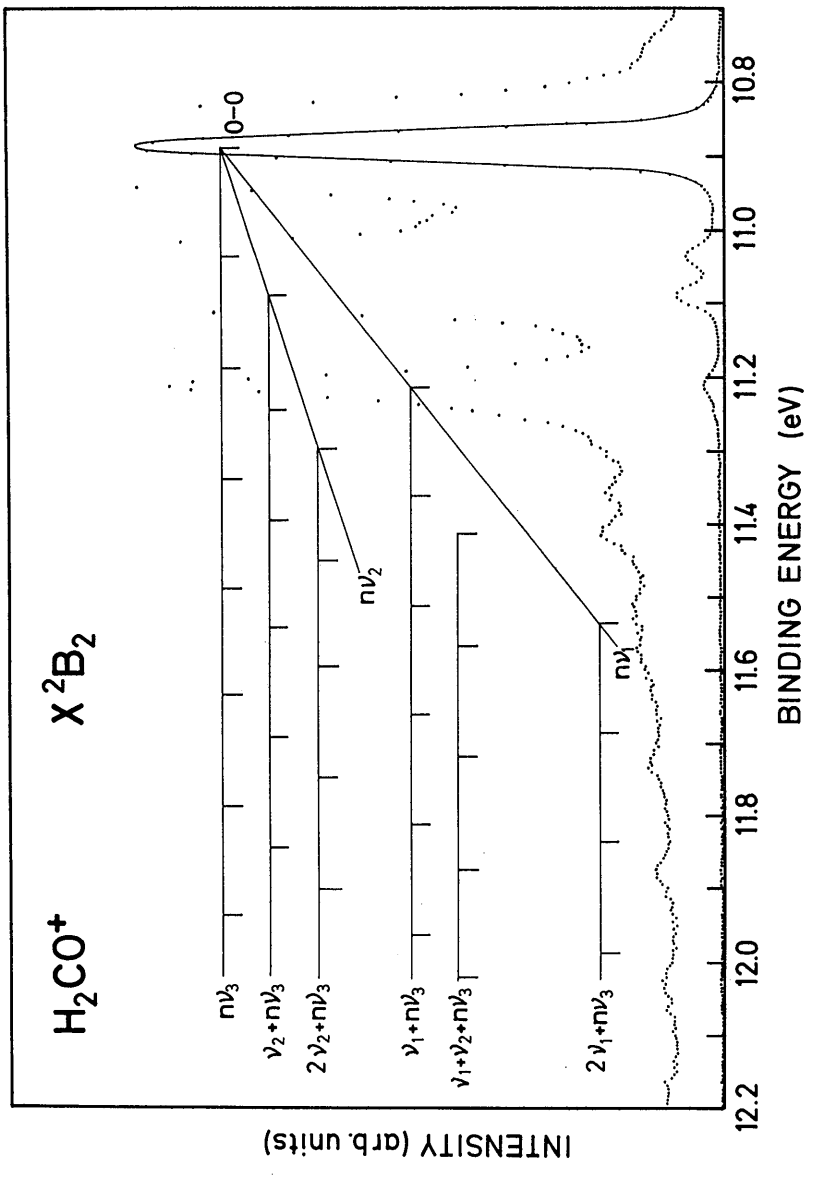

Fig.2. *A detail of the first photoelectron band of formaldehyde recorded between 10.7 and 12.2 eV. The bar diagram indicates the vibrational assignments. The strongest progressions are assigned as* $\nu_1+n\nu_3$ *and* $\nu_1+\nu_2+n\nu_3$.

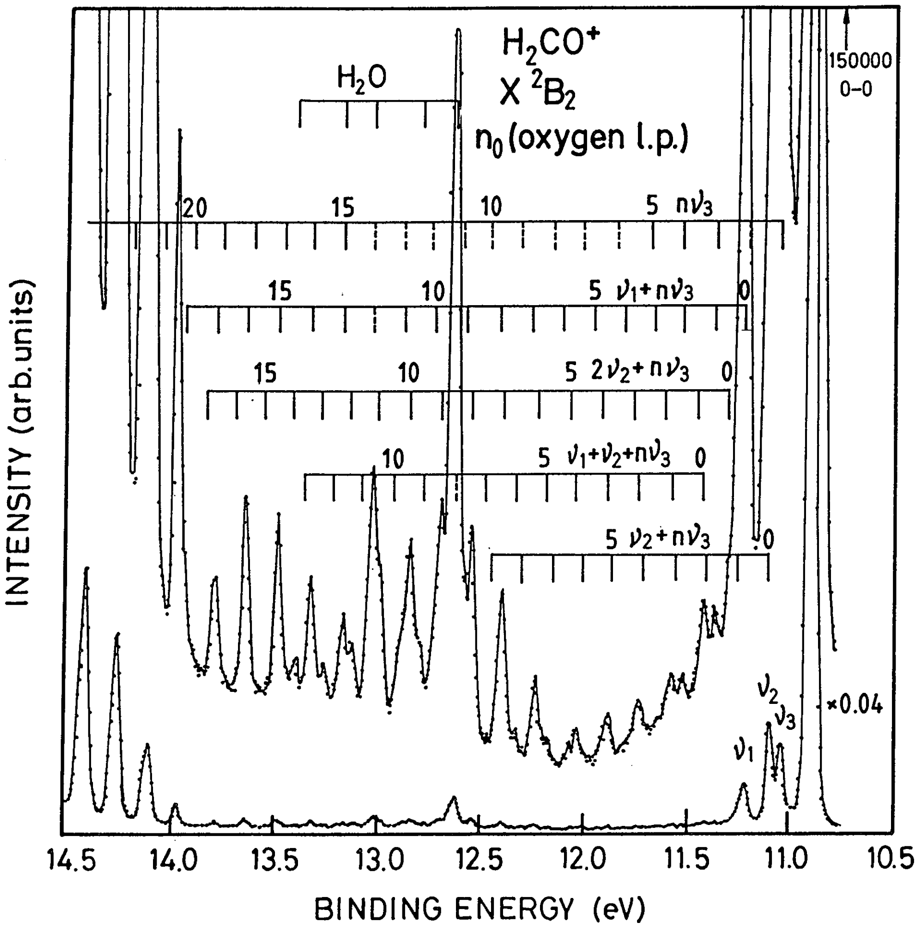

Fig.3. *A detail of the formaldehyde photoelectron spectrum in the region between 10.7 eV and 14.5 eV. The weak extended vibrational structure of the X state and the first part of the A state are exhibited.*

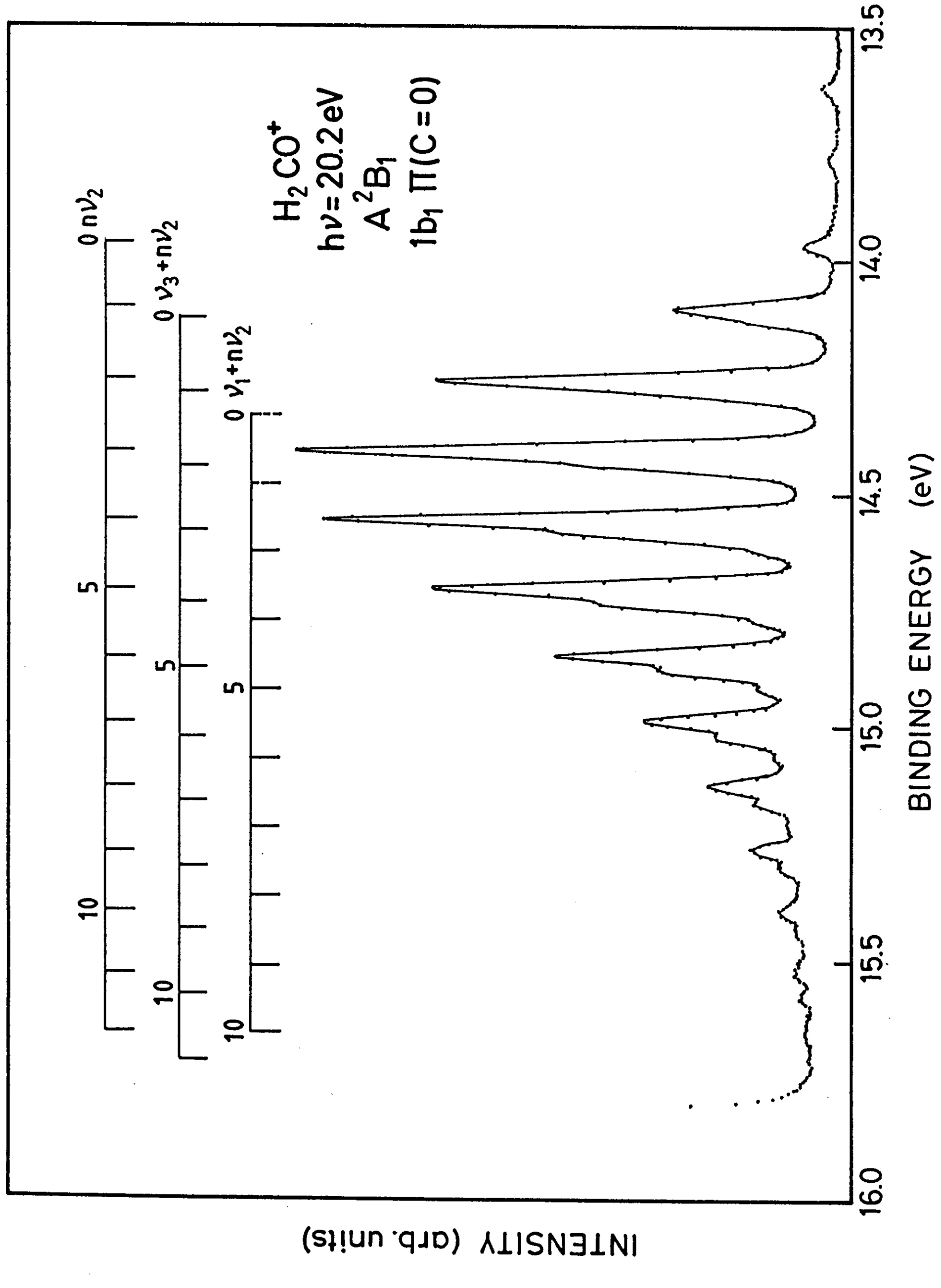

Fig.4. *The second photoelectron band of formaldehyde corresponding to transitions to the A $^2B_1$ ionic state. Vibrational assignments are indicated by the bar diagram in terms of the v_2 and v_3 modes.*

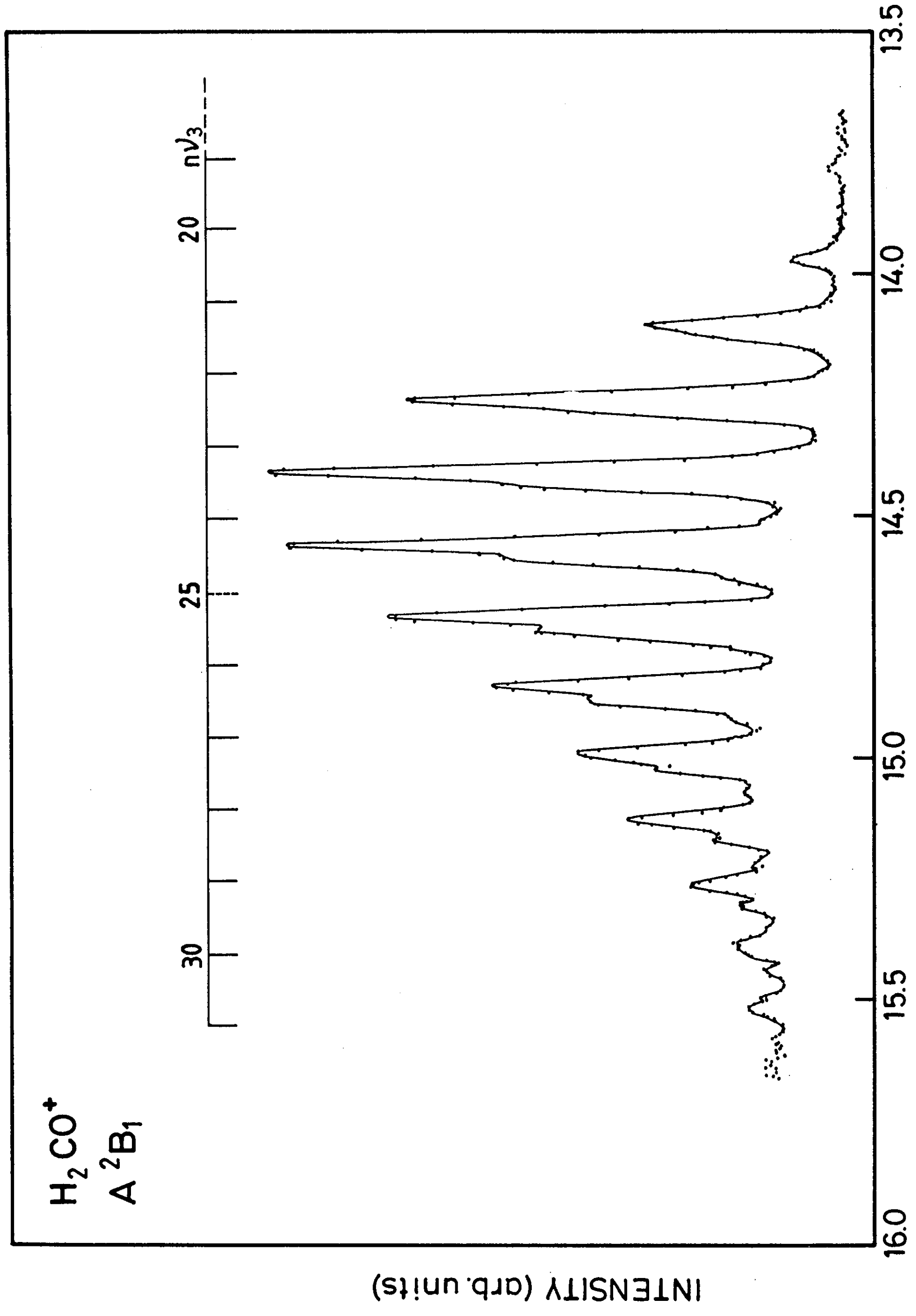

Fig.5. *The second photoelectron band of formaldehyde with vibrational assignments related to excitations of the* ν_3 *mode in the X state.*