The Carbonyl π-Ionization Potential of Formaldehyde

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ELECTRON-IMPACT experiments[1] have given the values 10·8, 11·8, and 13·1 ev respectively for the first three ionization potentials for formaldehyde. Numerous other determinations by spectroscopic and photoionization methods[2] also lead to values of 10·86—10·88 ev for the first ionization potential and this undoubtedly corresponds to the removal of a nonbonding electron mainly localised on the oxygen atom. The value 11·8 ev has been ascribed to the removal of a C=O π-electron, and appears widely in discussions of, for example, the electronic structure of formaldehyde and the conjugation that may occur between the carbonyl group and the carbon–carbon double bond.

Molecular photoelectron spectroscopy shows that neither of these higher values (11·8, 13·1 ev) can be true ionization potentials and gives the lowest value of the second ionization potential (adiabatic) as 13·99 ev. The photoelectron spectrum obtained with a retarding grid electron-velocity analyser[3] showed, in all, five bands giving the five adiabatic ionization potentials 10·8, 13·99, 15·86, 16·6, and 20·5 ev. Signs of vibrational structure in the third band lead us to speculate that this might be due to loss of a π-electron since only this ionization would be expected to excite mainly the C=O stretching vibration (ν_2) free from deformation and C–H stretching modes. With the higher resolution of a 180° magnetic velocity analyser (described in ref. 4) this conclusion was apparently confirmed. The present study using a 127° electrostatic

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velocity analyser* also showed that whilst vibrational structure could be resolved in the three highest energy bands (Figures 1 and 2) only in the third (vertical I.P. 16·0 ev) did it consist of an apparently single vibrational series of narrow lines with $\nu \sim 0{\cdot}15$ ev.

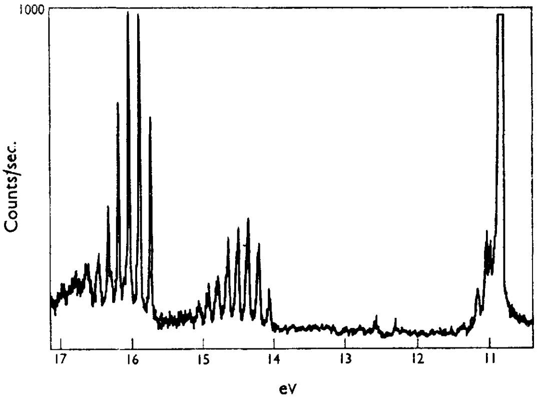

FIGURE 1. *Photoelectron energy spectrum excited in formaldehyde vapour by helium 584 Å radiation* ($h\nu$ = 21·21 ev). *Abscissa, ionization potential* (21·21 ev — *electron kinetic energy*). *Ordinate, electron flux* (*counts/sec.*).

Examination of the spectrum of a sample of deuteroformaldehyde (Figure 3), (kindly provided by Dr. J. H. Callomon) has shown this simplicity to be the result of an accidental equality between two vibrational modes one of which suffers on deuteration a decrease in frequency ($0{\cdot}147 \rightarrow 0{\cdot}110$ ev) whilst the other is unaffected. They probably correspond to the CH_2 deformation (ν_3) and the C–O stretching modes (ν_2) which in the H_2CO molecule have the values 0·186 and 0·216 ev, respectively. Both vibrational modes being strongly excited, we must infer the loss of an electron from an orbital which as well as having C–O bonding character also extends to the hydrogen atoms and is thus probably the C–O σ-orbital. In contrast, the second band (vertical I.P. 14·4 ev) shows little alteration as between formaldehyde and deuteroformaldehyde and can be analysed in terms of a progression ($\nu \sim 0{\cdot}15$ ev) of doublets (second component weak) in which only the doublet spacing alters on deuteration ($0{\cdot}16 \rightarrow 0{\cdot}13$ ev). We conclude that it is this band that corresponds to π-electron removal since only the C–O stretching mode is strongly excited and that whilst a change in C–O bond length and force constant occurs, there is little change in the C–H bonding.

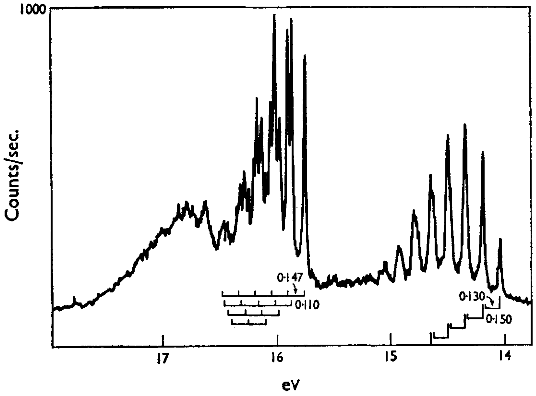

FIGURE 2. *A portion of the photoelectron spectrum of formaldehyde* (*see Figure* 1) *recorded more slowly with a longer integration time.*

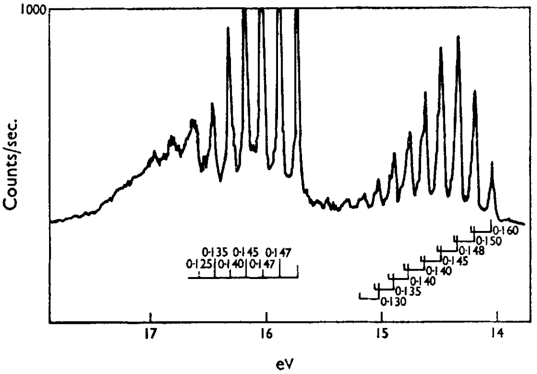

FIGURE 3. *Photoelectron energy spectrum excited in deuteroformaldehyde vapour by helium* 584 *Å radiation* ($h\nu$ = 21·21 ev). *Abscissa, ionization potential* (21·21 ev — *electron kinetic energy*). *Ordinate, Electron flux* (*counts/sec.*)

Calculated eigenvalues for the various molecular orbitals of formaldehyde have varied widely as the degree of refinement of the computation improved. The present results accord well with the most recent calculations by Newton and Palke[8] as shown in the summary of experimental results and calculations given in the Table.

TABLE

"Vertical" ionization potentials (I.P.) *and eigenvalues* (ϵ) *for formaldehyde*

		I.P. (ev)				ϵ (ev)			Location of electron
Method	S[9]	P.I.[2]	E.I.[10]	P.S.*	ref. 5	ref. 6	ref. 7	ref. 8	
	10·88	10·87	10·8	10·86	10·2	11·5	10·95	10·76	O:
			11·8	14·4	12·8	15·1	15·28	13·54	C–O π
			13·1	16·0	15·5	21·9	14·44	16·16	CH σ
				16·9		19·2	16·73	18·40	$C-O_2$
				~21		22·1	20·92	22·62	CH_2

* Present results.

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[1] T. M. Sugden and W. C. Price, *Trans. Faraday Soc.*, 1948, **44**, 116.
[2] R. W. Kiser "Tables of Ionization Potential Data", U.S. Atomic Energy Commission Publication, 1960.
[3] D. W. Turner and D. P. May unpublished work; D. P. May Ph.D. Thesis, London University 1966.
[4] D. W. Turner and D. P. May, *J. Chem. Phys.*, 1966, **45**, 471.
[5] J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, 1960, **32**, 303.
[6] P. J. Goodfriend, F. W. Biss, and A. B. Duncan, *Rev. Mod. Phys.*, 1960, **32**, 307.
[7] D. G. Carrol, L. G. Vanquickenborn, and S. P. McGlynn, *J. Chem. Phys.*, 1966, **44**, 2779.
[8] M. D. Newton and W. E. Palke, *J. Chem. Phys.*, 1966, **45**, 2329.
[9] W. C. Price, *Chem. Rev.*, 1947, **41**, 257.
[10] T. M. Sugden and W. C. Price, *Trans. Faraday Soc.*, 1948, **44**, 116.