The Photoelectron Spectrum and Ionisation Potentials of Carbon Suboxide

By C. BAKER and D. W. TURNER*

(*Physical Chemistry Laboratory, South Parks Road, Oxford*)

HERE we describe the 548 Å photoelectron spectrum of carbon suboxide, C_3O_2, obtained using the 127° electron velocity analyser described elsewhere.[1] The photoionisation of C_3O_2 has previously been studied by Kim and Roebber,[2] who reported a value of 10·60 ev for the first ionisation potential (I.P.). This result agreed exactly with the value obtained from the convergence of Rydberg series.[2,3] Two, and possibly up to four, series were obtained[3] leading to the first ionisation potential. None could be seen leading to higher ionisation potentials.

The highest energy band in the photoelectron spectrum (Figure) shows some indication of vibrational fine structure. The $0 \leftarrow 0$ vibrational component of this band corresponds to an I.P. of 10·60 ev, in exact agreement with previous results. The vibrational structure can be analysed in terms of excitation of vibrations of frequencies 1950 and 660 cm.$^{-1}$. These may correspond to ν_1', the symmetric C–O, and ν_2', the symmetric C–C, stretching frequencies, respectively (2200 and 830 cm.$^{-1}$ in the molecule).[4]

TABLE

The ionisation potentials of C_3O_2 measured from the photoelectron spectrum.

I.P.$_1$	10·60 ev	(adiabatic)
I.P.$_2$	14·45 ev	(,,)
I.P.$_3$	15·68 ev	(,,)
I.P.$_4$	16·98 ev	(,,)
I.P.$_5$	~19 ev	(measured in centre of broad band)
Alternatively (*see text*)		
I.P.$_5$	17·25 ev	(adiabatic)
I.P.$_6$	~19 ev	

The second band, adiabatic I.P. 14·45 ev, consists of four partly resolved vibrational peaks superimposed on a broad continuum. The separation of the peaks [0·08(7) ev] corresponds to a vibrational frequency of *ca.* 700 cm.$^{-1}$ (possibly ν_2'). The third band, adiabatic I.P. 15·68 ev, shows a similar partially resolved fine structure with a separation of 0·08(0) ev, corresponding to a vibrational frequency of 650 cm.$^{-1}$.

The fourth band admits of no simple analysis. The two strong peaks (I.P. 16·98, 17·25 ev) could be the first two members of a progression in ν_1' but the higher members of appropriate intensity are absent. If their absence is not due to the sudden onset of dissociative broadening, we must assign the two peaks to electrons from separate, weakly bonding orbitals, and the shoulder near 17·6 ev to a third, more strongly bonding orbital. The diffuse band between 18 and 21 ev indicates the presence of one or more strongly bonding occupied orbitals within this energy range The ionisation potentials observed are listed in the Table.

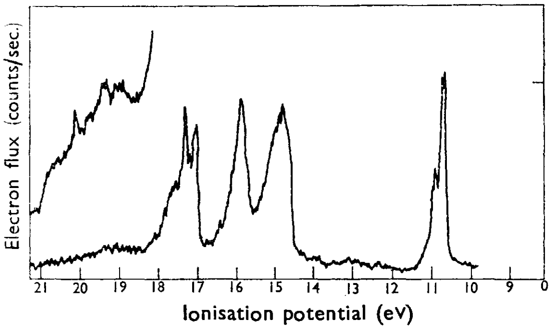

FIGURE. *Photoelectron energy spectrum excited in carbon suboxide vapour by helium* 584 Å *radiation* ($h\nu = 21{\cdot}21$ ev). (Inset, *part of spectrum recorded with increased slit width and recorder ordinate scale*).

The breadth of the few resolved vibrational peaks, and the general lack of resolved fine structure can possibly be explained either by excitation of low frequency bending modes,[5] or particularly in the second and third bands, as a result of the crossing of the potential energy surfaces of the first and second excited states of the ion with those leading to the fragment ions C_2O^+ and C_3O^+ respectively. The appearance potential of C_2O^+ (15·1 ev[6]) coincides with the second band, and that of C_3O^+ (15·9 ev[6]) with the third.

The electronic configuration of the ground state of C_3O_2 may be written as

$$\text{K–K}\ (s\sigma_g)^2(s\sigma_u)^2(s\sigma_g)^2(p\sigma_g)^2(p\sigma_u)^2(p\sigma_u)^2\text{-}\\ (p\pi_u)^4\,(p\pi_g)^4\,(p\pi_u)^4$$

The relative order of the deeper π levels and the highest σ levels cannot be deduced from the photoelectron spectrum. We note however that H.M.O. calculation[3] places the deeper π energies ($1\pi_u$, $1\pi_g$) at $-14{\cdot}8$ and $-15{\cdot}2$ ev, within the second highest energy band of our spectrum, which has approximately twice the integrated area of the first band.

(*Received, February 2nd*, 1968; *Com.* 126.)

---

[1] D. W. Turner, *Proc. Roy. Soc.*, in the press.

[2] H. H. Kim and J. L. Roebber, *J. Chem. Phys.*, 1966, **44**, 1709.

[3] J. L. Roebber, J. C. Larrabee, and R. E. Huffman, *J. Chem. Phys.*, 1967, **46**, 4594.

[4] F. A. Miller and W. G. Fateley, *Spectrochim. Acta*, 1964, **20**, 253.

[5] F. A. Miller, D. H. Lemmon, and R. E. Witowski, *Spectrochim. Acta*, 1965, **21**, 1709.

[6] R. Botter, Adv. Mass Spectrometry Proc. 2nd Conf., 1961 in Oxford, ed. R. M. Elliott, Pergamon, Oxford, 1963, vol. 2, p. 540.