1180. *Molecular Photoelectron Spectroscopy. Part IV.*[1] *The Ionisation Potentials and Configurations of Carbon Dioxide, Carbon Oxysulphide, Carbon Disulphide, and Nitrous Oxide*

By M. I. AL-JOBOURY, D. P. MAY, and D. W. TURNER

The photoelectron spectra excited by 21·21 ev photons in the vapours of carbon dioxide, nitrous oxide, carbon oxysulphide, and carbon disulphide, are described and shown to lead to all the adiabatic ionisation potentials less than 21·21 ev in each case. The bonding character of each orbital concerned is indicated. Comparisons between the spectra suggest correlations between the molecular orbital structures through the series of compounds.

IN Part III [1] of this Series we showed *inter al.*, how the photoelectron spectrum of a series of molecules of closely related electron structures (N_2, NO, O_2) reflected the progressive changes associated with the aufbau process. In the present Paper we show how the technique illuminates the variation of electronic structures through an isoelectronic series. Six valency-shell ionisation potentials are expected for each of these molecules whose ground state configurations may be written (for CO_2, COS, CS_2) *a priori* as: $(\sigma_g)^2{}_{\mathrm{X}}$ $(\sigma_u)^2{}_{\mathrm{X}}$ $(\sigma_g)^2{}_{\mathrm{C-X}}$ $(\sigma_u)^2{}_{\mathrm{C-X}}$ $(\pi_u)^4{}_{\mathrm{C-X}}$ $(\pi_g)^4{}_{\mathrm{C-X}}$, ${}^1\Sigma_g{}^+$, the consequences of the disymmetry present in carbon oxysulphide being neglected for the moment. Whilst there is a general measure of agreement concerning the first ionisation potential for carbon dioxide, carbon disulphide and nitrous oxide (removal of a π_g electron) some of the higher ionisation potentials are less surely based experimentally with large discrepancies between electron impact and spectroscopic values.

Experimental.—Photoelectron spectra were recorded by using the apparatus already described (cf. Part III [1]). Carbon oxysulphide was prepared by the method of Lochte-Holtgreven *et al.*[2] by dropping potassium thiocyanate (concentrated aqueous solution) into warm

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[1] Part III, M. I. Al-Joboury, D. P. May, and D. W. Turner, *J.*, 1965, 616.

[2] W. Lochte-Holtgreven and C. E. H. Bawn, *Trans. Faraday Soc.*, 1932, **28**, 698.

sulphuric acid (50%). The gas was carried in a nitrogen stream through potassium hydroxide solution (33%), animal charcoal, and calcium chloride (anhydrous). It was finally condensed at liquid nitrogen temperature and then stored at room temperature over a mixture of mercury and mercuric oxide. By these procedures CO_2, H_2S, CS_2, H_2O, N_2, and HCN were removed. Samples were further subjected to trap-distillation immediately before examination.

RESULTS AND DISCUSSION

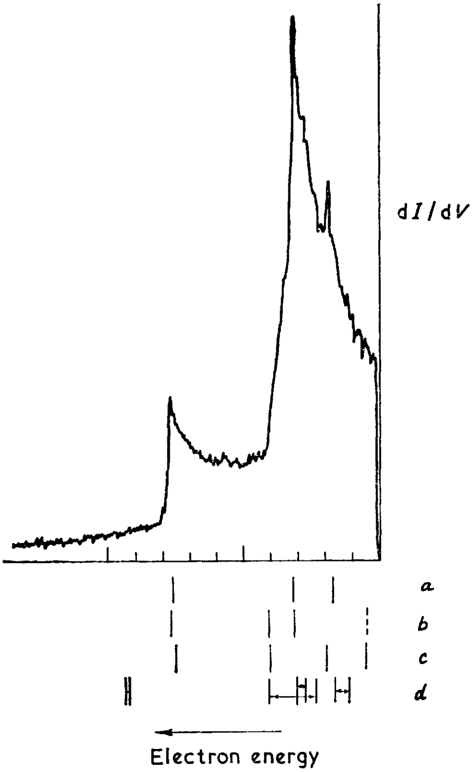

FIGURE 1. Above; the photoelectron spectrum for carbon dioxide (p = 0·025 mm.). Ionisation energy increases from left to right. Electron energy scale marked in 1 ev intervals

Below; alternative estimates of the ionisation potentials from (*a*) Rydberg series (ref. 3), (*b*) emission spectroscopy (ref. 6), (*c*) electron impact (ref. 10), (*d*) theoretical calculation (ref. 9)

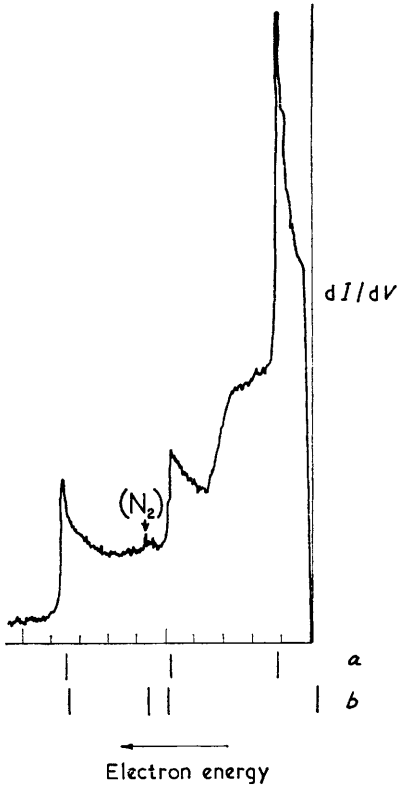

FIGURE 2. Above; the photoelectron spectrum for nitrous oxide (p = 0·028 mm) to the same electron energy scale as Figure 1

Below; alternative estimates of the ionisation potentials from (*a*) Rydberg series (ref. 12), (*b*) electron impact (ref. 15)

Carbon Dioxide.—The photoelectron spectrum excited by helium resonance radiation shows four bands for carbon dioxide (Figure 1) indicating only four ionisation potentials smaller than 21·21 ev. Three Rydberg series have been identified leading to ionisation potentials at 13·78 [3] (or 13·73 [4]) 18·00,[5] and 19·39 [3] ev. Clearly, the same levels give rise to the three sharp peaks in the photoelectron spectrum near 7·5, 3·1, and 1·9 ev the ionisation potentials being 13·68, 18·08, and 19·29, ev. The assignment of the first two to loss of a

[3] Y. Tanaka, A. S. Jursa, and F. J. Le Blanc, *J. Chem. Phys.*, 1960, **32**, 1199.

[4] W. C. Price and D. M. Simpson, *Proc. Roy. Soc.*, 1938, *A*, **169**, 501.

[5] H. J. Henning, *Ann. Physik*, 1932, **13**, 599.

π_g and a σ_u electron, respectively, follows from Mrozowski's study[6] of the emission bands of CO_2^+ where it was shown that the 2900 Å band system connects these two levels. The "adiabatic" first ionisation potential (13·68—13·78 ev) is only a little less than the electron impact value 13·85 ev (vertical ionisation). This is consistent with a very small change in molecular dimensions on ionisation, thus the π_g electrons are only weakly bonding as the shape of the first band in the photoelectron spectrum confirms. The 18·08 ev level also appears to be non-, or only weakly bonding in agreement with spectroscopic data for the $^2\Sigma_u^+$ state of CO_2^+ which has an internuclear separation only 0·018 Å greater than that in the ground state of carbon dioxide. On the basis of the photoelectron spectrum the 19·29 ev level is also non-bonding so that these last two which are undoubtedly σ orbitals may better be ascribed to the oxygen "lone pair" electron than to C–O bond orbitals as implied by the *a priori* configuration. This would be confirmed if the two deepest levels proved to be more strongly C–O bonding, some support for which comes from the structures of carbon oxysulphide and disulphide (see later).

There is a rather strong evidence for a Π_u state of CO_2^+ 3·54 ev above the ground state (*i.e.*, at 17·32 ev) from the work of Mrozowski[6] but this level remains unidentified with a Rydberg series. Also Mulliken[7] has predicted an ionisation potential somewhat above 17·1 ev for the π_u electrons and he further pointed out that this is a strongly bonding level. In our spectrum a broad band starts near 4 ev giving an "adiabatic" ionisation potential of 17·27 ev for what is clearly the most strongly bonding electron of all.

The experimental and theoretical (Koopmans' theorem being accepted) values for the first four ionisation potentials obtained by alternative methods[3,6,7-10] are summarised as an energy level diagram to the same energy scale as the spectrum in Figure 1, the zero on the electron energy scale corresponding to an ionisation potential of 21·21 ev. Similar presentations of comparative data are made in Figures 2—4 in respect of nitrous oxide, carbon oxysulphide,[11] and carbon disulphide.

Nitrous Oxide.—The first ionisation potential, measured from Rydberg series[12] is 12·82 ev which is close to the electron impact value 12·9 ± 0·5 ev observed by Smyth and Stueckelberg[13] and the photoionisation threshold 12·83 ± 0·07 ev measured by Walker and Weissler.[14] A non-bonding electron is thus indicated in agreement with the appearance (Figure 2) of the first peak in the photoelectron spectrum near 8·4 ev (12·82 ev). The second peak in the photoelectron spectrum near 4·8 ev (ionisation potential = 16·37 ev) is also clearly associated with a weakly bonding electron, and this value is in excellent agreement with the limit of several Rydberg series observed by Tanaka *et al.*[12] (16·39 ev). The next broad band (near 3·5 ev) leads to an ionisation potential of 17·67 ev apparently associated with a strongly bonding electron. This ionisation potential has not previously been observed by absorption spectroscopy or electron impact[15] and presumably is analogous to the $^2\pi_u$ level of CO_2^+ being difficult to observe on account of the weakness of the $0 \longleftarrow 0$ transition. The last sharp peak (~1 ev) gives an ionisation potential of 20·10 ev for another apparently weakly bonding electron. This value is the convergence limit given by Tanaka *et al.*[12] for four Rydberg series. No series converged to a vibrationally excited state of this ion but there is some indication of vibrational structure on the last peak of the photoelectron spectrum, in a shoulder which might correspond to the $\nu(1) \longleftarrow \nu(0)$ transition. The separation is 0·18 ± 0·02 ev (1300—1600 $cm.^{-1}$) which is similar in magnitude to the

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[6] S. Mrozowski, *Rev. Modern Phys.*, 1942, **14**, 216; *Phys. Rev.*, 1941, **60**, 730; 1942, **62**, 270; 1947, **72**, 682.

[7] R. S. Mulliken, *Rev. Modern Phys.*, 1942, **14**, 204.

[8] J. F. Mulligan, *J. Chem. Phys.*, 1951, **19**, 347.

[9] A. D. McClean, *J. Chem. Phys.*, 1963, **38**, 1347.

[10] J. Collin, *J. Chim. phys.*, 1960, **57**, 416, 424.

[11] E. Clementi, *J. Chem. Phys.*, 1962, **36**, 750.

[12] Ref. 3, p. 1205.

[13] H. D. Smyth and E. C. G. Stueckelberg, *Phys. Rev.*, 1930, **36**, 1205.

[14] W. C. Walker and G. L. Weissler, *J. Chem. Phys.*, 1955, **23**, 1962.

[15] R. K. Curran and R. E. Fox, *J. Chem. Phys.*, 1961, **34**, 1590.

symmetrical stretching vibration of the molecule (1285 cm.$^{-1}$) expected for ionisation of a non-bonding electron. It is in any case considerably smaller than the unsymmetrical vibrational frequency (2224 cm.$^{-1}$) which would be most likely to be excited by removal of a N–O or N–N bonding electron.

Carbon Oxysulphide.—The photoelectron spectrum (Figure 3) is remarkably similar in form to that of carbon dioxide (Figure 1) but with all spectral features moved some 2 ev to higher electron energies. In addition a fifth band has appeared at low electron energies. The highest energy peak leads to a first ionisation potential in close agreement with the photoionisation [16] value 11·17 ev and also with the Rydberg series limit of 11·23 ev tentatively assigned by Tanaka.[12] The great similarity between the two spectra suggests giving the same order of assignments so that the first four levels in carbon oxysulphide have ionisation potentials and assignments 11·06 (π_g, $O \leftrightarrow C{-}S$); 15·04 (π_u, O–C–S); 16·04 (σ_u, S:), 17·87 (σ_g, O:) ev. In addition we tentatively assign the extra level (19·9 ev) to σ_u (C–S). This order in which lone-pair orbital energies are higher than the corresponding σ bond orbitals seems to account best for the present results and is in accord with the results of calculations of the carbon oxysulphide molecule by Clementi.[11] The two ionisation potentials for weakly bonding levels at 16·04 and 17·87 ev are confirmed by Rydberg series [12] whereas the 19·9 ev value is not, which is consistent with the assignment of the

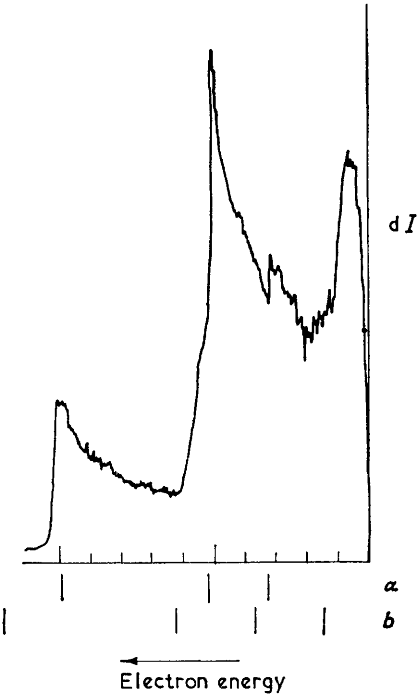

FIGURE 3. Above; the photoelectron spectrum for carbon oxysulphide (p = 0·011 mm.). Electron energy scale as Figure 1

Below; alternative estimates of the ionisation potentials from (*a*) Rydberg series (ref. 12), (*b*) theoretical calculation (ref. 11)

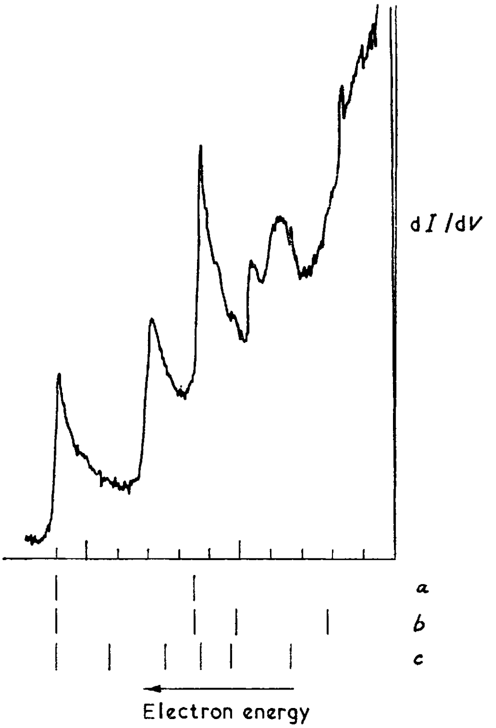

FIGURE 4. Above; the photoelectron spectrum for carbon disulphide (p = 0·013 mm.). Electron energy scale as Figure 1.

Below; alternative estimates of the ionisation potentials from (*a*) emission spectroscopy (ref. 17), (*b*) Rydberg series (ref. 12), (*c*) electron impact (ref. 10)

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[16] K. Watanabe, *J. Quant. Spectr. Radiactive Transfer*, 1962, **2**, 369.

latter rather than either of the first two to a bonding orbital. The second and fifth ionisation potentials are reported here for the first time.

Carbon Disulphide.—It seems probable that in carbon disulphide all the valency-shell orbital energies may lie above 21·21 ev, and six ionisation potentials should be observed in this range. In Part II we reported seven values one of which was regarded as doubtful. Collin [10] has extracted six ionisation potentials from electron-impact studies but of these only three (including the first) agree at all closely with spectroscopic values.[12, 17] These are the first, third, and fourth ionisation potentials according to the photoelectron energy spectrum (Figure 4). These appear to relate to non-bonding orbitals which for the third ionisation potential is confirmed as in the case of carbon dioxide by its assignment on spectroscopic grounds,[17] to the $^2\Sigma_u{}^+$, state of the ion with an internuclear separation increase of only 0·0099 Å compared with the molecule. As also in the case of carbon dioxide and carbon oxysulphide the more strongly bonding orbitals (ionisation potential 12·57, 16·64 ev) have not given sufficiently strong $0 \leftarrow 0$ Rydberg series for detection in the rather complex absorption spectra. The first five adiabatic ionisation potentials (10·06, 12·57, 14·46, 16·02 and 16·64 ev, respectively) can be derived with some confidence from the photoelectron energy spectrum, but the location of the sixth and last is less certain. Between 0 and 3 ev the broad band which underlies a small peak near 2 ev (ionisation potential 19·05) could represent a strongly-bonding or anti-bonding energy level whose adiabatic ionisation was near 18 ev. Tanaka *et al.*[12] have detected a weak Rydberg series leading to an ionisation potential of 19·5 ev close to the value for the sharp peak in the photoelectron spectrum. It seems improbable that the series is associated with a strongly bonding electron and it appears that the level concerned is the deepest of the six, $(\sigma_g)^2{}_{\text{C–S}}$, and is not strongly bonding. The broad band may be associated with electrons scattered at the first grid.

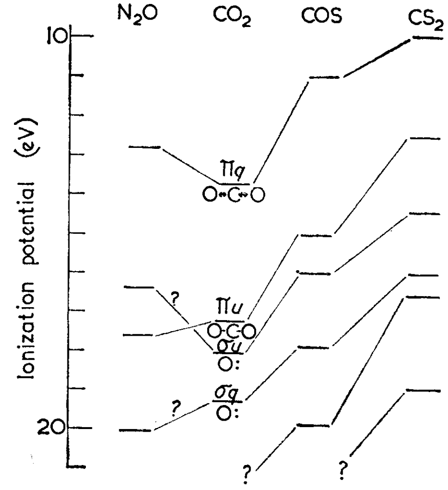

FIGURE 5. Electron energy level diagram for nitrous oxide, carbon dioxide, carbon oxysulphide, and carbon disulphide using the adiabatic ionisation potentials measured by photoelectron spectroscopy (see text). The correlations are based on the shapes of the bands in the photoelectron spectra

Correlations between Energy Levels.—Now that the energies of all the levels above 21·21 ev are measured, we can attempt to correlate orbital types on an experimental basis, using the appearance of the photoelectron spectra as a guide. The similarities are traced in the energy level diagram shown in Figure 5. The emission spectrum of $CO_2{}^+$ identifies the ground state of the ion as $^2\Pi_g$ and what we now see as its first two excited states as $^2\Pi_u$ and $^2\Sigma_u{}^+$, respectively. From the similarities in the photoelectron spectra and from the general absence of Rydberg series for the second level (indicating large bonding character) the first three levels in carbon oxysulphide and disulphide correspond in order to the first

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[17] J. M. Callomon, *Proc. Roy. Soc.*, 1958, *A*, **244**, 220.

three in carbon dioxide. That the π_u level is apparently less bonding in carbon disulphide can be associated with poor overlap between carbon 2*p* and sulphur 3*p* orbitals.

The third and fourth levels correspond to known Σ states of the CO_2^+ ion, $^2\Sigma_u^+$ (definitely) and $^2\Sigma_g^+$ (inferred by Mrozowski [6] to lie near 20·9 ev). We know from the photoelectron spectrum and from the small difference in vibrational frequency between CO_2 in its ground state and $^2\Sigma_u^+$ state of CO_2^+ that non-bonding orbitals are involved and thus that these must approximate to lone-pair orbitals largely confined to the terminal atoms, mainly $(2S_O + 2S_O)\ \sigma_g$, $(2S_O - 2S_O)\ \sigma_u$. The remaining two levels should then be C–O or C–S bonding and this seems to be confirmed since the band near 1·3 v in carbon oxysulphide (ionisation potential 19·9 ev) which is additional to those already seen in carbon dioxide and which appears near 4·6 v (ionisation potential 16·64 ev) in carbon disulphide is clearly broader than the two immediately higher in energy.

In nitrous oxide as in carbon dioxide four of the six expected ionisation potentials are less than 21·21 ev but the arrangement of the levels clearly differs, the order of the second and third being inverted. The present results suggest that this is due mainly to the increase in the energy of the higher lone-pair orbital in carbon dioxide to give one mainly localised on the terminal nitrogen atom whilst the lower orbital which remains localised on oxygen is affected to a less extent. The bonding π orbital which is non-localised would not be expected to be so sensitive to the nuclear charge redistribution and it is seen to change only slightly to lower energies.

We conclude that CO_2, COS, and CS_2 are better described by the configurations:

$$(\sigma_g)_{\text{C–O(S)}}\ (\sigma_u)^2_{\text{C–O(S)}}\ (\sigma_g)^2_{\text{O(S)}}\ (\sigma_u)^2_{\text{O(S)}}\ (\pi_u)^4\ (\pi_g)^4$$

and N_2O by:

$$(\sigma)^2_{\text{N–O}}\ (\sigma)^2_{\text{N–N}}\ (\sigma)^2_{\text{O:}}\ (\pi_u)^4\ (\sigma)^2_{\text{N:}}\ (\pi_g)^4$$

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