99. *Molecular Photoelectron Spectroscopy. Part III.*[1] *The Ionization Potentials of Oxygen, Carbon Monoxide, Nitric Oxide, and Acetylene.*

By M. I. Al-Joboury, D. P. May, and D. W. Turner.

Bands in the photoelectron spectrum of oxygen gas are ascribed to the four highest occupied molecular-orbital energy levels of oxygen. Vibration in the resulting positive ion in each case leads to a succession of subsidiary peaks within each band. $0 \longleftarrow 0$ Peaks can be identified, and the four resultant adiabatic ionization potentials are compared with values from other sources. Vertical ionization potentials are estimated from the intensity relationships within each group, and the magnitudes of the vibrational quanta are measured. Similar interpretations are made of the spectra of nitric oxide, carbon monoxide, and acetylene.

The ionization and dissociation of oxygen under photon and electron impact has been the subject of a number of detailed studies.[2] Considerable interest is attached to these processes, because of their relevance to solar photon absorption in the upper atmosphere, to chemical kinetics, and to the central place of oxygen in thermochemistry.

In its ground state, the oxygen molecule has the configuration

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2\ (^3\Sigma_g{}^-)$$

The valence-shell electrons with binding energies of up to *ca.* 30 ev occupy five different energy levels, and five ionization potentials should relate to the removal of one electron in turn from each level. The first ionization potential will correspond to the removal of one of the $\pi_g 2p$ electrons, which have parallel spins, and will lead to doublet $O_2{}^+$ ($^2\Pi_g$), a reduction of one in the number of unpaired spins. The four higher ionization potentials correspond to an increase in the number of unpaired spins from two to three, leading to the quadruplet excited states of $O_2{}^+$, $^4\Pi_u$, $^4\Sigma_g$, $^4\Sigma_u$, $^4\Sigma_g$, in order of increasing energy. In addition, four different higher ionization potentials are expected, corresponding to the doublet excited states $^2\Pi_u$, $^2\Sigma_g$, $^2\Sigma_u$, $^2\Sigma_g$, in which the electron left in the deeper level has a spin antiparallel to those in the highest levels, instead of parallel as in the quadruplet states. If the energy of each two-electron molecular orbital is to be related to an ionization potential, we may here select the quadruplet state of the particular configuration of the ion, which is its ground state (Hund's rule), and regard the doublet as an excited state (see below) of this configuration and hence less relevant as a measure of orbital energy in the parent molecule.

Two of these excited states of $O_2{}^+$ and one additional one, $^2\Pi_u$, are known from the band spectra of $O_2{}^+$.[3] The first negative system ($^4\Sigma_g{}^- \longrightarrow {}^4\Pi_u$) gives the difference between the second and fourth levels, and the absolute energies of both have been derived from the convergence limits of Rydberg series.[2b] The first ionization potential has been found by photoionization-yield measurements,[4] but no Rydberg series confirms it. Thus, the energies of three of the orbital energy levels are, for the most part, well known spectroscopically, and a fourth (20·3 ev), undesignated as yet, has been detected from a few numbers of an apparent Rydberg series between 610 and 650 Å.[2b]

Electron-impact studies [2a] have indicated the presence of up to four excited states of $O_2{}^+$. One of these, however, at 17·18 ev, appears to correspond to $^2\Pi_u$, since the energy difference between this level and the ground state of $O_2{}^+$ (5·11 ev) is close to the excitation energy $^2\Pi_g \longrightarrow {}^2\Pi_u$, known from the second negative-band system of $O_2{}^+$.

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[1] Part II, Al-Joboury and Turner, *J.*, 1964, 4434.

[2] See, for example (*a*) Frost and McDowell, *J. Amer. Chem. Soc.*, 1958, **80**, 6183; (*b*) Huffman, Tanaka, and Larrabee, *J. Chem. Phys.*, 1964, **40**, 356; (*c*) Schoen, *ibid.*, p. 1830.

[3] Herzberg, " Spectra of Diatomic Molecules," Van Nostrand, New York, 1950, p. 560.

[4] Watanabe, *J. Chem. Phys.*, 1957, **26**, 542.

The only vibrational parameters for the ion which are known with precision are those for the states which appear in the emission band spectra ($^2\Pi_g$, $^4\Pi_u$, $^2\Pi_u$, $^4\Sigma_g^-$).

Three pairs of single vibrational-quanta spacings ($n = 3, 4, 5$) have been identified in the Rydberg series leading to the 20·3-ev ionization potential,[2b] but the spectrum appears to be considerably more complex, and this state is not yet as well characterized as are the others.

The ground-state configuration of nitric oxide is $KK(\sigma_g2s)^2(\sigma_u2s)^2(\sigma_g2p)^2(\pi_u2p)^4(\pi_g2p)^1$, and would be expected to lead to a very similar electron-energy spectrum to that given by oxygen. Carbon monoxide has the same configuration as nitrogen, and the electron-energy spectrum should resemble the nitrogen spectrum closely; acetylene, which also has ten valence-shell electrons, would be expected to show some similarities. We have measured the photoelectron spectra of these gases, using the helium resonance line (21·21 ev) as the excitation source (cf. Parts I [5] and II [1] of this series), in order to determine, in each case, the number of occupied levels lying above 21·21 ev and their bonding characters.

Experimental.—The spectra were recorded, using the apparatus described in Part I; [5] calibration was effected with a digital voltmeter (DM. 2001 Mk. 2), instead of with the moving-coil voltmeter.

RESULTS AND DISCUSSION

Oxygen.—The spectrum (Fig. 1) shows only four bands, all of which are clearly composite, *i.e.*, are composed of overlapping groups of peaks. Starting from the left-hand, high-electron-energy side of Fig. 1, the first band corresponds to the first ionization potential, removal of a π_g2p electron to give O_2^+ ($^2\Pi_g$). Five subsidiary peaks can be discerned, and if the first is assigned to the $v'(0) \leftarrow v(0)$ transition, the value 12·10 ev is obtained for the first adiabatic ionization potential, agreeing well with Watanabe's value of 12·075 ev.[4] The subsequent peaks then correspond to the $v'(1) \leftarrow v(0)$, $v'(2) \leftarrow v(0)$, $v'(3) \leftarrow v(0)$, and $v'(4) \leftarrow v(0)$ transitions. The mean spacing over the 5 peaks is 0·21 ev, which agrees with the optical-spectroscopic mean value, 0·22 ev, within the limits of our measurement. From the relative heights of the peaks, the vertical ionization should occur near the $v'(1) \leftarrow v(0)$ peaks. This vertical ionization potential (12·32 ev) is slightly higher than the electron-impact value (12·21 ± 0·04 ev) obtained by Frost and McDowell.[2a]

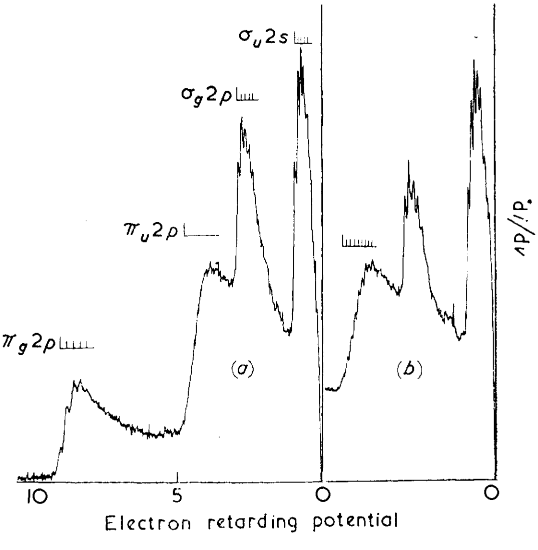

FIG. 1. Photoelectron spectrum for oxygen (p = 0·02 mm.). Ionization energy increases from left to right. Electron-collecting potential-difference (*a*) 12 v, (*b*) 2 v.

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[5] Part I, Al-Joboury and Turner, *J.*, 1963, 5141.

When the collecting potential difference [G_2–P (see Part I[5])] was reduced to 2v, to lessen unsymmetrical field-penetration through G_2 at low retarding potential differences, the second band consisted of at least nine distinct steps or peaks [Fig. 1(*b*)]; the first appears at an ionization potential of 16·26 ev and the ninth at 17·16 ev. The former value is close to the optical-spectroscopic value of 16·11 ev,[3] and can only correspond to the $^4\Pi_u$ state of O_2^+, a $\pi_u 2p$ electron having been removed in the process. The mean vibrational spacing over the nine peaks is 0·11(3) ev, which is in agreement with the corresponding spectroscopic value of 0·11(7) ev.[3] The difference between the spectroscopic ionization potential of 16·11 ev and the ionization potential of 16·26 ev corresponding to the first peak, together with the spectroscopic value of 0·12(7) ev for the first vibrational quantum, strongly suggests that the first distinct peak relates to the $v'(1) \longleftarrow v(0)$ transition and that, for some reason, the peak corresponding to the $v'(0) \longleftarrow v(0)$ transition is not readily apparent. The intensity of the peaks and the shape of the band indicate that the vertical ionization potential should lie close to the peak corresponding to the $v'(4) \longleftarrow v(0)$ transition. This gives a value of 16·6 ev, which is rather higher than the electron-impact value of 16·30 ± 0·03.[2a] The form of electron-energy spectrum suggests that the difference between the vertical and adiabatic ionization potentials is about 0·5 ev, which is larger than for the other three bands. This is consistent with the removal of one of the most strongly bonding electrons. A large change of internuclear distance, 1·20739 Å ⟶ 1·38126 Å, accompanies this ionization.

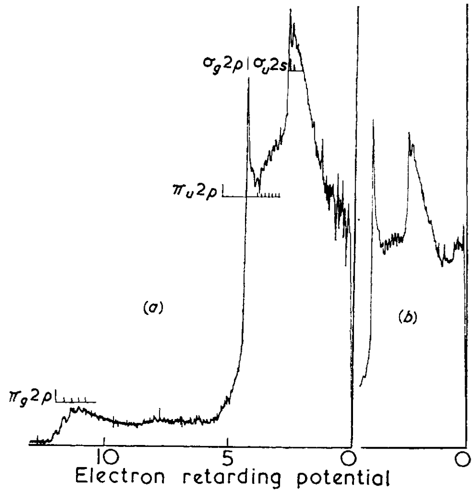

FIG. 2. Photoelectron spectrum for nitric oxide (p = 0·02 mm.). Ionization energy increases from left to right. Electron-collecting potential difference (*a*) 14 v, (*b*) 2 v.

The third band is clearly resolved into vibrational components; the first, assumed to be the $v'(0) \longleftarrow v(0)$ ionization, gives an ionization potential of 18·18 ev, close to the optical-spectroscopic value of 18·16 ev,[2b] thus confirming its assignment to the $^4\Sigma_g^-$ state of O_2^+. The mean vibrational spacing over the five subsidiary peaks is 0·13(7) ev, which agrees with the spectroscopic mean value of 0·13(8) ev.[3]

The fourth band shows five sharply defined peaks; the first, giving an ionization potential of 20·31 ev, is taken to be the $v'(0) \longleftarrow v(0)$ transition, and corresponds well with the value of 20·30(8) for the, as yet unclassified, state designated " x " by Huffman *et al.*[2b] The fifth peak, corresponding to the $v'(4) \longleftarrow v(0)$ transition, appears at 20·80 ev. This gives a mean vibrational spacing, over the first 5 peaks, of 0·12(3), which is to be compared with an estimate of 0·13 ev derived from the data of Huffman *et al.* The estimate refers to the mean spacing over the 3 peaks designated $x5_0$, $x5_1$, and $x5_2$, which occur at 19·7(9), 19·9(4), and 20·0(6) ev, respectively.

Nitric Oxide.—Four of the expected groups of electrons are indicated in the photoelectron spectrum [Fig. 2(*a*)]. The first and second groups give rise to broad bands, the third to a single sharp line, and the fourth is intermediate in character. Vibrational structure is most clearly resolved in the first and fourth bands, and some indication of such structure has also been found in the second, broadest band [Fig. 2(*b*)].

The first band is partially resolved into separate peaks; the first leads to an adiabatic ionization potential of 9·23 ev, close to the spectroscopic value of 9·26 ev.[6] Similar values (9·25 ev) have been obtained by means of photoionization-yield measurements.[7] The mean spacing of the first four peaks (0·29 ev) agrees with the spectroscopic value (0·29 ev) for the vibrational quantum of the ground state of NO^+. Steps have also been observed in the photoionization-yield curve,[7] with a separation of 0·30 ev, and have been ascribed to this vibration.

Although the second broad band is interrupted by a sharp, strong peak (see below), it appears to start at 5·8 v, and this leads to 15·4 ev for this second adiabatic ionization potential, which is evidently associated with a strongly bonding orbital. This value is considerably higher than the value (14·14 ev) for the supposed $^3\Sigma^+$ state of NO^+ (which is the convergence limit of the α Rydberg series described by Tanaka [8] and by Huber [9]), and might correspond to the so-far unobserved $^1\Sigma^+$ state of NO^+ (see below).

The third spectral feature is a single, remarkably sharp peak, giving an ionization potential of 16·53 ev, close to the convergence limit of Tanaka's β Rydberg series (16·5 ev).[8] In none of our nitric oxide spectra have any related peaks to lower electron energies been detected. The vibrational fine-structure (mean spacing, 0·16 ev) which is just resolvable when a low collecting potential is used [Fig. 2(*b*)] appears to relate to the second band, and the single strong peak does not fit into this series. Evidently only the $0 \longleftarrow 0$ transition of the third ionization is strongly excited, and a practically non-bonding orbital is indicated.

Huber [9] considered two possible origins for the β Rydberg series; he suggested that the promoted electron could come from either a π- or a σ-level, giving ions of the configuration $\sigma^2\sigma^2\pi^3\sigma^2\pi$ or $\sigma^2\sigma^2\pi^4\sigma\pi$, and he favoured the former. The similarity between the photoelectron spectra of nitric oxide and nitrogen strongly suggests that the latter was more correct. In addition, the slight increase in ν_e on going from NO to NO^+ ($1903 \longrightarrow 1980$ cm.$^{-1}$) favours the slightly antibonding character indicated for this level both theoretically and from our spectrum.

Non-empirical LCAO–MO calculations for nitrogen, carbon monoxide, nitric oxide, and oxygen [10] have given overlap populations (*i.e.*, bonding characters) for the $\sigma_g 2p$ orbitals (see Table 1), and these closely parallel the appearance, in the photoelectron spectra, of the bands which we assign to these electrons. In particular, this level is shown to have a minimum bonding character in nitric oxide.

TABLE 1.

Overlap populations of the $\sigma_g 2p$ molecular orbital.[10]

NO	CO	N_2	O_2
0·01	0·06	0·08	0·10

The last group of peaks is fairly well resolved. The first peak leads to the adiabatic ionization potential 18·34 ev, in fair agreement with the convergence limit of the first ($v' = 0$) γ Rydberg series, 18·24 ev.[8,9] The spacing of the first two peaks, 0·17 ± 0·02 ev, is to be compared with the difference between the convergence limits of the two ($v' = 0,1$) γ Rydberg series, 0·158 ev.[8] Tanaka originally considered the possibility that the series leads to the configuration $\sigma^2\sigma^2\pi^3\sigma^2\pi$, by comparison of the spectra of NO^+ and the isoelectronic CO. It now seems more probable that the configuration is $\sigma^2\sigma\sigma^2\pi^4\pi^1$.

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[6] Miescher, *J. Quant. Spectroscopy Radiative Transfer*, 1962, **2**, 421.

[7] Hurzeler, Inghram, and Morrison, *J. Chem. Phys.*, 1958, **28**, 76.

[8] Tanaka, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1942, **39**, 456.

[9] Huber, *Helv. Phys. Acta*, 1961, **34**, 929.

[10] Brion, Moser, and Yanamazaki, *J. Chem. Phys.*, 1959, **30**, 673.

Carbon Monoxide.—The photoelectron spectrum of carbon monoxide (Fig. 3) is remarkably similar to that of nitrogen (see Part II [1]). It is clear that a very similar description of the three bands is possible in terms of the (well known) spectroscopic properties of the three lowest states of the ion, which result from the removal of one electron in turn from the $\sigma_g 2p$, $\pi_u 2p$, and $\sigma_u 2s$ orbitals. As in nitrogen, the $\sigma_g 2p$ orbital appears to be nearly non-bonding. The three measured adiabatic ionization potentials are 13·98, 16·58, and 19·67 ev, being close to the direct spectroscopic values (13·94, 16·45, and 19·58 ev,[11] and 14·013, 16·536, and 19·674 ev [12]). The mean vibrational frequency in the second band (0·17 ev), taken over the first six levels, is close to the related value (0·18 ev) derived from the Baldet–Johnson bands ($A^2\Pi$ state), and that in the third ($v' = 0,1$ only 0·23 ev) is similar to the same interval (0·21 ev) derived from the first negative bands ($B^2\Sigma^+$ state) of carbon monoxide.

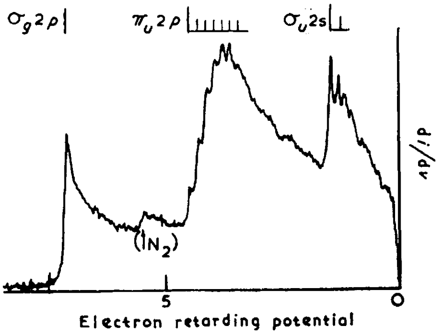

FIG. 3. Photoelectron spectrum for carbon monoxide ($p = 0{\cdot}02$ mm.). Ionization energy increases from left to right.

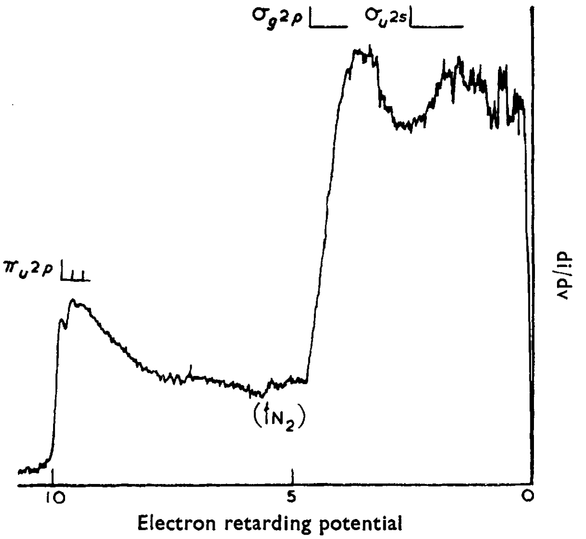

FIG. 4. Photoelectron spectrum for acetylene ($p = 0{\cdot}03$ mm.). Ionization energy increases from left to right.

Acetylene.—The three broad bands in the photoelectron spectrum (Fig. 4) lead to adiabatic ionization potentials of 11·36, 16·27, and 18·33 ev. The first is in good agreement with other determinations of the first ionization potential, in which photoionization-yield (11·41 ev) [13] and electron-impact (11·50 ev) [14] measurements were used. The higher ionization potentials are less well established experimentally; Collin [14] gives 13·25 and 16·95

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[11] Ref. 3, p. 522.
[12] Huffman, Tanaka, and Larrabee, *J. Chem. Phys.*, 1964, **40**, 2261.
[13] Mulliken, *J. Chim. phys.*, 1949, **46**, 497, 675.
[14] Collin, *Bull. Soc. chim. belges*, 1962, **71**, 15.

ev, but our spectra show no sign of an additional peak between the first two. (The small peak near 5·6 v in Fig. 4 is caused by nitrogen impurity.) It is possible that the 13·25-ev value corresponds to an autoionization rather than a direct ionization process. Several theoretical calculations of the ionization potentials, of varying degrees of refinement,[15–18] have been carried out and, although there is little variation in the calculated first ionization potential, the higher values vary widely, that for the $\sigma_g 2p$ orbital varying from 13·14 to 23·5 ev. Our results are in closest agreement with those of McLean [17] (see Table 2).

TABLE 2.

Calculated and experimental ionization potentials of acetylene (in ev).

Molecular orbital	Calculated values Ref. 15	16	17	18	Experimental values 13	19	4	14	Present work
$\pi_u 2p$	11·6	11·31	12·01	12·34	11·50	11·406	11·41	11·50	11·36
$\sigma_g 2p$	13·14	20·21	18·57	23·5				13·25	16·27
$\sigma_u 2s$	15·16		21·11	27·4				16·99	18·33
$\sigma_g 2p$			28·3	29·00					

In only the first band have we as yet detected vibrational fine-structure; the peaks at 11·36 and 11·56 ev represent the 0 ⟵ 0 and 1 ⟵ 0 ionizations, respectively. The vibrational quantum, 0·20 ev, is close to that recently detected in the photoionization-yield curve by Dibeler and Reese (0·23 ± 0·05 ev).[19]

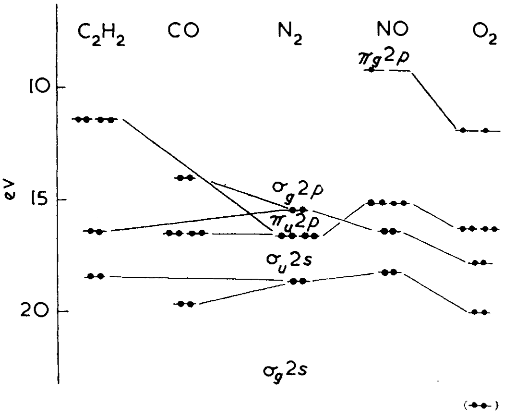

FIG. 5. Energy-level correlation diagram of (from left to right) acetylene, carbon monoxide, nitrogen, nitric oxide, and oxygen, using adiabatic ionization potentials.

Conclusion.—The close relationship between oxygen and its " aufbau precursors " nitric oxide and nitrogen is apparent from the small and regular changes which occur in the photoelectron spectra (Figs. 1—3). The large difference in energy between the highest occupied orbital ($\pi_g 2p$) in oxygen (2 electrons) and nitric oxide (1 electron), which is antibonding, and the next highest orbital levels ($\sigma_g 2p$ in nitrogen; $\pi_u 2p$ in oxygen and nitric oxide (Fig. 5) clearly illustrates the validity of the building-up principle described, for example, by Herzberg,[20] where a large gap is expected between the closed-shell nitrogen configuration and the subsequent levels.

The strongly bonding $\pi_u 2p$ level (4 electrons) can be followed through the series with little alteration in bonding character. The relative order of this level and the $\sigma_g 2p$ level exhibits the expected inversion; only in nitrogen is the $\sigma_g 2p$ level higher in energy. The change is regular and is apparently accompanied by a change in bonding character.

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[15] Mulliken, *J. Chem. Phys.*, 1935, **3**, 517.
[16] Mulliken, *Canad. J. Chem.*, 1958, **36**, 10.
[17] McLean, *J. Chem. Phys.*, 1960, **32**, 1595.
[18] Burnelle, *J. Chem. Phys.*, 1960, **32**, 1872.
[19] Dibeler and Reese, *J. Chem. Phys.*, 1964, **40**, 2035.
[20] Ref. 3, p. 366.

Although, to a first approximation, the $\sigma_g 2p$ level is expected to be bonding, recent non-empirical calculations have indicated that it is slightly anti-bonding, in agreement with the slight increase in bond length which accompanies ionization to N_2^+ ($^2\Sigma_g$) (1·094 $\longrightarrow$ 1·116 Å). In oxygen, an appreciable increase in bond length, from 1·2074 to 1·2795 Å, accompanies the corresponding ionization [O_2 ($^3\Sigma_g^-$) $\longrightarrow$ O_2^+ ($^4\Sigma_g^-$)], and, from the photoelectron spectrum, the level is clearly quite strongly bonding or antibonding.

The fourth band in the oxygen spectrum also indicates a somewhat bonding or anti-bonding electron. It seems to correlate with the nitrogen $\sigma_u 2s$ level, and for this reason we suggest its assignment to a $^4\Sigma$ state. The possibility (kindly pointed out by a Referee) that the third and fourth bands might correspond, respectively, to $^2\Sigma_g^-$ and $^4\Sigma_g^-$, formed by loss of a $\sigma_g 2p$ electron, can be eliminated by the confident assignment of the third band to $^4\Sigma_g^-$ on spectroscopic grounds, and the improbability of a quartet state lying 2·2 ev above the doublet when $^4\Pi_u$ is 0·88 ev below $^2\Pi_u$. No comparable spectral data are yet available for the various states of NO^+, but it seems clear from the photoelectron spectrum that this third level in NO, presumably $\sigma_g 2p$, is totally non-bonding, in that only the $v'(0) \longleftarrow v(0)$ transition appears on ionization. Rather smaller changes occur in the $\sigma_u 2s$ level, except in acetylene (Fig. 4) where a very broad band is produced in the electron-energy spectrum. We assume that this is to be explained by the strong C–H-bonding character of this orbital (it approximates to a $2s(C)1s(H)\sigma$-bond between the carbon and hydrogen atoms, with no C–C bonding).

Multiplicity in the excited states of O_2^+ *and* NO^+. The number of peaks in the photoelectron spectra of both oxygen and nitric oxide is equal to the expected number of different possible configurations of the ions, there being no indication of the formation of other electronically excited species. For example, only the $^4\Pi_u$ state of O_2^+ appears to be formed, and not the $^2\Pi_u$ state which should give rise to a series of peaks commencing at about $v' = 5$ in the $^4\Pi_u$ series, as no additional peaks are detectable. Similarly, in the nitric oxide spectrum there is no sign of doubling of the peaks due to the $\sigma_g 2p$ and $\sigma_u 2s$ electrons. These peaks are sufficiently well defined to render such a doubling more obvious. This is to be contrasted with electron-impact appearance-potential curves [2a] which seem to give similar weight to the triplet-to-quadruplet and triplet-to-doublet ionizations in oxygen. We cannot yet offer a reason for this distinction, but suggest that, in general, a considerable simplification in the study of the ionization of paramagnetic molecules may be expected when photoelectron spectroscopy is used.

It seems probable that if, as appears to be the case, only quadruplet excited states of O_2^+ are formed, then the 20·31 ev ionization process which appears strongly in our spectra must correspond to $^4\Sigma_u$ by its close analogy with the corresponding state in N_2^+. It is not clear, however, whether the higher states of NO^+ indicated here are singlet or triplet in character. Tanaka's α series is stated to lead to NO^+ ($^3\Sigma^+$), and this state is unobserved by us, whereas the γ series leads to NO^+ ($^1\Pi$), and this appears strongly. Strict analogy with the case of oxygen would indicate the latter state to be $^3\Pi$ and the former $^1\Sigma^+$. If Tanaka's assignments are correct, however, and the $^1\pi$ designation has been confirmed in a rotational analysis of its Miescher–Baer bands ($A^1\Pi \longrightarrow X^1\Sigma^+$), we must conclude that in nitric oxide, unlike oxygen, only the excited states of *lowest* multiplicity are formed, and the 15·40-ev ionization potential probably corresponds to NO^+ ($^1\Sigma^+$) and the 16·53-ev ionization potential (β series) to $^1\Pi$.

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Organic Chemistry Laboratories,
Imperial College, London S.W.7.

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