985. *Molecular Photoelectron Spectroscopy. Part I. The Hydrogen and Nitrogen Molecules.*

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A new method of determining ionization potentials is described. It is based upon the measurement of the energy imparted to photoelectrons liberated in the photo-ionization continuum. A photoelectron spectrometer is described which employs the helium resonance line (584 Å) as the excitation source. It is shown that the photoelectron energy spectra obtained for N_2 and H_2 agree in detail with other spectroscopic values and theoretical calculation; in particular the arrangement of the first three orbital energy levels is obtained directly. Vibrational structure, due to the ions H_2^+ and N_2^+, is also reported.

Ionization-potential measurements are the experimental observations which are related, in the most direct way, to the electron energy levels invoked in the theoretical development of the electronic structures of atoms and molecules. The accurate prediction of the first ionization potential of a molecule, I_1, is an important objective of molecular quantum theory and is regarded as a major test of the adequacy of the theoretical procedures. This first ionization potential, the energy required to remove the most loosely bound electron, has been the objective, since, at least in complex molecules (more than 3 atoms), the values of higher ionization potentials, I_2, I_3, etc., corresponding to the removal of more tightly bound electrons (*i.e.*, to the formation of excited ions), have been much less readily available, and when known have often not had the degree of confidence required for theoretical tests. Strictly, the ionization potential measured should be equated with the difference between the total energy of the positive ion and that of the parent molecule. It has been found, however, that since this is a small difference (*ca.* 10 ev) between two large (>500 ev) quantities the correlation is often poor and a better correlation is generally found [1] with the energy of the orbital occupied by the electron to be removed. That is to say that, at least in molecules, reorientation of the remaining electrons makes little contribution to the energy required to remove one electron. Therefore, in general the ith ionization potential of a molecule may be equated approximately and quite satisfactorily, for the purpose of making assignments, with the energy of its ith two-electron molecular orbital (the counting to exclude degeneracy). A general method of determination of *all* the ionization potentials of a molecule should thus reveal directly the system of molecular electron energy levels.

In the present paper we describe a new method for the direct measurement of all the ionization potentials of a molecule, smaller than a particular value (in our case 21·21 ev [2]), and illustrate it by considering its application to H_2 and N_2. In later papers we shall describe the results obtained for more complex molecules.

The principle of the method has been outlined in a preliminary communication [3] and depends upon an examination of the energy spectrum of the photoelectrons ejected by photons whose energy is much larger than the smaller ionization potentials. We are thus examining the processes occurring in the ionization continua. The important difference from the Rydberg series convergence method and the photo-ion current method of Watanabe [4] and from mass-spectrometric appearance-potential measurements, using electron impact, is that, unlike these, this is not a threshold technique. It seems, therefore, to be free from the limitations imposed by auto-ionization processes which frequently render higher ionization limits diffuse or unobservable by these methods.

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[1] Stewart, *Ann. Reports*, 1961, **58**, 14.

[2] Moore, " Atomic Energy Levels," Nat. Bur. Stand., Circ. **467**.

[3] Al-Joboury and Turner, *J. Chem. Phys.*, 1962, **37**, 3007.

[4] Watanabe, *J. Chem. Phys.*, 1954, **22**, 1564.

We suppose that a sufficiently energetic photon can cause the emission of an electron in a direction parallel to the electric vector of the incident light, *i.e.*, in a plane normal to its axis, with a velocity v such that its kinetic energy $mv^2/2$ is given very closely by $(h\nu - I)$.

Conservation of momentum results in energy partition between the electron and the ion in the inverse ratio of their masses; in the least favourable case (H_2) the mass ratio is *ca.* 10^4 and thus the error in equating the electron energy with $(h\nu - I)$ is *ca.* 1 part in 10^4; for larger ions it will usually be less than 1 part in 10^5.

An ideal molecular photoelectron energy spectrum (the number of electrons having a kinetic energy between E and $E + \mathrm{d}E$ plotted against the energy E) would thus, in the limit ($\mathrm{d}E \longrightarrow 0$) consist of a number of lines equivalent in order and spacing to the orbital energies in a conventional energy-level diagram of the ground state of the molecule. Each of these lines is then associated with the formation of a positive ion either in its ground or some excited state. An example of this is seen in Fig. 5 in the spectrum of N_2. The heavy lines, indicating the position of the vibrationless transitions (see below), correspond to such an energy-level diagram, a rotation of the figure clockwise through 90° giving the conventional arrangement with the orbital energy increasing towards the top.

The relative intensities of the various lines in such a photoelectron spectrum will be governed by the numbers of each type of electron present, *i.e.*, by the orbital degeneracy, and, provided that the total light absorption is small, by the photo-ionization cross-section σ_i. The relative intensities should also be independent of pressure until electron–molecule collisions become important (see below).

Since σ_i is known to decrease as the difference $(h\nu - I)$ increases (see, for example, the plots of σ against wavelength recorded in the "Handbuch der Physik"),[5] the peaks corresponding to high ionization potentials should be rather larger than those for the lower ones, but probably not by factors greater than about two under our conditions.

Franck–Condon Effects.—We should expect that energy partition between the nascent ion and electron, to give a vibrationally excited ion, would be determined by the Franck–Condon principle, and that only the removal of a non-bonding electron would allow the vibrationless ion to be formed with high probability. This would then lead to a single peak in the electron energy spectrum at the energy appropriate to the $v''0 \longleftarrow v'0$ transition. In contrast, the removal of a bonding (or antibonding) electron would lead ideally to a series of peaks in the electron energy spectrum corresponding in intensity [since only a small change in $(h\nu - I)$ and hence in σ_i occurs] to the relative probabilities of the $0 \longleftarrow 0$, $1 \longleftarrow 0$, and $2 \longleftarrow 0$ transitions. An increase in vibrational quantum number, v, upon excitation, results in a lower electron translational energy with usually a higher probability than that accompanying the formation of the vibrationless ion. If the energy resolution were less than the magnitude of the vibrational quantum in the ion, a broadened band in the electron energy spectrum would result, commencing at the electron energy corresponding to the $0 \longleftarrow 0$ transition. We shall show that, in favourable cases, this vibrational structure can be resolved and the vibrational frequencies of the ion measured.

EXPERIMENTAL

The apparatus (Figs. 1 and 2) consisted of a monochromatic light source separated from an electron spectrometer grid chamber by two aligned sections of a precision (0·5 mm.) bore capillary tube. Rapid pumping at the orifices O, in the side of the capillary tube, prevented mixing of the target vapour with the helium, in the light source.

Light Source.—Helium, purified by passage over red-hot copper oxide and liquid-nitrogen-cooled animal charcoal, was passed continuously through the discharge tube A, a 10 cm. Pyrex tube of 3 mm. int. diam., which had nickel electrodes in the side tubes. A high-voltage direct-current discharge was maintained by a 0—2000 v power supply (adjusted by a Variac transformer) using a 12,000 ohm ballast resistance in series with the lamp. This light source gave a

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[5] "Handbuch der Physik," ed. Flugge, Springer Verlag, Berlin, 1956, Vol. 21, p. 320.

stable output of the resonance line (584 Å) with discharge currents of up to about 100 mA. The helium flowing from the first section of capillary tube was removed by rapid pumping at B.

Electron Spectrometer.—A cylindrical retarding electrostatic field was established between two cylindrical grids, G_1 and G_2, coaxial with the light beam. Outside these grids was placed a collector cylinder P. The grids were of 10% rhodium–platinum alloy mesh (80 per in.; 0·002 in. diam. wire) spot-welded between 1 cm. long cylinders of platinum foil, and the electron collector, P, was a cylinder of Eureka-metal foil. The three electrodes were spot-welded to 1 mm. diam. tungsten supporting rods, C, which were glass-sheathed up to the seals to reduce surface leakage currents. The diameters of the electrodes were: G_1, 0·7 cm.; G_2, 2 cm.; and P, 4 cm. The grids were coated with gold by sputtering from a gold wire introduced along the axis through the socket D. Afterwards, a Pyrex glass tube (4 mm. int. diam.) was supported from a cone in this socket. This tube reached to the lower end of G_1 and prevented ions or electrons from reaching the collector without passing through the grids.

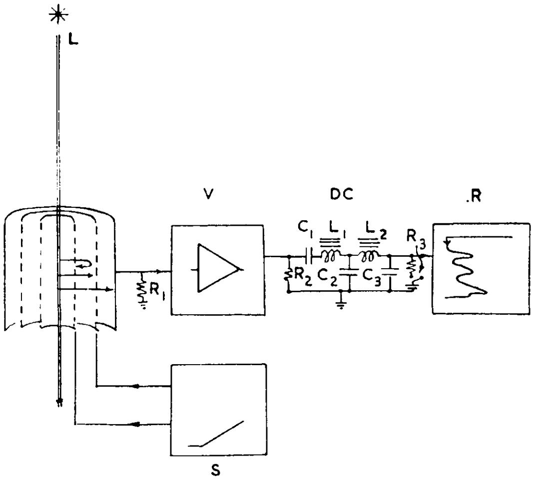

FIG. 1.

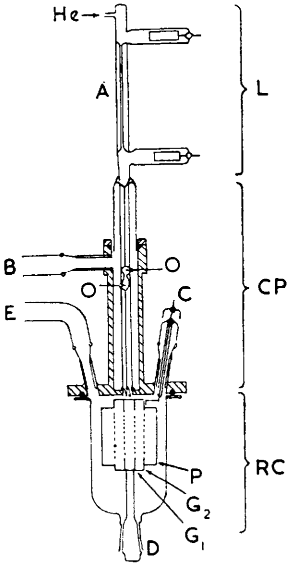

FIG. 2.

FIG. 1. Photoelectron spectrometer; general circuit arrangement (see text).
L, " Monochromatic " light source. V, Vibrating-reed electrometer. DC, Differentiating circuit. R, Recorder. S, Sweep generator.

FIG. 2. Photoelectron spectrometer; cross-section of the light source, collimator, and retarding-field grid chamber (see text).
L, " Monochromatic " light source. CP, Collimator and differential pumping section. RC, retarding-field grid chamber.

The electron energy spectrum was scanned by increasing the retarding potential difference between G_1 and G_2, initially zero, linearly with time by using the constant-current charging of a capacitance through a pentode valve (EF 91). The usual rate of potential increase was 60 mv/sec. An electron-collecting potential difference of up to 20 v was maintained between G_2 and P by maintaining G_2 (and G_1 before the start of a voltage sweep) at this value negative with respect to earth, P being returned to earth through the input resistance of a vibrating-reed electrometer. By keeping the G_2–P potential difference always greater than the maximum G_2–H_1 difference, the arrival of positive ions at P was prevented. Subject to this limitation, the lowest possible value (usually *ca.* 2v greater than the greatest electron energy) of the G_2–P potential difference gave, by reducing the field penetration through the G_2 spaces, the best energy resolution. This section of the apparatus was enclosed in a cylinder of " mumetal " to reduce magnetic field disturbances. The spectrometer chamber was connected, through E, to a separate pumping system and to a 1 l. pressure-stabilizing reservoir and vapour-admission manifold which had Teflon diaphragm valves. The pressure in this section of the system was measured by a Pirani gauge calibrated for air.

The photoelectron current collected at P (generally about 10^{-11} A) was amplified by a vibrating-reed electrometer (Ekco type N572). The first derivative with respect to time, di/dt (and, hence, with respect to voltage, di/dv, since a linear voltage sweep of 60 mv/sec. was used), was generated by operating on the electrometer output with the capacitative differentiating circuit shown in Fig. 1. The magnitude of $(C \times R)$ (*ca.* ⅓ sec.) was chosen to be less than the time (*ca.* 1 sec.) corresponding to the limit of the best energy resolution obtained (*ca* 60 mv). The filter network shown excluded signals due to electrode vibration from the recorder.

Calibration of the Potential Scale.—The potential difference between G_1 and G_2 was observed continuously by a 4½ in. mirror-scale voltmeter, standardized at 16 points on its range of 0—20 v. A marker circuit causing a " kick " of the recorder pen was operated manually at selected points on the scale, chosen to fall just above and just below the feature of interest in the spectrum. The potentials measured by interpolation are estimated to be accurate to ±20 mv.

In order to estimate the correction required for a possible surface potential difference between G_1 and G_2, the photoelectron energy spectra for argon, krypton, and xenon were examined (see Discussion and Fig. 3). The deviation between the potential at which each peak in the spectrum occurred and the value predicted on the basis of the spectroscopically known ionization potential[2] was not much greater than the limits of measurement of the position of the centre of the peak (see Table).

	21·21-Peak potential (v)		Spectroscopic ionization potential (v)		Differences (v)	
Rare gas	(i)	(ii)	(i)	(ii)	(i)	(ii)
Argon	15·79	15·93	15·755	15·933	0·03	0·00
Krypton	14·05	14·69	13·99	14·65	0·05	0·04
Xenon	12·17	13·49	12·127	13·427	0·04	0·06

Since, however, the deviations were all of the same sign, the mean value, 0·04 v, was assumed to arise from a surface potential difference and was applied as a correction to the measured ionization potentials.

RESULTS AND DISCUSSION

Energy Resolution and Peak Shape.—The energy resolving power was tested by examination of the electron energy spectra from Ar, Kr, and Xe (Fig. 3). The resolving power is not definable in quite the same way as in optical spectroscopy since in general the electron-optical properties of the grid structure produce some degree of asymmetry in the peaks, usually with the higher potential side steeper than the lower. However, in certain cases, notably the rare gases and completely non-bonding electrons in a few molecules (*e.g.*, NO, to be discussed later), an almost symmetrical peak has been observed, the half-height width being about 0·1 v. An additional peak broadening (below the point × in Fig. 3), which affects only the low-energy side, is ascribed to deflections experienced by electrons upon passing the first grid, the deflections being caused by local fields originating in surface-potential discontinuities. This effect, which results in a reduction of the component of velocity normal to the retarding field, proved particularly sensitive to the pretreatment of the grids, being progressively reduced as the gold-sputtering treatment was prolonged (chemical cleaning was ineffective). This progressive reduction (although we have been unable to eliminate the effect completely) suggests that the effect is not to be ascribed to initial ejections of electrons in directions other than normal to the incident light ray. Electron–molecule collisions can also be excluded since the peak shapes were quite unchanged by variations in gas pressure within the range 5—50 μ. At higher pressures (the particular value varying with the gas used), there is evidence of electron scattering by molecular collisions, in that a peak at nearly zero electron energy appears with a corresponding reduction in the height of the high-energy peak. The spectra presented here, however, have been obtained at pressures well below that at which onset of this phenomenon occurred.

The Nature of the Charge Carrier.—The possibility might arise that, in complex molecules, some of the peaks might be ascribable to negative ions, rather than electrons, as the result of photodissociation processes: $AB + h\nu \longrightarrow A^+ + B^-$. The peaks observed for the rare gases are undoubtedly due to electrons, as are those for simple diatomic molecules, since they coincide (as we shall show) in number and position with those expected from other measurements, and also on theoretical grounds. A test for the presence of negative ions is thus provided by the following argument. Some at least of the peaks observed for a more complex molecule must (from the above) be due to electrons. Molecular ions, however, have a much shorter collisional mean free path than electrons. Variation of relative peak intensity with change in pressure would result if some of the peaks were caused by negative ions and some by electrons. No such changes have yet been observed, and we ascribe all observed peaks to electron emission.

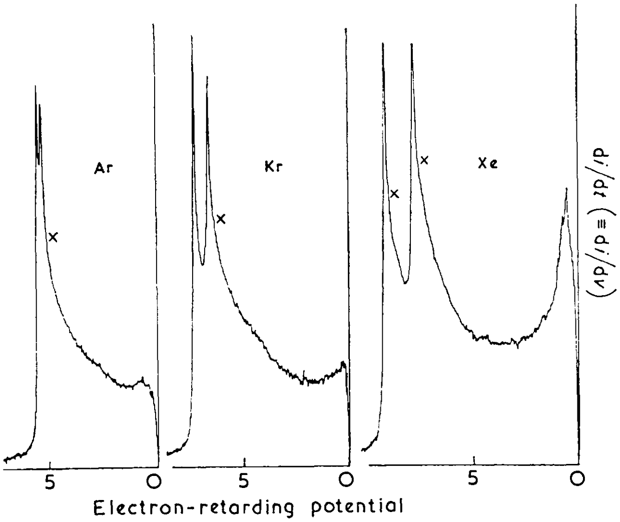

FIG. 3. Photoelectron spectra for argon, krypton, and xenon, excited by the helium resonance line (584 Å; 21·21 ev). Ionization energy increases from left to right within each section (see text).

Hydrogen.—The molecule H_2 has only one occupied molecular orbital ($\sigma_g 1s$) and this is within our energy range of 0 to —21·21 ev. The two electrons may be spoken of as strongly bonding and we should therefore expect a single band or ideally a group of lines in the molecular photoelectron spectrum, with a spacing corresponding to the vibrational energy intervals in H_2^+. The observed spectrum (Fig. 4) consists of a band on which is superimposed some fine structure in the form of a series of partially resolved peaks. The first of these, a shoulder, leads to an ionization potenial of 15·41 v which corresponds to the Rydberg convergence determined value[6] of 15·422 v for " adiabatic " ionization. We ascribe this first shoulder, therefore, to the $0 \longleftarrow 0$ transition; the most prominent peak (or step), $3 \longleftarrow 0$ (ionization potential = 15·95 v), accords well with the value for the vertical ionization potential measured from electron-impact studies (16·0 v). The molecular photoelectron curve continues to rise for higher ionization potentials, and this we ascribe to the curve being a summation of unsymmetrical components. No vibrational structure would be expected more than 2·65 v (the dissociation value for H_2^+) beyond the $0 \longleftarrow 0$ peak; none can be discerned beyond 1·6 v above the $0 \longleftarrow 0$ shoulder. Refinement in grid design (which is in hand), by revealing the convergence and disappearance of the vibrational structure, might be expected to lead to new direct estimates for the dissociation energies of simple ions. The mean spacing of the first four peaks (0·26 v) is in satisfactory agreement with the value (0·246 v) derived from data given by Richardson.[7]

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[6] Bentler and Junger, *Z. Physik*, 1936, **100**, 80.
[7] Richardson, *Proc. Roy. Soc.*, 1935, *A*, **152**, 503.

The vibrational origin of this fine structure was confirmed by examination of deuterium (Fig. 4). Here the fine structure is barely resolved but the mean value for the first four shoulders (0·17 v) is close to that ($\sqrt{\frac{1}{2}} \times 0{\cdot}246 = 0{\cdot}175$) expected from the change in reduced mass.

Nitrogen.—The photoelectron spectrum for nitrogen (Fig. 5) shows the presence of three groups of electrons, the first giving little more than a single line, the second a broad band, and the third being intermediate in character. Both the second and third clearly show (vibrational?) fine structure. The first (5·64 v) obviously corresponds to the first ionization potential (giving 15·57 ev) and is evidently associated with an almost non-bonding electron. Two small peaks can just be discerned in the photoelectron spectrum near 4·9 and 5·2 v, corresponding to ionization potentials 0·29 and 0·58 ev greater than the first. The mean separation (0·29 ev) is close to the value (0·294 ev) for the first vibrational interval in the ${}^2\Sigma_g{}^+$ state of N^{2+},[8] and we therefore ascribe these two peaks to $v'' = 1$ and $v'' = 2$ vibrational levels in this ion. Their weakness in relation to the $v'' = 0$ level implies that very little change in bond length occurs following this ionization. The value obtained for the $v'' = 0$ level agrees closely with the spectroscopic value[9] (15·576 ev) which is also close to the electron-impact value (15·63 ev),[10] a fact which supports the assignment to a

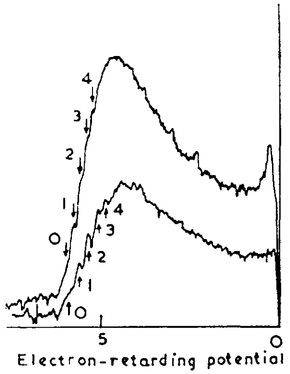

FIG. 4. Photoelectron spectra for H_2 ($p = 0{\cdot}06$ mm.)—lower curve, and D_2 ($p = 0{\cdot}06$ mm.)—upper curve, excited by the helium resonance line (584 Å, 21·21 ev). The pressures were indicated by a Pirani gauge, calibrated for air. The numbers adjacent to each curve indicate the vibrational quantum numbers in the ion ($H_2{}^+$ or $D_2{}^+$). Ionization energy increases from left to right (see text).

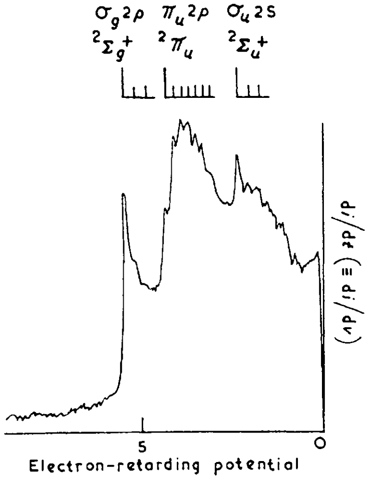

FIG. 5. Photoelectron spectrum for N ($p = 0{\cdot}024$ mm.), excited by the helium resonance line (584 Å, 21·21 ev). Ionization energy increases from left to right (see text).

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[8] Herzberg, " Spectra of Diatomic Molecules," Van Nostrand, New York, 1950, p. 554.

[9] Worley, *Phys. Rev.*, 1943, **64**, 207.

[10] Frost and McDowell, *Proc. Roy. Soc.*, 1955, *A*, **232**, 227.

non-bonding electron. The LCAO–MO calculations by Scherr[11] give the overlap populations and hence the bonding character of the three highest levels of the ground state of N_2, and indicate that the highest level is the least bonding, a prediction with which our results are in excellent agreement. The appearance of the middle band (showing fine structure) in our spectrum, is in agreement with its arising from the π-electron level ($\pi_u 2p$)[4] in Mulliken's[12] description of N_2 ($1\pi_u$ and $1\bar{\pi}_u$ in Scherr's nomenclature), orbitals which are strongly bonding in character. The mean spacing over the first four peaks is 0·22 v. This is sufficiently close to the value (0·23 ev) given by Worley[13] for the first vibrational interval ($\Delta G_{\frac{1}{2}}$) for this state of N_2^+ to confirm its assignment to the stretching vibration of this ion. The first member of this series of peaks is taken as the $v'', 0 \longleftarrow v', 0$ ionization. The value of —16·72 ev is in excellent agreement with Worley's spectroscopic values of —16·71 and —16·72 ev for the doublet components.

Although the vibrational components of this group are not completely resolved, it seems clear that the intensity distribution is such that a maximum occurs at $v'' = 1$ and that the $v'' = 0$ level is only slightly weaker; however, the intensity falls fairly rapidly for $v'' =$ 2, 3, and 4, $v'' = 6$ being the last level that can be discerned. A fairly large change in internuclear separation has therefore occurred in this case. The vertical ionization potential should lie between the values for $v'' = 0$ (16·72 ev) and $v'' = 1$ (16·94 ev), since these occur with similar strength in our spectrum. Frost and McDowell[10] give 16·84 v for the electron-impact appearance potential of $^2\pi_u$ N_2^+. The $^2\pi_u$ state of the N_2^+ ion has been, until recently, the least well described of the states of N_2^+. Its direct observation from a Rydberg series is difficult and, prior to Worley's study, its energy had only been inferred indirectly from auroral spectra. It appeared prominently, however, in Frost and McDowell's electron-impact study,[10] but the present study seems to be the first case of its appearing prominently in a photo-ionization experiment.

The last group of peaks in our photoelectron spectrum is quite well resolved, the first of the group (at 2·49 v) leading to an ionization potential of 18·72 ev. This is close enough to the spectroscopic value of 18·748 for the $^2\Sigma_u^+$ state of N_2^+ to confirm the peak as due to $v'', 0 \longleftarrow v', 0$ ionization from the $(\sigma_u 2s)^2$ level ($2\ \sigma_u$ in Scherr's nomenclature). The related peaks at 2·20 and 1·90 v appear to form the first three clearly detectable members of a series with a mean spacing of 0·3 v, which would agree with its assignment to the stretching vibration of $^2\Sigma_u^+$ N^{2+}, for which $\Delta G_{\frac{1}{2}}$ is 0·294 ev. From the relative strength of the peaks in this group, the $\sigma_u 2s$ electron is clearly intermediate in bonding (or antibonding) character between that of the two higher levels and closest to that of the highest ($\sigma_g 2\ p$) level. This agrees rather better with the order of the fractional bond-length changes ($\Delta R/R$) of Scherr[11] than with those given by Frost and McDowell.[10]

Conclusion.—We have shown that in two molecules whose valency electron structure is well understood and for which adequate spectroscopic ionization-potential data are already available, molecular photoelectron spectroscopy gives adiabatic ionization potentials, with a probable error of (at present) ±0·02 ev, in a form which is directly related to an MO energy-level diagram, and that resolution of the vibrational structure of the ion reveals the relative bonding or antibonding character of each level.

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[11] Scherr, *J. Chem. Phys.*, 1955, **23**, 569.
[12] Mulliken, *Rev. Mod. Phys.*, 1932, **4**, 1.
[13] Worley, *Phys. Rev.*, 1953, **89**, 863.