Photoelectron Spectra of Acetylene, Diacetylene, and their Deutero-derivatives

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THE 584 Å photoelectron spectrum of acetylene, obtained using a coaxial grid electron analyser,[1] showed three bands. It was therefore concluded that the molecule has three occupied orbitals having energies above −21·21 ev. The adiabatic ionization potentials observed were 11·36, 16·27 and 18·33 ev, and were assigned to the $2p\pi_u$, $2p\sigma_g$, and $2s\sigma_u$ orbitals, respectively. We have now re-examined the photoelectron spectrum of acetylene using a 127° electrostatic velocity analyser,† and have been able to measure vibrational fine structure in all three bands (Figure 1).

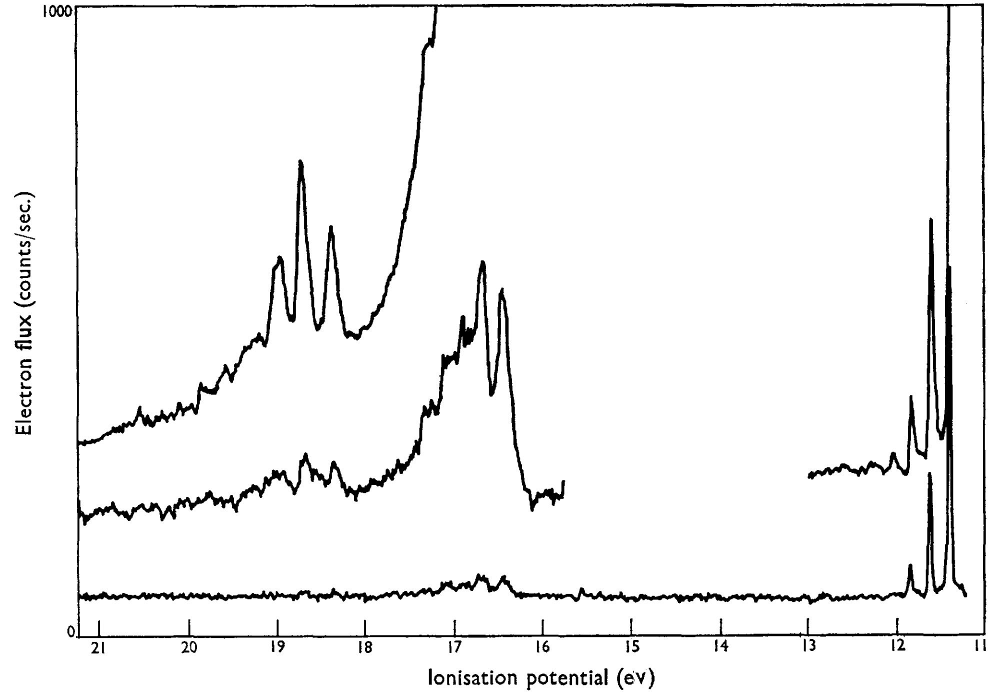

FIGURE 1

Photoelectron energy spectrum excited in acetylene vapour by helium 584Å *radiation* ($h\nu$ = 21·21 ev).

The first band in the photoelectron spectrum of acetylene, adiabatic ionization potential 11·40 ev, now consists of four well resolved peaks, having an average spacing of 0·22(0) ev, corresponding to a vibrational frequency of 1774 cm.$^{-1}$. This is in quite good agreement with that observed by Dibeler and Reese[2] (1855 cm.$^{-1}$), and is the C≡C stretching frequency, ν_2. In the spectrum of [$^2H_2$]acetylene, the average spacing is 0·20 ev, or 1614 cm.$^{-1}$. This is somewhat lower than Dibeler and Reese's value of 1775 cm^{-1}.

The second band, at ionization potential 16·44 ev, shows rather complex vibrational structure. There appears to be a superimposition of a low and a high frequency mode, the high frequency one (1774 cm.$^{-1}$) probably again being ν_2. This band is also complex in the C_2D_2 spectrum. The third band, adiabatic ionization potential 18·42 ev for C_2H_2 and C_2D_2, also appears to consist of two overlapping vibrational series. They have not, as

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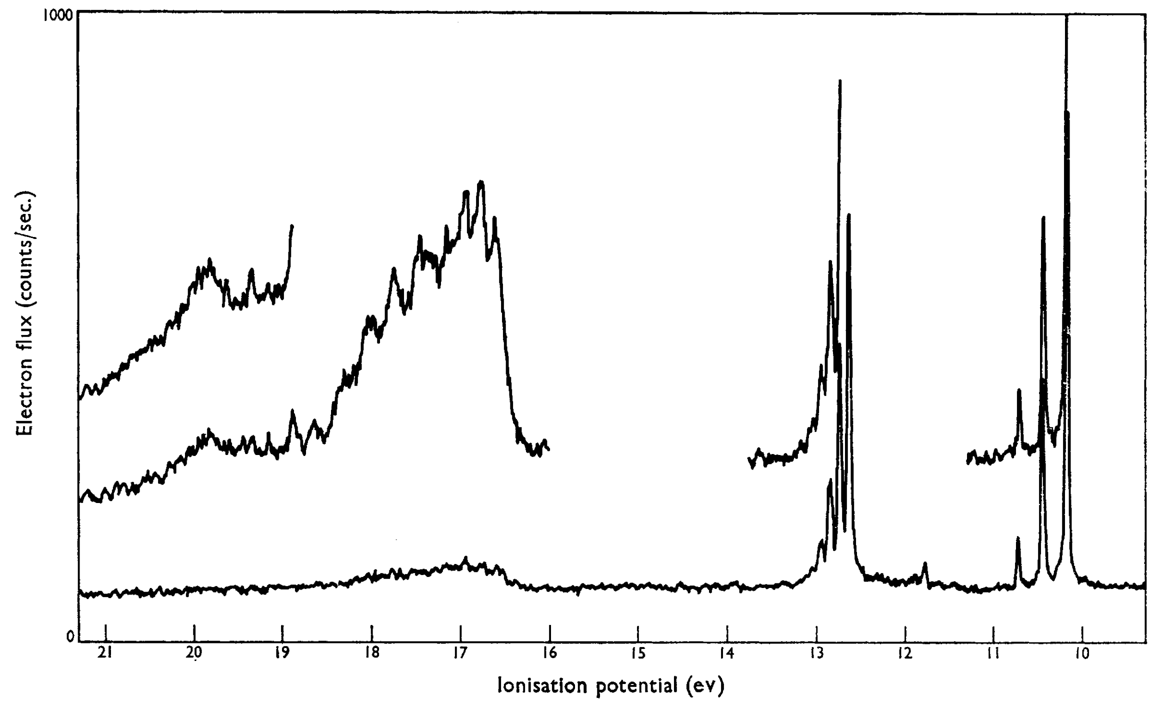

FIGURE 2

Photoelectron energy spectrum excited in diacetylene vapour by helium 584 Å *radiation* (*h*ν = 21·21 ev).

yet, been correlated with any known frequencies of the molecule or ion.

The observed Franck–Condon factors[3] agree with the calculations of Sharp and Rosenstock,[4] in that no isotope effect is observed on deuteration (*cf.*, Dibeler and Reese[2]), (Table 1).

TABLE 1

Observed Franck–Condon factors for the first ionization of acetylene and [$^2H_2$]*acetylene*

	Transition 0–0	1–0	2–0	3–0
C_2H_2	67%	25%	6·7%	1·0%
C_2D_2	66%	25%	7·4%	1·5%

The spectra of diacetylene (Figure 2) and [$^2H_2$]diacetylene show four bands, the first three of which have resolved vibrational structure. The first adiabatic ionization potential, 10·17 ev, agrees with the value obtained by Smith[5] (10·18 ev), from the convergence of Rydberg series. The fine structure spacing corresponds to a vibrational frequency of 2121 cm.$^{-1}$. This is the ν_2 mode; the symmetric C≡C stretch (*cf.*, 2184 cm.$^{-1}$ for C_4H_2, 2176 cm.$^{-1}$ for $C_4H_2^+$).[6] In the spectrum of C_4D_2, this spacing corresponds to 2041 cm.$^{-1}$. Calculation of the expected isotope effect gives the vibrational frequency in C_4D_2 as 2044 cm.$^{-1}$ (based on our C_4H_2 result). The peak at ionization potential 10·84 ev in the diacetylene spectrum could be the $v = 2$ level of the ν_4 vibrational mode (antisymmetric C–H stretch, 3329 cm.$^{-1}$ in C_4H_2).[6] This would be expected to appear in two quanta units. The 0–2 spacing observed is 5405 cm.$^{-1}$, suggesting that ν_4 is 2703 cm.$^{-1}$. The corresponding spacing in the C_4D_2 spectrum is 0·55 ev (4437 cm.$^{-1}$), *i.e.*, two quanta of 2219 cm.$^{-1}$.

The band corresponding to the second ionization potential of diacetylene, at 12·62 ev, has associated with it a vibrational frequency of 887 cm.$^{-1}$. This is comparable with the central C–C stretching mode ν_3 (874 cm.$^{-1}$ for C_4H_2, 860·6 cm.$^{-1}$ for $C_4H_2^+$).[6] In the deutero-derivative, the frequency is 823 cm.$^{-1}$.

The excitation of the ν_2 vibrational mode in the first ionization is consistent with loss of an electron from ψ_2, being the molecular orbital with a node between the two central carbon atoms, and the fact that ν_3 is excited by the second ionization is consistent with loss from ψ_1, which has no node.

TABLE 2

Ionization potential (ev)

	1st	2nd	3rd	4th
C_2H_2	11·40	16·44	18·42	
C_2D_2	11·40	16·54	18·42	
C_4H_2	10·17	12·62	16·61	19·8
C_4D_2	10·18	12·62	16·77	19·8

The bands associated with the third ionization potentials (C_4H_2 16·61 ev; C_4D_2 16·77 ev) consist of a complex vibrational structure, which has not yet been assigned.

The ionization potentials observed are given in Table 2.

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[5] W. L. Smith, private communication. We are grateful to Dr. Smith for making his results known to us prior to publication.

[6] G. Herzberg, "Electronic Spectra of Polyatomic Molecules", van Nostrand, New York, 1966, p. 633.