SPECTRA AND IONIZATION POTENTIAL OF CYANOACETYLENE

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ABSTRACT

The spectrum of cyanoacetylene has been photographed in the vacuum ultraviolet region and its analysis made. The ionization potential has been calculated from an observed Rydberg series to be 11.6 eV. The first Rydberg band has been compared with the photoelectron spectrum of the molecule and conclusions about the initial orbital have been drawn.

CYANOACETYLENE, HC≡C—C≡N is isoelectronic with cyanogen, N≡C—C≡N and diacetylene and these molecules provide simple examples of conjugation of two triple bonds. The spectrum of diacetylene has been analysed by Price and Walsh (1945) and recently in greater detail by Smith (1967). The spectrum of cyanogen has also been studied by Price and Walsh (loc. cit.) but no detailed analysis could be made due to its extreme diffuseness. Job and King (1966) have reported two absorption bands in cyanoacetylene, one extending from 2600–2300 Å and the other from 2300 Å into the vacuum region. In this paper its spectrum in the still shorter wavelength region is being reported.

Cyanoacetylene was prepared in the laboratory by the action of methyl alcohol and sulphuric acid on propiolic acid and treating the resultant ester with ammonium hydroxide when propioliamide was formed. This was vacuum-distilled with P₂O₅ and sand to obtain cyanoacetylene, which was further purified by fractional distillation.

The spectrum (Plate I) was photographed with Q₁ plates in the one-metre vacuum grating spectrograph at King’s College, University of London, using a Lyman tube as light source. The spectrum starts with an absorption band at 1508 Å which is followed by a region of broad absorption centred at 1453 Å. This second band has perhaps some diffuse structure superimposed on it. To the shorter wavelength side can be seen a system
of four bands that become progressively sharper and some of which are Rydberg in character. They fit into a formula of the type

\[ v_0^n = 93,670 - R (n - 1.45)^2. \]

The frequencies of the 1292 Å system of bands and those of the Rydberg ones are shown below:

<table>
<thead>
<tr>
<th>The 1,292 Å band system (cm(^{-1}))</th>
<th>The Rydberg bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>77,382</td>
<td>( n )</td>
</tr>
<tr>
<td>79,421</td>
<td>4</td>
</tr>
<tr>
<td>81,571</td>
<td>5</td>
</tr>
<tr>
<td>82,659</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>7</td>
</tr>
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<td></td>
<td>8</td>
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</tbody>
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Turner et al. (1968) have analysed the photoelectron (PE) spectrum of this molecule and it would be interesting to compare the results. The resemblance between the two spectra stems from the fact that the ultraviolet (UV) spectrum consists of the Rydberg bands going to the ionized state, which is given by the PE spectrum and whose geometrical configuration is not very much different from that of the molecule because the Rydberg electron hardly takes any part in the bonding of the molecule. The pattern and the energy spread of the two spectra should therefore be similar. The importance of this comparison lies in the fact that from their relative positions the band term values and hence the quantum defects associated with the excited electron can be determined. The nature of the excited state can then be deduced by the assumption that for elements in the first row of the periodic table \( ns \) electrons have a quantum defect 0.9–1.2, \( np \) electrons have 0.3–0.5, and \( nd \) electrons 0.1 (Herzberg, 1966).

The Rydberg band at 1292 Å has been plotted in Fig. 1 with intensity along ordinate and energy along abscissa and the PE spectrum of the ion corresponding to the removal of an electron from the upper of the two \( \pi \)-orbitals to which the Rydberg transition corresponds has been shown below this curve. It will be noticed that the energy states of the two curves have to be shifted relative to one another by 2.0 eV when they agree almost completely. This corresponds to a Rydberg denominator of \( (4 - 1.4) \). The high quantum defect of \( 1.4-1.45 \) no doubt points to an \( nσν \) Rydberg orbital and hence an \( np\pi \) initial orbital. The spacing of the vibrational bands in both the cases is \( ca \) 2100 cm\(^{-1}\) and compares favourably with that measured
by Turrell et al. (1957). This also confirms that the Rydberg electron takes hardly any part in the bonding of the molecule.

The ionization potential of 11.6 eV obtained both from the UV and the PE spectra should be compared with the corresponding value for acetylene (11.3 eV) and hydrocyanic acid (13.9 eV). It is well known that the effect of conjugation is to lower the ionization potential by stabilizing the ionic state, there being practically no effect on the ground state. It is remarkable therefore that the ionization potential of cyanoacetylene is slightly higher than that of acetylene. The discrepancy can perhaps be explained as the effect of a strong C≡N dipole which exerts an inductive effect on the C≡C bond, more than compensating the effect of conjugation. The situation is similar to cyanogen where the inductive effect of the strong C≡N dipole compensates the effect of conjugation so that its ionization potential (13.8 eV) is comparable to that of hydrocyanic acid (13.9 eV).

In conclusion, I would like to acknowledge gratefully my indebtedness to Professor W. C. Price for extending facilities for this work and for his continuous interest in it.
REFERENCES


5. ——. Ibid., 1966, 19, 185.
