# Vibrationally Resolved Study of the Fourth Photoelectron Band of Acetylene at 23.5 eV.

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## Abstract.

The inner valence $C^2\Sigma_g^+$ electronic state of the acetylene cation has been studied by means of ultraviolet photoelectron spectroscopy using HeII excitation. Vibrational structure is resolved and is interpreted in terms of a vibrational progression in the totally symmetric $\nu_2(\sigma_g^+)$ mode. A Franck-Condon analysis has been carried out and force constants corresponding to the CH stretching, CC stretching and CH-CC stretching interaction have been determined. The CH and CC bond lengths have been deduced and the values are found to be $1.088 \pm 0.005$ Å and $1.439 \pm 0.005$ Å, respectively.

## INTRODUCTION.

The valence electron configuration of the acetylene molecule can be written (in $D_{\infty h}$ symmetry)

$2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4$

The inner valence photoelectron spectrum of acetylene, comprising the $2\sigma_g^{-1}$ single hole and correlation satellites, has been studied extensively by means of XPS /1,2/, synchrotron radiation photoelectron spectroscopy (SRPS) /3/ and UPS /4/. Both the X-ray and synchrotron radiation excited photoelectron spectra show a main line centred at approximately 23.5 eV, primarily associated with transitions to the $C^2\Sigma_g^+$ single hole state, and several weaker satellite structures at higher binding energies associated with correlation effects. Several theoretical studies have been carried out in order to obtain the ionization energies, potential curves and intensities in the different transitions /5-7/. Due to the non-negligible electron correlation the difficulties in reproducing the experimental results for the inner valence region are considerable. In particular, it has been very difficult to calculate accurately the relative intensities in the photoelectron transitions to the various final states.

In a theoretical study /7/ it was suggested that vibronic interaction over a totally symmetric stretching mode may be responsible for a redistribution of intensity between the electronic states. In view of this, we have carried out the present UPS study with vibrational resolution in order to provide more detailed experimental information on the inner valence states. Since the well-known, prominent correlation satellite structures in the region around 27,5 eV are completely covered by the intense HeI excited spectrum, we focus in the present study on the band at 23.5 eV. Studies of the correlation satellites will have to await the introduction of monochromatized HeII radiation.

## EXPERIMENTAL DETAILS.

The spectrum was recorded on an electron spectrometer particularly adapted for high resolution studies using UV radiation for excitation. The analyzer consists of two truncated hemispherical electrodes giving a double focussing spherical electrostatic field. The electrons were detected using a microchannel plate arrangement and transformation of the electron pulses into light pulses through a phosphor plate. The light pulses were detected by a CCD camera and transferred into memory cells of a computer connected on line. A more detailed description of the various parts of the spectrometer and the electronics is given elsewhere /8/.

The study was carried out using HeIIα radiation with 40.8 eV energy for the photoionisation. This radiation was generated by means of a microwave source operating in the X-band and using cyclotron resonance to provide a high photon flux /9/. The magnetic field strength is relatively high, 0.36 T, and in order to isolate the gas cell, electron lens and energy analyser from the magnetic field double μ-metal shields were used. By this means the magnetic fields in these crucial parts of the spectrometer were practically eliminated.

During the recording of spectra a small amount of helium from the radiation source leaked into the gas cell, where the ionisation takes place. The ionisation of this neutral helium gives rise to a very well defined line in the photoelectron spectrum at 24.578 eV. This line is very close in energy to the investigated photoelectron band of the acetylene molecule and was therefore used to calibrate the energy scale of the spectrum.

## EXPERIMENTAL RESULTS.

Fig.1 shows the HeII excited photoelectron spectrum of acetylene in the energy region around 23.5 eV, containing the ionisation from the inner valence $2\sigma_g$ orbital. As can be seen, the band exhibits vibrational structure, which implies that the corresponding single hole state $C^2\Sigma_g^+$ is bound or quasi-bound. The fine structure is not very well resolved, but one vibrational progression can be clearly discerned with spacings of approximately 1370 $cm^{-1}$ (170 meV). Since the electronic state is non-degenerate, we expect that only totally symmetric modes will become strongly excited and assign the observed structure to a progression in the $\nu_2(\sigma_g^+)$ mode, which has an energy of 1973.2 $cm^{-1}$ (245 meV) in the neutral ground state. The lowering of the vibrational energy in the ionic state compared to the neutral ground state is 31%, which corresponds to a substantial decrease in the chemical binding energy upon the ionisation. Accordingly, a large increase in the equilibrium bond distance is expected as compared to the distance in the neutral ground state.

There is some ambiguity as to the position of the adiabatic (0-0) transition. The first clearly observed vibrational component has an energy of 23.03 eV. However, the intensity rises gradually and there are indications of still another component at 22.86 eV which we tentatively associate with the adiabatic (0-0) transition. Six more peaks are observed forming the progression. Table 1 gives the energies of these peaks. As can be seen, the spacings are practically constant, suggesting that the dissociation energy along the $q_2$ normal coordinate is high. The peak of highest intensity is observed at 23.54 eV which means that the difference in energy between the adiabatic and vertical transitions is very large as expected for a transition which involves a large change in geometry. Such a geometry change would also be accompanied by a more or less gaussian shaped photoelectron band with low Franck-Condon factors at the beginning of the band as is also observed (Fig.1).

## METHODS OF CALCULATION.

In order to evaluate the experimental results quantitatively a Franck-Condon analysis was performed. Since the observed vibrational structure can be well described by excitations of the totally symmetric $\nu_2(\sigma_g^+)$ mode alone, a linear shape was assumed for the acetylene cation in the calculation. For a linear acetylene like molecule, the internal symmetry coordinates S for the totally symmetric vibrational modes in the $\sigma_g^+$ irreducible representation can be expressed as /10/

$$S_1 = (\Delta r_1 + \Delta r_2) / \sqrt{2}$$

$$S_2 = \Delta R$$

with $r_i$ and R denoting the $CH_i$ and CC bond lengths, respectively. Force constant calculations were carried out on the two $\sigma_g^+$ vibrations through the use of the observed vibrational frequencies (cf Table 1). The QCMP 012 program from QCPE /11/ was employed in the computation.

The iterative Franck-Condon analysis procedure /12/ based on the generating function methods for harmonic oscillators /13/ was applied. The optimal shifts in the normal coordinates $\mathbf{D}^n$ between the $X^1\Sigma_g^+$ and the $C^2\Sigma_g^+$ states thus derived were converted into changes in internal symmetry coordinates $\Delta\mathbf{S}$ and hence into changes in bond lenghts through the expression /14/

$$\Delta\mathbf{S} = \mathbf{L'}_S \, \mathbf{D}^n$$

The $\mathbf{L}_S$ ( $\sigma_g^+$ ) matrix required in the calculation was for the $C^2\Sigma_g^+$ state deduced from force constant computations while that for the neutral ground state was obtained from reference /15/.

## RESULTS OF CALCULATIONS AND DISCUSSION

The symmetrized force constant matrix in the $\sigma_g^+$ representation consists of three quantities to be determined from observed vibrational frequencies. They are $F_S(1,1)$, $F_S(2,2)$ and $F_S(1,2)$ corresponding to the CH stretching, CC stretching and CH-CC interaction force constants, respectively. As was mentioned above, only the $\nu_2$ mode is observed with any appreciable intensity in the $C^2\Sigma_g^+$ state and no recordings were made on isotopic molecules. Hence, in the force constant analysis for the ion, the $\nu_1$ frequency was assigned to have the value of the neutral ground state /16/, while the interaction force constant was fixed to have a value of -0.1344 md $Å^{-1}$, which is the same as that in the $X^1\Sigma_g^+$ state

/17/. Thus, $F_S(1,1)$ and $F_S(2,2)$ are determined to have values of 6.1 ± 1.1 and 7.3 ± 0.4 md Å$^{-1}$, respectively, in the $C^2\Sigma_g^+$ state, compared to 6.3510 and 16.3410 md Å$^{-1}$ in the $X^1\Sigma_g^+$ state /17/. The error limits set for the ionic force constants were estimated from different calculations by varying the interaction force constants from -0.2688 to 0.1344 md Å$^{-1}$, as well as the $\nu_1$ and $\nu_2$ frequencies within 10% of the assigned values and the experimental error, respectively. It can be seen that there is a marked decrease in the CC stretching force constant in acetylene accompanying the $X^1\Sigma_g^+ \rightarrow C^2\Sigma_g^+$ transition.

The Franck-Condon analysis of the photoelectron band gave the value of $d^n_{CC}$ equal to 0.7774 x 10 $^{-20}$ g$^{1/2}$ cm with the theoretical vibrational intensities given in Table 1. The agreement between the computed and observed values is good considering the overlapping nature of the vibrational structure within the band as well as the harmonic oscillator approximation adopted in the intensity calculation. The $\mathbf{L}'_S$ matrix generated from the normal coordinate analysis was then employed to convert the shifts in the normal coordinates to the corresponding geometric changes, as mentioned previously. In this work, the matrix is found to be very insensitive to the magnitude of the interaction force constant as well as the $\nu_1$ frequency used. The CH and CC bond distances are determined to be 1.088 ± 0.005 and 1.439 ± 0.005 Å, respectively. Thus, in comparison to the neutral ground state values of 1.058 and 1.208 Å, the present values are much larger.

The $2\sigma_g$ orbital possesses CH and CC bonding character according to an INDO calculation /18/. Removal of an electron from the orbital weakens both the CH and CC bonds to different extents, resulting in a lengthening of the two bond distances as well as lowering of the corresponding vibrational frequencies, as was discussed above. In the present study, the vibrational energy of the CC stretching mode of acetylene is found to decrease drastically from 1973.5 /16/ to 1360 cm$^{-1}$, that is, by 31% accompanying the $X^1\Sigma_g^+ \rightarrow C^2\Sigma_g^+$ transition. Hence, the CC bond length is expected to increase appreciably in the process, in parallel with the calculated changes in structural parameters as well as with the variation of the force constant $F_S(2,2)$ upon ionisation.

The CH and CC bond distances of the ethylene molecule are respectively 1.086 and 1.339 Å /16/, respectively, while the corresponding values of ethane are 1.091 and 1.536 Å /16/. The structural parameters obtained for the acetylene cation in the present study are between these values. Hence, the CC bond order of the acetylene reduces from 3 in the molecule to about 1.5 in the ion.

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***Table 1.*** *Observed energies and relative intensities of the peaks in the $2\sigma_g^{-1}$ photoelectron band of the acetylene molecule. The intensities are taken as the peak heights.*

| Line no | Vibrational Energy quantum number | Observed (eV) | Calculated Relative Intensity | Relative Intensity |
|---|---|---|---|---|
| 1 | 0 | 22.86 | 0.14 | 0.04 |
| 2 | 1 | 23.03 | 0.35 | 0.24 |
| 3 | 2 | 23.21 | 0.73 | 0.60 |
| 4 | 3 | 23.37 | 0.97 | 0.93 |
| 5 | 4 | 23.54 | 1.00 [a] | 1.00 [a] |
| 6 | 5 | 23.71 | 0.87 | 0.78 |
| 7 | 6 | 23.87 | 0.63 | 0.45 |

[a] The peak with maximum intensity is assigned to have the value 1.00 .

## FIGURES

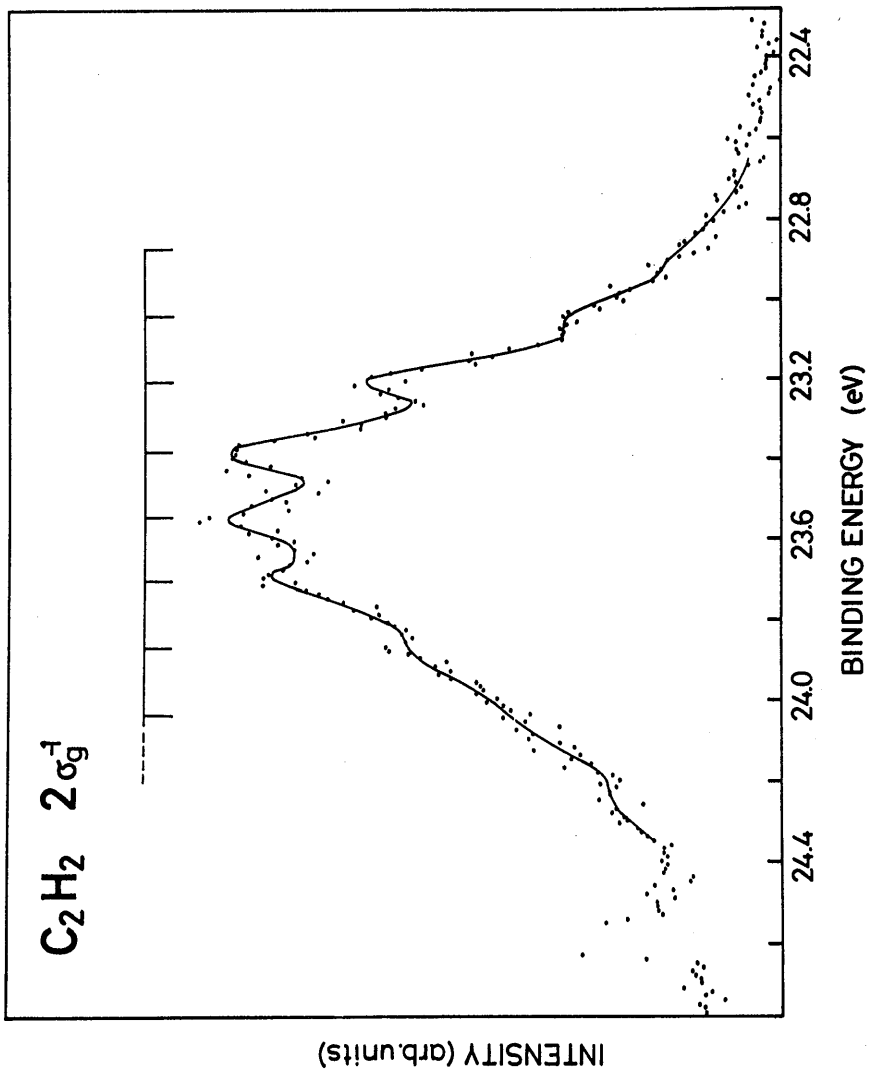


*Fig. 1.* *The fourth photoelectron band of the acetylene molecule associated with ionization from the $2\sigma_g$ inner valence orbital. A vibrational progression in the $\nu_2(\sigma_g^+)$ mode is indicated above the spectrum. A sharp line due to ionization of He with the HeIIa radiation is observed at 24.587 eV.*