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**Study of Correlation States in Molecular Systems by
Synchrotron Photoelectron Spectroscopy**

by

Maria Sabaye Moghaddam, B. Sc.

**A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfilment of the requirements for the degree of
Master of Science**

Department of Chemistry, Carleton University

Ottawa, Ontario

August 25, 1995

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2. Molecular Systems

2.1 Acetylene (C_2H_2)

2.1.1 Introduction

Acetylene, with a ground state electronic configuration ($^1\Sigma_g^+$) :

has been the subject of much attention due to its simple structure and very rich inner valence region in terms of correlation effects. It is the simplest hydrocarbon in the alkyne homologous series and one of the smallest triply bonded molecules. Of particular interest is its unusual chemical reactivity, for example in the formation of metal acetylides. Polymers of acetylene such as polyacetylene have been of growing importance due to their relatively high electrical conductivity⁵. A detailed knowledge of the electronic structure of acetylene is of importance in understanding its chemical and physical properties. In the last few decades, numerous experimental and theoretical studies have been performed in efforts to obtain as accurate and detailed a knowledge as possible of the electron interactions in this molecule. The following is a summary of the experimental and theoretical studies performed on acetylene.

Dixon et al.⁶ observed significant satellite structure in the inner valence region of C_2H_2 using binary (e,2e) spectroscopy (also known as electron momentum spectroscopy) and considered these structures to be associated with the $2\sigma_g^{-1}$ ionization process ($^2\Sigma_g^+$). On the other hand, Cavell and Allison⁷ considered the 27.5 eV satellite to be associated with the $2\sigma_u^{-1}$ ionization process ($^2\Sigma_u^+$) on the basis of discrete X-ray

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Synchrotron Photoelectron Spectroscopy**

submitted by Maria Sabaye Moghaddam, B. Sc.
in partial fulfillment of the requirements for the degree of
Master of Science

Thesis Supervisor

Chair, Department of Chemistry

Carleton University

August, 1995

Abstract

The inner valence photoelectron spectra of acetylene (C_2H_2) and isotopically labelled acetylene ($1,2\text{-}^{13}\text{C-C}_2\text{H}_2$) are obtained using high resolution synchrotron photoelectron spectroscopy (SRPES). Four distinct correlation (satellite) peaks are resolved. Three of these satellites (26.6 eV, 28.0 eV, and 29.8 eV binding energy) are found to be intrinsic with respect to $2\sigma_g^{-1}$ main peak while satellite four (31.2 eV binding energy) is found to be intrinsic with respect to $3\sigma_g^{-1}$ main peak as they exhibited constant photon energy dependence in their intensity ratio with respect to their parent peaks.

The SRPES spectra of pyridine ($\text{C}_5\text{H}_5\text{N}$) including inner and outer valence regions are obtained over a wide photon energy range (50-100 eV). Fifteen peaks corresponding to ionization out of fifteen main orbitals and two correlation peaks at binding energies 21.6 and 24.3 eV are observed. A comparison with the ADC(3) calculations is used to assign the overall dominant symmetry of the observed peaks in the photoelectron spectrum.

Acknowledgements

The most difficult part of writing my thesis was the acknowledgement. While it is very difficult to find the proper words that can describe the gratitude I feel toward many people for their support, it is impossible to find the space to mention the names of all these people. There are a few names, however, that have to be mentioned.

I would like to thank the Faculty, Staff, and Students of the Chemistry and Physics Departments for all their help over the last two years. In particular, I would like to thank Steve Desjardins, Behnaz Behroozian, and Dr. Ricardo Pascual. They have selflessly provided me with both academic and personal support any time I needed it.

I would also like to thank Professor Wolfgang von Niessen in Germany both for providing me with his ADC(3) calculations, and for helping me step-by-step to understand and interpret the results of his calculations.

As for my family, I can only ask for their forgiveness, for all the birthdays and weddings that I have missed, and for all their moments of need when I have not been there for them over the last seven years.

And to Jafar Shaker : thanks for everything.

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1. Introduction

1.1 Correlation Effects

Wigner and Seitz first used the term " electron correlation " in a study of the electronic structure of molecules in 1933 ¹. In order to understand electron correlations, different interactions between electrons in a system have to be examined. Whether these interactions are accounted for in models describing the electronic structure of different systems is of equal importance as this would allow for the knowledge of possible limitations of these models. This should ultimately lead to solutions that improve the present models and further the understanding of the complex electronic structures of different systems.

Due to Pauli exclusion principle, every electron in a system prevents electrons with the same spin occupying the same region of space. This type of correlation is accounted for in the Hartree-Fock (HF) model by the single determinantal wave function which requires the antisymmetry of the total wave function with respect to permutation of electron coordinates. In addition to this type of correlation, any given electron in a system moves in the instantaneous potential of all other electrons and its motion is therefore correlated with the motion of other electrons. That is, every electron in the system carries along a correlation hole to prevent other electrons from coming too close.² This interaction between the electrons in the system is formulated (in atomic units) as :

$$\frac{1}{2} \sum_{i \neq j}^N \frac{1}{|r_i - r_j|} \quad (1)$$

Consequently, the Hamiltonian for a many-electron system can be described as :

$$H = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 + V(i) \right) + \frac{1}{2} \sum_{i,j}^N \frac{1}{|r_i - r_j|} \quad (2)$$

In solving the Schrodinger equation for a many-body system, the independent electron models or orbital theories treat this potential (the second term on the right hand side of equation 2) as an effective potential (proportional to an average location of electrons) as opposed to an instantaneous potential (proportional to actual location of electrons). Independent electron models, therefore, suffer from two consequences of ignoring the effects of electron correlations. First, in calculating the energy of the systems, the energy associated with the interactions between electrons (E_{corr}) is ignored. Although small when compared to Hartree-Fock energy (E_{HF}), correlation energies ($E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$) are of the same order of magnitude as most energy differences of interest. Correlation energies make up to $\approx 0.5\%$ of the total energy of most systems. Yet, their importance can be better noted when they are compared to the binding energies. For example, the binding energy of N_2 is only $\approx 0.2\%$ of the total energy of the system. Second, these models are not capable of predicting full features of the photoelectron spectra of atoms and molecules. That is, they can predict only the peaks in the spectra that correspond to ionization out of the main orbitals. Other features of the photoelectron spectra, smaller peaks known as correlation peaks or satellites, are often ignored. These shortcomings reveal the importance of the study of electron correlations in efforts to gain a complete understanding of the electronic structure of atoms and molecules. More recent theoretical methods, being aware of the drawbacks associated with ignoring electron correlation effects, have included them in their calculations of the photoelectron spectra of different systems. For example, MRSDCI (multireference single and double

configuration interaction) calculations include electron correlation effects as symmetry allowed single and double excitations of electrons to (from) different orbitals. The result is their success in predicting full features of the photoelectron spectra of atoms and molecules. The results of MRSDCI calculations and recent Green's function calculations, presented in the following sections, will exhibit the success of these methods in predicting theoretical spectra that are in semi-quantitative agreement with the experimental spectra.

Efforts to understand the full effects of electron correlations have led to proposing different classification schemes. One such scheme, concerned with the mechanisms giving rise to these correlation peaks, is that proposed by Becker and Shirley.³ They divide the satellites (correlation peaks) into two categories: intrinsic and dynamic. Intrinsic correlation states are those whose intensity ratio with respect to the main line is independent of photon energy. In other words, satellite/main intensity ratio remains constant as the photon energy changes. These correlation states themselves can be divided into two classes: Initial State Correlations and Final State Correlations. These interactions occur between the electrons in the system in the absence of any other process. Photoionization does not trigger these interactions; it merely makes them visible. In contrast, dynamic correlation states are direct consequences of the photoionization process. As a photoelectron leaves the system, a hole is formed in its place. The system responds to this electron-hole "dipole": electrons in the vicinity of the hole try to get closer to fill the hole, while those closer to the electron leaving the system try to avoid it. There are subdivisions among the dynamic correlation states too. Examples include shake-up and conjugate shake-up correlation states which are the results of interactions between electrons in the system due to photoionization process. In the former case, a

photoelectron is ejected and another electron is excited to a higher level. In the latter case, the system receives the photon energy, and the photoelectron is excited to a higher energy level, while another electron leaves the system. Photon energy dependence studies of sat./main intensity ratios are one of the simplest and most direct methods of identifying the mechanisms that give rise to these different correlation states. Photoionization dependence studies of sat./main intensity ratios of acetylene, presented in the later sections, will illustrate the effectiveness of this method in identifying not only the mechanisms that give rise to these states but also the symmetry of these correlation peaks.

1.2 SRPES (Photoelectron Spectroscopy by Synchrotron Radiation)

SRPES refers to photoelectron spectroscopy by synchrotron radiation. Electron correlations become most evident in photoelectron spectra of molecules. The SRPES studies of different atoms and molecules have been indispensable tools in efforts to gain an accurate and complete understanding of the electronic structures of different systems. In photoelectron spectroscopy, a photon beam ($h\nu$) of sufficient energy ionizes the molecules (M) :

The ejected photoelectrons are detected at a particular angle relative to the light beam. The number of photoelectrons emitted in a unit of time is measured as a function of their kinetic energy (K) which is selected with an electron energy analyzer. Such a photoelectron intensity distribution plotted against K is the photoelectron spectrum in which ionization bands, corresponding to different ionization processes appear as individual bands. As the relationship between I and K is simply given by:

$$I = h\nu - K \quad (4)$$

the binding energies (I) of the different ionic states of a system can be directly obtained. The ordinate of photoelectron spectrum is usually given in units of counts (counts/s). i.e., the number of photoelectrons that reach the detector per second.

PES is the simplest method to determine the binding energies of the electrons in atoms and molecules directly. To provide accurate information about the electronic structure of different systems, PES is very much dependent on the choice of radiation source. The following example reveals how the choice of radiation source affects the information obtained by PES both qualitatively and quantitatively. The inner valence region of molecules has not been accessible by PES using traditional sources such as high energy resolution UV photon sources. High energy resolution photon sources such as HeI are not capable of providing photon energy beyond 21.2 eV. Consequently, they tend to miss the inner valence of most systems. High energy photon sources such as discrete X-rays (unmonochromatized), however, are not capable of energy resolutions of less than .80 eV fwhm. Therefore, they are not able to resolve the fine structures lying in the inner valence region. This region, particularly rich in correlation peaks, is accessible by PES using synchrotron as a radiation source. High energy resolution, high energy photons, high flux, and tunability of this radiation source allows for access to higher energy regions and for resolving fine structures which are normally obscured by the larger peaks.

Synchrotron radiation is emitted by charged particles such as electrons moving at relativistic speeds ($v/c \approx 1$) in a circular orbit. Fig. 1 shows a schematic drawing of a synchrotron radiation source. Electrons are injected into an electron synchrotron at a relatively low energy from a linear accelerator; in the synchrotron, these electrons are

accelerated on a fixed circular orbit. The synchrotron consists of an array of magnets for focusing and bending the beam and linear sections for accelerating the particles. When electrons reach the appropriate energy, they are transferred to the storage rings. Accelerator sections with the storage ring compensate for the losses due to synchrotron radiation. Around the storage ring, the radiation from the stored electrons can be used for various experiments. ⁴

Synchrotron radiation is the most versatile of electromagnetic radiation sources offering high intensity (photons. s^{-1} . mm^{-2} . $mrad^{-2}$) over broad spectral range (10^{-10} m - 10^{-4} m) and small angular divergence (1 to 10 mrad). These properties are of central importance in the development of high resolution studies of molecules as they allow access to the inner valence region of the molecules. Study of the electronic structure and in particular, the correlation effects in the molecules, is the main focus of this thesis. Two molecular systems have been studied: acetylene as the simplest representative of the triply-bonded hydrocarbons and pyridine as one of the simplest representative of the heteroatom aromatic structures.

Fig. 1. Schematic diagram of Aladdin Storage Ring at the University of Wisconsin at Madison.

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2. Molecular Systems

2.1 Acetylene (C_2H_2)

2.1.1 Introduction

Acetylene, with a ground state electronic configuration ($^1\Sigma_g^+$) :

has been the subject of much attention due to its simple structure and very rich inner valence region in terms of correlation effects. It is the simplest hydrocarbon in the alkyne homologous series and one of the smallest triply bonded molecules. Of particular interest is its unusual chemical reactivity, for example in the formation of metal acetylides. Polymers of acetylene such as polyacetylene have been of growing importance due to their relatively high electrical conductivity⁵. A detailed knowledge of the electronic structure of acetylene is of importance in understanding its chemical and physical properties. In the last few decades, numerous experimental and theoretical studies have been performed in efforts to obtain as accurate and detailed a knowledge as possible of the electron interactions in this molecule. The following is a summary of the experimental and theoretical studies performed on acetylene.

Dixon et al. ⁶ observed significant satellite structure in the inner valence region of C_2H_2 using binary (e,2e) spectroscopy (also known as electron momentum spectroscopy) and considered these structures to be associated with the $2\sigma_g^{-1}$ ionization process ($^2\Sigma_g^+$). On the other hand, Cavell and Allison ⁷ considered the 27.5 eV satellite to be associated with the $2\sigma_u^{-1}$ ionization process ($^2\Sigma_u^+$) on the basis of discrete X-ray

photoelectron spectroscopy experiments. These earlier studies were followed by extensive investigations using different experimental and theoretical techniques ⁸⁻²².

Later, better-resolved PES experimental studies resolved the broad satellite at 27.5 eV into two correlation (satellite) peaks at 26.7 eV and 28.0 eV ⁹. Theoretical calculations of Cederbaum et al. ¹¹ and Bradshaw et al. ¹² predicted a $^2\Sigma_g^+$ assignment for both correlation peaks. Furthermore, interference effects between the $2\sigma_g^{-1}$ and $3\sigma_g^{-1}$ processes were suggested as an explanation for the variations in the satellite/main intensity ratio as a function of photon energy.

A more recent PES study using monochromatic X-ray by Svensson et al. ¹³ resolved five correlation peaks (numbered 1-5 in order of increasing binding energy). Since then, various theoretical and experimental attempts have provided widely different interpretations as to the symmetry assignment of these correlation peaks. To mention a few, Chong ¹⁴ has considered $^2\Sigma_u^+$ symmetry for satellite 2 and $^2\Sigma_g^+$ symmetry for satellites 1 and 3, while Wasada and Hirao ¹⁵ have assigned $^2\Sigma_u^+$ for satellites 1 and 2 and $^2\Sigma_g^+$ symmetry for satellites 3 and 4 on the basis of theoretical calculations. More recently, Koch et al. ¹⁶ assigned $^2\Sigma_u^+$ symmetry for satellite 1 and $^2\Sigma_g^+$ for satellites 2 and 4 on the basis of synchrotron PES experiments. Weigold et al. ¹⁷ and Duffy et al. ¹⁸ assigned the symmetries of the satellites (1-4) to $^2\Sigma_g^+$ on the basis of electron momentum spectroscopy (EMS) experiments.

In the following sections, a comparison between high resolution photoelectron spectra of acetylene and MRSDCI(ANO) calculations, as well as photon energy dependence studies of intensity ratios of sat./main peaks is presented in an effort to assign

the proper symmetries to the correlation peaks in the photoelectron spectrum of acetylene.

2.1.2 Experimental method

The synchrotron PES spectra of acetylene and isotopically labelled acetylene (1,2- ^{13}C -acetylene) were obtained by Dr. Bawagan at the 3m-TGM beamline at the Aladdin storage ring, University of Wisconsin, Madison. The 600 grooves/mm (LEG) and 1800 grooves/mm (HEG) gratings were used in the 3m-TGM beamline. A toroidal grating is used to focus the photon beam between the entrance and exit slits in a TGM. A thin aluminum window isolated the spectrometer from the beamline and also removed higher order radiations which are the integer multiples of the selected photon energy.

The photon beam emerging from the monochromator exit slit is refocused to the gas cell in the Canadian Synchrotron Radiation Facility (CSRF) McPherson photoelectron chamber. A schematic diagram of the photoelectron spectrometer is shown in Fig. 2. A large (36 cm mean radius) McPherson electron energy analyzer provides the required high resolution and high transmission capabilities. A tunable guiding electric field in the spherical analyzer drives the photoelectrons towards the detector. The collecting efficiency of the energy analyzer is not constant for all electron energies for two main reasons. First, slower electrons have less of a chance of going through the analyzer to the detector as they are more affected by contact potentials, stray magnetic fields, and fringing electric fields than the higher energy electrons. To correct for transmission effects, all reported photoelectron intensity ratios are divided by the kinetic energy of the peaks²⁴. Secondly, photoelectrons are ejected with specific angular distributions that depend upon their energy and upon the orbit from which they are ejected (i.e., upon their angular momentum

state). To correct for this effect, the photoelectrons are collected at 55.8° (pseudomagic angle) relative to the polarization axis²³. At this pseudomagic angle, the number of electrons observed is independent of their angular distributions; therefore, no angular corrections to the derived cross sections are necessary. The detector used in this experiment was the Quantar open face multichannel plate position sensitive detector with a bias voltage of 3860 V and a gain of 5×10^7 .

High vacuum in the McPherson spectrometer is maintained by different pumping systems. Balzers turbomolecular pumps (models TPU 510 and 330) pumped the analyzer chamber and gas cell chamber respectively. The whole system is rough pumped by a Balzers rotary pump (DUO 008D). The gas inlet system is pumped by a small TRI VAC turbo pump. The entire beamline is at pressures of less than 2×10^{-10} Torr with pressures in the sample chamber of about 10^{-5} Torr.

The total experimental energy resolution (Γ_{total}) is ²³:

$$\Gamma_{\text{total}}^2 \approx \Gamma_{\text{natural width}}^2 + \Gamma_{\text{monochromator}}^2 + \Gamma_{\text{analyzer}}^2$$

As there are no experimental control on the natural widths ($\Gamma_{\text{natural width}}$) of the peaks, the total resolution is determined by the resolution of the electron energy analyzer (Γ_{analyzer}) and monochromator ($\Gamma_{\text{monochromator}}$) which for these experiments are about a total of 0.40 eV fwhm. A research purity sample of acetylene (99.9%) was supplied by Matheson Gas Products and 1,2-¹³C-acetylene (99%) was supplied by Isotec Inc.

2.1.3 Analysis

The obtained photoelectron spectra were converted from binary to ASCII format. The Jandel Scientific (PEAKFIT) program was used to fit gaussian peaks to the data. Two

Fig. 2. Schematic diagram of the McPherson photoelectron spectrometer. The photon beam is perpendicular to the plane of the diagram. The dashed line represents the path of the photoelectrons through the analyzer. The diagram is adapted from reference 23 and is not to scale.

additional gaussian peaks were fitted to the $2\sigma_g^{-1}$ main peak to account for the broad structure of this peak. In general, the gaussian fitting procedure is not a free-fit but constrained by several experimental parameters. In particular, the number of peaks and the peak positions are fixed based on previous XPS work.¹³ The peak widths are physically consistent with the measured total experimental energy resolution. The coefficient of determination (r^2) is generally 0.90-0.99 with a very good fit corresponding to $r^2 = 0.99$.

Linear and exponential backgrounds were fitted to the spectra obtained at high photon energies and low photon energies, respectively. The exponential backgrounds were obtained by running "no gas" background spectra.

For the photon energy dependence of intensity ratios, the transmission corrected areas under the specific peaks were calculated, and the respective ratios were taken. To correct for the transmission, the areas were divided by the kinetic energies²⁴ of the peaks.

The theoretical spectra were created by using a FORTRAN program to convolute the theoretical pole strengths, obtained from MRSDCI calculations, with gaussian peaks whose widths were consistent with the experimentally observed ones.

2.1.4 Results and discussion

A high resolution photoelectron spectrum of acetylene (at 68.8 eV photon energy) containing the main $2\sigma_g^{-1}$ peak and 4 correlation (satellite) peaks with binding energies of 23.5, 26.6, 28.0, 29.8, and 31.2 eV respectively is presented in Fig. 3. The energy scale was calibrated by aligning the main $2\sigma_g^{-1}$ peak to the well-known binding energy of the $2\sigma_g$ orbital obtained from a high resolution HeI spectrum²⁵. Additional Gaussian peaks

Fig. 3. A representative photoelectron spectrum of normal acetylene taken at photon energy of 68.8 eV with a total energy resolution of 0.40 eV fwhm. The spectrum as shown is not corrected for transmission effects. Gaussian curves are fitted to the correlation peaks (satellites 1-4) and the 2σ_g⁻¹ main peak. The 1π_u⁻¹ (11.43 eV binding energy), 3σ_g⁻¹ (16.7 eV binding energy) and 2σ_u⁻¹ (18.78 eV binding energy) main peaks are not shown.

Fig. 4. A representative photoelectron spectrum of isotopically labelled acetylene taken at photon energy of 72.4 eV with a total energy resolution of 0.40 eV fwhm. The spectrum as shown is not corrected for transmission effects. Gaussian curves are fitted to the correlation peaks (satellites 1-4) and the $2\sigma_g^{-1}$ main peak. The $1\pi_u^{-1}$ (11.43 eV binding energy), $3\sigma_g^{-1}$ (16.7 eV binding energy) and $2\sigma_u^{-1}$ (18.78 eV binding energy) main peaks are not shown.

to the high and low energy side of the $2\sigma_g^{-1}$ main peak were fitted to account for its broad structure. Single Gaussian peaks are fitted to correlation peaks 1-4 with widths of 0.51, 0.51, 0.85, and 0.85 eV fwhm, respectively. The width of the $2\sigma_g^{-1}$ main peak is 0.44 eV fwhm with additional peaks (of same width) on either side of the main peak to represent the broad structure.

To investigate whether these correlation peaks are of purely "electronic" origins, a PES spectrum of isotopically labelled acetylene (1,2- ^{13}C - C_2H_2) was obtained as shown in Fig. 4. No significant difference in terms of binding energy, peak widths, or peak areas of any of the ionization peaks was observed between acetylene and ^{13}C -labelled acetylene. The binding energy spectrum (Fig. 4), along with the photon energy dependence study of correlation peak intensity ratios (presented later), indicate that the correlation peaks are not influenced by extraneous electron-nuclear scattering processes.

To address the controversy surrounding the symmetry assignment of these correlation peaks, a study of the photon energy dependence of the intensity ratios of the correlation peaks relative to the $2\sigma_g^{-1}$ and $3\sigma_g^{-1}$ main peaks was performed. The results are presented in Tables 1-3 and shown in Figs. 5-8 for C_2H_2 and in Figs. 9-12 for 1,2- ^{13}C - C_2H_2 . It can be seen that the results are almost identical; there is no significant difference in the correlation peak to main $2\sigma_g^{-1}$ peak intensity ratios observed for normal C_2H_2 and 1,2- ^{13}C - C_2H_2 . This is further assurance that correlation peaks in acetylene are independent of electron-nuclear scattering effects.

It can be seen (Figs. 5-12) that satellites 1, 2, and 3 show relatively constant intensity ratios with respect to the main $2\sigma_g^{-1}$ peak, while satellite 4 exhibits an increase

Fig. 5. Photon energy dependence of the intensity ratio of satellite 1 at binding energy of 26.56 eV for normal acetylene. The intensity ratios are taken relative to the $2\sigma_g^{-1}$ main peak at binding energy of 23.51 eV. All reported intensity ratios are corrected for transmission effects. The corresponding XPS values¹³ are indicated by an arrow. The MRSDCI value was obtained by summing all the pole strengths in the respective satellite regions and dividing by the pole strengths in 22-24 eV region (see Table 4).

Fig. 6. Photon energy dependence of the intensity ratio of satellite 2 at binding energy of 28.01 eV for normal acetylene. The intensity ratios are taken relative to the $2\sigma_g^{-1}$ main peak at binding energy of 23.51 eV. All reported intensity ratios are corrected for transmission effects. The corresponding XPS values¹³ are indicated by an arrow. The MRSDCI value was obtained by summing all the pole strengths in the respective satellite regions and dividing by the pole strengths in 22-24 eV region (see Table 4).

Fig. 7. Photon energy dependence of the intensity ratio of satellite 3 at binding energy of 29.79 eV for normal acetylene. The intensity ratios are taken relative to the $2\sigma_g^{-1}$ main peak at binding energy of 23.51 eV. All reported intensity ratios are corrected for transmission effects. The corresponding XPS values¹³ are indicated by an arrow. The MRSDCI value was obtained by summing all the pole strengths in the respective satellite regions and dividing by the pole strengths in 22-24 eV region (see Table 4).

Fig. 8. Photon energy dependence of the intensity ratio of satellite 4 at binding energy of 31.2 eV for normal acetylene. The intensity ratios are taken relative to the $2\sigma_g^{-1}$ main peak at binding energy of 23.51 eV. All reported intensity ratios are corrected for transmission effects. The corresponding XPS values¹³ are indicated by an arrow. The MRSDCI value was obtained by summing all the pole strengths in the respective satellite regions and dividing by the pole strengths in 22-24 eV region (see Table 4).

Table 1: Transmission-corrected intensity ratios¹ of satellite peaks² to $2\sigma_g^{-1}$ for the spectra of normal acetylene obtained with high energy grating (HEG)

h ν	sat.1 ($\pm\sigma$)	sat.2 ($\pm\sigma$)	sat.3 ($\pm\sigma$)	sat.4($\pm\sigma$)
44	.152 (.011)	.155 (.014)	.164 (.022)	.183 (.034)
45	.075 (.023)	.078 (.024)	.111 (.019)	.118 (.040)
48	.085 (.010)	.094 (.011)	.010 (.016)	.070 (.025)
50	.081 (.010)	.101 (.009)	.026 (.014)	.100 (.015)
52	.102 (.008)	.125 (.009)	.057 (.014)	.098 (.021)
56	.112 (.010)	.133 (.010)	.068 (.014)	.086 (.015)
60	.118 (.005)	.131 (.005)	.070 (.008)	.065 (.009)
62	.119 (.007)	.132 (.007)	.067 (.010)	.068 (.010)
64	.121 (.009)	.131 (.009)	.066 (.013)	.065 (.013)
68	.129 (.042)	.137 (.006)	.070 (.008)	.060 (.009)
70	.134 (.009)	.137 (.009)	.072 (.009)	.057 (.008)
72	.145 (.006)	.138 (.006)	.084 (.009)	.062 (.010)

¹The quoted error limits are statistical errors and do not include systematic errors which are estimated to be $\leq 10\%$

²The binding energies of the satellite peaks 1-4 are 26.56, 28.0, 29.79, 31.2 eV respectively.

Table 2 : Transmission-corrected intensity ratios¹ of satellite peaks² to $2\sigma_g^{-1}$ for the spectra of normal acetylene obtained with low energy grating (LEG)

h ν	sat.1 ($\pm\sigma$)	sat.2 ($\pm\sigma$)	sat.3 ($\pm\sigma$)	sat.4 ($\pm\sigma$)
42	.156 (.011)	.149 (.011)	.154 (.015)	.274 (.019)
44	.092 (.019)	.096 (.020)	.071 (.034)	.118 (.033)
46	.183 (.107)	.168 (.012)	.145 (.019)	.114 (.024)
48	.132 (.012)	.133 (.012)	.103 (.021)	.093 (.020)
50	.115 (.008)	.127 (.007)	.068 (.011)	.084 (.013)
52	.126 (.007)	.138 (.007)	.084 (.011)	.098 (.010)
54	.109 (.045)	.130 (.048)	.063 (.009)	.082 (.010)
56	.113 (.049)	.146 (.018)	.127 (.023)	.018 (.020)

¹ The quoted error limits are statistical errors and do not include systematic errors which are estimated to be $\leq 10\%$

² The binding energies of the satellite peaks 1-4 are 26.56, 28.00, 29.79, and 31.2 eV respectively.

in intensity ratio with respect to the main $2\sigma_g$ peak as threshold (31.2 eV) is approached. In fact, all these correlation (satellite) peaks show constant photon energy dependence in the 50-75 eV photon energy range, with some variations at the lower photon energies (40-50 eV). The constant photon energy dependence is consistent with a predominantly $^2\Sigma_g^+$ symmetry assignment to these four correlation peaks; as correlation peaks which derive their intensity from different symmetry orbitals show strong variations in their intensity ratio with respect to one of the main peaks. Since experimentally determined $1\pi_u/2\sigma_g$ ¹² main peak and $3\sigma_g/2\sigma_g$ main peak ratios as well as the $2\sigma_u/2\sigma_g$ main peak ratios show a smooth decrease with increasing photon energy in the photon energy range 40-75 eV (see Appendix 1), we can use the correlation peak to $2\sigma_g^{-1}$ main peak intensity ratios for distinguishing the major contributor to a particular correlation peak. This is particularly true if there are contributions from ionic states with significant carbon 2p character such as $^2\Pi_u$ since the variations of the $1\pi_u/2\sigma_g$ main peak intensity ratio are very substantial¹². The variations in the $2\sigma_u/2\sigma_g$ main peaks are relatively smaller and the intensity ratio is constant in the photon energy range 55-75 eV (see Appendix 1). The photon energy dependence studies of the correlation peak to $2\sigma_g^{-1}$ as well as to $3\sigma_g^{-1}$ main peak intensity ratios which indicate predominantly $^2\Sigma_g^+$ symmetry are supported by MRSDCI calculations (see section 2.1.5).

The slight variations in the intensity ratio of satellites 1-3 in the 40-50 eV range can be due to a number of reasons. Close to threshold, autoionization (interchannel coupling) from doubly excited states introduces resonance structures in the photon energy dependence of correlation state cross sections^{26,27}. Thus observation of the correlation

Fig. 9. Photon energy dependence of the intensity ratio of satellite 1 at binding energy of 26.56 eV for isotopically-labelled acetylene. The intensity ratios are taken relative to the $2\sigma_g^{-1}$ main peak at binding energy of 23.51 eV. All reported intensity ratios are corrected for transmission effects. The corresponding XPS values¹³ are indicated by an arrow. The MRSDCI value was obtained by summing all the pole strengths in the respective satellite regions and dividing by the pole strengths in 22-24 eV region (see Table 4).

Fig. 10. Photon energy dependence of the intensity ratio of satellite 2 at binding energy of 28.0 eV for isotopically-labelled acetylene. The intensity ratios are taken relative to the $2\sigma_g^{-1}$ main peak at binding energy of 23.51 eV. All reported intensity ratios are corrected for transmission effects. The corresponding XPS values ¹³ are indicated by an arrow. The MRSDCI value was obtained by summing all the pole strengths in the respective satellite regions and dividing by the pole strengths in 22-24 eV region (see Table 4).

Fig. 11. Photon energy dependence of the intensity ratio of satellite 3 at binding energy of 29.79 eV for isotopically labelled acetylene. The intensity ratios are taken with respect to $2\sigma_g^{-1}$ main peak at 23.51 eV binding energy. All reported intensity ratios are corrected for transmission effects. The corresponding XPS values ¹³ are indicated by an arrow. The MRSDCI value was obtained by summing all pole strengths in the respective satellite regions and dividing by the pole strength in 22-24 eV (see Table 4).

Fig. 12. Photon energy dependence of the intensity ratio of satellite 4 at binding energy of 31.2 eV for isotopically labelled acetylene. The intensity ratios are taken with respect to $2\sigma_0^{-1}$ main peak at 23.51 eV binding energy. All reported intensity ratios are corrected for transmission effects. The corresponding XPS values ¹³ are indicated by an arrow. The MRSDCI value was obtained by summing all pole strengths in the respective satellite regions and dividing by the pole strength in 22-24 eV (see Table 4).

Table 3 : Transmission-corrected intensity ratios¹ of satellite peaks² to $2\sigma_g^{-1}$ for the spectra of labelled acetylene obtained with low energy grating (LEG)

h ν	sat.1 ($\pm\sigma$)	sat.2 ($\pm\sigma$)	sat.3 ($\pm\sigma$)	sat.4 ($\pm\sigma$)
42	.089 (.009)	.085 (.010)	.040 (.017)	.354 (.019)
46	.141 (.016)	.158 (.016)	.063 (.025)	.155 (.029)
48	.095 (.009)	.103 (.010)	.020 (.017)	.058 (.018)
50	.112 (.007)	.119 (.007)	.053 (.012)	.079 (.012)
52	.106 (.008)	.118 (.007)	.056 (.011)	.081 (.011)
56	.114 (.007)	.121 (.007)	.053 (.010)	.099 (.011)
60	.131 (.006)	.126 (.007)	.055 (.010)	.077 (.010)
62	.132 (.006)	.136 (.006)	.069 (.010)	.079 (.010)
68	.136 (.005)	.143 (.006)	.075 (.009)	.081 (.009)
70	.141 (.006)	.147 (.006)	.074 (.001)	.079 (.010)
70.4	.143 (.005)	.145 (.005)	.074 (.007)	.067 (.008)
72	.143 (.004)	.141 (.004)	.060 (.004)	.060 (.007)
72.5	.146 (.010)	.129 (.011)	.026 (.016)	.116 (.016)
73.5	.151 (.008)	.146 (.008)	.112 (.012)	.075 (.013)

¹The quoted error limits are statistical errors and do not include systematic errors which are estimated to be $\leq 10\%$

²The binding energies of the satellite peaks 1-4 are 26.56, 28.0, 29.79, and 31.2 eV respectively.

state cross sections as a function of exciting photon energy will show sharp resonance structures corresponding to the energies of doubly excited states of the neutral. Since the photon energy spacings between the present measurements are ≥ 2 eV, the resonance fine structures can not be observed; instead a scatter of data points can be seen in the 40-50 eV photon energy range (Figs.5-12). Another factor contributing to these variations is the experimental PES background. At low photon energies, especially below 40 eV, the sloping background prevents very accurate determination of intensity ratios. These errors are listed in Tables 1-3 and shown in Figs. 5-12. It can be seen that the observed variations are much larger than the error limits (1σ) of the intensity ratios. This indicates that these variations may be largely due to autoionization resonance structures yet to be identified.

It is worthwhile to note that the satellite/main $2\sigma_g^{-1}$ peak intensity ratios for satellites 1-3 (Figs. 9-11) are consistently lower than those obtained from the X-ray photoelectron (XPS) spectrum (at 1487 eV) of Svensson et al.¹³. The XPS values of Svensson et al are indicated by a horizontal arrow in Fig. 5-12. The discrepancy between the present measurements and the XPS values may be a real effect and can only be ascertained by performing synchrotron PES measurements at photon energies from 80 eV up to 1487 eV. However, it is most likely that the discrepancies are due to the higher atomic photoionization cross-section of C_{2s} orbital compared to C_{2p} orbitals at higher photon energies (ie. X-ray energies). At about 1487 eV photon energy, the photoionization cross-section of a C_{2s} orbital is 66 times larger than that of a C_{2p} orbital²⁸. This significant difference between the photoionization cross-section of C_{2s} and C_{2p} orbitals

Fig. 13. Comparison of (a) the experimental binding energy spectrum of acetylene with (b) the theoretical spectrum based on MRSDCI(ANO) calculation using a 171-CGTO basis set. The calculated pole strengths (solid poles) are convoluted with the experimental peak widths to yield the curve (solid line) which can be compared with the experiment (b). Poles associated mainly with the $2\sigma_g^{-1}$ and $3\sigma_g^{-1}$ ionization processes are labelled with a star. (see Table 4)

Table 4. The calculated line positions and intensities for the PES of acetylene¹

Symmetry	Ionization Energy ⁴ (eV)	Intensity ² S_j^2	Important Configurations ³
$^2\Sigma_g^+$	16.36	0.797	0.90 $(3\sigma_g)^{-1}$
			0.19 $(2\sigma_u)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$
			0.19 $(3\sigma_g)^{-1} (1\pi_u)^{-1} (n\pi_u)^1$
			0.18 $(3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
	23.17	0.519	0.72 $(2\sigma_g)^{-1}$
			0.48 $(2\sigma_u)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$
			0.17 $(2\sigma_g)^{-1} (1\pi_u)^{-1} (n\pi_u)^1$
			0.16 $(1\pi_u)^{-2} (n\sigma_g)^1$
			0.16 $(1\pi_u)^{-2} (n\delta_g)^1$
			0.15 $(2\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
			0.11 $(3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
			0.61 $(1\pi_u)^{-2} (n\delta_g)^1$
			0.51 $(2\sigma_u)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$
			0.32 $(1\pi_u)^{-2} (n\sigma_g)^1$
	26.93	0.061	0.25 $(2\sigma_g)^{-1}$
			0.19 $(3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
			0.88 $(1\pi_u)^{-2} (n\delta_g)^1$
			0.17 $(2\sigma_u)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$
	27.34	0.010	0.10 $(2\sigma_g)^{-1}$
			0.72 $(1\pi_u)^{-2} (n\delta_g)^1$
			0.39 $(2\sigma_u)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$
	28.13	0.112	0.34 $(2\sigma_g)^{-1}$
			0.16 $(3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
			0.87 $(1\pi_u)^{-2} (n\sigma_g)^1$
	30.09	0.005	0.15 $(3\sigma_g)^{-1} (1\pi_u)^{-2} (n\sigma_g)^1 (n\delta_g)^1$
			0.13 $(2\sigma_u)^{-1} (1\pi_u)^{-2} (n\sigma_u)^1 (n\delta_g)^1$
			0.09 $(3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
			0.07 $(2\sigma_g)^{-1}$
			0.53 $(3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
	30.29	0.034	0.38 $(2\sigma_u)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$
			0.36 $(1\pi_u)^{-2} (n\sigma_g)^1$
			0.34 $(1\pi_u)^{-2} (n\delta_g)^1$
			0.31 $(3\sigma_g)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$
			0.17 $(2\sigma_g)^{-1}$
	30.55	0.005	0.59 $(1\pi_u)^{-2} (n\delta_g)^1$
			0.49 $(3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
			0.38 $(1\pi_u)^{-2} (n\sigma_g)^1$
			0.06 $(2\sigma_g)^{-1}$

Table 4. Continued

			$0.06(3\sigma_g)^{-1}$
	30.77	0.008	$0.81 (3\sigma_g)^{-1} (1\pi_u)^{-1} (n\pi_u)^1$ $0.31 (3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$ $0.17 (3\sigma_g)^{-1} (1\pi_u)^{-2} (n\pi_u)^2$ $0.08 (2\sigma_g)^{-1}$
	31.15	0.016	$0.61 (2\sigma_u)^{-1} (1\pi_u)^{-1} (n\pi_g)^1$ $0.55 (3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$ $0.26 (3\sigma_g)^{-1} (1\pi_u)^{-1} (n\pi_u)^1$ $0.13 (1\pi_u)^{-2} (n\delta_g)^1$ $0.11 (2\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$ $0.09 (2\sigma_g)^{-1}$ $0.07 (3\sigma_g)^{-1}$
	31.66	0.016	$0.78 (3\sigma_g)^{-1} (1\pi_u)^{-1} (n\pi_u)^1$ $0.26 (2\sigma_u)^{-1} (1\pi_u)^{-1} (n\pi_g)^1$ $0.25 (3\sigma_g)^{-1} (1\pi_u)^{-2} (n\pi_u)^2$ $0.20 (2\sigma_u)^{-1} (1\pi_u)^{-2} (n\pi_g)^1 (n\pi_u)^1$ $0.13 (3\sigma_g)^{-1} (2\sigma_u)^{-1} (n\sigma_u)^1$ $0.13(3\sigma_g)^{-1}$
	32.23	0.004	$0.93 (3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
	34.26	0.005	$0.87 (1\pi_u)^{-2} (n\delta_g)^1$ $0.18 (3\sigma_g)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
$^2\Pi_g^5$	23.74	0.026	$0.90 (1\pi_u)^{-2} (1\pi_g)^1$
$^2\Pi_u$	11.40	1.64	$0.93 (1\pi_u)^{-1}$ $0.14 (1\pi_u)^{-2} (n\pi_u)^1$
	26.86	0.015	$0.88 (1\pi_u)^{-2} (n\pi_u)^1$ $0.10 (1\pi_u)^{-1}$
	31.65	0.005	$0.62 (1\pi_u)^{-1} (3\sigma_g)^{-1} (n\sigma_g)^1$ $0.44 (1\pi_u)^{-2} (n\pi_u)^1$ $0.31 (1\pi_u)^{-1} (2\sigma_u)^{-1} (n\sigma_u)^1$
	32.03	0.011	$0.64 (1\pi_u)^{-1} (2\sigma_u)^{-1} (n\sigma_u)^1$ $0.35 (1\pi_u)^{-2} (n\pi_u)^1$ $0.32 (1\pi_u)^{-1} (3\sigma_g)^{-1} (n\sigma_g)^1$ $0.31 (3\sigma_g)^{-1} (2\sigma_u)^{-1} (1\pi_g)^1$ $0.07 (1\pi_u)^{-1}$
	36.08	0.010	$0.53 (1\pi_u)^{-2} (n\pi_u)^1$ $0.47 (1\pi_u)^{-1} (3\sigma_g)^{-1} (n\sigma_g)^1$ $0.44 (1\pi_u)^{-1} (2\sigma_u)^{-1} (n\sigma_u)^1$
$^2\Sigma_u^+$	18.69	0.705	$0.87 (2\sigma_u)^{-1}$ $0.27 (3\sigma_g)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$

Table 4. Continued

23.82	0.010	$0.14 (2\sigma_u)^{-1} (1\pi_u)^{-1} (n\pi_u)^1$
		$0.13 (2\sigma_g)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$
		$0.89 (3\sigma_g)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$
		$0.19 (1\pi_u)^{-2} (n\sigma_u)^1$
		$0.14 (2\sigma_u)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
25.13	0.018	$0.10 (2\sigma_u)^{-1}$
		$0.88 (1\pi_u)^{-2} (n\sigma_u)^1$
		$0.17 (3\sigma_g)^{-1} (1\pi_u)^{-1} (1\pi_g)^1$
30.31	0.029	$0.13 (2\sigma_u)^{-1}$
		$0.82 (3\sigma_g)^{-1} (1\pi_u)^{-1} (n\pi_g)^1$
		$0.24 (2\sigma_u)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
32.79	0.004	$0.14 (2\sigma_u)^{-1}$
		$0.68 (2\sigma_u)^{-1} (1\pi_u)^{-1} (n\pi_u)^1$
		$0.47 (3\sigma_g)^{-1} (1\pi_u)^{-1} (n\pi_g)^1$
		$0.24 (2\sigma_g)^{-1} (1\pi_u)^{-1} (n\pi_g)^1$
		$0.17 (2\sigma_u)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
34.07	0.004	$0.09 (2\sigma_u)^{-1}$
		$0.73 (1\pi_u)^{-3} (n\pi_g)^1 (n\sigma_g)^1$
		$0.33 (2\sigma_u)^{-1} (1\pi_u)^{-1} (n\pi_u)^1$
		$0.30 (3\sigma_g)^{-1} (1\pi_u)^{-1} (n\pi_g)^1$
		$0.21 (2\sigma_u)^{-1} (1\pi_u)^{-2} (1\pi_g)^2$
34.12	0.013	$0.09 (2\sigma_u)^{-1}$
		$0.54 (3\sigma_g)^{-1} (1\pi_u)^{-1} (n\pi_g)^1$
		$0.44 (2\sigma_u)^{-1} (1\pi_u)^{-1} (n\pi_u)^1$
		$0.40 (1\pi_u)^{-3} (n\pi_g)^1 (n\sigma_g)^1$
		$0.09 (2\sigma_u)^{-1}$

1. For each symmetry, the MRSDCI wavefunctions are used for the cation and neutral molecule, and all calculations are based on the frozen average natural orbitals.
2. The values less than .004 are ignored.
3. Absolute value is used for every CI coefficient.
4. The first root energies have been adjusted to experimental data separately for each symmetry except for the $^2\Pi_g$ symmetry, and the same constant shift is used for the remaining roots in this symmetry. For symmetry $^2\Sigma_g^+$, the energy shift is -0.66 eV (to the lower binding energy direction), for symmetry $^2\Pi_u$, -0.12 eV and for symmetry, $^2\Sigma_u^+$ -0.45 eV.
5. The energy of the ground state of the neutral molecule is taken from our MRSDCI calculation based on the ionic frozen average natural orbitals of this symmetry ($^2\Pi_g$).

gives higher intensity to those satellites which are of symmetries with mostly C_{2s} character and lower intensity to those satellites which are of symmetries with more C_{2p} character. Since the main $2\sigma_g^{-1}$ peak has some $1\pi_u^{-1}$ poles as shown in the MRSDCI calculations (see section 2.1.5), there is some C_{2p} character in the main $2\sigma_g^{-1}$ peak. Satellites 1 and 4 are also predicted to have contributions from symmetry orbitals with strong C_{2p} character ($1\pi_u$ and $3\sigma_g$); thus the sat.1/ $2\sigma_g$ and sat.4/ $2\sigma_g$ intensity ratios in the 50-75 eV energy range are similar to the corresponding ratios at 1487 eV. In contrast, satellite 2 is of pure $2\sigma_g$ symmetry, whereas satellite 3 has $2\sigma_g$ and $2\sigma_u$ symmetry which are all symmetry orbitals with strong C_{2s} character. Therefore the sat.2/ $2\sigma_g$ and sat.3/ $2\sigma_g$ intensity ratios in the 50-75 eV energy range are lower than the corresponding ratios at 1487 eV. The C_{2s} and C_{2p} contributions provide a consistent explanation for the similarities as well as differences between the intensity ratios observed in the present experiment and those observed by Svensson et al.¹³ at 1487 eV.

Current interest in photon energy dependence of intensity ratios lies mostly in understanding the different mechanisms giving rise to these correlation peaks. Using the classification scheme of Becker and Shirley³, satellites 1, 2, and 3 can be regarded as intrinsic correlations and satellite 4 as a dynamic correlation based on the assumption that all peaks (1,2,3 and 4) are largely associated with the $2\sigma_g^{-1}$ ionization process. Intrinsic correlation (satellite) peaks are those whose intensity is independent of the photon energy while dynamic correlation (satellite) peaks are those whose intensity depends on photon energy.

An alternative and more plausible explanation can be advanced for the photon

energy dependence of the $\text{sat.4}/2\sigma_g$ intensity ratio. The theoretical PES of acetylene obtained from the MRSDCI(ANO) calculations is shown in Fig. 13(b) and Table 4. It can be seen that satellite 4 is composed primarily of $^2\Sigma_g$ correlation states. However, two of the correlation states (31.15 eV and 31.66 eV binding energy) corresponding to satellite 4 are associated with the $3\sigma_g^{-1}$ ionization process as opposed to the usual $2\sigma_g^{-1}$ ionization process (see Table 4); both of these processes have overall $^2\Sigma_g$ symmetry. The 31.15 eV state has a normalized Dyson orbital that is approximately $0.8(2\sigma_g) + 0.6(3\sigma_g)$ whereas the 31.66 eV state has a normalized Dyson orbital that is nearly pure $3\sigma_g$. Since the $3\sigma_g$ molecular orbital contains significant C_{2p} character, the $3\sigma_g/2\sigma_g$ main peak ratio will decrease as the photon energy increases. The same trend is observed experimentally for $\text{sat.4}/2\sigma_g$ main peak (see Figs. 8 and 12) which strongly suggests that $\text{sat.4}/3\sigma_g$ main peak intensity ratio is constant with increasing photon energy. The photon energy dependence of the $\text{sat.4}/3\sigma_g$ main peak intensity ratio is shown in Fig. 14 in comparison with the predicted MRSDCI pole strength ratio. The present intensity ratios (Fig. 14) were obtained using additional experimental PES data for the $2\sigma_g/3\sigma_g$ main peak ratio (see Appendix 1). The photon energy dependence curve is clearly constant in the photon energy range 45-75 eV. Very good agreement with the predicted MRSDCI ratio is also obtained.

Although the correlation states at 31.15 eV and 31.66 eV are only two of four other states in the satellite 4 binding energy region, on the basis of their relative pole strengths it can be said that the observed photon energy dependence of satellite 4 is associated mainly with the $3\sigma_g^{-1}$ ionization process rather than being a "dynamic"

Fig. 14. Photon energy dependence of the intensity ratio of satellite 4 (31.2 eV binding energy) for normal acetylene and isotopically-labelled acetylene. The intensity ratios are taken relative to the $3\sigma_g^{-1}$ main peak at binding energy of 16.36 eV. All reported intensity ratios are corrected for transmission effects. The MRSDCI value was obtained by summing all the pole strengths in 31-33 eV region and dividing by the pole strengths in 16-17 eV region (for details see Table 4).

correlation state associated with the $2\sigma_g^{-1}$ ionization process. It should be noted that this possibility (i.e., interference of $3\sigma_g^{-1}$ and $2\sigma_g^{-1}$ ionization processes in $^2\Sigma_g$ correlation states) was first suggested by Bradshaw et al. ⁸; however, it was made in relation to satellite 1 and not to satellite 4. The calculated $3\sigma_g^{-1}$ pole strengths in the satellite 4 binding energy region are small but not insignificant (≈ 0.03) and are in fact observable in the present synchrotron PES experiments. It can be seen that the predicted $^2\Pi_u$ correlation state at 26.86 eV is consistent with the value of the sat.1/ $2\sigma_g$ main intensity ratio (see above) relative to the corresponding intensity ratio at X-ray energies.

The experimental PES spectrum and the theoretical PES spectrum obtained from MRSDCI calculations are compared in Fig.13. As can be seen, there is reasonable agreement between experiment and theory in the inner valence region. The theoretical results lend support to the assignment of largely $^2\Sigma_g^+$ symmetry for the satellites 1-4. It can be seen from Fig. 13 (b) that most of the dominant poles are associated with the $2\sigma_g^{-1}$ and $3\sigma_g^{-1}$ ionization processes and are indicated by (*). Furthermore, these theoretical results predict that there are contributions to the intensity of satellites 1, 3, and 4 from $1\pi_u^{-1}$, $3\sigma_g^{-1}$, and $2\sigma_u^{-1}$ as well as $2\sigma_g^{-1}$ ionization processes. That is, there is an interleaving of correlation states. It is likely that the intensity ratio variations of correlation peaks 1,3 and 4 are due to intensity contributions from more than one symmetry. The MRSDCI calculations also predict some correlation states within the main $2\sigma_g^{-1}$ envelope itself. A $^2\Pi_g$ correlation state is predicted at 23.74 eV and a $^2\Sigma_u$ correlation state is predicted at 23.82 eV. These theoretical results are also consistent with experiment (Figs. 3 and 4) which showed an unusually broad $2\sigma_g^{-1}$ main peak which is represented by 3

Gaussian peaks in the deconvolution. The exact location of the correlation peak corresponding to the ${}^2\Pi_g$ state can not be quoted with certainty because there is no clear shoulder in the experimental data. The ${}^2\Pi_g$ state predicted at 23.74 eV is of special interest. It must be largely due to initial state configuration interaction as the $1\pi_g$ orbital is unoccupied in the Hartree-Fock neutral configuration.

According to the MRSDCI calculations (see table 4), satellite 2 can be considered as purely of ${}^2\Sigma_g^+$ symmetry ($2\sigma_g^{-1}$) and its intensity ratio relative to the $2\sigma_g^{-1}$ main peak (see Figs. 6 and 10), in fact, shows the least variation from the predicted constant trend expected for an intrinsic correlation state. The MRSDCI calculations indicate a single correlation state at 28.13 eV associated mainly with a 2h-1p configuration, $(1\pi_u)^{-2} (n\delta_g)^1$. There are no correlation states of other symmetry with significant intensity in the binding energy region of satellite 2. Satellites 1 and 4 are dominated by correlation states of ${}^2\Sigma_g^+$ symmetry ($2\sigma_g^{-1}$ and $3\sigma_g^{-1}$) with some contributions from ${}^2\Pi_u$ and ${}^2\Sigma_u^+$ correlation states. Satellite 3 is still largely of ${}^2\Sigma_g^+$ symmetry but contains a ${}^2\Sigma_u^+$ correlation state of large pole strength. The cumulative pole strength of ${}^2\Sigma_g^+$ correlation states in the 30-31 eV binding energy range is 0.054 while the single ${}^2\Sigma_u^+$ correlation state at 30.31 eV has a comparable pole strength of 0.029. Thus the observed variations in the intensity ratios for satellite 3 are clearly consistent with the theoretical predictions which indicate several correlation states of different symmetry.

2.1.5 Theoretical details

The photoionization transition amplitude (μ_j) is given by,
where $\Psi(N)$ is the ground state N-electron wavefunction, $\Psi_j(N-1)$ is the j^{th} ionic state

$$\mu_j = \langle \Psi_j(N-1) \chi^j(k) | \mu | \Psi(N) \rangle \quad (5)$$

wavefunction, μ is the dipole operator, and $\chi^j(k)$ is the continuum function for the outgoing photoelectron with momentum k and associated with state j . Here $\Psi(N)$ and $\Psi_j(N-1)$ are written as linear combinations of all possible configurations. This is referred to as the configuration interaction (CI) picture. The transition amplitude can also be written as,

$$\mu_j = \langle \chi^j(k) | \mu | \phi_{\text{Dyson}}^j \rangle S_j \quad (6)$$

where ϕ_{Dyson}^j is the Dyson orbital^{29,30} and S_j^2 is the so-called pole strength or the ionization probability for the j^{th} ionic state. The pole strength for the j^{th} ionic state is defined as,

$$S_j^2 = |\langle \Psi_j(N-1) | \Psi(N) \rangle_{N-1}|^2 \quad (7)$$

where the integration is performed over $N-1$ electrons.

In practice, PES measurements are taken at a fixed photon energy and the intensity ratio of the correlation (satellite) peak relative to a primary peak with a similar Dyson orbital is obtained. In this case, the intensity ratio of the j^{th} correlation peak to the p^{th} primary peak of the same symmetry (and under certain conditions) is given by the familiar expression^{29,30},

$$\frac{I(j)}{I(p)} = \frac{S_j^2}{S_p^2} \quad (8)$$

This approximation is valid only when the dipole matrix elements $\langle \chi^j(k) | \mu |$

Fig. 15. Calculated photoelectron spectrum reported by Wasada and Hirao¹⁵. The SAC-CI calculation predicts pole strengths at binding energies > 35 eV which are not included in the present diagram. The calculated pole strengths (solid poles) are convoluted with the experimental peak widths to yield the solid curve which can then be compared with experiment.

Fig. 16. Calculated photoelectron spectrum reported by Weigold et al.¹⁷ The calculated pole strengths (solid poles) are convoluted with the experimental peak widths to yield the solid curve which can then be compared with experiment.

ϕ_{Dyson}^j for the j^{th} correlation peak and the p^{th} primary peak are nearly equal. In this approximation, the explicit form of the continuum function ($\chi^l(k)$) is not specified. It is only assumed that the continuum functions for state j and state p are similar. More accurate calculations will definitely include explicit calculations of the continuum functions. Combining these MRSDCI calculations with explicit continuum state calculations is not feasible with current computer hardware and software technology.

As for acetylene, the MRSDCI(ANO) calculations of Wang and Davidson³¹ show semi-quantitative agreement with experimental photoelectron spectra of acetylene. This agreement between theory and experiment is beyond all comparisons that have been attempted in the past. In general, other theoretical calculations (Figs. 15 and 16) do not show as good an agreement as the MRSDCI results with the experimental results (Figs. 3 and 4). The previously reported calculations seem to suffer from limitations in their basis sets. For example, Weigold et al.¹⁷ use a 58-CGTOs (Contracted Gaussian Type Orbitals) basis set in their ADC(4) (Algebraic Diagrammatic Construction) Green's Function calculations, and Wasada and Hirao¹⁵ use a 42-CGTOs basis set in their SAC (CI) (Symmetry-Adapted-Cluster Configuration Interaction) calculations. Theoretical calculations prior to 1989 are not included in the comparison.

The MRSDCI(ANO) study uses a 171-CGTOs basis set which includes several Rydberg orbitals and diffuse functions. The improvement in the results can be observed by comparing each theoretical calculation with the experimental PES spectrum (cf. Figs. 13, 15, and 16). The MRSDCI(ANO) calculations are, clearly, superior in terms of the prediction of the binding energies and peak intensities (see Fig. 13). The SAC-CI

calculation of Wasada and Hirao (Fig. 15) is unsatisfactory in an overall sense. In particular, the SAC-CI calculation predicts two $^2\Sigma_u^+$ correlation states in the 26-32 eV region which is not consistent with the present experimental and theoretical results. The SAC-CI calculation predicts the first correlation state at about 31 eV whereas experiment clearly shows the correlation peak at much lower binding energy (25.56 eV). The symmetry assignments of the SAC-CI calculation is also inconsistent with EMS measurements^{17,18} and ADC(4) calculations¹⁷.

The ADC(4) calculation of Weigold et al (Fig. 16) is a significant improvement compared to the SAC-CI calculation. The overall profile of the ADC(4) calculation agrees better with the present experimental results except that it predicts only one main correlation state in the binding energy region of correlation peaks 1 and 2. These twin peaks (1 and 2) are clearly resolved in the present experiment as well as previous XPS measurements. The shortcoming of the most advanced Green's function calculation (ADC(4)) for acetylene may be due to the basis set chosen as opposed to the method itself. It has been observed in the MRSDCI calculation of the photoelectron spectrum of ethylene that "twining effects" are very sensitive to the choice of basis set^{29,30}.

2.2 Pyridine (C_5H_5N)

2.2.1 Introduction

Pyridine (C_5H_5N) is a prominent representative of heterocyclic aromatic molecules as it is closely related to benzene; it is suitable for the study of the influence of the presence of the hetero atom in the ring on the molecular properties. Numerous experimental and theoretical studies^{25,32-48} have been performed on pyridine in efforts to elucidate its electronic structure. The experimental studies of pyridine include ultraviolet PES of Turner⁴² and Kimura et. al²⁵. Neither of these works have been successful in obtaining a full PES spectrum of pyridine. That is, a PES spectrum containing the outer and inner valence regions of pyridine. The reason is that high energy resolution sources such as HeI can not go beyond 21.2 eV. For unknown reasons, there is no published account of an X-ray photoelectron spectrum of pyridine. The high brightness, variable photon energy, and high resolution of synchrotron radiation allows for access to the inner valence region of pyridine. It is therefore only now that inner valence region of pyridine is observed.

As for the theoretical studies, opinions have been divided over the symmetry assignment of the three outermost orbitals in the outer valence region of pyridine PES spectrum. In particular, the 3 outermost orbitals were found to be ($1a_2$ (π), $2b_1$ (π), $7a_1$ (n)) in order of increasing binding energy.^{25,43,44} This is in contrast to another theoretical (Green's function) calculation by von Niessen et al.^{32,41} which showed a slightly different orbital ordering of ($1a_2(\pi)$, $7a_1(n)$, $2b_1(\pi)$). The Green's function calculation also included computations on the correlation (satellite) state of pyridine using the 2ph-TDA

approximation. A good review of theoretical and experimental investigations of the electronic structure of pyridine is given by von Niessen et al.⁴¹

In this study, the full valence photoelectron spectra of pyridine (C_5H_5N) is obtained over an energy range of 50-100 eV photon energy. In addition to the outer valence ionization peaks, seven peaks at binding energies of 19.8, 20.6, 21.6, 23.4, 24.3, 24.5, and 28.0 eV are observed in these spectra for the first time. The outer valence binding energy spectrum of pyridine was previously obtained by Kimura et al. using HeI (21.2 eV). Orbital symmetry assignments for the 10 outermost orbitals were made by Kimura et. al. based on SCF MO(4-31G) calculations.²⁵ In the present work, an ADC(3) Green's function calculation is used to confirm the previous orbital symmetry assignments as well as to assign symmetries to the newly observed peaks in the PES spectrum of pyridine.

2.2.2 Experimental Method

The synchrotron PES spectra of pyridine over a range of photon energies from 50 eV to 100 eV were obtained at the grasshopper beamline (091) at the Synchrotron Radiation Center (University of Wisconsin) using the Canadian Synchrotron Radiation Facility (CSRF) McPherson photoelectron spectrometer ²³ (For details about the McPherson spectrometer refer to section 2.1.2.). The full spectrum of pyridine containing inner and outer valence region was obtained at 90.8 eV photon energy. The inner valence spectrum of pyridine was obtained over the energy range 50-100 eV. It should be noted that the second order radiations have been found to be minimal (1% of the first order intensity at about 45 eV ⁴⁹). As the spectra obtained in this experiment were taken at photon energies higher than 45 eV (50-100 eV), there is no interference from second order

radiation in this experiment. A thin carbon window isolated the spectrometer from the beamline and also removed higher order radiation.

" Grasshopper" monochromators were initially designed and built for monochromatization of synchrotron radiation. They give the ultrahigh vacuum required for synchrotron radiation studies and also very high resolution and intensity at high photon energies (50-500 eV). A schematic diagram of optical elements and basic arrangements of the grasshopper monochromator⁵⁰ is given in Fig. 17. The light beam from synchrotron hits the mirror M_1 which focuses the beam in a vertical plane on the entrance mirror-slit S_1 . The grazing angle on M_1 is one degree and optimizes the throughput of the higher photon energies. This mirror-slit combination at S_1 directs the incoming radiation onto the grating (G) during scanning. The beam is then focused through the exit slit by the grating.

The total experimental resolution is described in more detail in section 2.1.2. In this experiment the monochromator resolution is that of the grasshopper monochromator. The energy resolution of the grasshopper becomes poorer with increasing photon energy and slit width. At higher photon energies, the entrance and exit slits have to be opened wider to increase the light intensity coming out of the monochromator to have higher count rate of electrons reaching the detector. The grasshopper allows a larger distribution of energy ($h\nu \pm dE$) to pass through (dE increases as the slit is opened wider). Consequently, the energy resolution becomes poorer with increasing photon energy. To obtain better statistics (count rate) for the inner valence region, the slit width of 52 μ was chosen. For the outer valence region, however, the slit width of 37 μ was chosen. The total experimental energy resolution (electron energy analyzer and monochromator) for these

Fig. 17. Optical elements and basic arrangement of the "Grasshopper" monochromator. Angles are exaggerated, and two positions are shown, zero order and a wavelength λ . The diagram is adapted from reference 50.

experiments was about 0.50 eV fwhm.

No angular corrections to the derived cross sections were necessary since the photoelectrons were collected at the pseudomagic angle. All reported photoelectron intensity ratios were corrected for transmission effects²³. Instrumental calibrations of the photoelectron spectrometer and multichannel detector were done with Ne. A research purity sample of liquid pyridine (99.9%) was supplied by Aldrich Chemicals and was purified using repeated freeze-thaw cycles.

2.2.3 Results and Discussion

A high resolution photoelectron spectrum of pyridine (at 90.8 eV) is presented in Fig. 18. The binding energy scale was calibrated by aligning peak 3 (2b₁) with the corresponding peak in the HeI spectrum²⁵. Peaks (11-15) at binding energies of 19.8, 20.6, 23.4, 24.5, and 28.0 eV, corresponding to ionization from the inner valence orbitals, have not been observed before. The photoelectron spectrum presented in Fig. 18 can be described as the first PES of pyridine containing both inner and outer valence regions. The numbers (1-15) in Fig. 18 represent the symmetry assignment for the peaks by comparison of the experimental PES with the ADC(3) theoretical calculations (see later section). On the basis of this comparison, the ground state valence electronic configuration of pyridine (C_{2v}) is :

The reported spectrum (Fig. 18) has been corrected for slight nitrogen (N₂) contamination. The subtraction procedure involved digitizing nitrogen spectra at different photon energies reported by Krummacher et. al.⁵¹ and subtracting the digitized nitrogen spectra from the raw pyridine (+ N₂) spectra with appropriate scaling (see Appendix 3).

Fig. 18. A representative photoelectron spectrum of pyridine taken at photon energy of 90.8 eV with a total energy resolution of 0.50 eV fwhm. The spectrum as shown is not corrected for transmission effects. The numbers correspond to the symmetry assignments based on the comparison of the experimental PES with the ADC(3) calculation of von Niessen⁵². The vertical bars (1-10) refer to the experimental binding energies from HeI (21.2 eV) PES spectrum²⁵.

Table 5. The symmetry assignments and experimental binding energies (eV) of pyridine (C₅H₅N)

Symmetry ¹	Binding Energy ² ($\pm\sigma$)
1a ₂	9.60 ³
7a ₁	9.75 ³
2b ₁	10.51 ³
5b ₂	12.61 ³
1b ₁	13.1 ³
6a ₁	13.8 ³
4b ₂	14.5 ³
5a ₁	15.6 ^{3,4}
3b ₂	15.8 ^{3,4}
4a ₁	17.2 ³
2b ₂	19.8 (0.1)
3a ₁	20.6 (0.1)
S ₁	21.6 (0.2)
1b ₂	23.4 (0.1)
S ₂	24.3 (0.3)
2a ₁	24.5 (0.1)
1a ₁	28.0 (0.1)

¹C_{2v} molecular symmetry with molecule lying in the xy-plane. The orbital labels refer to the corresponding molecular orbital associated with the dominant configuration for the particular ionic states. (see text for details)

²Energy scale was established by aligning synchrotron PES with HeI spectrum (peak 3, 2b₁). The error limits ($\pm\sigma$) were estimated from several spectra (see text for detail).

³ Reference 25. Note that the symmetry assignment for 7a₁ and 2b₁ are switched.

⁴ Values may be inaccurate. See text for details.

The shoulder on the higher binding energy side of the peak corresponding to ionization out of $4a_1$ orbital (peak 10) is very likely an artefact of the subtraction procedure although a broad $4a_1$ peak has been observed in the HeI spectrum²³. The subtraction procedure was highly successful as shown in Table 5 and Fig. 18 where general agreement in the binding energies of the outer valence orbitals (peaks 1-7) and previous experiments²⁵ is observed. It can be seen that the vertical bars (1-7) shown in Fig. 18 which correspond to the binding energies from the HeI spectrum matches well with the present synchrotron PES spectrum. The slight misalignment of peaks 8 and 9 with the peak energies obtained from HeI spectrum²³ may be due to inappropriate consideration of N_2 impurities in the previous HeI spectrum. For example, Turner⁴² has noted the possibility of N_2 contamination in an earlier HeI spectrum.

The experimental PES of pyridine, along with the theoretical spectra calculated by von Niessen⁵² is presented in Fig. 19(b) and Table 6. The theoretical spectrum was obtained by convoluting the calculated pole strengths (solid poles) with the experimental peak widths. It can be seen that there is reasonable agreement between the experimental (PES) spectrum and the theoretical spectrum calculated by a Many Body Green's Function method (ADC(3)). The agreement is relatively better in the outer valence region in terms of binding energies. To compare the intensities, which are proportional to the photoionization cross sections, the pole strengths have to be multiplied by the corresponding dipole matrix elements.

The theoretical spectrum (ADC(3))⁵² is used to assign symmetries to the peaks observed in the experimental spectrum. Based on the comparison between these two spectra, the symmetries have been assigned and marked on Fig. 18. The symmetries of

Fig. 19. Comparison of (a) the experimental binding energy spectrum of pyridine at 90.8 eV photon energy with (b) the theoretical spectrum based on ADC(3) calculations of von Niessen⁵². The calculated pole strengths (solid poles) are convoluted with the experimental peak widths to yield the solid curve which can then be compared with experiment.

Table 6. The calculated energies and pole strengths of pyridine based on the ADC(3) calculation⁵²

Symmetry ^a	Ionization Energy(eV)	Pole Strength ^b (S ²)
1a ₂	9.34	0.892
7a ₁	9.60	0.889
2b ₁	10.11	0.882
5b ₂	12.61	0.903
1b ₁	13.14	0.733
6a ₁	13.81	0.854
4b ₂	14.40	0.162
4b ₂	14.57	0.716
6a ₁	14.95	0.021
1b ₁	15.21	0.023
5a ₁	15.58	0.081
1b ₁	15.78	0.024
3b ₂	15.83	0.399
5a ₁	15.90	0.769
3b ₂	16.07	0.457
4a ₁	17.01	0.134
4a ₁	17.51	0.693
1b ₁	17.58	0.088
1b ₁	18.27	0.037
5a ₁	18.69	0.012
3a ₁	18.85	0.023
4b ₂	19.15	0.018
3a ₁	19.35	0.034
3a ₁	19.52	0.024
2b ₂	19.60	0.016
3a ₁	20.06	0.323
2b ₂	20.12	0.034
2b ₂	20.15	0.041
2b ₂	20.23	0.178
3a ₁	20.31	0.067
2b ₂	20.42	0.262
2b ₂	20.45	0.161
3a ₁	20.63	0.092
3a ₁	20.77	0.093
3a ₁	20.81	0.020
3a ₁	21.22	0.031

Table 6. Continued

2b ₂	21.33	0.017	
3a ₁	21.53	0.086	} ^c
3a ₁	21.76	0.028	
3b ₂	21.77	0.020	} S ₁
3a ₁	21.87	0.025	
2b ₂	21.92	0.013	
2b ₂	22.03	0.022	
2b ₂	22.19	0.034	
4a ₁	22.33	0.016	}
3a ₁	22.42	0.014	
2b ₂	22.83	0.025	
2b ₂	23.11	0.020	
3a ₁	23.17	0.028	
2a ₁	23.69	0.012	
1b ₂	23.69	0.071	
1b ₂	23.76	0.090	
1b ₂	23.82	0.043	
1b ₂	23.92	0.165	
2a ₁	24.13	0.015	
1b ₂	24.28	0.047	} ^c
2a ₁	24.40	0.022	
1b ₂	24.44	0.040	} S ₂
3a ₁	24.44	0.032	
1b ₂	24.62	0.047	
1b ₂	24.72	0.066	
1b ₂	24.81	0.015	
2a ₁	25.01	0.047	}
2a ₁	25.09	0.011	
1b ₂	25.29	0.021	
2a ₁	25.35	0.011	
2a ₁	25.40	0.019	
2a ₁	25.50	0.188	
2a ₁	25.65	0.174	
2a ₁	25.77	0.039	
2a ₁	25.85	0.021	
2a ₁	26.04	0.020	
4a ₁	26.38	0.011	
2a ₁	26.68	0.018	
2b ₂	26.88	0.013	

Table 6. Continued

1a ₁	27.70	0.011
1b ₂	27.70	0.013
2a ₁	27.76	0.011
2a ₁	27.86	0.010
2a ₁	28.17	0.014
1a ₁	28.19	0.019
3a ₁	28.43	0.012
1a ₁	28.66	0.010
1a ₁	28.81	0.035
1a ₁	28.88	0.013
1a ₁	29.01	0.024
1a ₁	29.19	0.032
1a ₁	29.22	0.015
1a ₁	29.35	0.011
1a ₁	29.38	0.024
1a ₁	29.48	0.024
1a ₁	29.59	0.023
1a ₁	29.64	0.048
1a ₁	29.71	0.026
1a ₁	29.81	0.031
1a ₁	29.83	0.019
2a ₁	30.05	0.014
1a ₁	30.20	0.045
1a ₁	30.23	0.030
1a ₁	30.27	0.012
1a ₁	30.31	0.013

-
- a. Refers to the molecular orbital associated with the dominant configuration of the particular ionic state. (see text for detail)
- b. Pole strengths less than 0.01 are not included.
- c. Approximate regions corresponding to the experimental correlation (satellite) peaks S₁ and S₂.

the newly observed peaks at binding energies 19.8, 20.6, 23.4, 24.5, and 28.0 eV have been determined as $3a_1$, $2b_2$, $1b_2$, $2a_1$, and $1a_1$ respectively. The actual ordering of the inner valence peaks is not very obvious from the ADC(3) calculation, nor from the experiment. The poles redistribute the ionization strength of both orbitals such that it is very difficult to establish a unique symmetry assignment. The ordering for peaks 8 and 9 are arbitrary but made consistent with an earlier study³². The ordering of peaks 11 and 12 are based on the relative order of the dominant poles in the ADC(3) calculation.(see Table 6)

The other two peaks, at 21.6 eV and 24.3 eV can be considered as correlation peaks receiving intensity from a number of ionization processes. For instance, according to the ADC(3) results, the correlation peak at 24.3 eV (S_2) receives major intensity contributions from $2a_1$ and $1b_2$ and minor intensity contributions from $3a_1$. Likewise, the correlation peak at 21.6 eV (S_1) receives main intensity contributions from $3a_1$ with minor contributions from $3b_2$, $2b_2$, and $4a_1$ (see Table 6). It has been discussed that at higher binding energies, in the inner valence region, the strong breakdown of one-particle picture occurs and ordering does not bear much meaning^{41, 53}. Thus caution must be exercised in interpreting the reported orbital ordering which is considered the "best" possible ordering within a single particle picture of photoionization.

The photoelectron spectrum of the inner valence region of pyridine (at 80.6 eV) is presented in Fig. 20. Gaussian curves are fitted to all seven peaks observed in the spectrum. At least two correlation peaks (S_1 and S_2) at 21.6 and 24.3 eV are seen; they are marked with arrows. It should be noted that peak assignments for the inner valence region in the PES spectrum of pyridine were made on the basis of additional PES spectra

Fig. 20. The photoelectron spectrum of the inner valence region of pyridine taken at 80.63 eV photon energy. The spectrum as shown is not corrected for transmission effects. Gaussian curves are fitted to 5 inner valence peaks and 2 correlation peaks (S_1 and S_2). The peak widths are 0.333 ($3a_1$), 0.364 ($2b_2$), 0.442 ($1b_2$), 0.437 ($2a_1$), and 1.04 ($1a_1$) eV fwhm for the valence peaks and 0.511 (S_1) and 0.908 (S_2) eV fwhm for the correlation peaks.

taken at 50, 60, 70, 90, and 100 eV photon energies. A template corresponding to the 5 orbitals and 2 correlation peaks was devised and fitted consistently to all the PES spectra taken at 50-100 eV using PEAKFIT. The error limits obtained from this analysis are quoted in Table 5.

The inter-leaving of correlation states has been predicted by MRSDCI(ANO) calculations in the PES of other molecules such as acetylene³¹. This effect is usually considered to be responsible for variations observed in the photon energy dependence of intensity ratio of the satellites to one of the main peaks. A similar photon energy dependence of the intensity ratios is also observed for $1b_2/2a_1$ peaks in the inner valence region of the pyridine (see Appendix 2). The variation of the intensity ratios could be due to a number of factors most important of which is the existence of a broad correlation peak at 24.3 eV (.908 eV fwhm) which receives intensity contributions from $1b_2$, $3a_1$, and $2a_1$. Other factors include intensity contributions from more than one symmetry to both peaks corresponding to the $1b_2^{-1}$ and $2a_1^{-1}$ ionization processes. This is predicted by ADC(3) calculations as presence of poles of different symmetries over the region of about 23-25 eV (see Table 6).

2.2.4 Theoretical Details

In Green's function method, the ionization potentials and transition amplitudes are calculated directly, usually as the poles and residues of the one-particle Green's function. Both ionization potentials and transition amplitudes appear explicitly in the expressions for the 1-particle Green's function⁵³. Ignoring the part related to electron attachment, in energy space this function reads⁵⁴:

$$G_{pq}(\omega) = \sum_n \frac{\chi_q^{(n)} \chi_p^{(n)}}{\omega + I_n - i0^+} \quad (9)$$

where ω and I_n represent the photon energy and the ionization potential respectively, and

$$\chi_q^{(n)} = \langle \psi_n^{N-1} | a_q | \psi_0^N \rangle \quad (10)$$

represents the transition amplitude of finding the state $a_q | \psi^N \rangle$ in the final ionic state, a_q is the annihilation operator. The probability of finding the exact initial molecular state (ψ^N) in the final ionic state (ψ_n^{N-1}) is given by the square of the transition amplitude $|\chi_q^{(n)}|^2$.

The calculation of the pole strengths and ionization potentials involves the solution of the Dyson equation⁵⁵:

$$G(\omega) = G^0(\omega) + G^0(\omega) \Sigma(\omega) G(\omega) \quad (12)$$

which connects the Green's function G , with the Hartree-Fock (or free) Green's function (G^0) via the quantity called the self-energy ($\Sigma(\omega)$). The self-energy is the exact potential seen by an electron due to the interactions with the surroundings and in the surroundings³². It can be expanded in series according to different orders of perturbation as:

$$\Sigma(\omega) = \Sigma^{(1)} + \Sigma^{(2)}(\omega) + \dots + \Sigma^{(n)}(\omega) \quad (13)$$

and calculated using the so-called algebraic diagrammatic construction (ADC(n)) to a certain order of perturbation theory n (Rules and diagrams concerning the calculation of self-energy are discussed in reference 56). These calculations are very sensitive to the order of perturbation used in the self-energy expansion as well as the choice of basis set^{53,56}.

The 1995 calculations of von Niessen⁵² consider all terms up to and including the

Fig. 21. Calculated photoelectron spectrum reported by von Niessen³². The calculated pole strengths (solid poles) are convoluted with the experimental peak widths to yield the solid curve which can then be compared with experiment.

third order self-energy and are called ADC(3). The results of these calculations are shown in Fig. 19(b) as a theoretical spectrum and in Table 6 as ionization potentials, pole strengths, and symmetries. The basis set used for these calculations include a double-zeta quality basis set plus polarization of Huzinaga⁵⁷. The d-type polarization functions have the exponents 0.6 for carbon and 0.7 for nitrogen, and the p-type functions on hydrogen have an exponent of 0.75.

Comparison of the experimental PES spectrum of pyridine and the ADC(3) calculations (Fig. 19) shows that the separation of $7a_1$ from $2b_1$ (peak 2 and 3) is better defined in the experimental PES than in the ADC(3) theoretical spectrum; the same can be noted with regards to the separation of $5b_2$ from $1b_1$ (peaks 4 and 5). Comparison of the present ADC(3) calculations (Fig. 19(b) and Table 7) and many body Green's function calculations previously reported by von Niessen et. al in 1979³²(Fig. 21), however, shows a distinct improvement in terms of the position of the peaks, especially in the inner valence region, and the number of peaks in the spectrum (see Figs 19 and 21). The small peaks (indicated with a star) on the lower binding energy side of $2b_2$, $1b_2$, and on the higher binding energy side of $1a_1$ in the 1979 calculation do not appear in the present ADC(3) calculation. The shifts in the binding energies of the former two peaks in the ADC(3) calculations compared to the 1979 calculations result in the better agreement observed between the results of ADC(3) calculation and the experimental PES than between the 1979 calculation and the experimental PES. In the 1979 many-body calculations³² (Fig. 21), there is a sudden shift in binding energies of the peaks with binding energies greater than about 16 eV. This is due to the fact that for the first 8 peaks, ionization energies are based on an outer valence Green's function (OVGF)

calculations. The rest of the theoretical spectrum (Fig. 21), is based on the 2ph-TDA (Tamn-Dancoff approximation) calculations³²

In general, there is good agreement between the synchrotron PES spectrum and the present ADC(3) calculation (Fig. 19). The ADC(3) calculation is a definite improvement of a previously reported Green's function calculation³² (Fig. 21) and reflect the improved basis set and the inclusion of higher order terms in the perturbation series. Unfortunately, a comparable configuration interaction (MRSDCI) study of pyridine has not been reported. Based on previous studies on smaller molecules^{30,31}, MRSDCI calculations with large basis sets can provide a similar degree of agreement as the present ADC(3) calculation.

3. Conclusions

The photon energy dependence of intensity ratios of satellite/main peak of acetylene and labelled acetylene reveal the overall symmetries of the four correlation peaks. Satellites 1-3 are intrinsic with respect to $2\sigma_g^{-1}$ main peak while satellite 4 can be considered intrinsic with respect to $3\sigma_g^{-1}$ main peak. These symmetry assignments are consistent with the MRSDCI calculations.

The full photoelectron spectrum of pyridine containing the outer and inner valence regions is obtained. The symmetries of the observed fifteen peaks in this PES spectrum are determined by comparison with ADC(3) calculations. These peaks can be identified as $1a_2$, $7a_1$, $2b_1$, $5b_2$, $1b_1$, $6a_1$, $4b_2$, $5a_1$, $3b_2$, $4a_1$, $3a_1$, $2b_2$, $1b_2$, $2a_1$, and $1a_1$ in the order of increasing binding energy.

These studies show the essential role of SRPES as an experimental tool in the study of electron correlations in molecular systems. In the case of pyridine, SRPES allowed for access to the inner valence region for the first time. As for acetylene, the high resolution SRPES spectra allowed for photon energy dependence studies over a wide range of photon energies. The results of photon energy dependence studies of intensity ratios (satellite/main) are helpful both in understanding the mechanisms that give rise to these correlation peaks and in their symmetry assignment.

The agreement between the high resolution synchrotron photoelectron experiments and the theoretical calculations prove the success of the present theoretical methods,

which include the correlation effects, in accurately predicting the ionization spectrum of molecular systems in terms of binding energies and intensities.

The work on acetylene was an extension of the previous work done by S. J. Desjardins on ethylene as part of a series of studies of electron correlations in hydrocarbons. Future directions for this work may explore any trends in terms of binding energies and/or intensity distributions of correlation peaks of homologous series of alkenes and alkynes.

The work on pyridine was also an extension of the previous SRPES studies of electron correlations. However, it was quite different from previous works for two main reasons. First, this work explored the effect of the presence of a heteroatom (nitrogen) in a ring structure. That is, in studying pyridine, in addition to carbon-carbon and carbon-hydrogen interactions, carbon-nitrogen and hydrogen-nitrogen interactions were considered. Secondly, this work was the first thorough examination of the PES spectrum of this molecule to reveal its inner valence region as well as correlation peaks.

Numerous computational efforts have already investigated possible patterns in terms of chemical effects in azabenzenes. These calculations, however, are not supported by any SRPES experimental studies as there are no high resolution SRPES spectra of these molecules. Future SRPES studies can explore possible chemical trends in these molecules by obtaining high resolution SRPES of azabenzenes, performing photon energy dependence studies of intensity ratios, and comparing them with the available theoretical calculations.

4. Appendix 1 : Intensity Ratio of Main Peaks of Acetylene

Figure 22 presents the intensity ratios of $2\sigma_v/2\sigma_g$ and $3\sigma_g/2\sigma_g$ main peaks of acetylene. All reported intensity ratios are corrected for transmission effects. For photon energies higher than 45 eV the intensity ratio of $2\sigma_v/2\sigma_g$ is constant, while that of $3\sigma_g/2\sigma_g$ is decreasing with increasing photon energy.

Fig. 22. The intensity ratios of $2\sigma_u/2\sigma_g$ and $3\sigma_g/2\sigma_g$ main peaks of acetylene. All reported intensity ratios are corrected for transmission effects.

5. Appendix 2 : Intensity Ratio of Main Peaks

Figure 23 presents the intensity ratios of $1b_2/2a_1$ main peaks of pyridine. All reported intensity ratios are corrected for transmission effects.

Fig. 23. The intensity ratios of $1b_2/2a_1$ main peaks of pyridine. All reported intensity ratios are corrected for transmission effects.

6. Appendix 3: Nitrogen Subtraction Procedure

A summary of the procedure acquired in subtracting nitrogen from pyridine spectrum at 90.86 eV photon energy is presented as follows. First, reported nitrogen spectra of Krummacher et al⁵¹ at different photon energies were digitized. A representative of these digitized nitrogen spectra at 50.3 eV is presented in Fig. 24. These spectra could not be used directly to subtract N₂ from pyridine since they were different from the pyridine spectrum in terms of energy resolution, step size, and photon energy. These digitized nitrogen spectra were curve-fitted using PEAKFIT to obtain widths and areas of all peaks. The widths and the areas of nitrogen peaks at 90.8 eV were extrapolated using these data. The amplitudes for different peaks of nitrogen at 90.8 eV were obtained using the relationship:

$$Area = \sqrt{2\pi} \cdot amplitude \cdot width$$

Having the widths, amplitudes, and binding energies of all nitrogen peaks, a FORTRAN program was used to synthesize a nitrogen spectrum (presented in Fig. 25) with the same step size as the pyridine spectrum at 90.8 eV photon energy. The synthesized nitrogen spectrum was then subtracted from the pyridine + N₂ spectrum (see Fig. 26) taken at 90.8 eV photon energy. The final result is a (pyridine - N₂) spectrum, presented in Fig. 18.

Fig. 24. A representative digitized spectrum of nitrogen by Krummacher et al⁵¹ at 50.3 eV photon energy.

Fig. 25. A representative of synthesized nitrogen spectrum at 90.8 eV photon energy. For details regarding the widths, amplitudes, and positions of the peaks refer to text.

Fig. 26. A representative spectrum of pyridine + nitrogen at 90.8 eV photon energy.

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