PHOTOELECTRON SPECTROSCOPY  
OF MOLECULAR ANIONS  

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Advances in Gas Phase Ion Chemistry  
Volume I, pages 121–166.  
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ABSTRACT

Ultraviolet photoelectron spectroscopy is used to study the vibrational and electronic structure of molecular anions and the corresponding neutral molecules. The negative ion photoelectron spectrometer and ultraviolet laser system are described. Interpretation of the photoelectron spectra, including Franck-Condon simulations of vibrational intensities and analysis of photoelectron angular distributions, provides information about the vibronic structure of the anions and corresponding neutral molecules. Case studies are presented for $C_4H_{2n-}^-$ ($n = 0, 1, 2$) hydrocarbons and transition metal dimers and trimers. Electron affinities obtained from the photoelectron spectra are used in a thermochemical cycle to determine bond dissociation energies.

I. INTRODUCTION

In negative ion photoelectron spectroscopy, a beam of mass-selected anions is intersected by a fixed frequency laser beam. In the interaction, an electron is ejected from the molecular anion in the photodetachment process,

$$AB^- + h\nu \rightarrow AB + e^- .$$

To obtain the photoelectron spectrum, the kinetic energies of the photodetached electrons are measured. Energy conservation requires that the kinetic energy of the photoelectron be equal to the photon energy minus the transition energy between the initial state of the anion and the final state of the neutral molecule. The final state of the neutral may be the ground state or vibrationally or electronically excited states. Thus, measurement of the electron kinetic energy (eKE) yields a vibrational and electronic spectrum of the transitions between the anion and the neutral.

Negative ion photoelectron spectroscopy has several strengths relative to other spectroscopic methods. First, because the ions can be selected with a mass spectrometer, the signal carrier of the photoelectron spectrum is unambiguously established. Second, it is a general method of obtaining the vibrational and electronic spectra of neutral molecules, including reactive, short-lived, and radical species, for which the corresponding anions can be synthesized by ion-molecule chemistry techniques. Modern ion source technology allows a wide
variety of anionic species to be produced and formed into a beam. Third, electron affinities of the neutral molecules can be reliably and precisely measured by photoelectron spectroscopy. Electron affinities are important fundamental quantities and are also useful in thermochemical cycles, which yield bond dissociation energies. Finally, because an electron is removed in the photodetachment process, the selection rule for electron spin is $\Delta S = \pm \frac{1}{2}$ and neutral electronic states of different spin multiplicity may be observed in the photoelectron spectrum. For example, a doublet anion yields both singlet and triplet states of the neutral in the photoelectron spectrum, and singlet–triplet energy splittings can be measured directly. Singlet–triplet transitions are strongly forbidden in optical spectroscopy.

Several previous reviews cover various aspects of negative ion photodetachment. Corderman and Lineberger surveyed experimental methods for negative ion spectroscopy. Lineberger reviewed negative ion photoelectron spectroscopy of atoms and molecules. In 1984, Drzaic et al. discussed photodetachment threshold experiments on polyatomic anions and compiled molecular electron affinities. In the same volume, Mead et al. described high resolution photodetachment of atomic and diatomic anions, as well as photoelectron spectroscopy investigations of molecular anions. Hotop and Lineberger examined photodetachment of atomic ions and critically evaluated atomic electron affinities. We present here a summary of photoelectron spectroscopy experiments on molecular anions that we have carried out using the latest generation of the negative ion photoelectron spectrometer.

There has been rapid growth in the area of negative ion photoelectron spectroscopy in recent years. Although this review is limited in scope to photoelectron spectroscopy investigations of molecular anions carried out by the authors at the University of Colorado, others have made many significant contributions. It must suffice here to list the molecules studied by negative ion photoelectron spectroscopy since the 1984 reviews. Kit H. Bowen and co-workers at Johns Hopkins University have investigated $\text{M}_2^-$, $\text{M}_3^-$, $\text{MO}^-$, $\text{MO}_2^-$, and $\text{M}^-(\text{M = Te or Se})$, $\text{P}_2^-$, $\text{SeO}_3^-$, $\text{N}_2\text{O}^-$, $(\text{N}_2\text{O})_2^-$, $\text{NH}_4^-$, $\text{H}^-(\text{NH}_3)_n(n = 1,2)$, $\text{NO}^-(\text{N}_2\text{O})_n(n = 1,2)$, $\text{NO}^-(\text{Rg} = \text{Ar}, \text{Kr}, \text{Xe})$, $(\text{SO}_2)_2^-$, $\text{Rb}_n^-$, $\text{Rb}_3^-$, $\text{Cs}_2^-$, $\text{Cs}_3^-$, $\text{K}_n^-(n = 1 - 7)$, and $\text{Na}_n^-(n = 1 - 5)$. G. Barney Ellison and co-workers at the University of Colorado have studied $\text{HO}_2^-$, $\text{SiH}_3^-$, $\text{CH}_3\text{N}^-$, $\text{CH}_2\text{S}^-$, $\text{C}_2\text{H}_5\text{S}^-$, $\text{CH}_3\text{S}^-$, $\text{CH}_3\text{SCH}_2^-$, $\text{CH}_3\text{CN}^-$, $\text{CH}_3\text{NC}^-$, $\text{CH}_4\text{CO}^-$, $\text{C}_2\text{H}_5^-(n = 1,2,3,5)$, $\text{CCO}^-$, $\text{HCCO}^-$, $\text{C}_2\text{O}^-$, $\text{C}_3\text{O}_2^-$, $\text{C}_4\text{O}^-$, $\text{CS}_2^-$, $\text{Si}_2^-$, $\text{Si}_3^-$, $\text{SiO}_2^-$, $\text{SO}_2^-$, $\text{S}_2^-$, $\text{S}_2\text{O}^-$, $\text{C}_3\text{H}_3^-$, $\text{BH}_3^-$, $\text{O}_2^-$, $\text{NO}^-$, $\text{C}_2\text{H}_5^-$, $\text{CH}_3\text{N}^-$, and $\text{CH}_3\text{N}^-$. Mark A. Johnson and co-workers at Yale University have examined $\text{N}_2\text{O}_2^-$, $(\text{CO}_2)_n^-(n = 2 - 13)$, and $(\text{O}_2)_n^-(n = 1 - 6)$. A. Kaldor and co-workers at Exxon Research have reported photoelectron spectra of $\text{Au}_2^-$ and $\text{Ag}_5^-$. Doreen G. Leopold and co-workers at the University of Minnesota have studied transition metal carbonyls, for example $\text{W(CO)}_n^-(n = 1,2,3)$, $\text{Cr(CO)}_3^-$, $\text{Mo(CO)}_3^-$, and $\text{Re}_2\text{(CO)}_2^-$.
Berkeley, have obtained the photoelectron spectra of XHY\(^-\) (X, Y = F, Cl, Br, I), FH\(_2\)^-, NO\(_2\)^-, Si\(_2\)^-, Si\(_4\)^-, and HS\(^-\). From the Lineberger laboratory,\(^{41-67}\) spectra have been reported for CH\(_2\)^-, C\(_6\)H\(_4\)^-, HCO\(^-\), NaX\(^-\) (X = F, Cl, Br, I), KX\(^-\) (X = Cl, Br, I), MCl\(^-\) (M = Li, Rb, Cs, Mg), F\(^-\) (NaF)\(_n\), Na(NaF)\(_n\)\(^-\), (NaF)\(_n\)\(^-\) (n \leq 17), CHX\(^-\) (X = F, Cl, Br, I), CF\(_2\)^-, CCl\(_2\)^-, MH\(^-\) (M = Cr, Co, Ni), MH\(_2\)^- (M = Mn, Fe, Co, Ni), M\(_2\)^- (M = Fe, Co, Re, Pd), M\(_3\)^- (M = Ni, Pd, Pt), Cu\(_n\)\(^-\) (n = 1-10), Ag\(_n\)\(^-\) (n = 1-10), Au\(_n\)\(^-\) (n = 1-5), NO\(_2\)^-, NH\(_2\)^-, H\(_2\)CC\(^-\), HCC\(^-\), C\(_2\)^-, and SO\(^-\).

Photoelectron spectra of additional large metal, semiconductor, and molecular cluster anions have been reported by Richard E. Smalley and co-workers at Rice University; by K.-H. Meiwes-Broer, H. O. Lutz, and co-workers at Universität Bielefeld; and by K. H. Bowen and co-workers. Cluster anion systems studied by photoelectron spectroscopy have been reviewed by Cheshnovsky et al.\(^{64}\) and by Arnold et al.\(^{65-66}\) These reviews present excellent discussions of photoelectron spectroscopy of clusters; our work on the photoelectron spectroscopy of transition metal cluster anions\(^{56-62}\) is therefore not included in this review.

We describe the negative ion photoelectron spectrometer and ultraviolet laser system in Section II. The principles of the analysis of negative ion photoelectron spectroscopy are reviewed in Section III, including Franck–Condon simulations and photoelectron angular distributions. Section IV contains case histories of several molecular anion systems we have examined: C\(_2\)H\(_n\)\(^-\) hydrocarbons (n = 0, 1, 2) and transition metal diatomics and triatomics. The thermochemical implications of electron affinities determined from the photoelectron spectra are considered in Section V.

## II. ULTRAVIOLET NEGATIVE ION PHOTOELECTRON SPECTROMETER

### A. Overview

The principal components of the negative ion photoelectron spectrometer are the ion beam, the laser, and the electron energy analyzer. Ions from a flow tube source are mass-selected, focused into a beam, and then crossed at 90° with a high-intensity laser beam. Photoelectrons are collected in the direction perpendicular to the ion and laser beams and are sent through an electrostatic energy analyzer, which disperses the electrons according to their kinetic energy. The photoelectron intensity is monitored as the analyzer is scanned over electron kinetic energies.

The first negative ion photoelectron spectrometer was constructed in the late 1960s by Hall and co-workers\(^{70}\) at the University of Colorado. It consisted of a Branscomb discharge ion source, a Wien filter for ion mass selection, an argon ion visible laser, and a hemispherical electrostatic energy analyzer with 50 meV resolution. The ancestry of the photoelectron spectrometer currently used in the
Lineberger laboratory at the University of Colorado can be traced to that instrument, although it has undergone a number of reconstructions. Here, we briefly describe the photoelectron spectrometer including three major enhancements incorporated since 1983: a flowing afterglow ion source for producing and synthesizing thermalized anions, a laser system for routine operation in the near-ultraviolet, and an electron energy analyzer with 5–10 meV resolution.

A schematic drawing of the photoelectron spectrometer is presented in Figure 1.

Figure 1. Negative ion photoelectron spectrometer and ultraviolet laser build-up cavity system. Labels: AOM, acousto-optic modulator; λ/2, half-wave plate; D5, deflectors, R1, and R2, build-up cavity mirrors.
B. Flowing Afterglow Ion Source

The flowing afterglow ion source consists of an 5 cm diam. stainless steel tube, through which an inert buffer gas (helium or argon) flows at a rate of $5 \times 10^7$ cm$^3$ min$^{-1}$ and a pressure of 0.3–1.0 torr. Ions are produced in the flow tube by any of several ion sources. The ions are carried down the field-free flow tube with the buffer gas. At the end of the flow tube, the ions are gently extracted through a 1-mm diam. aperture into a 10$^{-4}$ torr pressure region, while the buffer gas is pumped away by a Roots blower system. Details of the design and construction of the flowing afterglow source have been reported.47

The flowing afterglow ion source is distinguished from other discharge ion sources by three qualities. First, because the ions undergo $10^4$–$10^5$ collisions with the buffer gas, most ions become vibrationally and rotationally relaxed to near room temperature, even though the ions may be initially formed in highly excited states. Thermal relaxation suppresses hot band peaks, which can congest the photoelectron spectrum and confuse the assignment of the vibrational origin. Second, the flowing afterglow system is extremely versatile. Ion sources that have been used in the flow tube include an electron impact ionization source, a microwave discharge, and a metal cathode discharge. Desired ions can be synthesized by carrying out ion–molecule reactions in the flow tube; ions formed initially are allowed to react with a neutral gas leaked into the buffer gas flow at a downstream inlet. We may rely upon the extensive literature of ion–molecule chemistry48 to produce virtually any anion of interest. Third, the flowing afterglow ion source is remarkably reliable and easy to use, especially with the microwave discharge source.

Several of our experiments on small organic radical anions have relied on a simple ion–molecule reaction of atomic oxygen anions. O$^-$ reacts efficiently with many neutral hydrocarbon or other hydrogen-containing species to abstract H$^+$ or H$_2^+$, often with good specificity. For example, O$^-$ reacts with acetylene by abstraction of H$^+$ to form C$_2$H$_2^{-}$. O$^-$ abstracts H$_2^+$ from halomethanes to produce halocarbenic anions (e.g., O$^-$ + CH$_3$Cl $\rightarrow$ CHCl$^-$ + H$_2$O). In the reaction with ethylene, O$^-$ + C$_2$H$_4$ $\rightarrow$ H$_2$CC$^-$ + H$_2$O, the hydrogen atoms are removed from the same end of the ethylene molecule to produce the vinylidene anion.49 The high efficiency of these reactions is at least partly due to the formation of the stable neutral products, H$_2$O or OH. The initial O$^-$ anions are easily produced in the microwave discharge from O$_2$ or N$_2$O.

A recent addition to our ion source repertoire is a metal cathode discharge source$^{50,51}$ for producing transition metal dimers, trimers, and cluster anions. In this source, a cathode fabricated from the metal of interest is used in the flow tube with a helium/argon buffer gas mixture. A voltage of $-3$ to $-5$ kV on the cathode relative to the grounded flow tube initiates a discharge. Cluster ions form when ions (probably Ar$^+$) in the discharge are accelerated to the surface of the metal cathode and sputter away small particles. No evidence for ion clustering
downstream of the discharge has been observed, although some is possible. A
distribution of cluster sizes up to a dozen atoms has been obtained for a variety
of transition metals.\textsuperscript{56,57,61,67} The principle for initial formation of ions is the same as
for laser vaporization metal cluster sources,\textsuperscript{48} although the plasma at the metal
surface is much less focused and concentrated in our discharge source. In the
laser vaporization sources, aggregation in the gas expansion following ablation
can produce larger clusters.

After extraction from the flow tube, ions are focused into a beam and passed
through a Wien velocity filter (crossed electric and magnetic fields) for mass
selection. The Wien filter chamber is differentially evacuated by a diffusion
pump (10\textsuperscript{-7} torr). Following mass selection, the ions are decelerated and
refocused at the point of interaction with the laser, in a high vacuum chamber
differentially pumped by ion pumps (10\textsuperscript{-9} torr). The ion current is measured at
an isolated Faraday cup, with a sensitivity of 0.1 pA, after the interaction region.
Usable ion currents range from 0.5 to 300 pA, above which shifts (1–3 meV) in
the apparent electron kinetic energy are sometimes observed, probably due to
charging effects in the analyzer.

C. Ultraviolet Laser System

Typical photodetachment cross sections are small, 10\textsuperscript{-18} cm\textsuperscript{2} or less. Therefore,
for sufficient photoelectron signal intensity, the spectrometer requires both
sensitive electron detection and a powerful laser beam, at least tens of watts of
continuous power on a single line. Such powers are not available in commercial
lasers; the largest argon ion lasers provide 8–10 W in the visible (488 nm) or 2–3
W in the near-ultraviolet (351 nm). One method for increasing the available
power is to use the intracavity radiation of the laser—in effect, placing the
experiment inside the laser. By extending the laser cavity around the interaction
region of the photoelectron spectrometer (via a folded cavity mirror system and
Brewster-angle windows on the vacuum chamber), circulating powers of 100–200
W can be achieved at 488 nm. The intracavity method was used previously for
our photoelectron spectrometer\textsuperscript{42} and is in use in several other laboratories.\textsuperscript{4,37,75}

Use of ultraviolet light is attractive for photoelectron spectroscopy because the
higher photon energy extends the available spectral range. It is possible to
operate an intracavity laser system on the ultraviolet lines of the argon ion laser,\textsuperscript{34}
but the available power levels are too low for routine operation. We have
modified the laser system of the photoelectron spectrometer for operation in the
near-ultraviolet region (351–364 nm).\textsuperscript{55,61} The UV laser system is briefly de-
scribed in the following.

In the new UV laser system (Figure 1) the output of an argon ion laser is
amplified in an external optical power build-up cavity,\textsuperscript{75} which is essentially a
Fabry–Perot interferometer\textsuperscript{89} that is locked to its resonant frequency. The ion
beam intersects the laser inside the build-up cavity. The circulating power inside
the build-up cavity is amplified to several hundred times that of the incident laser beam. The fundamental requirement for laser amplification is that the resonant frequencies of the laser and build-up cavities be exactly matched. Because the resonant frequencies are subject to noise from acoustic vibrations and thermal fluctuations, active steps must be taken to match the frequencies of the two cavities. The matching is accomplished by a servoamplifier system that adjusts the lengths of the two cavities using piezoelectric translators on the cavity mirrors.

The argon ion laser is operated with a wavelength-specific output coupler to select one of the lines in the Ar III system, 351 nm or 364 nm. The wavelength-specific output coupler, a narrow band pass reflectivity filter, eliminates the need for an external prism to separate the UV lines. An intracavity, temperature-stabilized solid etalon selects a single longitudinal mode, which is necessary for matching the frequency to the external build-up cavity. The standard rear high reflector mirror of the laser is replaced by a smaller mirror mounted on a fast piezoelectric translator for control of the cavity length by the servoamplifier system. This laser mirror translator is used to compensate for acoustic noise up to 5 kHz.

The build-up cavity mirrors are attached to the vacuum chamber of the photoelectron spectrometer by stainless steel bellows and kinematic mirror mounts, and also serve as vacuum windows. The input mirror mount can be moved with a piezoelectric translator to change the cavity length. This translator is driven by the servoamplifier system to compensate for thermal drift and other noise up to 100 Hz and to keep the resonant frequency of the build-up cavity within the free spectral range of the laser.

A lens and mirror system (Figure 1) between the laser and the external cavity provides for alignment of the laser beam and focusing to match the spatial beam parameters (beam radius and wave-front curvature) of the two cavities. A good match of spatial parameters is required for efficient injection of the laser beam into the external cavity. A half-wave plate is placed between the laser and the build-up cavity to rotate the polarization of the light inside the build-up cavity to any desired angle. Routine control of the polarization angle is an important improvement over the previous intracavity laser system, for which the polarization angle was fixed by the Brewster angle windows on the laser tube and the vacuum chamber.

A servoamplifier system keeps the laser and the build-up cavities locked in resonance, using a laser stabilization scheme similar to those in which the laser frequency is locked to a stable reference cavity. The frequency stabilization system relies on an acousto-optic modulator (AOM) to modulate the laser frequency. An error correction signal is extracted by the servoamplifier system from the modulated power of the light transmitted through (or reflected from) the build-up cavity. The AOM also optically isolates the laser and build-up cavities, and provides for fast fine tuning of the laser frequency by the servoamplifier.
Further details of the build-up cavity and servoamplifier system are presented elsewhere.\textsuperscript{61}

Laser power amplification factors of 150–250 have been achieved by the build-up cavity system. For 150–200 mW incident laser power (single frequency, single mode), this produces 30–60 W circulating power inside the build-up cavity. Although this power is lower than possible for intracavity systems in the visible, it is sufficient for taking photoelectron spectra with picoampere or larger ion currents.

D. Electron Kinetic Energy Analyzer

The kinetic energy of the photodetached electrons is measured by a hemispherical electrostatic energy analyzer,\textsuperscript{47,11} shown in Figure 2. Photoelectrons produced at the point of intersection of the ion and laser beams fly in all directions, but only a fraction of these are selected by an aperture with acceptance cone of 5\textdegree half-angle. This aperture discards 99.8\% of the photoelectrons, but it is necessary to select a single velocity component in order to achieve good

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Cross-sectional view of the electrostatic energy analyzer and interaction region.}
\end{figure}
energy resolution. A zoom lens\textsuperscript{11,74} accelerates or decelerates the photoelectrons to the constant analyzer transmission energy of 1.5–5 eV. The first stage of the zoom lens is set for constant magnification (typically 6 × or 20 ×) from the initial photoelectron kinetic energy, but the center focusing element of the second stage is computer controlled, with its voltage optimized prior to the experimental scan for the best sensitivity and resolution at each electron kinetic energy.

The hemispherical analyzer\textsuperscript{74} is designed without entrance or exit slits. Herzog correction lenses\textsuperscript{69} compensate for fringe fields at the entrance and exit of the analyzer. Because there are no slits, all electrons within a band of kinetic energies are transmitted by analyzer at any given setting. This energy window is 30–100 meV wide for analyzer transmission energies of 1.5–5 eV. Photoelectrons exiting the analyzer are accelerated and magnified by a system of exit lenses, then imaged onto a two-dimensional position-sensitive array detector. The array detector consists of a dual microchannel plate electron multiplier in front of a resistive anode. Photoelectrons are detected at different positions on the anode, dispersed according to their kinetic energy, giving an effective energy resolution of 5–10 meV FWHM. In this manner, a 30–100 meV segment of the photoelectron spectrum is collected at one time, providing a multiplexing effect, which increases the sensitivity of the analyzer while maintaining high electron energy resolution.

The photoelectron spectrometer is interfaced to a microcomputer, which controls the analyzer voltages and collects the photoelectron counts as a function of position on the array detector in the energy-dispersing direction. A series of 30–100-meV segments of the spectrum are acquired at incremented nominal electron kinetic energies spaced by 5–20 meV. These segments are then combined to build up the entire photoelectron spectrum over the full range of electron kinetic energies.

The electron kinetic energy scale is calibrated from the photoelectron spectra of atomic anions. The absolute kinetic energy is calibrated against the precisely known electron affinities of atoms\textsuperscript{1} such as O, S, or P. The instrumental kinetic energy scale is slightly compressed from the nominal scale based on analyzer potential settings, possibly because of end effects in the hemispherical analyzer. A kinetic energy compression factor, an empirical linear correction to the relative energy scale,\textsuperscript{11,74} is calibrated against the spacings of known energy levels\textsuperscript{11} in phosphorous or tungsten atoms. The typical value of this correction is 0.4% at an analyzer transmission energy of 2 eV (or 1.0% at 5 eV). The experimental uncertainty of the absolute electron kinetic energy of well-resolved peaks in the photoelectron spectra is ±0.005 eV.

Figure 3 presents the photoelectron spectrum of O\textsuperscript{−} under conditions optimized for high resolution, at an analyzer transmission energy of 1.5 eV. Five of the six expected spin-orbit transitions are observed; the sixth is unresolved from the largest transition. The peak widths are 4.5 meV FWHM. Under more routine conditions, we are able to obtain resolutions of 6–10 meV FWHM, depending on
Figure 3. Photoelectron spectrum of O$^-$ at 488 nm. The inset shows an energy level diagram and transitions for spin-orbit states of O$^-$ ($^3P$) and O ($^3P$).

focusing and alignment conditions, constant over the electron kinetic energy range from 0.3 eV to the photon energy. Below about eKE = 0.3 eV, the sensitivity and resolution degrade somewhat due to the effects of stray fields on low-energy electrons; no photoelectrons are detected below 0.1 eV. The instrumental energy resolution and line shape are determined by observing isolated atomic transitions. The resolution function can typically be approximated by the sum of a Gaussian peak and a broader Gaussian "pedestal" of 3-4 times width and 5-10% intensity relative to the main component.

E. Comparison of Photodetachment Techniques

There are two major classes of negative ion photoelectron spectrometers presently in use. The type described previously employs a continuous ion beam, continuous laser, and continuous electrostatic energy analysis. Pulsed systems are also possible, for which a pulsed ion source is used (typically involving a pulsed supersonic expansion), a pulsed laser is used for photodetachment, and the electron kinetic energies are analyzed by time-of-flight methods. Because continuous and pulsed ions sources lend themselves to making different classes of molecules, the continuous and pulsed photoelectron spectrometers provide
complementary information. Two recent reviews are available on pulsed ion experiments. 68,92

The resolution of negative ion photoelectron spectrometers is limited by the electron kinetic energy analysis. At the present state of the art, the best resolution is 5–10 meV for either electrostatic energy analysis (used in continuous ion/laser experiments) or time-of-flight energy analysis (used in pulsed systems). An advantage of continuous electrostatic energy analyzers is that the resolution is constant over the entire kinetic energy range. In time-of-flight analyzers, the resolution in the time frame is constant, which means that the energy resolution degrades with increasing electron kinetic energy as $E^{3/2}$. Thus, time-of-flight analyzers have lower effective resolutions.

Pulsed systems currently have an advantage over continuous systems in that higher photon energies are available in pulsed lasers. Continuous photoelectron spectrometers use argon ion lasers operating in the visible or near-ultraviolet, while time-of-flight machines can employ YAG or excimer lasers operating in the deep ultraviolet. At photon energies above 4–5 eV, precautions must be taken to avoid background photoelectrons produced by stray laser light striking metal surfaces.

Much higher resolution can be obtained by photodetachment threshold measurements, 34 in which the total photodetachment cross section is measured as a function of laser wavelength. The resolution in photodetachment threshold spectroscopy is in principle limited by the laser linewidth. If the photodetachment threshold is sharp, precise electron affinities and onsets of neutral excited states may be measured. According to the Wigner threshold laws, 45 thresholds are sharp, $\sigma(E) \propto (E - E_m)^{1/2}$, when $p$-like electrons are photodetached ($s$-wave detachment), but threshold onsets are gradual for detachment of $s$- or $d$-like electrons [e.g., $\sigma(E) \propto (E - E_m)^{3/2}$ for $p$-wave detachment]. Therefore, sharp thresholds are observed only for anions with $s$-wave detachment at threshold. Above the threshold region, these onsets are obscured by the background from lower energy states, unless resonances occur for which the laser frequency matches a transition to a bound excited level of the anion. Photodetachment threshold measurements require a tunable laser with a frequency range matching the threshold energy, whereas photoelectron spectrometers may use any available laser with a photon energy exceeding the electron affinity.

Zero electron kinetic energy photodetachment spectroscopy 64 is a hybrid of photodetachment threshold and photoelectron spectroscopy methods. A tunable, pulsed laser is used for photodetachment. After a short delay following photodetachment, a voltage pulse extracts the photoelectrons. The delay ensures that fast electrons have left the viewing region, such that the instrument is sensitive only to near zero kinetic energy threshold electrons. The energy resolution is limited by the ability to separate zero-kinetic energy electrons from faster electrons. A resolution of 0.4 meV has been demonstrated, 41 a significant advance over traditional photoelectron spectrometers. The method is limited, however, to
molecules that have sufficiently large photodetachment cross sections within a few wavenumbers of the energy threshold. Zero electron kinetic energy methods will therefore be applicable only to systems that exhibit s-wave detachment at threshold (see earlier). In the continuum region at photon energies well above threshold, where traditional photoelectron spectrometers operate, the photodetachment cross sections are typically large regardless of electron orbital symmetry and only weakly dependent on photon energy (in the absence of resonant processes). Thus, photoelectron spectrometers employing electron energy analysis are generally applicable to a larger set of molecular anions than are zero kinetic energy methods.

III. ANALYSIS OF NEGATIVE ION PHOTOELECTRON SPECTRA

A. Diatomic Molecules

A cartoon of the photodetachment process and photoelectron spectrum is shown in Figure 4 for the case of a simple diatomic, \( \text{O}_2^- \). The potential energy curves of the ground states of \( \text{O}_2 \) and \( \text{O}_2^- \) are represented as Morse oscillators. The energies of the dissociation asymptotes of the potential energy curves of \( \text{O}_2^- \) (\( \text{O} + \text{O}^- \)) and \( \text{O}_2 \) (\( \text{O} + \text{O} \)) are separated by the electron affinity of atomic oxygen. Photons induce transitions from the ground state of \( \text{O}_2^- \) to a virtual level in the \([\text{O}_2^- + \text{e}^-]\) continuum. Electrons are ejected with kinetic energies

![Diagram of the photodetachment process and resulting photoelectron spectrum for \( \text{O}_2^- + h\nu \rightarrow \text{O}_2 + \text{e}^- \).](image)
corresponding to the various final states of neutral \( \text{O}_2 \). The resulting spectrum is shown in Figure 4 on the same vertical energy scale as the potential energy curves. The relative intensities of the various vibrational transitions are determined by the Franck–Condon overlap of the vibrational wavefunctions of the anion and the neutral molecule.

The identification of the vibrational origin (0–0) peak allows direct determination of the electron affinity (EA) of the neutral molecule, according to

\[
EA = h\nu - \text{eKE}(0-0).
\]  

(2)

For thermal ions, minor corrections to this EA value may be necessary to account for a shift due to the rotational contour of the vibrational peak and for unresolved sequence band transitions (1–1, 2–2, etc).

If vibrationally excited anions are populated under the experimental conditions, these may also photodetach to produce hot band transitions. Hot band transitions appear shifted to higher electron kinetic energy by the initial vibrational excitation of the anion (for the same final states in the neutral). The origin peak (0–0 vibrational transition) can often be unambiguously identified in a vibronic band by an abrupt change in spacing between the peaks from the neutral vibrational frequency to that of the anion vibrational frequency. This assignment is possible for most diatomics but can fail if the anion and neutral frequencies are similar (e.g., for removal of a nonbonding electron) or for polyatomics where several vibrational modes are active and the spectrum is congested. In such cases, it is often still possible to identify hot bands experimentally by changing the vibrational temperature of ions produced by the ion source, which changes the intensities of the hot bands relative to the ground state transitions. If changing the ion vibrational temperature is not possible, careful Franck–Condon analysis of the vibrational progressions may permit identification of the origin. Finally, isotopic substitution can be used to identify the origin, because all the transitions except the origin are subject to isotopic vibrational frequency shifts. (Zero-point energy shifts of the origin are negligible in most cases.)

Transitions from the anion to excited electronic states of the neutral molecule may occur if these excited states are within the photon energy range. A vibrational progression is observed for each electronic state, with intensities controlled by the Franck–Condon factors for that transition. Unlike neutral molecules, which may have an infinite number of excited electronic states, anions support only one or a few bound electronic states. If an electronically excited state of the anion is populated in the experiment, an electronic hot band transition may also be observed in the photoelectron spectrum.

An experimental photoelectron spectrum of \( \text{O}_2^- \), obtained with the ultraviolet photoelectron spectrometer described earlier, is presented in Figure 5 as an example. The actual spectrum is more complicated than the simulated spectrum in Figure 4 for three reasons. First, there are three vibrational progressions corresponding to transitions from the ground electronic state of the anion to the
three low-lying electronic states of O$_2$: $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$. Vibrational assignments for each of the electronic transitions are labeled in Figure 5. Second, vibrationally excited anions are populated, giving rise to hot band transitions, ($v' = n$)$\leftarrow$($v'' = 1$) and ($v' = n$)$\leftarrow$($v'' = 2$), for each electronic state. Third, each vibronic transition is actually a doublet, having a partially resolved shoulder on the high-KE side. The doublets arise from the two spin-orbit states of the anion, $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$. The measured spacing between the peaks is 20 $\pm$ 2 meV, which yields an approximate spin-orbit coupling constant of $A = 160 \pm 16$ cm$^{-1}$, compared with $A = 124$ cm$^{-1}$ for isoelectronic NO.$^{44}$ For an estimated ion temperature of 300 K, the calculated thermal population of the excited $^2\Pi_{3/2}$ spin-orbit state for the observed energy splitting is about 30%, in reasonable agreement with the observed intensity ratio of the spin-orbit doublets. The electron affinity and O$_2$$^-$ molecular constants obtained from the spectrum agree with those of Travers et al.$^{29}$

B. Polyatomic Molecular Anions

Polyatomic molecules differ from diatomics in that more than one vibrational mode may be active. According to the Franck–Condon principle, vibrational
modes that correspond to a large change in geometry between the anion and neutral (for example, a large change in bond angle for a bending vibration) have an extended Franck–Condon progression. When the geometry change is small for a vibrational coordinate, a vertical transition is observed, with greatest Franck–Condon intensity for the 0–0 transition and small intensities for higher \((v' = n)\leftarrow(v'' = 0)\) transitions. This behavior is exemplified in the photoelectron spectrum\(^{15}\) of \(\text{NO}_2^–\), reproduced in Figure 6. The major vibrational progression is a series of peaks in the \(v_2\) bending mode with an intensity maximum at \(v_2' = 4\), corresponding to the large change in the ONO bond angle between \(\text{NO}_2^–\) and \(\text{NO}_2\). A shorter progression in the \(v_1\) symmetric stretching mode, peaking at \(v_1' = 2–3\), arises from the relatively smaller change in NO bond length. Additional combination bands arise from excitation in both of these modes. The \(v_3\) asymmetric stretch mode is not active. The geometry change corresponding to the asymmetric stretch is identically zero because both \(\text{NO}_2^–\) and \(\text{NO}_2\) have \(C_2v\) symmetry. As a result, the Franck–Condon overlap for the asymmetric stretch (and for all non-totally symmetric normal modes of polyatomics) is significant only for the 0–0 transition, corresponding to \(\Delta v = 0\). Other even changes of vibrational quanta (\(\Delta v = \pm 2, \pm 4, \pm 6, \ldots\)) are also

**Figure 6.** Photoelectron spectrum of \(\text{NO}_2^–\) at 351.1 nm. The upper trace is for a polarization of \(\theta = 0^\circ\); the lower trace is for \(\theta = 90^\circ\). The vibrational origin is indicated by an arrow. Vibrational assignments are indicated by symbols above the transitions: the \(1_{1u}^2\) bend mode overtone progression is marked by circles, the \(1_{2u}^2\) progression is marked by triangles, and the \(1_{0u}^2\) progression is marked by squares.
allowed for non-totally symmetric modes, but these are weak if the anion and neutral frequencies are similar.

Vibrational assignments for diatomics are straightforward once the origin peak is identified. For polyatomics, the various modes can be identified by their characteristic vibrational frequencies or by isotopic substitution. Neutral vibrational frequency constants may be obtained from the vibrational peak spacings, and anion vibrational constants from the spacings of hot band transitions.

C. Franck–Condon Analysis

The total cross section for photodetachment is given by

$$\sigma = \left( \frac{32\pi^4}{m_e^2} \right) \cdot \left( \frac{e^2}{\nu^3 \hbar c^2} \right) \cdot |M|^2,$$

where $m_e$ and $e$ are the electron mass and charge, $v_e$ is the asymptotic electron velocity, $\nu$ is the photon frequency, $\hbar$ is Planck’s constant, $c$ is the speed of light, and the transition moment $M$ is given by,

$$M = \langle \Psi''(q) \mid \mu(q) \mid \Psi'(q) \rangle,$$

where $\mu$ is the electronic transition moment between the vibrational wavefunction of the initial state (anion) $\Psi''$ and of the final state (neutral) $\Psi'$, as a function of nuclear coordinates $q$. In equation 4, we have made the approximations that the electronic, vibrational, and rotational wavefunctions are separable and that the rotational overlap integrals are the same for all vibrational states. Furthermore, the electronic transition moment is assumed constant over the range of vibrational coordinates sampled (Condon approximation), i.e.,

$$\mu(q) = \mu_0.$$

With these approximations, we obtain,

$$\sigma \propto v_e \cdot |\langle \Psi''(Q'') \mid \Psi'(Q') \rangle|^2,$$

where the nuclear coordinates are expressed in terms of the normal vibrational coordinates of each species, $Q''$ and $Q'$, and constant factors from equation 3 have been dropped. In equation 6, $\langle \Psi'' | \Psi' \rangle$ is the vibrational overlap integral and its square is the Franck–Condon factor. The electron velocity factor in equation 6 usually varies little over the range of a vibrational progression in the photoelectron spectrum. The magnitudes of Franck–Condon factors are extremely sensitive to geometry changes between the anion and neutral states. Therefore, the Franck–Condon intensity profile of a vibrational progression can be analyzed to extract the changes in geometry between the anion and the neutral molecule.

For many of the systems of interest, there is limited independent information available on spectroscopic constants of the anions or even of the neutrals. Moreover, in a medium resolution spectral technique like photoelectron spectroscopy, the data seldom justify using highly sophisticated vibrational models. Therefore, we generally use simple harmonic oscillator or Morse oscillator
models for the vibrational potentials. Franck–Condon simulations using these simple models allow extraction of geometry changes from the spectra, as described in the following sections.

For diatomics, the one-dimensional vibrational overlap integral can be calculated directly. For harmonic oscillators, we use the recursion formula method of Hutchisson,\textsuperscript{46} which gives analytical expressions for the Franck–Condon factors as a function of bond length change. For systems that exhibit significant anharmonicity, we use a Morse oscillator model. The Morse wavefunctions are calculated analytically using the Laguerre series functions\textsuperscript{57} on a fixed grid of bond lengths for all vibrational quantum levels of interest for the initial and final states, taking advantage of the efficiency of the Laguerre recursion formulas. The wavefunction overlaps are then integrated numerically (Simpson’s rule). Franck–Condon factors for Morse oscillators calculated by a perturbation correction to the Hutchisson recursion formulas\textsuperscript{46} have been found to be inaccurate for large anharmonicities or for high vibrational quantum levels (i.e., when it is most necessary to use a Morse oscillator model instead of a harmonic oscillator in the first place).

To evaluate the Franck–Condon factors for polyatomics, we make the further simplification that the normal modes in the anion and neutral states are independent. The total wavefunction is then the product of one-dimensional vibrational wavefunctions $\psi_i$ for the $n$ vibrational modes of the molecule,

$$|\Psi(Q)\rangle = |\psi_1(Q_1)\rangle|\psi_2(Q_2)\rangle|\psi_n(Q_n)\rangle,$$

where $Q_i$ is the normal mode coordinate for vibrational mode $v_i$. These one-dimensional wavefunctions are usually modeled as harmonic oscillators or Morse oscillators, reducing the problem to the equivalent of a diatomic molecule in each mode. Certain vibrational modes in polyatomic molecules cannot be adequately represented by a harmonic or Morse oscillator model, for example, an inversion mode with a barrier. For such cases, we model the vibrational potential with an appropriate functional form and calculate the vibrational wavefunction, energies, and overlap integrals numerically, using a variational calculation with a splines basis set.\textsuperscript{45,58} The adjustable parameters of the potential function are optimized to fit both the observed energy levels and the Franck–Condon intensities.

If the normal coordinates of the initial and final states of a polyatomic molecule are different from each other, it is necessary to take into account the transformation between the normal coordinates of the initial and final states, $Q'$ and $Q''$ respectively, in the integration of the overlap integral of equation 7, as originally described by Duschinsky.\textsuperscript{47,48} The multi-dimensional overlap integrals including the Duschinsky rotation between modes must then be calculated explicitly. We use the generating functions method of Sharp and Rosenstock.\textsuperscript{50} Details of the Franck–Condon analysis including Duschinsky mixing are given in our report\textsuperscript{48} on NO$_2^-$ . Duschinsky mixing can be important when the frequencies or geometries (and therefore the normal modes) change drastically between the anion and the neutral.
In many cases, it is not necessary to include Duschinsky mixing in the Franck-Condon analysis. This parallel mode approximation leads to a major simplification because the Franck-Condon factors can be expressed as the product of Franck-Condon factors for each mode,

$$\text{FCF}(\nu^\nu, \nu^\nu; \mathbf{K}) = |\langle \Psi'^\nu(\mathbf{Q}'') | \Psi'(\mathbf{Q}) \rangle|^2 =$$

$$|\langle \psi'^\nu, \nu^\nu (\mathbf{Q}') | \psi'_\nu, \nu' (\mathbf{Q}) \rangle|^2 |\langle \psi'_\nu, \nu' (\mathbf{Q}) | \psi''_\nu, \nu'' (\mathbf{Q}'') \rangle|^2 - |\langle \psi'_\nu, \nu' (\mathbf{Q}) | \psi''_\nu, \nu'' (\mathbf{Q}'') \rangle|^4,$$

and only one-dimensional overlap integrals need to be calculated. The values of the Franck-Condon factors, FCF(\nu^\nu, \nu^\nu; \mathbf{K}), for initial state vibrational quantum numbers \(\nu^\nu = (v_1^\nu, v_2^\nu, \ldots, v_n^\nu)\) and final state vibrational quantum numbers \(\nu' = (v'_1, v'_2, \ldots, v'_n)\), are functions of the vector of normal coordinate displacements in each mode, \(\mathbf{K} = (\Delta Q_1, \Delta Q_2, \ldots, \Delta Q_n)\). The displacements define the change in geometry between the initial and final states in each normal coordinate direction.

D. Spectral Simulation

Once the Franck-Condon factors are calculated, we may simulate the photoelectron spectrum. The relative intensities of vibrational transitions, including hot bands, are given by,

$$I(\nu^\nu, \nu'') = \sigma_0 \nu_c \text{FCF}(\nu^\nu, \nu''; \mathbf{K}) \exp[-G_0''(\nu'')/kT'']. \quad (9)$$

where \(\sigma_0\) is a scaling factor, \(\nu_c\) is the electron velocity corresponding to the final electron kinetic energy \(\text{eKE}(\nu^\nu, \nu')\), and the exponential term gives the relative Boltzmann population of vibrational states of the anion for a vibrational temperature \(T''\). The initial and final vibrational energies, \(G_0''(\nu'')\) and \(G_0'(\nu')\), are calculated according to the vibrational model used (e.g., from the harmonic or Morse oscillator constants). The peak positions (electron kinetic energies) of vibrational transitions are given by,

$$\text{eKE}(\nu^\nu, \nu') = \hbar \nu - \text{EA} - G_0'(\nu') + G_0''(\nu''). \quad (10)$$

Equations 9 and 10 together yield a simulated stick spectrum of intensities versus electron kinetic energy.

For comparison with the experimental spectrum, the calculated stick spectrum must next be convoluted with the transition line shapes. The experimental line shape is a combination of the instrumental resolution function and the rotational contour. The rotational contour can be calculated by modeling the process as an electronic transition between the anion ground state and the anion virtual state, with appropriate rotational selection rules. Our report\(^25\) on the photoelectron spectrum of \(\text{NH}_3^-\), which exhibits partially resolved P, Q, and R branches, relates details on the rotational contour modeling for the case of an asymmetric rotor. Rotational constants for the anion and neutral species are obtained from independent measurements or estimated from the Franck-Condon analysis itself. The rotational contour line shape generally does not affect the Franck-Condon
analysis but may shift the origin by a few millivolts because of a difference between the rotationless origin and the center of the peak.

The final step in the spectral simulation is to compare the calculated spectrum to the experimental data and to obtain the best values for molecular constants. The adjustable parameters are the anion and neutral vibrational constants, the anion and neutral geometries, the electron affinity, the anion vibrational temperature, and a scaling factor for the relative intensity. For harmonic oscillators, the Franck–Condon factors depend only on the magnitude of the geometry change, not its sign. Therefore, the direction of the geometry change must be determined from independent information or inferred from molecular orbital arguments considering the bonding or anti-bonding nature of the electron removed upon photodetachment.

An interactive computer program\textsuperscript{99} has been developed for calculating the Franck–Condon factors, simulating the photoelectron spectra, and optimizing the adjustable parameters by comparison with experimental spectra. A simulated spectrum is calculated from initial guesses of the molecular parameters and is displayed graphically in superposition with the experimental data. The experimental parameters may be modified until a reasonable visual fit is obtained. Then any of the adjustable fitting parameters may be refined by an iterative nonlinear least-squares optimization procedure.\textsuperscript{99} The quality of the fit is determined by the sum of squared residuals as well as by visual inspection (good overall residuals may be meaningless if a particular transition is not reproduced by the vibrational model and assignments). The fitting procedure may be repeated as necessary to evaluate different origin and vibrational assignments. The simulations provide more reliable frequency constants and electron affinities than can be obtained by simple measurement of peak positions, because the peaks are subject to shifts due to overlapping transitions. The complete Franck–Condon simulation accounts for unresolved bands explicitly by fitting the simulated spectrum to all data points in the spectrum.

The fitting procedure provides the electron affinity and vibrational frequency constants directly. Geometry displacements are obtained in terms of the mass-weighted Cartesian normal coordinate displacements [units of (g/mol)$^{-1/2}$ · Å], so that no explicit information about the actual geometry of the molecule is necessary for the fitting procedure. A normal coordinate analysis of the molecule must then be performed in order to transform the Cartesian displacements into changes in bond lengths and bond angles. For a diatomic molecule, the transformation is simply $\Delta Q = \mu^{1/2} \Delta r$, where $\mu$ is the reduced mass, $\Delta r = r_n^+ - r_n^-$ is the change in bond length between the anion and neutral, and $\Delta Q$ is the displacement in mass-weighted normal coordinates. For polyatomics, calculating the transformation matrix requires a full normal coordinate analysis,\textsuperscript{99} which in turn necessitates the vibrational force field for the molecule. Unfortunately, the vibrational frequency data from the photoelectron spectrum itself are rarely sufficient to determine uniquely a force constant matrix. If force constants are available from
an independent experimental determination, then these can be used for the normal coordinate analysis. For several systems, we have relied upon ab initio calculations of the harmonic force field.\textsuperscript{54,55} Because the Franck–Condon factors are sensitive to geometry changes, but only weakly dependent on frequencies, approximate calculated force constants or empirical estimates are often sufficiently accurate.

E. Photoelectron Angular Distributions

The angular dependence of the photodetachment intensity is given by\textsuperscript{54}

$$\frac{d\sigma}{d\Omega} = (\alpha/4\pi) \cdot [1 + \beta \cdot P_2(\cos \theta)],$$

where $\theta$ is the angle between the electric field vector of the light and the direction of electron ejection, $P_2(\cos \theta) = (3\cos^2 \theta - 1)/2$, $\sigma$ is the total photodetachment cross section, and $\beta$ is the asymmetry parameter ($-1 < \beta < +2$). Photoelectron spectra are routinely taken at the "magic" angle of $\theta = 54.7^\circ$, for which the asymmetry term is zero, giving intensities proportional to the total photodetachment cross section. The value of $\beta$ is measured by monitoring the photodetachment intensity of a transition in the photoelectron spectrum while rotating the polarization of the light, then fitting the data to equation 11. If a precise value of $\beta$ for each transition is not needed, measurement of the photoelectron spectrum at $\theta = 0^\circ$ and $\theta = 90^\circ$ provides a quick measure of $\beta$ from the relationship,

$$\beta = \frac{I_0 - I_{90}}{\frac{1}{2}I_0 + I_{90}},$$

where $I_0$ and $I_{90}$ are the relative photoelectron intensities at $\theta = 0^\circ$ and $\theta = 90^\circ$.

The angular distribution of photoelectrons provides information about the symmetry of the orbital from which the electron is detached. In atoms, the angular distribution is directed related\textsuperscript{54} to the angular momentum state of the detached electron orbital. The photodetachment selection rule is $\Delta l = \pm 1$. For example, an electron detached from an $s$ orbital ($l = 0$) becomes a $p$ wave ($l = 1$), which gives an asymmetry parameter $\beta = 2$ [i.e., the intensity maximum is along the electric field vector of the light ($\theta = 0^\circ$)]. An electron in an atomic $p$ orbital can depart either as an $s$ wave or a $d$ wave ($l = 0$ or 2). Near the photodetachment threshold (low kinetic energy of the detached electron), the lower angular momentum state predominates, giving an isotropic angular distribution, $\beta = 0$. At photon energies above the threshold, the $s$ and $d$ waves interfere to give a negative asymmetry parameter\textsuperscript{54,55}

For molecular photodetachment, the situation is complicated by the random initial orientation of the molecular frame. The orientation of the molecule is partially selected by the electronic transition moment of the anion, and the angular distribution of photoelectrons is an average over this orientational dependence and the intrinsic photodetachment angular distribution. It is unnecessary to
do a thorough theoretical analysis of the photoelectron angular distributions for molecular systems, however, to obtain valuable qualitative information from polarization measurements. First of all, each electronic state is expected to have a characteristic value of the asymmetry parameter $\beta$. For example, the photoelectron angular distribution for NO$_2^-$ (Figure 6) exhibits an asymmetry parameter of $\beta = 1.4$ over the entire ground state transition. The value of $\beta$ does vary slightly with the electron kinetic energy within an electronic band because of interference terms between electron waves of different $l$ values, but this variation is often weak over the range of the band. Therefore, measurement of the angular distribution can be used to identify peaks in the photoelectron spectrum that belong to different electronic states. This is especially useful in the case of overlapping electronic bands, for example, for the singlet and triplet states of the halocarbenes. A second use for the asymmetry parameter values is as an indication of the molecular orbital symmetry. We take the simplistic viewpoint that the $\beta$ parameter for a molecular detachment reflects the atomic orbital parentage of the molecular orbital from which the electron is detached. We may then use our knowledge of the trends in $\beta$ for atomic photodetachment as rules of thumb to identify $s$-like, $p$-like, or $d$-like molecular orbitals. For example, an angular distribution with $\beta \approx 2$ can be associated with an $s$-parentage molecular orbital such as $\sigma$. These rules have proven useful in identifying electronic states in both organic species and transition metal dimers.

IV. CASE STUDIES

In the following sections, we discuss several illustrative examples of negative ion photoelectron spectroscopic studies of molecular species.

A. Dicarbon

The dicarbon anion, C$_2^-$, is unusual in that it has three bound electronic states: $X^1\Sigma_g^+$, $A^3\Pi_u$, and $B^3\Sigma_u^+$. Because of its rich vibronic structure, C$_2^-$ has been the subject of study by high resolution spectroscopic techniques$^{55-57}$; these studies have established precise electronic term energies and vibrational and rotational constants for each of the three states. The low-lying electronic states of neutral C$_2$, $X^1\Sigma_g^+$ and $a^3\Pi_u$, are also well characterized. The spacing between the anionic and neutral manifolds, given by the electron affinity EA(C$_2$), has been more difficult to ascertain. Here we relate previous attempts to determine the electron affinity and our recent measurement,$^{58}$ EA(C$_2$) = 3.269 ± 0.006 eV.

The electron affinity of dicarbon is too high for C$_2^-$ to be detached by visible laser light. This had prevented the measurement of the photoelectron spectrum of C$_2^-$ until the availability of ultraviolet negative ion photoelectron spectroscopy.
An early xenon lamp photodetachment threshold measurement\(^{10}\) gave \(EA(C_2) = 3.54 \pm 0.05\) eV. However, because the ground state transition, \(C_2 X^1\Sigma_u^+ \leftarrow C_2^+ X^2\Sigma_u^+\), involves \(p\)-wave detachment, the threshold is expected (in hindsight) to have a gradual onset, which would be difficult to detect.

Autodetachment spectroscopy experiments on \(C_2^-\) performed by Jones et al.\(^{96}\) in the Lineberger group provided a potentially more precise electron affinity. Jones et al.\(^{96}\) observed autodetachment from the \(v = 5\) level of the \(B^2\Sigma_u^+\) state of \(C_2^-\), which gave a strict upper limit of \(EA(C_2) \leq 3.408\) eV. A lower bound was chosen on the basis of observed autodetachment rates. In particular, it was observed that autodetachment for the \(B^2\Sigma_u^+ (v = 5)\) level is more than 10 times slower than that from higher vibrational levels. To account for the large change in autodetachment rates between \(v = 5\) and \(v = 6\), it was postulated that the \(B^2\Sigma_u^+ (v = 5)\) level of \(C_2^-\) lay between the ground vibrational levels of the \(C_2 X^1\Sigma_u^+\) and \(C_2 a^3\Pi_u\) states, thus energetically allowing autodetachment to the neutral triplet state (expected to be rapid) for \(v = 6\) but not for \(v = 5\).

Because the \(X^1\Sigma_u^+\) and \(a^3\Pi_u\) states of \(C_2\) are separated\(^{94}\) by only 612 cm\(^{-1}\), this conclusion gave a tight lower limit of \(EA(C_2) \geq 3.374\) eV.

Our ultraviolet photoelectron spectrum\(^{94}\) of \(C_2^-\) is shown in Figure 7. Five irregularly spaced transitions are observed, which can be uniquely assigned on

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![Diagram](image.png)

**Figure 7.** Photoelectron spectrum of \(C_2^-\) at 351.1 nm. Vibrational and electronic assignments of the observed transitions are labeled.
the basis of the established molecular constants of the low-lying states of C_2 and C_2^-. The assignments are labeled in Figure 7. The assigned origin transition yields an electron affinity of EA(C_2) = 3.269 ± 0.006 eV, below the lower limit from the autodetachment lifetimes. Because the photoelectron spectrum is unambiguous, the original interpretation of the autodetachment lifetimes* must be in error. Although we have no definitive reinterpretation, one possible explanation* for the lifetimes is nonradiative transitions to the C_2^- A ^3Π_u state, for which the v = 16 level is near-resonant with v = 5 level of the ground state.

B. Ethynyl

Ethynyl radical, C_2H, is the subject of spectroscopic interest because of its strong vibronic coupling between the X ^2Σ^+ ground electronic state and the low-lying A ^2Π excited state. Although a number of vibronically coupled levels have been observed, the term energy of excited state has not been determined. Like C_2, ethynyl has a large electron affinity and was not accessible by photoelectron spectroscopy with visible light. An initial goal of our ultraviolet photoelectron spectroscopy study of C_2H^- was to observe the term energy spacing, but unfortunately the excited state lies beyond our energy range, giving only a lower limit of T_0(A ^2Π) > 3400 cm^-1. A number of new vibrational levels in the ground state are observed, however, as well as unusual non-Franck–Condon effects.

The photoelectron spectra* of ^12C_2H^- and ^13C_2H^- are presented in Figure 8. Because the geometry change between the anion and the neutral is small, the vibrational origin has the largest Franck–Condon intensity. The other vibrational transitions can be identified by their characteristic isotopic frequency shifts: the ν_3 CC stretch mode shows only a small shift, while the ν_2 CCH bend shows a larger relative shift. The assignments are labeled in Figure 8. The assignments of the fundamental transitions, 2_0^1 and 3_0^1, and the 2_0^1 3_0^1 combination band are confirmed by high resolution infrared spectroscopy on the C_2H radical. Other vibrational levels of the neutral and anion are observed for the first time by photoelectron spectroscopy.

The appearance of odd vibrational transitions of the bending mode (Δν_2 = 1 and 3) is surprising because odd transitions are not Franck–Condon allowed for a non-totally symmetric mode. These transitions are indicative of strong vibronic interactions between the X ^2Σ^+ ground state and the low-lying A ^2Π excited state. The odd bending vibrational levels have π vibronic symmetry, which allows coupling with the Π excited electronic state. Further evidence for the vibronic coupling is seen in the unusual photoelectron angular distributions shown in Figure 9. The Franck–Condon allowed (even) vibrational transitions exhibit a strong maximum at θ = 0°, while the odd levels are at a maximum of θ = 90°. This behavior is contrary to the usual expectation that all transitions within an electronic band should have approximately the same angular distribu-
Figure 8. Photoelectron spectra of $^{12}$C$_2$H$^-$ (top) and $^{13}$C$_2$D$^-$ (bottom) at 351.1 nm. The upper trace in each spectrum is magnified 20 times and offset from zero. Assignments of prominent vibrational transitions are labeled.
Figure 9. Laser polarization dependence of the photoelectron spectrum of \(^{12}\text{C}_2\text{H}^-\). The solid line represents a laser polarization of \(\theta = 0^\circ\) and the connected circles represent \(\theta = 90^\circ\). Vibrational assignments are labeled.

A simplistic explanation for the observed behavior is that photodetachment resulting in the allowed vibrational levels (\(\sigma\) symmetry) corresponds to removal of an electron from the \(\sigma\) molecular orbital, whereas those transitions leading to the odd vibrational levels (\(\pi\) symmetry) effectively involve removal of an electron of \(\rho\pi\) symmetry. As discussed earlier, detachment of \(s\)-like electrons leads to strong preference for ejection along the electric field vector of the light (\(\theta = 0^\circ\)), whereas detachment of \(p\)-like electrons leads to perpendicular ejection.

C. Vinlylidene

Vinlylidene, \(\text{H}_2\text{C}=	ext{C}\), is a highly excited isomer of acetylene and is the simplest unsaturated carbene. Vinlylidene undergoes a rapid, exothermic 1,2-hydrogen shift to form acetylene:
\[
\begin{align*}
\text{H} & \quad \text{C} = \text{C}: \longrightarrow \text{H} - \text{C} \equiv \text{C} - \text{H}.
\end{align*}
\]

Figure 10 shows an energy level diagram for the acetylene-vinylidene system. The predicted classical barrier height for the isomerization on the neutral singlet surface is only 3 kcal/mol, leading to a predicted vinylidene lifetime of about a picosecond. We can investigate the transient vinylidene molecule by starting with the stable H₂C = C⁻ anion, whose structure has been established by ion-molecule reaction studies. When H₂CC⁻ is photodetached to produce singlet H₂CC, the asymptotic velocity of the ejected electron is about 10 Å/fs, so the information provided by the photoelectron spectrum corresponds to the early time evolution on the vinylidene potential energy surface. Thus, we are able to obtain the full vibrational spectrum of a species that lasts for a picosecond or less. Vinylidene also has excited triplet states (Figure 10) that have barriers against isomerization to triplet acetylene and are therefore longer lived.

\textbf{Figure 10.} Energy level diagram for the anion, singlet, and triplet surfaces of the vinylidene-acetylene system.
The photoelectron spectrum of $\text{H}_2\text{CC}^-$ is shown in Figure 11. We observe both the ground singlet and excited triplet states. The geometry changes are small, so the vibrational origins are the strongest peaks in each electronic transition. The electron affinity, $\text{EA}(\text{H}_2\text{CC}) = 0.490 \pm 0.006 \text{ eV}$, and the singlet–triplet splitting, $\Delta E(3^3\text{B}_2) = 47.6 \pm 0.2 \text{ kcal mol}^{-1}$, are obtained directly from the energies of the origin peaks.

The vibrational spectra of the $3^3\text{B}_2 \text{H}_2\text{CC} \leftrightarrow \tilde{X}^2\text{B}_2 \text{H}_2\text{CC}^-$ and $1^1\text{A}_1 \text{H}_2\text{CC} \leftrightarrow \tilde{X}^2\text{B}_2 \text{H}_2\text{CC}^-$ electronic transitions are shown in Figure 12 for three isotopomers, $\text{H}_2\text{CC}^-$, $\text{HDCC}^-$, and $\text{D}_2\text{CC}^-$. Because the triplet transition is not subject to the complication of the isomerization channel, we will examine it first. For $\text{H}_2\text{CC}$ and $\text{D}_2\text{CC}$, we observe transitions of the three totally symmetric modes: CC stretch mode (small isotopic shift), CH$_3$ in-plane scissors mode (larger shift), and CH symmetric stretch (largest shift). For HDCC, the C$_{2v}$ symmetry is reduced to C$_s$ symmetry and there are five totally symmetric modes. We observe both CH and CD stretches and an extra transition for the CH$_2$ in-
plane rock mode. The appearance of these additional bands for HDCC is a dramatic example of the role of symmetry in vibrational spectroscopy. A Franck–Condon simulation reproduces all of these transitions and provides estimates of geometry changes between the anion and the triplet.61

The singlet state transition (Figure 12) is more congested than the triplet transition because a slightly larger change in geometry produces additional overtone and combination bands. The vibrations can be assigned according to their characteristic isotopic shifts as for the triplet. Note that the CH stretch, CC stretch, and CH2 scissors transitions all lie at energies above the calculated barrier for isomerization of vinylidene into acetylene. They can nevertheless be adequately described as zero-order vinylidene normal modes because these vibrational coordinates are orthogonal to the isomerization reaction coordinate. An "extra" vibrational transition occurs at low frequency, 450 cm\(^{-1}\) (0.056 eV) for H2CC, and appears in all three isotopomers. The only vinylidene mode with a frequency this low is the CH2 rock, but the \((\nu' = 1) \leftarrow (\nu'' = 0)\) transition is symmetry allowed only for HDCC. Its appearance for all three isotopomers indicates that it must be the \((\nu' = 2) \leftarrow (\nu'' = 0)\) transition. Consideration of the nature of the rock mode shows why this transition is active. The CH2 rock normal coordinate closely corresponds to the reaction coordinate for the vinylidene-acetylene isomerization. Because the isomerization barrier is small, the vibrational potential in this coordinate is both shallow and anharmonic, as shown by the model potential energy curve in Figure 13. The large change in frequency between the anion rock mode and the neutral, as well as the anharmonicity on the neutral surface, yields relatively large Franck–Condon factors for the \(2 \leftarrow 0\) transition. A Franck–Condon simulation61 using the model potential shown in Figure 13 reproduces the transition frequency and intensities for all three isotopomers (Figure 12) with reasonable accuracy considering the simplistic one-dimensional model. We have used photoelectron spectroscopy in effect to determine the potential energy surface along the isomerization reaction coordinate.

Examination of Figure 12 shows another significant difference between the singlet and triplet transitions: the lines are wider for the singlet. Much of the difference can be attributed to different rotational contours, because different rotational selection rules apply to the \(a^3\text{B}_2 \leftarrow X^2\text{B}_2\) (parallel) and \(X^1\text{A}_1 \leftarrow X^1\text{B}_2\) (perpendicular) transitions. However, careful modeling of the rotational contours61 indicates there is additional broadening in the singlet band, which can be ascribed to lifetime broadening. The estimated lifetime for singlet vinylidene based on the linewidth analysis is 0.04–0.2 ps. A comparison of this lifetime with theoretical calculations of the tunneling lifetime,60 as well as the well-depth of the model CH2 rock potential optimized in the Franck–Condon analysis, suggests61 that the isomerization barrier height is close to 2 kcal mol\(^{-1}\). This is in good agreement with a theoretical value60 of 3 kcal mol\(^{-1}\) for the classical isomerization barrier height.
Figure 12. Photoelectron spectra of \( \text{H}_2\text{CC}^- \) (top), \( \text{HDCC}^- \) (middle), and \( \text{D}_2\text{CC}^- \) (bottom) in the region of the triplet (left) and the singlet (right) bands. Points are experimental data, vertical sticks are the transitions calculated in Franck-Condon simulations, and the solid lines show these convoluted with the observed peak shape. Vibrational assignments are indicated for prominent transitions, with normal modes indicated by letter codes: \( \text{CH} \), \( \text{CD} \), and \( \text{CC} \) stretches; \( S \), \( \text{CH}_2 \) scissors; and \( R \), \( \text{CH}_2 \) in-plane rock.
Figure 13. Potential energy curves for the CH$_2$ rock normal coordinate of the $X^1\text{A}_1$ H$_2$CC $\leftarrow X^2\text{B}_2$ H$_2$CC$^-$ transition in vinylidene. The lower curve is a harmonic potential for the anion. The upper curve shows a symmetric well potential used to model the CH$_2$ rock in the neutral. Horizontal lines indicate the calculated vibrational energy levels and vertical lines show symmetry-allowed transitions ($\Delta v = 0, \pm 2, \pm 4$). The dashed lines schematically represent the presence of the deep potential energy well corresponding to HCCCH geometries.

D. Coinage Metal Dimers

In addition to studies of small organic radicals, another major effort in our laboratory has been in the area of transition-metal–containing molecules and clusters. We describe here photoelectron spectroscopy investigations of the coinage metal (nickel and copper group) dimers and trimers. These two groups provide an illustrative contrast in electron configuration and bonding. In the copper group, the ground state atoms have $s^1d^{10}$ electronic configurations. Because the atomic d shells are fully occupied, the bonding in the dimers and
trimers is due predominantly to the valence $s$ electrons (one per atom). Because there are a limited number of molecular orbital combinations of the atomic $s$ orbitals, the copper group molecules have a small number of low-lying electronic states. The nickel group atoms have one fewer electron and an open $d$ shell. The $s$ and $d$ orbitals have similar energies, which is demonstrated by the different neutral ground state configurations—Ni ($s^2d^8$), Pd ($d^{10}$), and Pt ($s^1d^{10}$)—and the presence of low-lying atomic excited states, for example, Ni ($s^1d^9$) and Ni ($s^2d^9$) are nearly degenerate. The open $d$ shell creates the possibility for involvement of $d$-$d$ interactions in the molecular bonding, and the similar $s$ and $d$ orbital energies can give rise to many low-lying molecular orbital configurations. Thus, the spectra of the nickel group molecules are expected to be much more complex than those of the copper group.

Photoelectron spectra of copper group metal dimers are shown in Figure 14. The spectra of Cu$_2^-$ and Ag$_2^-$ are nearly identical, exhibiting two electronic transitions. The higher eKE band in Cu$_2^-$ and Ag$_2^-$, and the only feature for Au$_2^-$, corresponds to the ground state transition $M_2X^2\Sigma_u^+ (\sigma g)^2 \leftarrow M_2X^2\Sigma_u^+ (\sigma g)^2 (\sigma u)^1$. Vibrational levels of the neutral are resolved, and a Franck-Condon analysis was used to determine molecular constants.

At lower eKE, an excited triplet state transition, $M_2X^3\Sigma_u^+ (\sigma g)^1(\sigma u)^1 \leftarrow M_2X^2\Sigma_u^+ (\sigma g)^1(\sigma u)^1$, is observed for Cu$_2$ and Ag$_2$, while the comparable transition for Au$_2$ is shifted beyond our photon energy range. The triplet transitions have no resolved vibrational structure, because the triplet states have very shallow vibrational wells with vibrational transitions too closely spaced to be resolved in our experiments. Considering that the $(\sigma g)^1(\sigma u)^1$ configuration has a formal bond order of zero, it is perhaps surprising that the triplet state is bound at all. Calculations by Bauschlicher et al. show that the $\sigma u^*$ orbital is extensively polarized by mixing in $p$ orbital character, reducing its anti-bonding character. Thus, the triplet dimers are slightly bound. Another reason for lack of vibrational structure is that the vertical transition lies partially in the unbound continuum region of the triplet potential because the triplet state has a significantly longer bond length than does the anion.

Although the copper group dimers have only one excited state within 2 eV of the ground state, the nickel group dimers are predicted to have many low-lying electronic states because of the many nearly equivalent configurations of the $d$ electrons. Balasubramanian calculated 41 electronic states for Pd$_2$ within 1 eV. The photoelectron spectrum of Pd$_2^-$ is shown in Figure 15. The spectrum is indeed more congested than those of the copper group dimers, but it would be difficult to identify as many electronic states as predicted by Balasubramanian. There are two explanations for observing a smaller number of electronic states than actually exist. First, photodetachment cross sections are small for two-electron processes involving a change in electronic configuration in addition to removal of an electron from an orbital. Therefore, transitions will be observed only for the subset of neutral states that have molecular orbital configurations
Figure 14. Photoelectron spectra of the copper metal dimer anions at 351.1 nm: Cu$_2^-$, Ag$_2^-$, and Au$_2^-$.  

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corresponding to that of the anion ground state (or low-lying excited states populated in the beam) less one electron. Second, $s$ electron detachments are expected to have larger cross sections than $d$ electron detachments. Detachment of different $d$ shell electrons from the anion leads to different neutral electronic states. These processes are therefore likely to contribute to the many overlapping transitions observed with low intensity in the photoelectron spectrum.

The two most prominent features in the photoelectron spectrum of Pd$_2^-$ (Figure 15) should, according to these arguments, involve $s$ electron detachment. This is confirmed by the polarization dependence of those transitions. Large positive values of the $\beta$ parameters (characteristic of $s$ electron detachment) are found for the two strongest transitions (labeled X and I in Figure 15), whereas most of the weak features have negative $\beta$'s (characteristic of $d$ electron detachment). The two strong transitions are also observed to have vibrational progressions with identical Franck-Condon factors, indicating that the bonding structure is similar. Based on these observations, the two strong features are assigned to Pd$_2^- [d^{19}]s\sigma^1 \leftarrow$ Pd$_2^- [d^{19}]s\sigma^2$ transitions (using notation that neglects the detailed molecular orbital configuration of the $d$ shell electrons). The difference between the two neutral states is in the spin coupling of the $s$ electron with the hole in the $d$ shell. The calculations of Balasubramanian indicate the ground triplet and an excited singlet stage of Pd$_2^-$, corresponding to the same $d$ shell

![Figure 15. Photoelectron spectrum of Pd$_2^-$ at 351.1 nm. Band X corresponds to the ground triplet state of Pd$_2^-$, whereas band I corresponds to an excited singlet state.](image-url)
configuration, are separated by 4443 cm⁻¹, in agreement with the 3985 cm⁻¹ splitting observed in the photoelectron spectrum for these two transitions.

E. Coinage Metal Trimers

The photoelectron spectra of the nickel⁰¹ and copper⁰² group trimer anions are presented in Figure 16. As in the case of the copper and silver dimers, there is a striking similarity between the spectra of the copper and silver trimers. Each of these two trimer spectra has a single, narrow electronic transition devoid of resolved vibrational structure. Theoretical calculations⁰¹,⁰² indicate that the trimer anion ground states are linear, with a \((\sigma_g)^3(\sigma_u)^3\) configuration of the four s

![Figure 16. Photoelectron spectra of the coinage metal trimer anions: Ni₃⁻, Pd₃⁻, and Pt₃⁻ (468.0 nm) and Cu₃⁺, Ag₃⁺, and Au₃⁻ (351.1 nm).](image-url)
valence electrons. Removal of a $\sigma_u$ electron produces the linear form of the neutral in a vertical transition, yielding the observed narrow feature. However, the ground state of the neutral trimer is not linear but rather triangular with a $(a_1')^2(e')^1$ molecular orbital configuration.\textsuperscript{112} Addition of an electron gives a preference for the linear geometry in the anion because the $\sigma_u$ orbital is partially bonding, while the $e'$ orbital is nonbonding. Because the ground state of the neutral is not accessed by a vertical transition, in this case the photoelectron spectrum does not yield a value for the adiabatic electron affinity.

The gold trimer is a special case.\textsuperscript{52,114} The third row transition metal electron affinities trend significantly higher than for the first and second rows, such that the vertical transition in Au$_3^-$ corresponding to those observed for Cu$_3^-$ and Ag$_3^-$ is expected to be beyond our energy range. What is observed instead is a two-photon process, in which the first photon dissociates Au$_3^-$ into Au + Au$_2^-$ or Au$^-$ + Au$_2$, and the second photon detaches an electron from the product anion. The spectrum consists of two features: a sharp peak corresponding to free Au$^-$ and a broader peak corresponding to free Au$_2^-$. The latter transition is broadened compared to the normal Au$_2^-$ spectrum because the photodissociation process produces vibrationally hot dimer anions.

The nickel group trimers,\textsuperscript{13} also shown in Figure 16, exhibit spectra different from the copper group trimers and from each other. Instead of the single narrow transitions observed for Cu$_3^-$ and Ag$_3^-$, broad and congested spectra are observed. Nickel trimer exhibits only broad features corresponding to many overlapping electronic states. Palladium trimer also has broad features, but superimposed upon the broad background are sharp features with spacings that could correspond to either vibrational progressions or separate electronic states. For the platinum trimer, the spectrum is less congested with two low-lying bands. Each of these bands has structure corresponding to vibrational progressions of one or a few electronic transitions.

The basic reason for the congested spectra for the nickel group trimers is the large number of low-lying electronic states resulting from the open $d$ shells and the comparable energies of the $s$ and $d$ orbitals. The many nearly equivalent configurations of the $d$ electron "hole" on each metal atom lead to a large number of low-lying electronic states. Spin-orbit coupling further increases the number of electronic states. Balasubramanian\textsuperscript{135} has calculated 19 states lying within 0.5 eV of the ground state for Pd$_3$, consistent with the observed spectrum.

The congestion of the nickel group trimer spectra makes it impossible to make detailed assignments of electronic states or vibrational spectrum. We can compare the apparent density of states, which decreases from nickel to palladium to platinum. This decrease reflects an increase in the amount of bonding interaction from the $d$ orbitals—as one goes down the column in the periodic table, the size of the $d$ orbitals increases relative to the $s$ orbitals. For nickel trimer, the $d$ orbitals are largely localized on each atom and there is little $d-d$ bonding, leading to closely spaced electronic states and only broad features. For platinum trimer, $d$
orbital overlap is significant and there are a few most favorable configurations leading to a relatively small number of low-lying electronic states. Palladium trimer is intermediate in character.

V. THERMOCHEMISTRY

In addition to information about the vibrational and electronic structure, a primary result from the photoelectron spectrum of an anion R$^-$ is the electron affinity of the neutral, EA(R). This value can be combined with the gas-phase acidity of RH and the ionization potential of the hydrogen atom according to the following thermochemical cycle$^{114}$ to obtain the bond dissociation energy, $D(RH)$:

$$
\begin{align*}
R^- & \rightarrow R + e^- & \text{EA}(R) \\
RH & \rightarrow R^- + H^+ & \Delta H_{\text{acid}}(RH) \\
H^+ + e^- & \rightarrow H & -\text{IP}(H)
\end{align*}
$$

\[ RH \rightarrow R + H \quad D(R-H) \]

Gas-phase acidities can be obtained from gas-phase proton transfer equilibrium measurements using selected ion flow tube techniques.$^{115}$ The ionization potential of the H atom is precisely known, so measurement of the electron affinity and gas-phase acidity yields the bond dissociation energy according to,

$$
D_0(R-H) = \text{EA}(R) + \Delta H_{0,\text{acid}}(RH) - \text{IP}(H). \quad (13)
$$

Entropy and thermal corrections$^{116}$ are incorporated to convert the measured gas phase acidity free energy at room temperature, $\Delta G_{298,\text{acid}}(RH)$, to the 0 K enthalpy, $\Delta H_{0,\text{acid}}(RH)$.

We have recently carried out a collaboration at the University of Colorado with G. B. Ellison, C. H. DePuy, V. M. Bierbaum, and their co-workers, using this thermochemical cycle to determine the CH bond dissociation energies of C$_2$H$_n$ hydrocarbon molecules.$^{118}$ Electron affinities measured by the Lineberger and Ellison groups were combined with gas-phase acidities measured in the laboratory of DePuy and Bierbaum to determine $D_0$(HCC-H), $D_0$(CH$_2$CH-H), and $D_0$(CH$_3$C-H). These values could be combined with accepted values for the heats of formation of C$_2$H$_4$, HCCCH, CH$_2$, CH, C$_2$, C, and H to derive the energies required to break up acetylene and ethylene into all possible fragments, one bond at a time in any order. Figure 17 shows each of the CH bond dissociation energies of ethylene and acetylene.$^{118}$

A striking result is the wide variation in values of CH bond dissociation energies (Figure 17). The larger CH bond dissociation energy for acetylene, $D_0$(HCC-H) = 131.3 ± 0.7 kcal mol$^{-1}$, than for ethylene, $D_0$(CH$_2$CH-H) = 109.7 ± 0.8 kcal mol$^{-1}$, can be attributed to the stronger $sp$ $\sigma$ bond in acetylene compared to the $sp^2$ $\sigma$ bond in ethylene. However, breaking a similar $sp^2$ $\sigma$ bond
in vinyl radical requires much less energy, $D_d(H-\text{HCCH}) = 33.6 \pm 0.8$ kcal mol$^{-1}$. The reason for the large variation is that the bond dissociation energy reflects not only the "intrinsic" strength of the bond in the molecule, but also the stabilization or destabilization of the fragments upon cleavage. In the case of vinyl, breaking the $\beta$ CH bond leaves acetylene as the molecular fragment, converting a double CC bond into a triple CC bond. Thus, much of the energy required to break the CH bond is returned in the form of extra CC bond strength in the product molecule. This example demonstrates that bond dissociation energies are not necessarily a valid indication of the intrinsic strengths of chemical bonds at the equilibrium geometry of a molecule. Bond dissociation energies are the important quantities of interest for modeling the kinetics of combustion processes and other chemical reactions where bonds are broken and created.

There has been a controversy over the value for the CH bond dissociation energy of acetylene. Although the heat of formation of acetylene, and therefore its atomization energy, was precisely determined by calorimetry techniques in the 1940s, the bond dissociation energies of individual bonds have been surprisingly poorly known. Table 1 presents a summary of recent experimental and theoretical values. Molecular beam photodissociation measurements by Wodtke and Lee in 1985, giving $D_d(\text{HCC-H}) = 132 \pm 2$ kcal mol$^{-1}$, received support from upper limits obtained from spectroscopic predissociation but combustion kineticists favored a lower value of 124 kcal mol$^{-1}$. In 1989, while our collaborative work was under way, two experimental reports of lower values appeared: Field and co-workers reported an upper limit of 126.6 kcal mol$^{-1}$ based on Stark anticrossing spectroscopy, in which observed lifetime decays were assigned to predissociation. Wittig and co-workers found
Table 1. CH Bond Dissociation Energy of Acetylene (kcal mol⁻¹)\(^a\)

<table>
<thead>
<tr>
<th>(D_0)(HCC—H)</th>
<th>Method</th>
<th>Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>131.1 ± 0.7</td>
<td>Experiment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>131. ± 1</td>
<td>HCCH + e⁻ (K.E.) (\rightarrow) C₂H⁻ + H</td>
<td>1990</td>
<td>125</td>
</tr>
<tr>
<td>123. ± 1</td>
<td>proton affinity kinetics</td>
<td>1990</td>
<td>126</td>
</tr>
<tr>
<td>131.3 ± 0.7</td>
<td>(\Delta H_{\text{mol}}) (HCCH) + EA(C₂H) (-) IPA(H)</td>
<td>1990</td>
<td>116</td>
</tr>
<tr>
<td>127. ± 1.5</td>
<td>HCCH + (h\nu) (\rightarrow) C₂H + H(K.E.)</td>
<td>1989</td>
<td>120</td>
</tr>
<tr>
<td>(\leq 126.647 \pm 0.002)</td>
<td>Stark anticrossing spectroscopy</td>
<td>1989</td>
<td>119</td>
</tr>
<tr>
<td>(&lt; 132.3 \pm 0.004)</td>
<td>Zeeman anticrossing spectroscopy</td>
<td>1988</td>
<td>122</td>
</tr>
<tr>
<td>(&lt; 132.9 \pm 1.2)</td>
<td>fluorescence yield cut-off</td>
<td>1988</td>
<td>121</td>
</tr>
<tr>
<td>132.6 ± 1.2</td>
<td>HCCH + (h\nu) (\rightarrow) H⁺ + C₂H + e⁻ threshold</td>
<td>1987</td>
<td>123</td>
</tr>
<tr>
<td>124. ± 2</td>
<td>acetylene pyrolysis kinetics</td>
<td>1987</td>
<td>124</td>
</tr>
<tr>
<td>132. ± 2</td>
<td>HCCH + (h\nu) (\rightarrow) C₂H(K.E.) + H</td>
<td>1985</td>
<td>118</td>
</tr>
</tbody>
</table>

**Theory**

| 129.7 ± 1      | GVB-CCCI | 1990 | 128 |
| 131.54 ± 0.45  | QC1-CBS  | 1990 | 130 |
| 130.1 ± 1.0    | MRCl     | 1990 | 129 |
| 133.5 ± 2.0    | G1       | 1988 | 131 |

\(^a\)Literature values for \(\Delta H_{\text{mol}}(\text{C}_2\text{H})\) and \(\Delta H_{\text{mol}}(\text{C}_2\text{H})\) have been converted to \(D_0\)(HCC-H) using auxiliary heats of formation and heat capacity data given in Ref. 116.

\(D_0\)(HCC-H) = 127 ± 1.5 kcal mol⁻¹ from Doppler-resolved photodissociation experiments. Since our value of \(D_0\)(HCC-H) = 131.3 ± 0.7 kcal mol⁻¹ was published, two independent experiments have confirmed the higher value: Rusiec and Berkowitz\(^{15}\) found a value of 131.1 ± 0.7 kcal mol⁻¹ using a dissociative electron attachment technique. Chandler and co-workers\(^{16\dagger}\) repeated the photodissociation experiments using a proton imaging detection scheme and obtained 131 ± 1 kcal mol⁻¹; they also found evidence for intense multiphoton effects, which could have been an artifact in the Wittig experiments.

Further experiments by Field and co-workers\(^{10}\) suggest that anomalous lifetime decays seen in the anticrossing spectra of acetylene are due to a triplet isomerization barrier, rather than the onset of predissociation as originally thought. It is perhaps interesting to compare the high resolution acetylene anticrossing spectroscopy\(^{11\dagger}\) to the resonant autodetachment lifetime studies on C₂⁻ (discussed earlier). In both cases, a reasonable and apparently the simplest interpretation of spectroscopic data did not stand up to more direct (though less precise) measurement of a thermochemical quantity [\(D_0\)(HCC-H) or EA(C₂⁻)]. Rather, more complex explanations for the spectroscopic observations must be invoked, Occam’s razor is not infallible!

We believe a consensus has developed for a value for the acetylene CH bond dissociation energy near 131 kcal mol⁻¹. A recent value of \(D_0\)(HCC-H) = 123 ± 1 kcal mol⁻¹ from proton affinity measurements\(^{17}\) contradicts these results.
but it relies on kinetic correlations rather than equilibrium measurements and may therefore be subject to error.

Theoretical values for the bond dissociation energy of acetylene (Table 1) are in excellent agreement with the experimental consensus value. Accurate ab initio bond energies require large basis sets and extensive treatment of electron correlations, but such calculations are now feasible for small molecules even with multiple bonds. However, the theoretical agreement seen for $D_\text{h}(\text{HCCH})$ does not extend to the further fragmentation of acetylene. Theoretical values for $D_\text{h}(\text{HC})$ at comparable levels of theory fall over a wide range: 111.6 (QCICBS),\textsuperscript{115} 102 kcal mol\textsuperscript{-1} (GVB-CCCI),\textsuperscript{128} and 112.4 ± 2.0 kcal mol\textsuperscript{-1} (MRCI).\textsuperscript{122} The experimental value we reported\textsuperscript{116} is $D_\text{h}(\text{HCC}) = 116.3 ± 2.6$ kcal mol\textsuperscript{-1}. This value is derived from our measurement of $D_\text{h}(\text{HCCH})$ using a thermochemical cycle that also depends on the bond energy of $\text{C}_2$. We adopted\textsuperscript{116} $D_\text{h}(\text{C}_2) = 141.0 ± 2.5$ kcal mol\textsuperscript{-1} based on an evaluation of literature values; however, there is experimental evidence\textsuperscript{133} in favor of a higher value, $D_\text{h}(\text{C}_2) = 145.2 ± 0.2$ kcal mol\textsuperscript{-1}. This value would yield $D_\text{h}(\text{HCC}) = 112.1 ± 0.8$ kcal mol\textsuperscript{-1}, in agreement with the higher theoretical estimates. The low theoretical prediction of 102 kcal mol\textsuperscript{-1} by Wu and Carter\textsuperscript{128} can be ruled out. Further independent experiments and theoretical analyses are indicated for both $D_\text{h}(\text{C}_2)$ and $D_\text{h}(\text{HCC})$.

When both the electron affinity, $\text{EA}(R)$, and the gas phase acidity, $\Delta G_{\text{acid}}(RH)$, can be measured, an accurate and reliable value for the bond dissociation energy, $D_\text{h}(R-H)$, may be obtained. As with most experimental methods, both measurements are subject to possible errors of interpretation (e.g., mis-assignment of the origin in the photoelectron spectrum or undetected excited ions in the proton transfer kinetics), but these pitfalls can be avoided by careful experimentation.\textsuperscript{116}

VI. SUMMARY AND OUTLOOK

Negative ion photoelectron spectroscopy is a productive technique well suited for studying the vibrational and electronic structure of both anions and the corresponding neutral molecules. In this review, we have discussed our work in this area at the University of Colorado during the past few years.

Our negative ion photoelectron spectrometer continues to provide a wealth of spectroscopic data. In the six years since the last review,\textsuperscript{4} the electron energy analyzer and detection system has been refurbished to give 10 × better resolution and 1000 × higher sensitivity. The addition of the flowing afterglow ion source has solved the problem of excessive anion internal excitation, and the flowing afterglow has been further exploited to synthesize a number of interesting molecular anions as well as transition metal cluster anions. Finally, the new build-up cavity laser system has extended the photon energy from the visible to the near-ultraviolet. Future directions of instrumental improvements will likely include pushing the photon energy to the 5-eV region by intracavity doubling the
visible light of an argon ion laser for injection into the external build-up cavity, as well as upgrading the mass spectrometer to cover higher masses, which are increasingly important for investigations of cluster anion species. Although further increases in the electron energy resolution are possible, traditional negative ion photoelectron spectrometers with electrostatic energy analysis are unlikely to rival the resolution of zero electron kinetic energy techniques. However, they retain a unique strength in their general applicability to a large variety of molecular anions.

More than in technological advances, the true future of negative ion photoelectron spectroscopy lies in the chemistry to be explored. This is perhaps best conveyed by touching upon a few of the recent accomplishments by other groups, which we have not been able to include in this review. Bowen and co-workers\cite{Bowen} have produced ammonia and water cluster anions with over a thousand molecules and have traced the evolution of the solvated electron from the molecular level to the bulk limit. Smalley and co-workers have examined copper clusters of over 400 atoms,\cite{Smalley} observing the onset of bulk metal electron band behavior, and have also used negative ion photoelectron spectroscopy to characterize buckminsterfullerene, C\(_{60}\), and other carbon clusters.\cite{Smalley} Neumark and co-workers\cite{Neumark} have obtained spectra of the transition state in a heavy-light-heavy bi-molecular reaction, XH + X, by photoelectron spectroscopy of the corresponding stable anion, XHX\(^-\) (X = halogen). Ellison and co-workers continue to examine a variety of organic molecules, including for example CH\(_3\)N\(^-\), which exhibits low-lying singlet and triplet states,\cite{Ellison} and have recently upgraded their electron energy analyzer to make available higher resolution. Leopold and co-workers\cite{Leopold} are opening up the field of inorganic chemistry in negative ion photoelectron spectroscopy, beginning with coordinatively unsaturated transition metal carbonyl compounds. In the Lineberger laboratory, investigations of small organic radicals and transition metal clusters are continuing.

Determination of electron affinities has always been an emphasis of negative ion photoelectron spectroscopy, both as fundamental physical quantities and because of their use in thermochemical cycles for the determination of bond strengths. Our recent collaborative effort\cite{Feigerle} in the determination of the bond dissociation energies of acetylene and ethylene demonstrates again that the systematic application of ion kinetics and ion spectroscopy toward thermochemical determinations can greatly benefit the wider chemical community beyond gas-phase ion chemistry. A further collaboration at the University of Colorado aimed at obtaining bond dissociation energies for the C\(_3\)H\(_8\) hydrocarbons is under way.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the prodigious accomplishments of our colleagues in the photoelectron spectroscopy laboratory. C. S. Feigerle, Amy E. Stevens Miller, Thomas M. Miller, Kermit K. Murray, Doreen G. Leopold, Joe Ho, Mary K. Gilles, and Mark L.
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