Laser Spectroscopy of Gas Phase Ions

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I. INTRODUCTION

This chapter surveys the state of our knowledge of the interactions of small, free atomic and molecular negative ions with radiation, and the structural information that can be obtained from the interaction. The primary emphasis is on recent advances made possible by the utilization of lasers as light sources. Excellent reviews of earlier work have been published

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by Berry (1969), Steiner (1972), Herzberg (1971), and Smith (1968). We include in this discussion electron affinities, excited electronic states, and the experimental methods for studying these properties. The myriad problems associated with polyatomic negative ions, solvation of ions, ion–molecule reactions, and ion–ion interactions are beyond the scope of this work. We thus emphasize those aspects of negative ion properties that are related to equilibrium conditions, thermodynamics, comparisons with structure calculations, and interactions with radiation fields. In view of the central theme of this volume, we give only cursory attention to some of the new theoretical techniques being applied to negative ion structure and interactions with radiation.

One of the most important properties associated with a negative ion is the minimum energy required to remove the least tightly bound electron from the ion, forming a neutral atom or molecule and an electron at rest far away. This quantity is called the electron affinity of the corresponding neutral species. Theoretical calculations of electron affinities have been particularly difficult, since the electron affinity is typically of the same magnitude as the difference in correlation energies between the ion and the corresponding neutral molecule. There have been many attempts to determine precise electron affinities over the past forty years. Among the many techniques employed are \textit{ab initio} calculations, semiempirical calculations, isoelectronic extrapolations, studies of thermodynamic cycles, surface ionization, endothermic charge transfer, ion pair production in photoionization, studies of continuous absorption or emission in plasmas, and photodetachment. In spite of such extensive studies, by 1970 electron affinities accurate to better than 1% were known (Steiner, 1972) for only about ten atoms or molecules. The question immediately arises why such an important thermodynamic property has been so extensively studied, and yet is, on the scale of accuracy for other simple atomic and molecular properties, so poorly known. We shall attempt to provide a partial answer to this question in the remainder of this section.

It is not surprising that direct theoretical calculations have been successful only for small atoms, simply because of the difficulty and/or expense of large scale calculations of multielectron systems. The experimental techniques, with the exception of photoabsorption and photodetachment (which will be discussed shortly), generally suffered from substantial inaccuracies either because approximations had to be made which could not be readily verified, or because the measurement was a very indirect determination of an electron affinity. As an example, let us consider the surface ionization technique, which has provided (Bakulina and Ionov, 1964; Smirnov, 1965; Zandberg and Paleev, 1970; Zandberg \textit{et al.}, 1971) the only electron affinity determination for many atoms. The basic idea is to allow a beam of atoms to strike a
hot surface and to measure the ratio of the positive ion current to the negative ion current emitted from the surface. If one assumes complete equilibrium on the surface, then this ratio is determined by the ionization potential of the atom, the electron affinity of the atom, and the work function of the surface. The problem of measuring the work function can be circumvented by using two atomic beams, for one of which both the ionization potential and the electron affinity are known. In effect, the second beam is used to measure the work function of the surface; the question of equilibrium on the surface, however, has not yet been answered. In fact, recent work (Hotop et al., 1973a; Hotop and Lineberger, 1973) suggests that large errors exist when the two atomic beams have different surface chemistries; the assumption of surface equilibrium thus appears to be not generally valid.

Upon cursory examination, the photoabsorption technique would appear to be a very simple and direct method for obtaining accurate electron affinities. We need only to fill a container with negative ions and measure the extinction coefficient of the sample as a function of wavelength. The longest wavelength at which one detects absorption will be essentially the photon energy corresponding to the removal of an electron with zero kinetic energy from the ion, namely, the electron affinity. The result is direct and unambiguous. The problem, of course, is that in order to obtain a sufficient negative ion density to do such a measurement, one must study negative ions in a rather hot plasma. The other components of the plasma introduce other absorptions and emissions, making analysis very difficult. This technique, however, has been successfully applied to the halogens in an important series of measurements by Berry and co-workers at the University of Chicago (Berry and Reimann, 1963; Berry et al., 1965a,b).

The difficulties associated with the plasma can be circumvented by performing a crossed beam photodetachment measurement, in which a mass selected beam of negative ions is crossed by an energy resolved photon beam. One then measures a cross section for production of electrons as a function of photon energy; the electron affinity then corresponds to the threshold photon energy for production of electrons. Since the only ions in the interaction volume are the mass selected ions under study, there is no ambiguity in the interpretation. Several elegant experiments of this type were performed by Branscomb and his colleagues at the National Bureau of Standards in the 1960's (Branscomb et al., 1958, 1965; Branscomb, 1966; Steiner et al., 1962). The photodetached electron signal is directly proportional to the product of the negative ion density in the interaction region and the photon flux. Thus the meager photon fluxes attainable with conventional light sources restricted such studies to those ions for which copious beams could be produced. The low intensity of these light sources also required that, in order to have sufficient photon flux to see a signal, the photon energy
resolution be no better than approximately 50–500 Å in the visible spectrum.

Clearly, in order to improve these measurements, one needs a brighter light bulb. The advent of lasers has, of course, removed the serious light source restrictions previously encountered and has made a qualitative change in the accuracy with which electron affinities can be measured. The increased photon flux has also removed the requirement for intense negative ion beams and made it possible to study ions that were not previously accessible. Two such experimental techniques will be discussed below: (1) measurement of photodetachment cross sections in a crossed beam apparatus using a tunable dye laser as the light source, and (2) studies of the photoelectron spectra of negative ions excited by a fixed wavelength laser.

In the following section we will discuss in some detail a tunable laser photodetachment apparatus, a fixed wavelength laser photoelectron spectroscopy apparatus, and a laser photodissociation apparatus. The remaining sections will deal primarily with results and applications. Atomic and molecular negative ion photodetachment results are treated separately because the problems of analysis are quite different. Some very recent photodissociation studies by groups in Amsterdam and Orsay will be discussed, as well as applications of multiphoton photodetachment of negative ions. Finally, we will attempt to make some speculations concerning future developments in this rapidly changing field.

II. EXPERIMENTAL TECHNIQUES

At present, three essentially different laser techniques are being utilized for the study of these spectra of gas phase ions: (1) tunable laser photodetachment cross section measurements, (2) fixed laser photoelectron spectroscopy, and (3) fixed laser photodissociation fragment spectroscopy. While the latter two techniques sound quite similar, the experimental arrangements and problems differ considerably. In the former case, the photodetached electron carries a very small fraction of the total center-of-mass energy, while in the latter, the heavy photofragment carries a substantial fraction of the c.m. energy. The reader primarily interested in experimental results may wish to omit reading this section. The discussion of the laser sources will be limited to an enumeration of the properties of the laser; more information on the laser sources may be found in Chapter 1.

A. Tunable Laser Photodetachment Apparatus

A schematic diagram of a tunable laser photodetachment apparatus (Hotop et al., 1973b) is shown in Fig. 1. The basic idea is to intersect a
several keV mass analyzed negative ion beam with the focused output of a pulsed, tunable dye laser and to measure the relative cross section for production of neutral atoms as a function of the laser wavelength. The negative ions are extracted from an ion source, accelerated to several keV, mass analyzed and focused onto a 15-stage particle multiplier located 20 cm beyond the laser beam–ion beam intersection. After passing through the interaction region, but before reaching the multiplier, the remaining negative ions are electrostatically deflected into a Faraday cup, so that only the neutral atoms, produced by charge stripping on the background gas and by laser photodetachment, reach the neutral detector. As a result of the large number of neutrals striking the multiplier in a short time interval, this detector is operated in a linear, charge amplifying mode rather than as a particle counter. The quantities measured are the ion beam current, the photon flux, the neutral signal, and the photon wavelength. The result of the measurement is a relative cross section for production of neutrals as a function of photon wavelength.

Two variations on this scheme, in which one measures the decrease in the ion signal rather than the appearance of products, have been utilized to date. Brauman and co-workers (Smyth et al., 1971; Smyth and Brauman, 1972) have trapped the negative ions of interest in an ion cyclotron resonance trap and, following irradiation of the trap with a photon beam, measured the decrease in the number of ions in the trap. Using conventional light
sources this technique has been successfully used to study a number of molecular negative ions. Smyth and Brauman (1972) reported photodetachment of NH$_2^-$ using a tunable parametric oscillator as the light source. Sinnott and Beatty (1971) have investigated photodetachment of thermally relaxed molecular ions drifting in a weak electric field. While these techniques are basically quite similar, the detailed discussion which follows relates specifically to the tunable laser photodetachment apparatus of Lineberger and his colleagues.

1. Ion Source and Optics

A variety of different sources have been used to produce the negative ions. These include a magnetically confined hot cathode discharge source (Lineberger and Woodward, 1970; Lineberger 1973), a sputtering source (Hotop and Lineberger, 1973), and an oven-type discharge source used to volatilize solid samples. In general, the hot cathode discharge has been most useful for gaseous compounds, the sputtering source for relatively unreactive refractory materials, and the oven source for alkalis. A detailed discussion of all three can be found in the literature cited above.

The negative ions are extracted from the source, accelerated to 2 keV, and focused by means of an electrostatic quadrupole doublet onto the entrance aperture of a 90° sector magnetic mass spectrometer having a resolution $m/\Delta m$ of about 40. A second quadrupole doublet then focuses the mass selected ion beam onto the first stage of the multiplier normally used for neutral atom detection. Included in the ion optical system is a 5° deflection just prior to the interaction region. This deflection is adequate to permit spatial separation of the laser-produced neutrals from those produced by charge stripping in the relatively high pressure region (approximately 10$^{-6}$ Torr) prior to the small deflection. A considerable reduction in noise is afforded by this deflection, since the differentially pumped interaction and neutral detector chambers are operated at pressures of 10$^{-8}$ Torr.

2. Tunable Laser

As can be seen in Fig. 1 the ion beam is intersected normally by the output of a flashlamp-pumped, pulsed tunable dye laser (Jennings and Baldwin, 1971). The laser dye cell located at one focus of an elliptical cavity is pumped by a linear xenon flashlamp located at the other focus. The laser optical cavity is defined by a partially transmitting mirror and an 1800 lines/mm grating blazed at 5000 Å in first order. A 4 x beam expander is used to better define the angle at which the laser light strikes the diffraction grating. Wavelength tuning is accomplished by rotating the grating using a computer controlled stepping motor. A small portion of the laser output
energy is diverted with a beam splitter to a solid state photodiode for laser power measurement. The laser is normally operated at 5 Hz, and produces an output pulse whose time duration is approximately 0.3 μsec. A number of different dyes are used to cover the wavelength region 4500-7000 Å. The line width of a single pulse is not measured, but the envelope of several hundred pulses (which is a parameter relevant to our data) has a width of 1-2 Å.

3. Signal Detection

The neutral particle multiplier, operated in a linear, charge amplifying mode, is monitored by a pair of fast sample/holds (S/H). The first samples the stripped neutral signal approximately 1 μsec before the laser-produced neutrals reach the multiplier, providing a neutral background correction obtained in a time short compared to the coherence time of the negative ion beam. The second samples the total signal at the arrival time of the laser-produced neutrals; namely, after a delay (following the laser pulse) equal to the flight time from the interaction region to the detector. The S/Hs used have a response time of 0.3 μsec.

The ion beam current from the Faraday cup is monitored with an electrometer whose output is fed directly to the small computer. A third S/H is used to monitor the integrated signal from the laser photodiode. The triggers for the laser and the S/Hs are controlled by a combination of computer generated pulses and delay gates. For a more detailed description of the apparatus, see Hotop et al. (1973b).

4. Data Acquisition and Analysis

Using a small computer to control the laser firing and to read the various S/H outputs, an apparent neutral production cross section is determined for each shot of the laser. A single datum point in one run is the average of, typically, 300 such shots. The quantity actually measured, $Q_{AP}$, is given in terms of the experimental parameters by

$$Q_{AP} = \sum_{i=1}^{N} \frac{[AS(i) - AB(i)] - AN}{[LS(i)IS(i)]},$$  \hspace{1cm} (1)

where $N$ is the number of laser shots for the datum point, $AS(i)$ is the output from the S/H detecting laser-produced neutrals and background gas stripped neutrals for the $i$th laser shot, $AB(i)$ is the signal from the S/H looking at stripped neutrals alone for the $i$th laser shot, $AN$ is the net laser-induced electrical noise in the atom channel, $LS(i)$ is the laser signal measured by the photodiode for the $i$th laser shot, and $IS(i)$ is the ion beam current measured at the Faraday cup for the $i$th laser shot.
The implicit assumption is made that the spatial overlap between the ion beam and laser beam is time invariant. In order to correct this relative cross section for slow drifts in the ion beam–laser beam overlap, one particular wavelength is chosen as a benchmark and the cross section at this wavelength is measured after every three data points. A linear interpolation is then performed between successive values of the benchmark cross section and the data points are normalized to a particular value for the cross section at the benchmark. Under normal conditions, the benchmark cross section varies less than 3% from run to run.

Data are taken as a function of the laser grating angle and are converted to wavelengths by calibrating the laser output with a 0.35 m monochromator whose resolution is better than 0.1 nm. In order to be certain that the observed cross section is the result of an unsaturated single photon process, the apparent cross section is measured as a function of laser power. Neutral density filters are used to vary the laser power, insuring a constant laser line width.

If desired, one can obtain an estimated absolute photodetachment cross section by measuring relative photodetachment cross sections, under identical experimental conditions, for O⁻ (whose absolute cross section is known) and the ion of interest at some fixed wavelength. These apparent relative cross sections are then converted to true relative cross sections by making the appropriate ion velocity determination (to convert measured ion current to ion density) and measuring the ratio of secondary electron yields for the two neutrals (to determine relative detector sensitivity) (Hotop et al., 1973b).

B. Fixed Laser Photoelectron Spectroscopy Apparatus

The details of this experimental technique as well as the complete theoretical justification for the analysis have been published elsewhere (Siegel et al., 1972; Celotta et al., 1972) and only the most important points are mentioned here. Thus, in the following two sections we shall describe only a few salient features of the experimental method and data analysis.

1. Experimental Method

A pictorial diagram of the interaction region is shown in Fig. 2. A 680 eV beam of negative ions is illuminated by the linearly polarized intracavity field of an argon–ion laser (4880 Å) in an otherwise field-free region. Those electrons entering a small solid angle, 4π/2000 sr, at right angles to both the ion and photon beams are filtered by a hemispherical electron monochromator and, if transmitted, are detected by a particle counter and stored
Fig. 2. Pictorial view of the interaction region of the laser photoelectron spectroscopy apparatus developed by Hall and co-workers.

digitally. As one sweeps the transmission energy of the filter, the energy spectrum of the photodetached electrons is accumulated.

With a laser discharge current of 20 A the circulating power in the laser cavity is about 20 W on the 4880 Å line. The intracavity laser beam enters the vacuum chamber through a normal incidence, antireflection coated optical window. The polarization independence of the window transmission permits us to use a half-wave plate in the laser cavity to rotate the plane of polarization of the laser light in the interaction region. In this manner it is possible to determine the photoelectron count rate as a function of the angle between the electric vector of the laser light and the electron collector, thereby determining the angular distribution of the photoelectrons.

The negative ion sources utilized in this apparatus are essentially the same as those described in Section II.A.2. The negative ion optics employ a Wein velocity filter for mass analysis of the monoenergetic negative ions. A unique advantage of the Wein filter is that it can be operated at zero resolution, thus providing the capability to photodetach simultaneously all of the negative ions in the beam from the ion source. This feature is very useful in obtaining, under identical conditions, energy differences between electrons from an ion of known electron affinity and the ion under study.
The photodetached electron collection and energy analysis are described in detail elsewhere. Basically the analyzer is a hemispherical electrostatic electron analyzer operated at a constant transmission energy of 12.18 eV. The electron energy spectrum is swept by varying the potential of the interaction region. The design of the optical system is such that an electron ejected into the acceptance cone of analyzer with kinetic energy $W$ eV will be accelerated to the transmission energy of the analyzer only when the interaction region is at a potential $W$ eV. The resolution of the analyzer (fwhm) is approximately 54 meV.

2. Data Analysis

Electrons transmitted by the hemispherical electron monochromator are detected by a particle counter and stored digitally in the appropriate energy bin. By sweeping the transmission energy, the energy spectrum of the photodetached electrons is accumulated. The vertical detachment energy $E_{vd}$ for an electron with energy $\Omega$ measured in the laboratory frame, can be determined from the simple energy balance relation

$$E_{vd} = h\nu - \Omega + E_{cp} - (m/M)W,$$

where $h\nu$ is the incident photon energy (2.540 eV), $\Omega$ is the measured lab frame energy of the outgoing electron, $m/M$ is the ratio of the mass of the electron to the mass of the ion, $W$ is the kinetic energy of the ion, and $E_{cp}$ is a contact potential term. The last term in Eq. (2) is a kinematic correction which comes from the coordinate transformation from the c.m. frame to the laboratory frame. This equation holds for mutually perpendicular photon, ion, and electron beams. It has been shown that additional terms having to do with mechanical misalignments and higher order terms yielding small kinematic shifts are negligible (Siegel et al., 1972).

The contact potential term is a slowly varying function of time which must be measured in order to calibrate the energy scale. The simultaneous photodetachment of two species, one of which has a well-known detachment energy $A$, allows us to eliminate the contact potential from the differential energy measurement and avoids possible errors due to contact potential changes. Thus if $A_2$ is the unknown electron affinity for an ion of mass $M_2$ and $A_1$ is the known electron affinity of an ion of mass $M_1$, then applying Eq. (2) to both ion 1 and ion 2 and subtracting we obtain

$$A_2 = A_1 + \Omega_1 - \Omega_2 + mW \left( \frac{1}{M_1} - \frac{1}{M_2} \right).$$

The ions which have been generally used as reference ions are $O^-$ (Hotop et al., 1973a), $OH^-$ (Lineberger, 1973; Hotop et al., 1974), $S^-$ (Lineberger and Woodward, 1970), and $K^-$ (Lineberger, 1974).
These electron differences are determined by a nonlinear least squares
fitting procedure to the observed detached electron peak. The procedure
is to fit the data to a Gaussian with a small asymmetry parameter. Since
one is measuring only energy differences, the exact definition of the center
of the peak does not matter so long as all the peaks involved have the same
shape. By this technique energy differences can be determined to better
than 1% ± 1 meV for pairs of ions whose masses are greater than approxi-
mately 30 amu.

C. Ion Photofragment Spectroscopy Technique

Two groups of workers have recently reported kinetic energy spectra
of H⁺ ions produced by laser photodissociation of fast H₂⁺ ions (Ozenne
et al., 1972, 1974; van Asselt et al., 1974). The principal differences between
this experimental technique and that discussed in the previous section arise
from the fact that, in this case, the photofragment carries away a large
fraction of the total c.m. energy.

In the Ozenne apparatus, a beam of H₂⁺ ions is produced by electron
impact ionization of H₂, accelerated to 4 keV, and crossed at right angles
by the output of a pulsed ruby laser delivering about 10 J in a 400 μsec
pulse. The H⁺ ions arising from photodissociation of H₂⁺ are collimated,
momentum analyzed, and collected at zero scattering angle. The product
ions are detected by a multiplier and counted in a gated 100 MHz scaler.
A background correction is obtained by opening the gate for a similar period
of time when the laser is not fired.

One wishes to be able to distinguish H⁺ fragments originating from
different vibronic levels of the H₂⁺ ions. If the angular divergence of either
the incident H₂⁺ ion beam or that of the detected H⁺ fragments is too large,
this resolution will not be obtained. These fragment peaks were just barely
resolved with angular apertures of 2.5 and 7.5 mrad for the primary and
secondary beams, respectively; subsequent reductions in the angular
aperture have made these peaks clearly resolvable. The photodissociation
apparatus of van Asselt and colleagues is quite similar to Ozenne's, except
that a continuous argon–ion laser (5145 Å) with lower peak power is used
as a light source, and ultrahigh vacuum conditions are essential to eliminate
the collisional dissociation background.

III. ATOMIC NEGATIVE ION PHOTODETACHMENT

The primary information we hope to obtain from a negative ion photo-
detachment cross section measurement is, of course, the electron affinity of
the atom. In order to interpret the cross section correctly, however, we first need to understand the threshold behavior of the photodetachment cross section. The theoretical foundations for the interpretation, together with typical experimental results, are presented in Section III.A. Processes involving photodetachment into excited final states are discussed in Section III.B, with primary emphasis on the alkali ions. Finally, Section III.C summarizes electron affinity determinations to date and includes new estimates for the electron affinities for the three long series of the periodic table.

A. Threshold Cross Section Behavior

If a bound p-electron is detached, such as in Se\(^-\), the dipole selection rules tell us that the outgoing electron can be in an s or d wave. Very close to threshold, the s-wave behavior will dominate the cross section behavior, since the d-wave cross section will be suppressed by a centrifugal barrier. The quantitative statement of this behavior is contained in the work of Wigner (1948) on threshold laws for processes in which pairs of particles are formed in the final state. He shows that the leading term of the energy dependence of photodetachment cross sections near threshold is given by

\[ \sigma \propto k^{2L+1} \propto E^{(2L+1)/2}, \]  

(4)

where \( L \) is the orbital angular momentum of the detached electron, \( k \) is the magnitude of its linear momentum, and \( E \) is the kinetic energy of the electron. In deriving Eq. (4), it is assumed that the long-range forces between the departing electron and the atom (other than the centrifugal potential) fall off faster than \( 1/r^2 \), a condition which is fulfilled for all atoms except \( H (n \geq 2) \) (O'Malley, 1965).

We see from Eq. (4) that the energy dependence of the threshold photodetachment cross section tells us the orbital angular momentum of the detached electron, and hence provides some information on the orbital from whence it came. This threshold behavior is in marked contrast with the threshold behavior for photoionization of neutrals, where the threshold cross section is a step function, independent of the orbital angular momentum of the ejected electron. The reason for this difference is that, in the case of photoionization the dominant long-range interaction is the \( 1/r \) coulomb interaction, while in the photodetachment case, the dominant long-range interaction is the \( l(l + 1)/r^2 \) centrifugal potential. In a high resolution photodetachment threshold cross section measurement one would like both to verify the Wigner threshold law and to determine the energy range over which it gives a satisfactory description of the cross section.
Experimentally, the simplest case to study is photodetachment of a bound p-electron, because the threshold law \( (\sigma \propto E^{1/2}) \) leads us to expect an infinite derivative for the cross section at the threshold, an experimentalist's dream. As an example of such threshold behavior, consider photodetachment of Se\(^-\); a schematic diagram of the relevant energy levels is shown in Fig. 3.

![Energy level diagram](image)

**Fig. 3.** Diagram of Se and Se\(^-\) energy levels relevant to tunable laser photodetachment studies.

One expects to observe some or all of the six \( E^{1/2} \) thresholds, corresponding to transitions from Se\(^-\) \( 2P_{1/2,3/2} \) to Se \( 3P_{2,1,0} \). Since the spin-orbit splittings in the neutral atom are well known from optical spectroscopy, identification of each transition will be straightforward.

The measured Se\(^-\) photodetachment cross section (Lineberger, 1973; Hotop *et al.*, 1973b) is shown in Fig. 4; four sharp onsets are readily observable. The three onsets at the highest photon energies correspond to transitions from Se\(^-\) \( 2P_{3/2} \) to Se \( 3P_{2,1,0} \); the energy differences correspond to those known from neutral spectroscopy to within \( \pm 2 \text{ cm}^{-1} \). The onset at about 16,000 cm\(^{-1}\) is the transition Se\(^-\) \( 2P_{1/2} \) to Se \( 3P_1 \). It cannot be \( 2P_{1/2} \rightarrow 3P_0 \), because then we would see an onset around 15,450 cm\(^{-1}\), which we do not observe; it cannot be \( 2P_{1/2} \rightarrow 3P_2 \), because the cross section is nonzero below this energy. The range of the tunable lasers was not sufficiently great to observe the \( 2P_{1/2} \rightarrow 3P_2 \) onset around 14,000 cm\(^{-1}\). The \( 2P_{1/2} \rightarrow 3P_0 \) onset is buried in the rising portion of the first large threshold near 16,550 cm\(^{-1}\).

Since the electron affinity of Se corresponds to the Se\(^-\) \( 2P_{3/2} \rightarrow 3P_2 \) threshold energy we find \( \text{EA(Se)} = 2.0206 \pm 0.0004 \text{ eV} \). The spin-orbit
Fig. 4. Se\textsuperscript{-} photodetachment cross section in the energy range 14,000–19,000 cm\textsuperscript{-1}. The individual fine structure transition thresholds are labeled.

splitting in the Se\textsuperscript{-} ion was also derived from these threshold measurements and was found to be \(\Delta E(2P_{3/2} \rightarrow 2P_{1/2}) = 2279 \pm 2\) cm\textsuperscript{-1}.

The range of validity of the Wigner threshold law can be tested by plotting one of the partial cross sections as a function of electron momentum. A straight line then corresponds to the Wigner threshold law; such a plot for the Se\textsuperscript{-}(2P_{3/2}) \rightarrow Se^{3P_2} partial cross section is shown in Fig. 5. It is seen that the Wigner threshold law is valid for only approximately 5 meV above threshold. There has been an attempt (Lineberger, 1973; Hotop et al.,

Fig. 5. Se\textsuperscript{-} 2P_{3/2}, Se\textsuperscript{3P_2} partial photodetachment cross section plotted as a function of the magnitude of the electron momentum. The straight line corresponds to the Wigner threshold law, which is seen to be valid for only the first 5 meV (0.02 a.u.) above threshold.
1973b; O’Malley, 1965) to utilize these deviations from the threshold law to determine the polarizability of the neutral atom and the low-energy electron–atom elastic scattering cross section. The results, however, are not definitive to date.

In order to complete the picture of threshold photodetachment cross section behavior, one should study photodetachment of a bound s-electron. The H\(^-\) ion is the most logical candidate for such a test since its structure is so simple and a very accurate calculation of EA(H) (0.75421 eV) by Pekeris (1962) is available. The H\(^-\) threshold, however, lies in a portion of the infrared not currently accessible with tunable lasers. Consequently, negative ions of the noble metals were chosen for study.

Au has a 5d\(^{10}\)6s\(^2\)S\(_{1/2}\) ground state, and the first excited state lies more than 1 eV higher. The ground state of Au\(^-\) should be 5d\(^{10}\)6s\(^2\)1S, with no other stable negative ion state likely. The photodetachment cross section near threshold should exhibit the p-wave behavior, since an s-electron is detached. Figure 6 shows Au\(^-\) photodetachment data (Hotop and Lineberger, 1973) obtained in the photon wave number range 18,500–19,500 cm\(^{-1}\). The cross section is zero below 18,620 cm\(^{-1}\) (2.3086 eV); above that energy the cross section behavior is compatible with the Wigner threshold law for p-wave electrons (\(\sigma \propto k^2\)). This behavior is clearly demonstrated in Fig. 7, where we plot (\(\sigma/h\nu\))\(^{1/3}\) versus \(h\nu\); a straight line then corresponds to the Wigner threshold law for a p-wave continuum electron. In this case, the Wigner law seems to be valid for approximately 50 meV above threshold.

![Figure 6. Au\(^-\) photodetachment cross section.](image-url)
The rather large range over which the threshold law is valid (ten times greater than Se\(^-\)) is fortuitous, being due to a near cancellation of the first two correction terms to the Wigner law.

**B. Excited State Thresholds**

As a result of the fact that present dye lasers do not operate at wavelengths sufficiently long to observe photodetachment thresholds for many atomic negative ions, it is of interest to consider the possibility of observing thresholds for photodetachment processes that leave the resulting atom in an excited electronic state. One is substantially aided in this task by the fact that selection rules do not preclude photodetachment into a final state of multiplicity different from the atomic ground state. For example, consider photodetachment of O\(^-\) \(2\ ^3P_{1/2,3/2}\) forming O(2p\(^+\)) plus a free electron. If the photon energy is sufficiently high, then all electronic terms resulting from 2p\(^+\), namely, \(^3P\), \(^1D\), and \(^1S\), have cross sections of the same magnitude. Thus, one can observe the photodetachment threshold for O\(^-\), leaving the O atom in the \(^1D_2\) state, and determine the electron affinity of O from a photodetachment cross section measurement in a wavelength region more convenient than that of the first threshold (8500 Å). Such a measurement has been performed by Hotop et al. (1973a) and Branscomb et al. (1965). If one can observe photodetachment thresholds for both ground and excited
terms of the neutral, then it may be possible to determine the energy differences for multiplet series of atoms which have not been accurately determined to date.

In addition to these direct threshold measurements, there exists the possibility of observing interference effects in photodetachment at photon energies corresponding to the opening of a new channel which competes with the already open channel. This fact was pointed out in detail by Norcross and Moores (1974) in the case of Na\(^-\) photodetachment at photon energies corresponding to the opening of the lowest \(^2\)P exit channel in the neutral. A schematic energy level diagram showing the various competing continua is depicted in Fig. 8.

Norcross and Moores (1974) have shown that, as a result of extensive configuration mixing in the alkali negative ion wave function, both the \(^2\)S\(_{1/2}\) and \(^2\)P\(_{1/2,3/2}\) final state channels are significantly allowed, resulting in an interference (a Wigner cusp) at the \(^2\)P channel openings. Figure 9 shows Na\(^-\) photodetachment data (Patterson et al., 1972) in the region of the Na(3 \(^2\)P\(_{1/2,3/2}\)) thresholds; the individual fine structure thresholds could not be resolved. The shape of the cross section near threshold corresponds to a Wigner cusp, and is essentially in agreement with calculations by Norcross and Moores. Since the energy location of the peak corresponds essentially to a weighted average energy for forming Na \(^2\)P, one can determine that EA(Na) is (0.543 ± 0.010) eV. This result is in remarkable agreement with the \textit{ab initio} calculation of the electron affinity of Na (0.54 eV) by Weiss (1968).

The K\(^-\) ion is a more favorable case for experimental study both because the spin-orbit splitting in the excited state is much larger than for Na, and because the expected threshold falls in a more convenient spectral region. Figure 10 shows the K\(^-\) photodetachment cross section (Patterson et al., 1974) in a broad energy region containing the \(^2\)P excited state thresholds.
Fig. 9. Na \(^{+}\) photodetachment cross section in the region of the Na (3\(^{2}P_{1/2,3/2}\)) thresholds. The individual fine structure thresholds were not resolved. Curve indicates dipole length (Moores and Norcross, 1974); dots indicate data of Patterson et al. (1974). See text for more details.

Fig. 10. K \(^{+}\) photodetachment cross section in the region (5500-6100 Å) containing the 2\(^{2}P\) thresholds. The solid line is a dipole velocity calculation of the photodetachment cross section performed by Moores and Norcross (1974); the broken line is dipole length; dots represent data of Patterson et al. (1974).
On this energy scale, the principal feature is the sharp drop in the total cross section. Figure 11 is a twenty-fold expansion of these data (Lineberger, 1974) in the vicinity of the threshold. The energy difference between the two minima corresponds to the $^2P_{1/2,3/2}$ energy separation in $K(4^2P_{3/2,1/2})$. From the location of the minimum near 17,025 cm$^{-1}$, one finds $\Delta B(K)$ to be $(0.5012 \pm 0.0005)$ eV. While the shape of the cross section near threshold is quite different from the Na case, it is still consistent with the general treatment of the threshold behavior, which predicts only a discontinuity in the cross section derivative at the channel opening, but not necessarily a change in the sign of the derivative of the cross section with respect to energy. In addition, calculations by Moore and Norcross (1974) confirm the general shape of the $K^-$ photodetachment cross section in this region.

Recent studies (Patterson et al., 1974) of Rb$^-$ and Cs$^-$ photodetachment near the $^2P$ thresholds show even more pronounced structure. For example, the Cs$^-$ photodetachment cross section drops by approximately three orders of magnitude within a few millivolts near the $^2P_{1/2}$ threshold. It is possible that this structure is the result of a doubly excited negative

---

**Fig. 11.** Twenty-fold expansion of the $K^-$ data of Fig. 10, near the $^2P$ thresholds. The individual fine structure thresholds are now well resolved, and the energy difference between the two sharp decreases corresponds within 2 cm$^{-1}$ to the $^3P_{1/2}-^3P_{3/2}$ energy difference in K 4 $^2P$.  

---
ion configuration lying very close to the $^2P$ threshold. Such a state would give rise to a Fano line shape (Fano, 1961; Fano and Cooper, 1965; Schulz, 1973). Since the continuum consists of one partial wave, one expects a true zero in the total cross section. A full explanation, however, must wait until further measurements and calculations are available.

Photodetachment of alkali negative ions has also been studied with the laser photoelectron spectroscopy apparatus. In some preliminary measurements, we (Patterson et al., 1974; Kasdan and Lineberger, 1974) have found $EA(\text{Cs}) = (0.470 \pm 0.003)$ eV and $EA(\text{Rb}) = (0.486 \pm 0.003)$ eV. In addition to the electron energy measurements, the photoelectron spectroscopy machine has been used to measure the angular distributions of the ejected electrons. This angular distribution measurement provides a very sensitive test of theoretical calculations, since the angular distributions result essentially from interference of two partial waves.

C. Atomic Electron Affinities

In addition to the atomic negative ions already discussed, there have been laser photodetachment determinations (Lineberger, 1974) of electron affinities for Ag, C, Cu, Li, Pt, and S. These atoms together with H and the halogens, represent all of the atoms in the periodic table whose electron affinities are presently known to better than 10 meV. Within the next few years it is likely that similar accurate electron affinities will be known for most of the atoms in the periodic table.

Until that time, however, we can substantially improve upon our knowledge of many electron affinities by employing isoelectronic extrapolations, using these accurately known electron affinities as benchmarks. In particular, one can estimate the EA's of the elements in the three long series ($K \rightarrow \text{Cu}, \text{Rb} \rightarrow \text{Ag}, \text{Cs} \rightarrow \text{Au}$) via horizontal isoelectronic extrapolations (Hotop et al., 1973a).

Charkin and Dyatkina (1965) and Zollweg (1969) showed that the energy difference between the two configurations $d^{10}S^2$ and $d^KS$ ($K = 0, \ldots, 10$) increases nearly linearly with $K$. Since it is rather well established that the ground state configuration of negative ions in the three long periods is $d^{10}S^2$, one can estimate the electron affinities for these atoms, based on alkali and noble metal EA determinations as benchmarks.

For example, the benchmark EA's of K and Cu determine the slope of the straight line representing the $d^{10}S^2 \rightarrow d^KS$ energy differences between the negative ion and the $d^KS$ neutral atom state. Using this procedure, one arrives at the values shown in Table 1, in which the EA's of the elements of the three long periods (excluding the rare earths), as determined by this extrapolation, are listed.
TABLE 1

ELECTRON AFFINITIES OF THE ELEMENTS IN THE THREE LONG SERIES (eV) AS DETERMINED BY ISOELECTRONIC EXTRAPOLATIONS

<table>
<thead>
<tr>
<th>K</th>
<th>Ca</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>-1.95</td>
<td>-0.78</td>
<td>-0.09</td>
<td>0.53</td>
<td>0.86</td>
<td>-1.18</td>
<td>0.15</td>
<td>0.65</td>
<td>1.13</td>
<td>[1.23]</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
</tr>
<tr>
<td>0.49</td>
<td>-1.68</td>
<td>-0.71</td>
<td>0.13</td>
<td>0.81</td>
<td>0.89</td>
<td>0.66</td>
<td>1.06</td>
<td>1.14</td>
<td>0.41</td>
<td>[1.30]</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
</tr>
<tr>
<td>0.47</td>
<td>-0.46</td>
<td>0.51</td>
<td>-0.72</td>
<td>0.00</td>
<td>1.02</td>
<td>0.12</td>
<td>1.12</td>
<td>1.59</td>
<td>2.13</td>
<td>[2.31]</td>
</tr>
</tbody>
</table>

There are very few experimental data with which these numbers can be compared. The value for EA(Pt) obtained from this extrapolation (2.13 eV) agrees remarkably well with the photodetachment value of Hotop and Lineberger (1973): (2.128 ± 0.002) eV. Such excellent agreement is certainly fortuitous. Further comparisons can be made with the surface ionization determinations of Scheer (1970), whose results are as follows:

\[
\begin{align*}
\text{EA(Mo)} &= (1.0 \pm 0.2) \text{ eV} ; \\
\text{EA(Ta)} &= (0.8 \pm 0.3) \text{ eV} ; \\
\text{EA(W)} &= (0.5 \pm 0.3) \text{ eV} ; \\
\text{EA(Re)} &= (0.15 \pm 0.10) \text{ eV} .
\end{align*}
\]

Except for Ta, the agreement between Scheer's (1970) data and these extrapolated numbers is quite reasonable. As a result of using more accurate benchmarks, these extrapolations represent an improvement over earlier extrapolations, but they should be viewed as guidelines with errors of order 0.1 eV being entirely possible in this estimate.

IV. MOLECULAR NEGATIVE ION PHOTODETACHMENT

Detailed interpretation of the tunable laser atomic negative ion photodetachment data has been a relatively straightforward task; molecular negative ions present a very different case. Since one cannot prepare a negative ion beam in a single rotational, vibrational state, one must contend with unfolding a large number of photodetachment thresholds from various negative ion rotational states, all opening in a rather narrow photon energy interval. Moreover, the exact form of the photodetachment threshold law is unknown for a rotating molecular ion with a permanent dipole moment. Geltman (1958) has predicted photodetachment threshold laws for a non-rotating diatomic negative ion possessing no permanent electric dipole moment. O'Malley (1965) has studied photodetachment in a system \([hv + H^- \rightarrow H(n = 2) + e]\) in which there is an aligned permanent dipole
in the final state. He finds that the form of the threshold law depends upon
the magnitude of the dipole moment, varying from \(E^{1/2}\) to a step function
as the dipole moment increases. Unfortunately, neither of these treatments
is adequate to tell us the exact form of the threshold law for molecular
negative ion photodetachment. It is, however, clear that the form of the
threshold law will be dependent upon both the permanent electric dipole
moment of the final state molecule and the rotational energy of the molecule.

The simplest case one can consider is a measurement of the \(\text{OH}^-\)
photodetachment cross section. It has been established (Branscomb, 1966;
Cade, 1967; Celotta et al., 1974) that the potential curves of the neutral
molecule and the negative ion are virtually identical; moreover, threshold
law determinations lead one to expect that the individual rotational thresh-
holds will be at least as sharp as \(E^{1/2}\). Figure 12 shows the measured \(\text{OH}^-
\)
photodetachment cross section (Hotop et al., 1974) in the range 7000–6500 Å (14,300–15,400
cm\(^{-1}\)).

![Figure 12](image)

**Fig. 12.** \(\text{OH}^-\) photodetachment cross section in the range 7000–6500 Å (14,300–15,400
cm\(^{-1}\)).

The sharp onset, covering a range of 50 cm\(^{-1}\), is due to the opening
of what can be called the \(Q\)-rotational branches for transitions from \(\text{OH}^-(\Sigma)\)
to \(\text{OH}(^3\Pi_{3/2})\). Even in much higher resolution data than are shown in
Fig. 12, individual rotational thresholds could not be clearly identified.
These data were analyzed by constructing synthetic photodetachment cross
sections based on the known spectroscopic constants of the neutral molecules
and the measured equilibrium internuclear separation of the negative ion,
assuming some form for the threshold law. A crude attempt to fit the data
shown in Fig. 12 suggested that \(E^{1/4}\) was a reasonable “average” threshold
law. Based upon a number of such fits one obtains \(\text{EA(OH)} = (1.825 \pm 0.002)\)
eV and \(\text{EA(OD)} = (1.823 \pm 0.002)\) eV. The observed isotope shift \((2.5 \pm 1)\)
meV can almost entirely be ascribed to differences in the position of the ground rotational state in OH($^2\Pi_{3/2}$) and OD($^2\Pi_{3/2}$).

Smyth and Brauman (1972) have employed a similar but less detailed analysis in the case of NH$_2^-$ photodetachment, obtaining an electron affinity for NH$_2$ of (0.744 ± 0.022) eV. The substantial problems encountered in the analysis of these “simple” molecular negative ions indicate that in many cases it will be very difficult to understand in detail such cross sections for molecular negative ions unless some special fortuitous circumstances occur, such as the structures of the negative ion and the corresponding neutral being very similar. The basic difficulty, of course, is that the cross sections one measures are effectively integral spectra of the transitions involved, folded with an unknown threshold law. Since the fixed laser photoelectron spectroscopy technique provides differential electron spectra directly, it has a significant advantage over the tunable laser photodetachment measurements for molecular ions.

The laser photoelectron spectroscopy apparatus (Breth et al., 1967; Hall and Siegel, 1968; Siegel et al., 1972; Celotta et al., 1972) has been used to study NO$^-$, O$_2^-$, OH$^-$, NH$_2$, SO$_2^-$, and SO$^-$. As an example, let us consider the photodetached electron energy spectrum of SO$^-$ (Bennett, 1972) shown in Fig. 13. The spectrum consists of a series of peaks characteristic

![Photodetached electron energy spectrum of SO$^-$](image)

**Fig. 13.** Photodetached electron energy spectrum of SO$^-$, resulting from absorption of a 2.54 eV photon. The individual peaks correspond to transitions from a specific SO$^-$ vibrational level to a particular vibrational level in either SO $^1\Sigma$ or SO $^1\Delta$. The individual peaks are identified by an analysis procedure discussed in the text. Note that there is very little intensity difference between the $^3\Sigma$ and $^3\Delta$ final states.
of transitions from the \( ^v \nu = 0 \) level of SO\(^-\) to various vibrational levels of SO(\( X^3\Sigma \)) and SO(a \( ^1\Delta \)). The principal task involved in the analysis of these data is placing the correct vibrational assignment on each of the peaks shown in the figure. Once the vibrational assignments have been made, computation of the electron affinity is a trivial matter. The most direct method for making the vibrational peak assignment is to measure peak shifts upon isotopic substitution; the energy difference between the same two peaks in S\(^{16}\)O and S\(^{18}\)O is a unique function of the vibrational energy of the molecule. The energy shifts in SO, however, which are of order 1 meV, are near the resolution limit of the apparatus; while successful in this case, one will not, in general, be able to resolve the shift. An alternate means of identification is by a Franck-Condon factor analysis of the intensities of the various transitions. This analysis has been described in detail by Siegel \textit{et al}. (1972). Both analyses lead to the same vibrational assignments.

It should be noted that the \( ^1\Delta \) state of SO is prominently observed in the photodetached electron energy spectrum. The SO \( ^3\Sigma \rightarrow SO \:^1\Delta \) absorption is highly forbidden, has never been observed, and, as a consequence, the term energy of the \( ^1\Delta \) state was unknown. Thus these data provide the first measurement (Bennett, 1972) of the term energy of SO(a \( ^1\Delta \)), which is \((0.730 \pm 0.003)\) eV. There are a number of cases in which the energy differences between terms of different multiplicities are completely unknown particularly for free radicals. It may well be that this technique will provide the most direct method for measuring these energy differences.

V. MULTIPHOTON PHOTODETACHMENT

A possible way to preserve the inherently high energy resolution of the tunable laser photodetachment technique and, at the same time, directly obtain differential spectra, would be to make use of multiphoton processes. If a molecular negative ion possesses a bound electronically excited state, then one can study two-photon photodetachment of the ion, utilizing the bound excited state as a real intermediate state. For those intermediate states lying at energies greater than half of the vertical detachment energy, and for photon energies corresponding to excitation of this state, one will see a two-photon photodetachment signal which is the product of the resonant bound-bound excitation function and the relatively smooth single photon photodetachment cross section from the intermediate state being pumped. Since the photon energies are below the single photon photodetachment threshold, there is essentially no neutral background. One can easily keep the laser power sufficiently low that there will be a detectable photodetachment signal only for near resonant pumping of the
real intermediate states. The $C_2^-$ ion was chosen (Lineberger and Patterson, 1972) for the first such study because there was considerable evidence (Herzberg and Lagerquist, 1968; Milligan and Jacox, 1969; Frosch, 1971) for a $C_2^-$ state lying approximately 2.3 eV above the ground state, and the electron affinity of $C_2$ is approximately 3.5 eV (Feldman, 1970).

Figure 14 shows the $C_2^-$ resonant two-photon photodetachment cross section near the origin of the Herzberg–Lagerquist band system. The laser flux employed in obtaining these data was sufficiently large that the photodetachment signal depended linearly, rather than quadratically, upon the photon flux; this result was obtained because at these fluxes the resonant bound-bound excitation step was completely saturated. Only at much lower laser fluxes could the expected quadratic intensity dependence be observed (Fig. 15).

The data shown in Fig. 14 have the appearance of a low resolution spectrum of a $\Sigma-\Sigma$ absorption, and in fact it is possible to analyze these spectra to obtain the molecular parameters for both of the states involved in the bound-bound excitation. The wavelength resolution of the tunable laser could be easily improved to the point that individual rotational transitions are resolved. Since the data in Fig. 15 show the transition from unsaturated to saturated excitation of the ion, it is possible, by measuring the absolute intensity of the laser, to determine an absolute oscillator strength for the absorption. This latter measurement has been performed by Mackie and Cathro (1973) in a shock tube experiment.
Fig. 15. Laser flux dependence of the apparent single photon photodetachment cross section at the 5415 Å peak of Fig. 14. The solid line is the flux dependence expected if one of the two steps in the photodetachment process can be saturated. The data of Fig. 14 were taken at laser fluxes much greater than any fluxes shown in this figure.

VI. PHOTODISSOCIATION OF POSITIVE IONS

Studies of the photodissociation of positive ions using laser sources are in their infancy, the first such investigations having just been completed by Durup and colleagues in Orsay and Los and co-workers in Amsterdam. The objective of these early experiments has been to obtain a detailed understanding of the techniques employed; a wealth of new information, however, should become available in the near future.

The ion chosen for the first such studies was H$_2^+$, since it is possible to solve exactly the Schrödinger equations for the electronic wave function. The potential energy curves, the energies of the vibrational–rotational levels of the ground state, and the vibrational wave functions have been known for years. The cross sections for the process

$$h\nu + H_2^+(1s\sigma_g) \rightarrow H_2^+(2p\sigma_u) \rightarrow H^+ + H(1s)$$

have been calculated theoretically for all vibrational levels of H$_2^+$ and D$_2^+$ at any wavelength by Dunn (1968).

The photodissociation experiments observe the H$^+$ ions formed by photodissociation at a fixed wavelength, from different vibrational levels of the initial H$_2^+(1s\sigma_g)$ state. Since the laser wavelength is fixed, these H$^+$ ions will have different translational energies in the c.m. system. Since the photodissociation cross sections are known, the intensities of the H$^+$ ions...
resulting from various vibrational states may be used to determine relative vibrational populations in the \( \text{H}_2^+ \) beam.

The \( \text{H}^+ \) ions resulting from different vibrational states of \( \text{H}_2^+ \) are very easily energy resolved because of the expansion of the c.m. energy scale upon conversion to the laboratory frame. A simple velocity analysis yields

\[
T = \frac{1}{2} T_0 + (W T_0)^{1/2} \cos \theta + \frac{1}{2} W,
\]

where \( T_0 \) is the incident \( \text{H}_2^+ \) translational energy, \( T \) is the laboratory energy of the product \( \text{H}^+ \), \( W \) is the total translational energy of \( \text{H}^+ + \text{H} \) in the c.m. frame, and \( \theta \) the ejection angle of \( \text{H}^+ \) (with respect to the incident flight direction) in the c.m. frame. Thus, in the Orsay experiment (\( T_0 = 2000 \) eV, \( h\nu = 1.786 \) eV, \( \theta = 0 \)) the energies \( T \) of the \( \text{H}^+ \) ions produced from photodissociation of levels \( v = 8 \) and \( 9(W = 0.891 \) and \( 1.047 \) eV, respectively) are \( 1042.66 \) and \( 1046.28 \) eV, energy differences which are easily resolved. This result, of course, holds only for \( \theta = 0 \) and in order to be able to resolve these vibrational peaks, \( \Delta \theta \) must be of the order of a few milliradians (Ozenne et al., 1974).

With the tight collimation required to resolve these vibrational peaks, one sees only groups of protons scattering near \( \theta = 0 \) and \( \pi \) in the c.m. frame. Thus by rotating the plane of polarization of the laser light with respect to the ion beam, and observing the intensity variation of the photofragment peaks, one can determine the orientation of the transition moment.

In the experimental apparatus employed at Orsay (Ozenne et al., 1973), the \( \text{H}_2^+ \) ions are produced in a low pressure electron impact ion source such that the vibrational populations of the \( \text{H}_2^+ \) ions are determined by the Franck–Condon principle. An example of the \( \text{H}^+ \) kinetic energy spectra obtained at Orsay is shown in Fig. 16. Only half of the spectrum (corresponding to forward ejection of \( \text{H}^+ \)) is shown. The dotted vertical lines show the expected energy locations for \( \text{H}^+ \) ions resulting from the indicated vibrational levels of \( \text{H}_2^+ \). The height of each dotted line represents the intensity expected from Franck–Condon population distributions in the ion beam and the photodissociation cross sections at this wavelength as calculated by Dunn (1968). The individual thin lines are the predicted analyzer line shapes with intensities determined by the best fits (heavy lines) to the observed spectra (dots). The agreement is impressive and indicates that one understands what is happening in the apparatus.

These data were obtained with the ruby laser light polarized parallel to the direction of the \( \text{H}_2^+ \) ion beam; upon \( 90^\circ \) rotation of the laser polarization, the signal essentially disappeared, confirming our knowledge that the transition moment is parallel to the vibrational axis of the \( \text{H}_2^+ \) ions. This interpretation takes advantage of the fact that the dissociation time is very
short compared to a rotational period, and thus most ions absorbing the laser photons will dissociate in a direction corresponding to their orientation upon absorption of a photon. This experiment is, of course, primarily intended to be applied to ions other than H₂⁺. It may then yield spectroscopic information on states of molecular ions, on some dissociative or predissociated states, and on the symmetries of optical transitions (Dunbar and Kramer, 1973). If one increases the power of the lasers so as to saturate photodissociation, one can then obtain direct information on the vibrational populations of the ions in the beam.

A very intriguing example of where these studies may lead is provided by the work of Dunbar and colleagues (Dunbar, 1973a,b; Kramer and Dunbar, 1973; Dunbar and Fu, 1973) at Case Western Reserve University. Using a conventional light source they have studied the disappearance of positive ions in an ion cyclotron resonance trap as a function of photon energy. As an example they have studied the photodissociation spectra for C₇H₈⁺ formed from toluene, cycloheptatriene, and norbornadiene. This study attempts to answer the question of whether the C₇H₈⁺ ions arising from isomeric parents have the same geometrical conformation or not. Even after the C₇H₈⁺ ions had undergone a number of collisions, all three photodissociation spectra were very different, providing the strongest evidence to date for different geometries of the ions arising from isomeric parents. The application of tunable lasers in this type of experiment should
lead to even greater versatility, and the answers to a number of very important chemical questions.

VII. FUTURE DEVELOPMENTS

The preceding sections have hopefully made it clear that advances in laser technology have opened a new era of gas phase ion spectroscopy. Since this technology is still rapidly expanding and, since the experiments are yet in a rather primitive state, rapid and significant advances can be expected in the near future. Already, much more extended wavelength regions, much higher resolution, and much higher laser powers than those used in any of the experiments discussed in this chapter have been reported in the literature. As these newer laser devices are further developed, it will become much easier to utilize them as reliable components in an already complicated apparatus. Such developmental improvements require no extrapolation of today’s technology, and these lasers should be available within the next few years.

The photoelectron spectroscopy technique is limited at present by the fact that the argon–ion laser is the bluest laser readily available which has sufficiently high photon output to provide a useful signal-to-noise ratio. Recent advances in argon–ion laser output powers make it possible to do these experiments using a frequency doubled argon–ion laser. This possibility means that one can study photodetachment and photodissociation of the so-called “terminal” negative ions frequently encountered in many chemical or atmospheric applications.

At present, one can easily build tunable lasers with line widths of several hundred megahertz (Walther and Hall, 1970; Hänsch, 1972; Marowsky, 1973) sacrificing very little power in the reduction from the 1 Å line width employed in the studies reported here. Thus it is possible to measure electron affinities to accuracies of the order of microelectron volts. Utilizing such a narrow band laser in the multiphoton photodetachment processes reported in Section V it is possible to saturate bound-bound transitions with oscillator strengths of order $10^{-6}$. Thus the two-photon photodetachment technique could be used for spectroscopy on partially forbidden transitions in positive and negative ions. A similar two-step photodissociation technique (Ambartzumian and Letokhov, 1972) can be used to study bound-bound transitions in positive ions.

The photodissociation studies are so new that it is not yet easy to recognize the limitations on the experimental techniques. Certainly the ability to determine vibrational populations in ion beams, and to distinguish between isomeric forms of ions will lead to a great variety of interesting and important results.
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REFERENCES

3. LASER SPECTROSCOPY OF GAS PHASE IONS


