Advances in
CHEMICAL PHYSICS

VOLUME LXXXI

54.2088
A244
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Advances in CHEMICAL PHYSICS

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JOHN WILEY & SONS, INC.
NEW YORK · CHICHESTER · BRISBANE · TORONTO · SINGAPORE

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Library of Congress Catalog Number: 58-9935

ISBN 0-471-54570-8

Printed and bound in the United States of America
by Braun-Brumfield, Inc.

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VOLUME LXXXI

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE
STUART A. RICE

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TRANSITION STATE SPECTROSCOPY OF BIMOLECULAR REACTIONS USING NEGATIVE ION PHOTODETACHMENT

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Advances in Chemical Physics, Volume LXXXI, Edited by I. Prigogine and Stuart A. Rice.
ISBN 0-471-54570-8 © 1992 John Wiley & Sons, Inc.

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I. INTRODUCTION

A primary objective of experimental and theoretical investigations in chemical physics has been to gain a detailed understanding of the transition state region in a chemical reaction. The transition state region is the region of the reactive potential energy surface where chemical change occurs, and studies which probe this region offer the promise of qualitative improvements in our understanding of the microscopic forces that govern the course of a chemical reaction. Although much of the effort in this area has concentrated on the extraction of properties of the transition state region through scattering experiments, a parallel and considerably smaller effort has focused on the development of spectroscopic methods which can be applied directly to the transition state. These "transition state spectroscopy" experiments are complicated by the short-lived nature of the transition state (10^{-15}–10^{-12} sec). In addition, the transition state region must be accessed in a sufficiently well-defined manner so that one can observe meaningful structure associated with the transition state.

A number of frequency and time-resolved techniques have been applied to the transition state in recent years. These have been admirably reviewed by Brooks[1] and Zewail.[2] Zewail and co-workers[3,4] have carried out a particularly noteworthy set of experiments in which chemical reactions and photodissociation are monitored in real time using femtosecond lasers. This chapter focusses on a complementary type of transition state spectroscopy experiment performed in our laboratory in which photodetachment of a stable negative ion is used to probe the transition state region in bimolecular chemical reactions.

The principle behind photodetachment-based transition state spectroscopy is that if the geometry of a stable anion is similar to that of the neutral transition state, then one can photodetach the anion and prepare the unstable transition state complex in a well-defined manner. The idea of using photodetachment to create an unstable neutral species has been in the literature for some time. In 1968 Golub and Steiner[5] reported the total photodetachment cross section of the anion $OH^-(H_2O)$; the resulting $OH{\cdot}H_2O$ complex dissociates rapidly. More recently, Brauman and co-workers[6] measured total cross sections for the photodetachment of a series of anions $ROHF^-$, in which the neutral ROHF complex dissociates to HF + RO.

To obtain more detailed information on the dissociating neutral complex, one can use techniques such as negative ion photoelectron spectroscopy[7,8] and threshold photodetachment spectroscopy.[9] These methods can yield vibrational structure associated with the transition state even if dissociation occurs in as little as 10^{-14} sec. These techniques can be applied to unimolecular decomposition, as in the photoelectron spectrum of HCO^- obtained by Lineberger and co-workers,[10] which shows resolved transitions to vibrationally excited levels of HCO which lie up to 4000 cm^{-1} above the H + CO dissociation limit. One can also study unimolecular isomerization, as in Lineberger's photoelectron spectrum of the vinylidene anion $C_2H_2^-$.[11] Although the neutral vinylidene radical rapidly isomerizes to acetylene, vibrational features attributed to the vinylidene structure are observed in the spectrum.

During the last few years, we have applied photodetachment spectroscopy to the study of transition states in *bimolecular* chemical reactions. We have studied several hydrogen transfer reactions $A + HB \rightarrow HA + B$, where A and B are atomic or polyatomic species, via photodetachment of the stable anion AHB^-.[12] In many cases, the AHB^- anion is strongly hydrogen-bonded with a dissociation energy of ~1 eV or higher, and its overall size and geometry are such that one obtains good overlap with the neutral transition state region upon photodetachment. One then obtains resolved vibrational progressions which reveal the spectroscopy and dissociation dynamics of the neutral AHB complex, and from this one can learn about the features of the A + HB potential energy surface near the transition state.

One of the primary motivations for conducting these studies was that they appeared to hold high promise for experimentally observing *reactive resonances*. In the early 1970s, quantum mechanical scattering calculations on model collinear potential energy surfaces for the $H + H_2$ reaction by Truhlar and Kuppermann[13] and Wu and Levine[14] revealed pronounced oscillatory structure in the reaction probability as a function of translational energy. This structure was attributed[15] to reactive resonances which occur because of quasi-bound states with high probability density in the transition state region. In the following years, resonances were found in collinear scattering calculations for the $F + H_2$ reaction.[16-19] Especially sharp resonance structure due to long-lived states of the collision complex was predicted in calculations by Pollak[20] and Bondi et al.[21] for heavy + light-heavy reactions such as Cl + HCl or I + HI. This is the mass combination relevant to most of the experiments performed in our laboratory.

Clearly, the experimental observation of resonances would be an important step in understanding the vibrational structure of the transition state.[22] However, while resonances have been shown to exist in scattering calculations on three-dimensional (rather than collinear) potential energy sur-

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faces,[23] their experimental detection in a scattering experiment is complicated by the contribution of many partial waves to the total reaction cross-section. This has been predicted[24,25] to cause substantial blurring of resonances in total cross-section measurements, such as those recently performed on the H + H_2 reaction.[26] Differential cross-section measurements on the F + H_2 reaction[27] show evidence for reactive resonances, but the ultimate interpretation of these results requires a more accurate potential energy surface than is currently available.

The photodetachment experiment offers an excellent opportunity for the observation of reactive resonances. Long-lived quasi-bound states on the A + HB potential energy surface should appear as sharp structure in the AHB^- photoelectron spectrum, provided these quasi-bound states have good Franck–Condon overlap with the anion. In our experiments, the anions are produced in a free-jet expansion which should result in substantial rotational cooling. This means that, subsequent to photodetachment, the total angular momentum available to the reaction is much more restricted than in a reactive scattering study of the same system. Resonances should therefore be more pronounced in the photodetachment experiment. The results and analysis presented below will show that resonances are responsible for some, but not all, of the structure seen in the AHB^- photodetachment spectra.

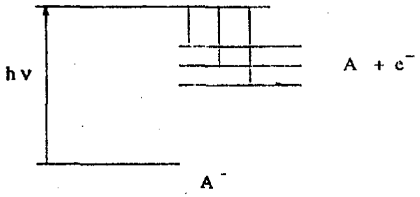
The organization of this chapter is as follows. In Section II the experimental methods used in this work are described. Section III presents a general discussion of the theoretical methods useful in analyzing these spectra. Section IV covers the symmetric Br + HBr and I + HI reactions, which are studied by photodetaching the bihalide anions $BrHBr^-$ and IHI^-. Finally, several asymmetric hydrogen exchange reactions are discussed in Section V.

II. EXPERIMENTAL METHODS

The spectra shown below were obtained using two negative ion photodetachment methods: "fixed-frequency" photoelectron spectroscopy and threshold photodetachment spectroscopy. Both experiments involve the generation of an internally cold, mass-selected negative ion beam, but different photodetachment and electron detection schemes are employed. The two instruments are described briefly in this section; more detailed descriptions may be found elsewhere.[9,28]

Figure 1 illustrates the principles behind the two techniques. In photoelectron spectroscopy (Fig. 1*a*), the negative ions are photodetached with a fixed-frequency laser and the kinetic energy distribution of the ejected photoelectrons is measured. All energetically accessible levels of the neu-

a) 'fixed-frequency' photoelectron spectroscopy
(8 meV resolution)



b) threshold photodetachment spectroscopy (0.4 meV)

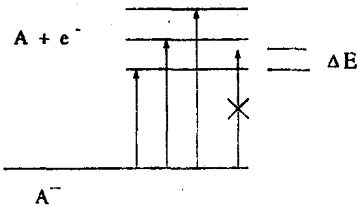


Figure 1. Energy levels and laser excitation scheme for (*a*) photoelectron spectroscopy and (*b*) threshold photodetachment spectroscopy.

tral are populated according to their Franck–Condon overlap with the initial state of the anion. For a single photodetachment event, the electron kinetic energy (eKE) is given by

$$\mathrm{eKE} = h\nu - E_b^{(-)} - E_i^{(0)} + E_i^{(-)} \tag{1}$$

Here $h\nu$ is the photon energy and $E_b^{(-)}$ is the energy difference between the anion and neutral ground states. In the case of IHI^- photodetachment, where the IHI complex is unstable with respect to dissociation, $E_b^{(-)}$ is the energy required to remove an electron from the ground state of IHI^- to form I + HI($v = 0$). $E_i^{(-)}$ and $E_i^{(0)}$ are the internal energies of the anion and neutral, respectively. For IHI^- photodetachment, $E_i^{(0)}$ is measured relative to I + HI($v = 0$).

Thus, the electron kinetic energy distribution exhibits peaks resulting from transitions between ion and neutral energy levels. In nearly all cases, the energy resolution of photoelectron spectroscopy is insufficient to discern rotational structure and one only learns about vibrational energy levels of the neutral and (occasionally) the anion. In our spectrometer,

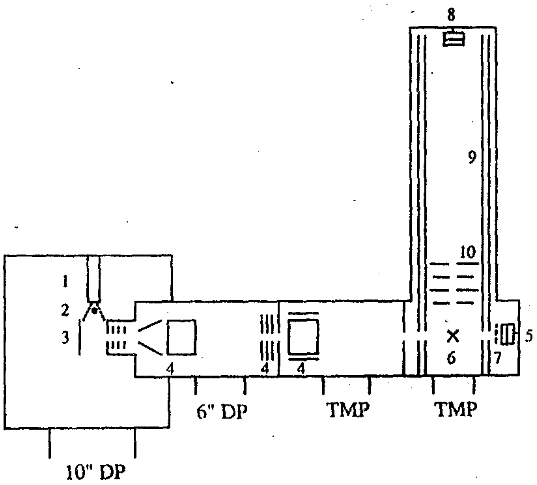


Figure 2. Schematic diagram of time-of-flight photoelectron spectrometer. Salient features are described in text (Ref. 28).

for example, the energy resolution of our time-of-flight analyzer is 8 meV at eKE = 0.65 eV and degrades at higher electron kinetic energies as $(eKE)^{3/2}$. This is the instrumental resolution function used in the simulations of Sections IV and V.

Figure 2 shows a schematic of the negative ion photoelectron spectrometer used in these studies.[28] A similar instrument is described by Posey et al.[29] Because many of the AHB^- anions of interest have high electron binding energies (3.80 eV for IHI^-, 4.27 eV for $BrHBr^-$), a pulsed UV laser is the most appropriate photodetachment light source, and the entire instrument is based on pulsed technology. An excellent review of pulsed methods in ion spectroscopy is provided by Johnson and Lineberger,[30] and several components of our instruments are described in more detail therein.

In the photoelectron spectrometer, negative ions are generated by expanding a mixture of neutral gases through a pulsed molecular beam valve (1) and crossing the molecular beam with a 1-keV electron beam (2) just outside the valve orifice. The fast electrons produce relatively slow secondary electrons by ionization. These slow electrons, which rapidly thermalize due to the high gas density in front of the beam valve, efficiently produce negative ions through low-energy attachment processes. To make $BrHBr^-$, for example, a 5% HBr/Ar mixture is used. The likely mechanism is formation of Br^- via dissociative attachment to HBr, and formation of $BrHBr^-$ via three-body clustering reactions:

$$Br^- + HBr + M \rightarrow BrHBr^- + M \tag{2}$$

The ions are formed in the continuum flow region of the supersonic expansion and cool internally as the expansion progresses.

A time-of-flight mass spectrometer of the Wiley–Maclaren design[31] is used to select the mass of the ion of interest. A small volume of negative ions is extracted at 90° from the molecular beam by applying a negative pulse to the electrode (3). The ions then pass through a 1-kV potential drop. As they traverse the 140-cm drift region (4), the ions separate into bunches according to mass. The photodetachment laser pulse is timed so that it crosses the ion beam at (6) and interacts with the ion bunch of the desired mass. The spectra shown below were obtained with the fourth harmonic (266 nm, 4.660 eV) or fifth harmonic (213 nm, 5.825 eV) of a Nd:YAG laser. A small fraction (10^{-4}) of the ejected photoelectrons is detected (8) at the end of a 100-cm field free-flight tube (9) and energy analyzed by time of flight.

Considerably higher resolution can be obtained with threshold photodetachment spectroscopy. The principle of this method is shown in Fig. 1*b*. In this experiment, negative ions are photodetached with a tunable pulsed laser. At a given laser wavelength, only electrons produced with nearly zero kinetic energy are detected. The zero-kinetic energy spectrum plotted as a function of laser wavelength consists of a series of peaks, each corresponding to an ion → neutral transition. The width of the peaks is determined by the ability of the instrument to discriminate against photoelectrons produced with high kinetic energy. By adapting the methods developed by Müller–Dethlefs et al. for threshold photoionization of neutrals,[32] we have achieved a resolution of 3 cm^{-1} (0.37 meV) with this instrument and were able to obtain a spectrum of SH^- in which transitions between individual rotational levels of the anion and neutral were resolved.[9]

Figure 3 shows a schematic of the threshold photodetachment spectrometer.[9] The ion source (1, 2) is similar to that shown in Fig. 2, but the ions pass through a skimmer and into a differentially pumped region prior to being accelerated to 1 keV. A coaxial time-of-flight mass spectrometer (3) of the design proposed by Bakker[33] is used for mass separation. The anions are photodetached using an excimer-pumped dye laser with frequency-doubling capability.

In order to selectively detect zero-kinetic-energy photoelectrons, the region in which detachment occurs (4) is initially field-free. A weak extrac-

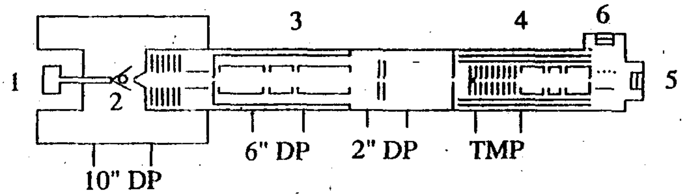


Figure 3. Schematic diagram of threshold photodetachment spectrometer: (1) pulsed beam valve, (2) electron beam, (3) coaxial time-of-flight mass spectrometer, (4) photodetachment region, (5) ion detector, (6) electron detector. Laser–ion beam interaction region is marked by ● (Ref. 9).

tion pulse is applied along the ion beam axis 200–300 ns after the photodetachment laser pulse. The purpose of this delay is to allow the higher energy electrons to spatially separate from the zero-kinetic-energy electrons. The higher-energy electrons that scatter perpendicularly to the ion beam axis are discriminated against since they will not pass through one of the many apertures between the detachment region and the electron detector (6). The higher-energy electrons that scatter along the beam axis will be in different regions of the extraction field when it is applied. They therefore emerge from the extraction region with different kinetic energies from the electrons produced with zero kinetic energy, arrive at the electron detector at different times, and are discriminated against by gated detection of the electron detector signal. The combination of spatial and temporal filtering is essential to achieving the ultimate resolution of this detection scheme.

III. THEORETICAL METHODS

In most negative-ion photodetachment experiments, a stable neutral species is formed by photodetaching a negative ion. Photoelectron spectra are typically analyzed by invoking the Born–Oppenheimer and Condon approximations. The electronic and vibrational degrees of freedom in the anion and neutral are assumed to be separable, so that the cross-section for photodetachment from anion vibrational level υ'' to neutral vibrational level υ' is given by

$$\sigma(\upsilon' \leftarrow \upsilon'') \propto |\tau_e|^2 |\langle \psi_{\upsilon'}^{(0)} | \psi_{\upsilon''}^{(-)} \rangle|^2 \qquad (3)$$

Here τ_e is the dipole matrix element between the electronic state of the anion and the (neutral + e^-) continuum, which is assumed constant for a given electronic band. The approximations in Eq. (3) have been used in all theoretical treatments of photodetachment-based transition state spectroscopy experiments to date. In general, neither the anion or neutral potential energy surface is sufficiently well known to warrant a more sophisticated treatment.

The application of Eq. (3) to the spectra presented below is problematic since they all involve formation of an unbound, short-lived neutral complex. Thus, the vibrational wavefunction $\psi_{v'}^{(0)}$ in Eq. (3) must be replaced by a scattering wavefunction. One can then simulate the photoelectron spectrum within a time-independent formalism, in which the Franck–Condon overlap between the anion and neutral scattering wavefunctions is calculated as a function of energy. Alternatively, the spectrum can be simulated using time-dependent wavepacket analysis. Both types of simulations are discussed below.

A. Time-Independent Analysis

The time-independent analysis of these photodetachment experiments has been summarized nicely by Schatz.[34] Equation (3) is replaced by

$$\sigma(E) \propto |\langle \psi^{(0)}(E) | \psi_{v''}^{(-)} \rangle|^2 \tag{4}$$

where $\psi^{(0)}(E)$ is the scattering wavefunction supported by the neutral potential energy surface at energy E. In most scattering calculations, E is measured relative to the neutral potential energy minimum in the asymptotic region for either reactants or products and differs from $E_i^{(0)}$ in Eq. (1) by the zero-point energy of the neutral fragments.

The accurate simulation of a photoelectron spectrum using Eq. (4) therefore requires the determination of A + HB scattering wavefunctions over the energy range for which $\sigma(E)$ is nonnegligible. This is a formidable task which, so far, has only been attempted for triatomic systems, in which case a three-dimensional scattering wavefunction must be determined. Schatz has simulated the ClHCl^- and IHI^- photoelectron spectra in this manner[35,36] using model London–Eyring–Polanyi–Sato (LEPS) potential energy surfaces for the Cl + HCl and I + HI reactions. The neutral wavefunctions are calculated with a coupled-channel method using hyperspherical coordinates.[37] The calculations assume the anions to be ground-state harmonic oscillators and are restricted to total angular momentum $J = 0$ for the anion and neutral. Both of these assumptions are justified by the low anion temperatures attained in the free-jet ion source, although the small rotational constants for ClHCl^- ($B_e = 0.09685\ \text{cm}^{-1}$)[38] and IHI^- mean that several rotational levels will be populated even at 10 K.

Using a different method for calculating the scattering wavefunctions, Zhang and Miller[39] have performed a three-dimensional simulation of the

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