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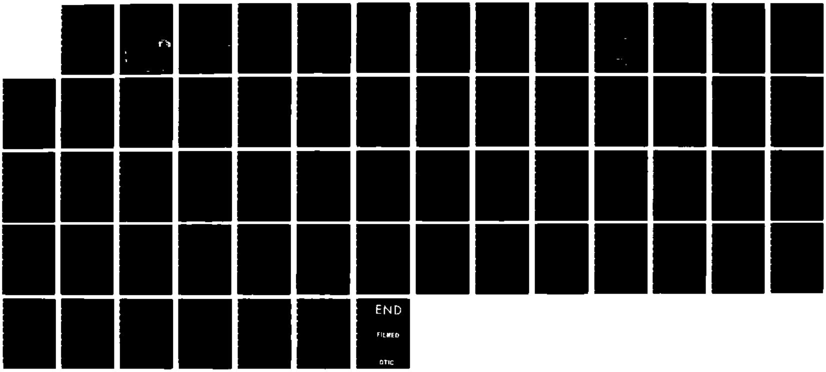

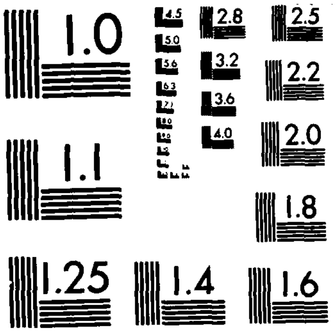

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EXPERIMENTAL STUDIES IN MOLECULAR FRAGMENTATION: PROCESSES, ENERGETICS AND DIAGNOSTICS

Contract N00014-83-K-0134

Final Report

For the period 1 January 1983 through 31 March 1985

Principal Investigator

John L. Kohl

Prepared for

The Office of Naval Research

September 1985

Smithsonian Institution
Astrophysical Observatory
60 Garden Street
Cambridge, MA 02138

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We have developed a new technique and apparatus for studying photodestruction processes in molecules. Proof of method experiments have been carried out using H_2^+ as the prototypical molecule. A paper describing this work has been submitted to the Review of Scientific Instruments. Application of the method to polyatomics and more than two fragments per dissociation event has been investigated. Beams of the ions of nitromethane and its fragments have been produced in sufficient quantities for experimentation using our technique. The absorption spectrum of nitromethane has been measured in the range

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190-300 nm with 0.001 nm resolution. A feasibility study of induced fluorescence experiments to determine the spectra of polyatomic free radicals has been carried out. Experiments on the photodissociation of CH^{+} and OH^{+} and CH have been initiated. Keywords:

I. Abstract

We have developed a new technique and apparatus for studying photodestruction processes in molecules. Proof of method experiments have been carried out using H_2^+ as the prototypical molecule. A paper describing this work has been submitted to the Review of Scientific Instruments. Application of the method to polyatomics and more than two fragments per dissociation event has been investigated. Beams of the ions of nitromethane and its fragments have been produced in sufficient quantities for experimentation using our technique. The absorption spectrum of nitromethane has been measured in the range 190-300 nm with 0.001 nm resolution. A feasibility study of induced fluorescence experiments to determine the spectra of polyatomic free radicals has been carried out. Experiments on the photodissociation of CH^+ and OH^+ and CH have been initiated.

II. Introduction

This final report describes the accomplishments of our program under Contract N00014-83-K-0134 from its initial funding on October 1, 1982, until its termination on March 31, 1985. During this period we have presented papers at three scientific meetings and submitted one paper to a scientific journal. Copies of the abstracts for the meetings and a copy of the paper are included as Attachments A through D. We also participated in two contractors workshops in Chestertown, Maryland. One of these occurred before the initiation of our contract.

III. Discussion

Molecular fragmentation and radiative decay, whether induced by photons, electrons, or heavy particles, are processes of central importance to the physics of energetic materials. Accurate molecular data on many atoms, radicals, and ions are needed in order to diagnose tests of energetic materials as well as, through model calculations, to understand the physics of detonation and combustion.

The combination of internal Smithsonian Institution support and Office of Naval Research support has allowed us to design, construct and test a unique experimental apparatus for the study of photodissociation processes in a wide variety of molecules and radicals. This apparatus produces a fast beam of neutral or charged molecules that undergo photodissociation. The fragments are subsequently detected, their kinetic energies are measured and absolute cross sections are determined. The experiments are capable of providing knowledge of the mass and kinetic energy of each fragment from the dissociation of a single molecule of known mass. When the bond energy of the parent molecule is known *a priori*, the method also provides information regarding the internal excitation of the fragments. The accumulated data from many dissociation events may be used to provide branching ratios for different sets of fragments from the same parent or different final states of the same fragments. Details of the method are provided in Appendix A and Attachment D.

Experiments on the photodissociation of H_2^+ have been carried out and a paper describing the work submitted to the Review of Scientific Instruments. This work was intended as a proof of method experiment only, and was consistent with that of prior investigators. The experiment gave us confidence in our ability to apply our experimental methods to more interesting species. The reader is referred to Attachment D, a preprint of the submitted paper describing this work.

We have carried out extensive development tests in order to ascertain our ability to generate beams of the negative ions of nitromethane and its fragments. To date we have observed beams of the following molecular ions using nitromethane vapor as the source gas in our discharge ion source:

$CH_3NO_2^-$; $CH_2NO_2^-$; $CHNO_2^-$; CNO_2^-; NO_3^-; NO^-; CNO^-; CH_3^-; CH^-.

The beam currents obtained have, in general, been sufficient for carrying out photodissociation experiments on the neutral for all of these but the first.

We have carried out measurements on the absorption spectrum of nitromethane vapor in the wavelength range 350 to 190 nm with 0.001 nm resolution. We see no difference in the shape of the absorption spectrum from the lower resolution results reported by Taylor et al. (Int. J. Chem. Kinetics **12**, 231 (1980)). We find only a diffuse spectrum, which indicates a high probability for the occurrence of dissociation following photon absorption. This is consistent with the work of Y. T. Lee, and collaborators, (invited talk at the Workshop on the Fundamentals of Initiation of Chemical Decomposition of Energetic Materials, Chestertown, MD, May 4-6, 1982) who have observed the breakup of nitromethane at the discrete excimer laser wavelengths 248 and 196 nm.

The possibility of using a variation on our photodissociation experimental technique to determine fluorescence wavelengths from free radicals has been investigated. A brief discussion of the technique devised can be found in Appendix B.

We have carried out some preliminary experiments on the photodissociation of CH^+ and OH^+. The intent of the experiments was to investigate the photodissociation of the lowest metastable state in each ion. In CH^+, for example, the lowest metastable state is the $a^3\Pi$. This state can be laser excited to the $b^3\Sigma^-$ state which is expected to predissociate through interactions with the repulsive $c^3\Sigma^-$ state. This state has the same dissociation limit as the ground state $x^1\Sigma^+$. By measuring the final kinetic energy of the H fragment so produced, we could place the triplet and singlet state manifolds on the same absolute energy scale, something that has not been done experimentally. There is a similar problem in the OH^+ ion, but here the metastable is a singlet and the upper laser excited singlet state is predissociated by triplets. In all other respects the experiments are similar. To date we have not had success with these experiments due apparently to an insufficient number of metastable ions in the respective beams. Further pursuit of these problems will await modification of the ion source.

Experiments on the photodissociation of the CH neutral free radical have been initiated. The photodetachment of CH has been observed. It is expected that this experiment will be completed with internal Smithsonian support.

Appendix A–Description of the Experimental Apparatus and Technique

The experimental arrangement is illustrated in Figure A.1. The fast molecular beam is produced by neutralizing a fast negative ion beam. Negative ions of the molecule of interest are produced in an appropriate ion source, extracted, and accelerated to keV energies. They are then magentically momentum analyzed and directed onto the main axis of the apparatus. The resolution of the magnetic analysis is sufficient to ensure that a beam of ions of single known mass is obtained. A pulsed laser beam is directed between the pole faces of the analyzing magnet and along the main beam axis. This laser light has a photon energy just sufficient to produce photodetachment of the ions in the beam. The light intensity is made sufficiently high that a very large fraction of the ions present in the machine during the light pulse are converted into neutral molecules. After a flight length of about 100 cm the remaining ions are deflected off axis using a small parallel plate electrostatic analyzer and the current is monitored with a Faraday cup or particle multiplier. The neutrals drift undeflected through the ion removal region and into the region where photodissociation will occur.

In the second region of the apparatus the neutral beam is crossed at right angles by another pulsed laser beam. Absorption of this laser light by the molecules is expected to cause photodissociation. The firing of this second laser is delayed relative to the firing of the first laser by an amount between one and about four microseconds so that the neutrals have sufficient time to pass into the interaction region. Assuming proper timing of the laser pulses, there will typically be a few molecules in the volume of overlap of the laser and molecular beams, and occasionally one will absorb a photon and dissociate into two or more fragments.

The center of mass of the fragments will continue essentially unchanged along the main beam axis. The fragments themselves, however, will in general have non-zero velocity components perpendicular to the original beam direction due to the conversion of some of the photon energy into kinetic energy. The fragments will therefore move away from the axis as they travel toward the end of the machine where they will strike a position sensitive particle detector. This detector with its accompanying electronics will provide knowledge of the positions of the fragments and their arrival times. The use of such a detector in a similar experimental arrangement has been independently suggested by de Bruijn and Los [Rev. Sci. Instr. **53**, 1020 (1982)]. In general, <u>all</u> fragments from most single dissociation events will be detected in coincidence. The knowledge of the impact positions of the fragments, their arrival times, the mass of the parent molecule, the initial beam energy, the flight distance, and the photon energy enable the determination of the masses and kinetic energies of <u>each</u> fragment. From the impact positions and arrival times correlated angular distributions may be compiled for sets of the same fragments. Additional measurements of initial molecule and photon fluxes and their overlap then allow the evaluation of absolute cross sections and branching ratios.

The following examples of photodissociation events illustrate how measurements of the parent molecule's velocity, the flight distance, the photofragment impact positions and arrival times at a detector together with *a priori* knowledge of the parent molecule's mass and the photon energy, lead to a complete determination of the kinetics of the photodecomposition process.

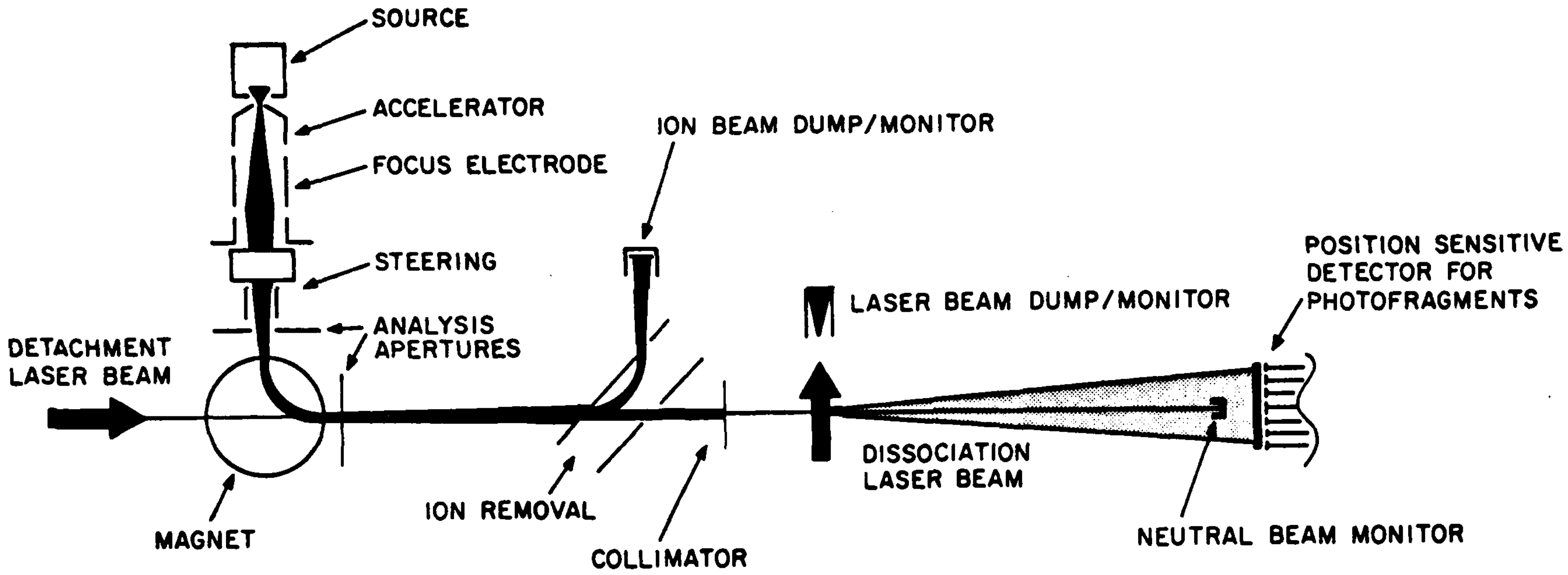

Figure A.1. Schematic Diagram of the Experiment.

Fragmentation into Two Products

Consider the breakup of the molecule CH_3NO_2 into two fragments as shown in Figure A.2. The fragments will strike the detector at times t_1 and t_2 after the dissociation and at radial positions $\mathbf{R}_1$ and $\mathbf{R}_2$. These quantities are determined experimentally. They can be related in a straightforward way to the total axial flight distance ℓ, the velocity of the center of mass v_0, the velocity vectors $\mathbf{v}_1$ and $\mathbf{v}_2$ in the center of mass frame, and the angle θ between these vectors and the direction of flight of the center of mass (see Fig. A.2).

$$|\mathbf{R}_1| = |\mathbf{v}_1| t_1 \sin\theta \tag{1a}$$

$$|\mathbf{R}_2| = |\mathbf{v}_2| t_2 \sin\theta \tag{1b}$$

$$t_1 = \frac{\ell}{v_0 + |\mathbf{v}_1|\cos\theta} \tag{2a}$$

$$t_2 = \frac{\ell}{v_0 - |\mathbf{v}_2|\cos\theta} \tag{2b}$$

Conservation of linear momentum forces a relationship between the velocities and masses of the fragments:

$$M_1\mathbf{v}_1 + M_2\mathbf{v}_2 = 0 \tag{3}$$

where the momentum of the absorbed photon is taken to be small. Combining Eq. (3) with (1) and (2) leads to the independent relationships:

$$\frac{M_1}{M_2} = \frac{|\mathbf{R}_2|}{t_2}\frac{t_1}{|\mathbf{R}_1|} \tag{4}$$

$$\frac{M_1}{M_2} = -\frac{v_0 - \ell/t_2}{v_0 - \ell/t_1} \tag{5}$$

Equations (4) and (5) thus provide the same information and constitute a check on the internal consistency of the data. Since the sum of M_1 and M_2 is the total mass M of the parent molecule, and M is known, it may be concluded that:

$$M_1 = M\Big/\left(1 + \frac{|\mathbf{R}_1|t_2}{t_1|\mathbf{R}_2|}\right) \tag{6}$$

A similar equation can be obtained for M_2 by interchanging the subscripts 1 and 2 in Eq. (6). The individual masses M_1 and M_2 are therefore fully determined.

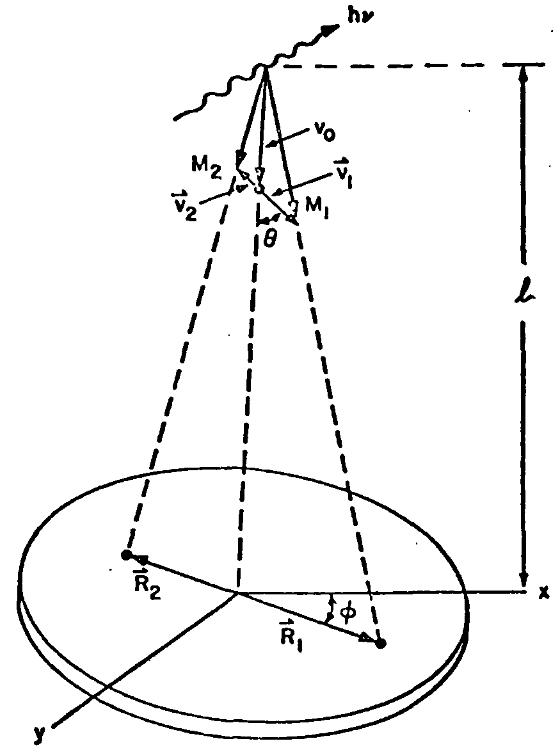

Figure A.2. The Breakup of a Molecule into Two Fragments.

Combining Eqs. (1a) and (2a) to eliminate the angle θ and solving for $\mathbf{v}_1$ gives:

$$|\mathbf{v}_1| = \left[\left(\frac{|\mathbf{R}_1|}{t_1}\right)^2 + \left(\frac{\ell}{t_1}\right)^2\left(1 - \frac{v_0 t_1}{\ell}\right)^2\right]^{1/2} \tag{7a}$$

A similar equation can be obtained for $\mathbf{v}_2$:

$$|\mathbf{v}_2| = \left[\left(\frac{|\mathbf{R}_2|}{t_2}\right)^2 + \left(\frac{\ell}{t_2}\right)^2\left(1 - \frac{v_0 t_2}{\ell}\right)^2\right]^{1/2} \tag{7b}$$

Since each mass and velocity has been determined, the kinetic energy of each fragment can be calculated. This experimentally determined parameter and knowledge of the photon energy can be used to draw conclusions about the effective dissociation energy of the parent molecule and/or the degree of internal excitation of the fragments.

Equations (1) and (2) may also be used to solve for θ:

$$\tan\theta = +\frac{\mathbf{R}_1}{(v_0 t_1 - \ell)} \tag{8a}$$

$$\tan\theta = -\frac{\mathbf{R}_2}{(v_0 t_2 - \ell)} \tag{8b}$$

The two independent results obtained, provide the consistency check mentioned above. Observation of a large number of dissociation events provides a distribution of θ's that together with knowledge of the laser polarization can be used to infer characteristics of the quantum states of the parent molecule. [See, for example, R.N. Zare, Ph.D. Thesis, Harvard University (1964); R. Bersohn and S.H. Lin, Adv. Chem. Phys. **16**, 67 (1969); C. Jonah, J. Chem. Phys. **55**, 1915 (1971); J. Soloman *et al.*, J. Chem. Phys. **55**, 1908 (1971); G.E. Busch and K.R. Wilson, J. Chem. Phys. **56**, 3838 (1972).]

Now that we have shown how data for two fragments would be analyzed, let us return to Figure A.2 and consider some reasonable values of experimental parameters for the purpose of illustrating the feasibility of the experiments. Suppose, for example, that the parent molecule were nitromethane, CH_3NO_2, and that we observe its breakup into CH_3 and NO_2.

If we use photons of 200 nm wavelength, then there will be about 4.1 eV excess photon energy converted into kinetic energy ($D = 2.52$ eV) [B. de B. Darwent, Nat. Stand. Ref. Data Serv., NBS (U.S.) **31**, 23 (1970)]. Using conservation of momentum, energy, and mass, it is straightforward to show that:

$$\frac{|\mathbf{v}_1|}{v_0} = \left(\frac{h\nu - D}{E_0}\right)^{1/2} \left(\frac{M_2}{M_1}\right)^{1/2} \tag{9a}$$

$$\frac{|\mathbf{v}_2|}{v_0} = \left(\frac{h\nu - D}{E_0}\right)^{1/2} \left(\frac{M_1}{M_2}\right)^{1/2} \tag{9b}$$

where E_0 is the kinetic energy of the parent molecule ($E_0 = 1/2\, M v_0^2$) and all other symbols are as previously defined.

Applying Eqs. (9) to the CH_3NO_2 breakup, choosing $E_0 = 7.6$ eV, and picking subscript 1 to correspond to CH_3 and subscript 2 to NO_2, one has

$$\frac{|\mathbf{v}_1|}{v_0} = 4.06 \times 10^{-2} and \frac{|\mathbf{v}_2|}{v_0} = 1.32 \times 10^{-2}$$

Thus after a flight distance ℓ of 50 cm, CH_3 fragments would strike the detector at radius vectors of length 20 mm and less, and NO_2 fragments at 6.5 mm and less. Fragment arrival times would be centered on 3.234 μs and have a range of +126 ns and -137 ns for CH_3 fragments and +42 ns and -43 ns for NO_2 fragments. Uncertainties in the measurements of impact positions of 0.3 mm and in arrival times of 1 ns lead to uncertainties in fragment masses and kinetic energies of less than 5% and 8%, respectively. We expect to produce $CH_3NO_2^-$ fluxes of $\sim 4\, pA/cm^2$.* Assuming a 1 mm diameter CH_3NO_2 beam of the same flux, and a laser operating with a 10 Hz repetition rate, there will be on average one dissociation event every 80 seconds at saturation. This is a quite reasonable data acquisition rate. The primary background process in this experiment will be collisionally induced dissociation from scattering of beam molecules off the background gas in the vacuum system. However, since the electronics system can reject events occurring outside a $\sim 0.5\,\mu s$ window (centered on 3.2 μs for the case in point) where laser induced events are expected, the collisionally induced events counted will be, at most, 1% of the photon induced events. Thus signal to noise will be on the order of 100 to 1, a quite acceptable value.

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*$CH_3NO_2^-$ fluxes of 0.4 pA/cm^2 have been easily produced in our present ion source. It is reasonable to expect at least an order of magnitude improvement if the source operation is optimized.

Fragmentation into Three Products

Consider the instantaneous breakup of a molecule into three fragments as shown in Figure A.3. Then using conservation of momentum and conservation of mass it is straightforward to show that:

$$\frac{M}{M_1} = 1 - \frac{v_1^y v_2^x - v_1^x v_2^y}{v_3^x v_2^y - v_3^y v_2^x} - \frac{v_1^y v_3^x - v_1^x v_3^y}{v_2^x v_3^y - v_2^y v_3^x} \tag{10}$$

where the v_j^x, v_j^y refer to the x and y coordinates of the vectors v_j, referring to particles 1, 2, and 3 as drawn in Figure A.3. Each of the components in Eq. (10) are readily obtained from the measured vectors $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{R}_3$ and the arrival times t_1, t_2, and t_3. Similar equations can be obtained for M/M_2 and M/M_3. The third components of the velocity vectors $\mathbf{v}_j$ can be obtained from the flight distance ℓ and the arrival times:

$$v_j^z = \frac{\ell}{t_j} - v_0$$

Thus the kinetic energy of each fragment is determined accordingly as

$$E_j = \frac{1}{2} M_j |\mathbf{v}_j|^2 = \frac{1}{2} M_j \left(\left(\frac{x_j}{t_j} \right)^2 + \left(\frac{y_j}{t_j} \right)^2 + \left(\frac{\ell}{t_j} - v_0 \right)^2 \right)$$

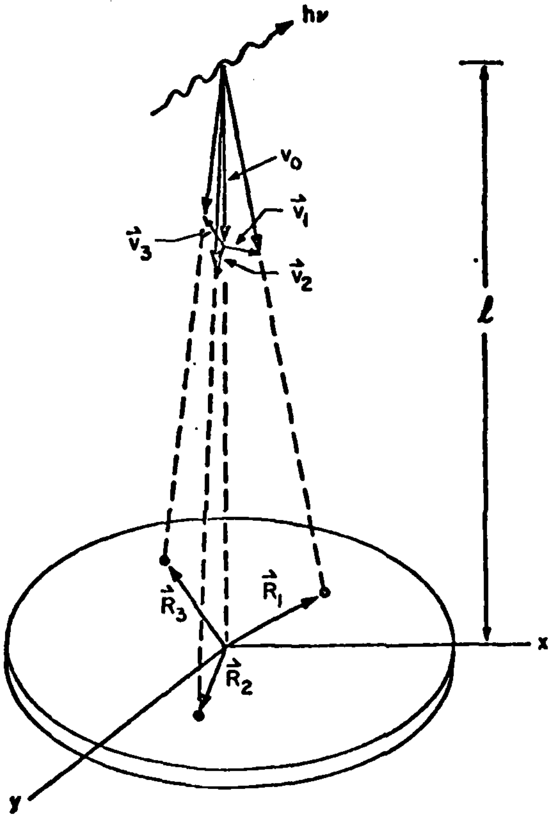

Figure A.3. Simultaneous Breakup of a Molecule into Three Fragments.

As in the two fragment case it may be possible to determine details of the quantum mechanical states involved by studying the distributions of arrival positions and times. However, at present we are not aware of any theoretical models useful for interpreting such angular distributions.

As an example to illustrate the sensitivity of the experiments, suppose CH_3NO_2 with a beam energy of 7.6 keV absorbed a 200 nm photon and broke up into the three fragments CH_3, NO, and O. The 2.52 eV of the photon's energy would be required to break the C-N bond, and 3.12 eV required to break one of the N-O bonds [H. Zacharias *et al.*, J. Chem. Phys. **74**, 218 (1981)]. Thus 0.56 eV of the photon's energy would be left over and, for example, could be converted into center of mass kinetic energy of the fragments. If, for example, the fragments velocity vectors $\mathbf{v}_1$, $\mathbf{v}_2$, and $\mathbf{v}_3$ (see Fig. A.3) were all perpendicular to the original direction of the parent molecule's motion, the angles between $\mathbf{v}_1$ and $\mathbf{v}_2$ and between $\mathbf{v}_2$ and $\mathbf{v}_3$ were each 120°, and the flight distance ℓ were chosen to be 1.5 m, then CH_3 will strike the detector at $|\mathbf{R}_1| = 17\,mm$, NO at $|\mathbf{R}_2| = 9\,mm$, and O at $|\mathbf{R}_3| = 16\,mm$. In this case, the arrival times will all be the same, 9.701 μs, which is a typical time for the general case. These values are all quite reasonable and measurable numbers. Uncertainties in the measurements of the impact positions of 0.3 mm and in the arrival times of 1 ns lead to uncertainties in fragment masses and center of mass energies of less than 6% and 10%, respectively.

Now consider a three fragment breakup as shown in Figure A.4. Here is is assumed that the parent molecule breaks up after photon absorption essentially instantaneously into a mass M_1 and an excited complex M^*, which then proceeds to breakup a short time later into masses M_2 and M_3. In this case the velocities $\mathbf{v}_2$ and $\mathbf{v}_3$ cannot be simply determined from $\mathbf{R}_2$, $\mathbf{R}_3$, t_2, and t_3 for the lifetimes of the intermediate M^* greater than about 100 ns. Repeated experiments at different values of ℓ would allow one to identify such processes. In some cases it may be possible to determine the intermediate M^* lifetime, should it be in the range 0.1 to 5 μs. For example, a situation can be envisioned where τ is long enough that the intial breakup pair M_1 and M^* could be detected at some relatively small value of ℓ before there was a significant amount of breakup of M^*, and yet short enough that the final breakup partners M_1, M_2, and M_3 could all be detected at some significantly larger value of ℓ.

Breakup into Four or More Fragments

Determination of center of mass velocity vectors $\mathbf{v}_1$, $\mathbf{v}_2$, $\mathbf{v}_3$, and $\mathbf{v}_4$ by measurement of individual detector impact positions and arrival times together with *a priori* knowledge of the mass of the parent molecule is sufficient information for the determination of fragment masses in the case of photodissociation into four fragments, since conservation of momentum and of total mass provide four independent equations. The kinetic energy of each fragment can then be calculated in the usual way.

For breakup into five fragments, *a priori* knowledge of the total excess energy would give an additional equation, conservation of energy, thereby providing a fifth independent equation containing the five unknowns M_1 through M_5. Of course, in the case of five detected fragments, there are very few reasonable possibilities for the identities of the fragments.

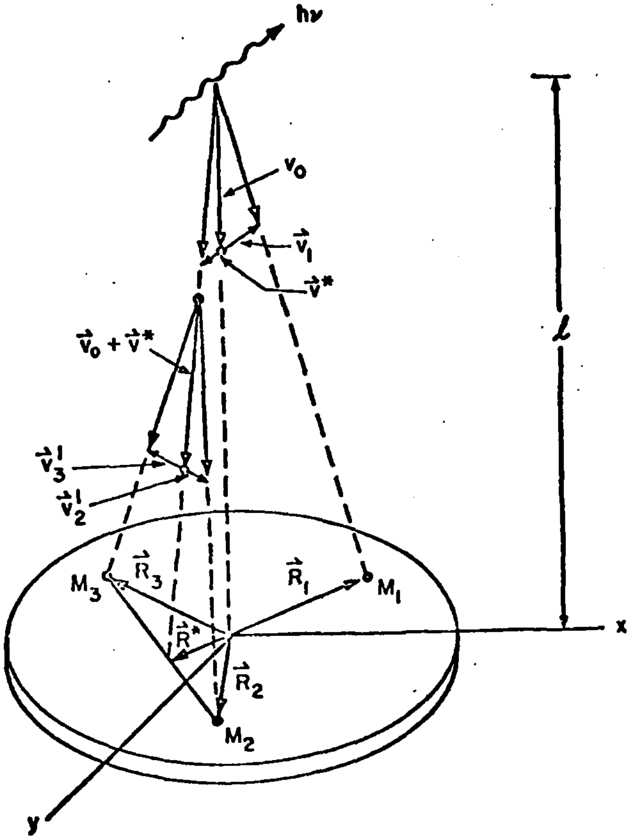

Figure A.4. Three Particle Fragmentation Involving a Long Lived Intermediate.

The problem is in general under-determined for breakup into more than five fragments unless some additional information is provided.

The consideration of long lived intermediates complicates the problem further by adding lifetimes to the list of unknowns and making it difficult to calculate the velocities $\mathbf{v}_j$ in a simple fashion from the measured impact positions and arrival times. We feel, therefore, that our technique is best suited to photodissociations producing no more than four fragments per single event.

Appendix B: Experimental Approach for Fluorescence Experiments

The experimental arrangement of choice for these experiments is shown in Figure 1. The neutral molecules formed from laser photodetachment events would be excited by photons from a second coaxial laser beam. Photons emitted by some of the excited molecules would be captured by a light condensing system employing a spherical reflector and focused onto the entrance slit of a spectrometer. Visible photons dispersed in wavelength would arrive at the focal plane of the instrument and be simultaneously detected using a multichannel system composed of individual fiber optic collectors positioned along the focal plane. Each fiber optic would lead to a photomultiplier. This basic light dispersion and detection system has been used in this laboratory to study spectral line broadening (M.J. Eckhart, Ph.D. Thesis, Harvard University, 1974). For wavelengths shortward of 350 nm the fiber optics would be eliminated and a single photomultiplier would be used behind the spectrometer exit slit. In this way spectra spanning about 10 nm in wavelength with wavelength resolution of at least 2 nm and perhaps as low as 0.2 nm could be obtained. For initial beam currents in the range of 1 nA, we would expect to detect one fluorescence photon for every 50 laser shots in those cases where photon emission is the dominant mode of excited state decay. (If predissociation is a competing decay mechanism, the number of photons emitted would be lower.) Backgrounds, such as photomultiplier dark currents, would contribute at most 10% to the fluorescence signal, since the data acquisition system would be gated on for only a period of from 1 to at most 10 μsec after the firing of the fluorescence inducing laser. For lasers operating at a 10 Hz repetition rate, time periods of the order of two to three hours would be required

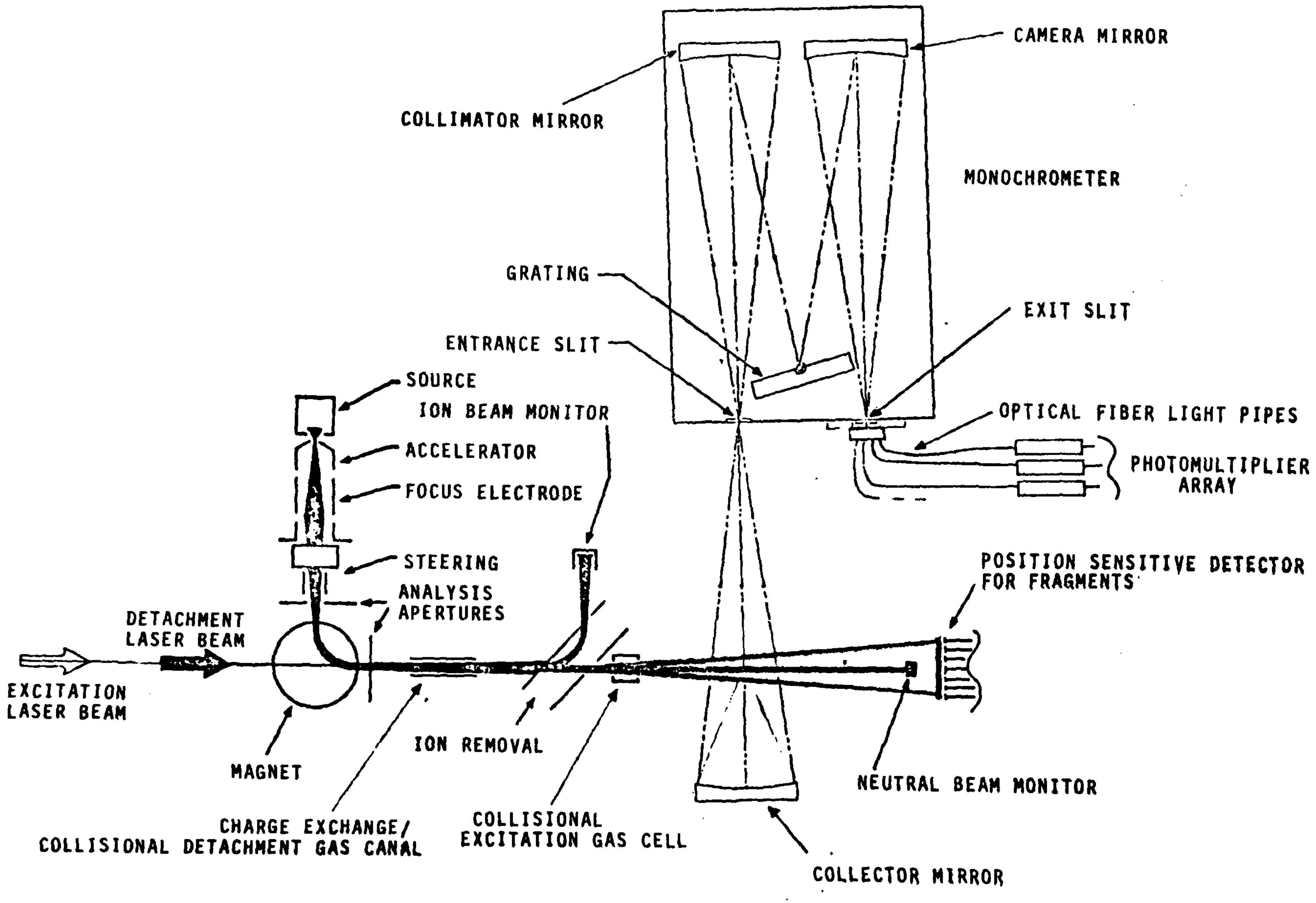

Figure 1. Schematic of Apparatus for Fluorescence Experiments.

to obtain spectra over a 10 nm range with 2 nm resolution.

Our experiments from the outset have been designed to detect the fragments of photodissociation. A fragment detection system should be "on line" while carrying out any induced fluorescence experiments. This system will allow us to know immediately whether there are any fragmentation processes competing with fluorescence emission. In particular, should fragments be detected, we would then have reason to suspect that any emission feature also detected could be coming from a fragment. (If so, the photon wavelength from a fragment, would be an indicator of the final state of that fragment.) Confirmation of the source of the emission would be obtained in a second induced fluorescence experiment on the fragment itself.

Attachment A

FAST NEUTRAL BEAM MEASUREMENTS OF MOLECULAR PHOTODISSOCIATION

L.D. Gardner and J.L. Kohl

in *Electronic and Atomic Collisions, Contributed Papers*,

J. Eichler, I.V. Hertel, and N. Stolterfoht, eds.

(North Holland, 1983)

FAST NEUTRAL BEAM MEASUREMENTS OF MOLECULAR PHOTODISSOCIATION

L. D. Gardner and J. L. Kohl

Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138 U.S.A.

We are using a new technique to measure photodissociation cross sections for neutral molecules that is especially promising for chemically unstable species. The experimental arrangement (see Fig. 1) produces negative ions of the molecule of interest which are accelerated, mass analyzed and subsequently undergo photodetachment by a coaxial pulsed laser beam. The fast neutral beam of molecules so prepared is then photodissociated by a second pulsed laser beam which is perpendicular to the molecular beam. Fragments from the photodissociation can be detected away from the beam axis with either an array of discrete secondary electron type particle multipliers or a single large area position sensitive particle detector such as a channelplate with a multiple anode array.[1,2] The detection of all fragments from a single dissociation event together with measurements of their impact positions on the detector and the time of detection, permit the mass of each fragment as well as the kinetic energy of each fragment to be determined.

To date we have constructed the apparatus and made measurements on the photodetachment of several molecular and atomic ions.[3] Additional measurements on the photodetachment of CH^- and OH^- will be reported here. Recently, to test the apparatus, we have observed the photodissociation of excited states of H_2^+ using a pulsed Nd:YAG pumped dye laser that is operated near 640 nm. Fast neutral fragments, i.e., H atoms, are detected away from the beam axis with an array of discrete particle multipliers. Charged fragments, i.e., H^+ ions, are deflected out of the beam by a low resolution parallel plate electrostatic analyzer, and are detected with a particle multiplier. Efforts to record both the H^+ and H fragments in coincidence are underway.

Experiments are also being carried out on the photodissociation of the CH radical through its predissociating $C^2\Sigma^+$ state.[4] This state can be reached from the CH ground state with photon wavelengths near 314 nm.[5] Progress on these experiments will be reported.

This work was supported by the Smithsonian Institution through its Scholarly Studies Program and by the Office of Naval Research Contract N00014-83-K-0134 to the Smithsonian Astrophysical Observatory.

References

1. J.G. Timothy, G.H. Mount, and R.L. Bybee, IEEE Trans. Nucl. Sci. NS-28, 689 (1981).
2. D.P. de Bruijn and J. Los, Rev. Sci. Instr. 53, 1020 (1982).
3. L.D. Gardner, Electronic and Atomic Collisions, Abstracts of Contributed Papers to the XII International Conference on the Physics of Electronic and Atomic Collisions, S. Datz, ed. (Gatlinburg, TN, 1981), p. 52.
4. J. Brzozowski, P. Bunker, N. Elander, and P. Erman, Astrophys. J. 207, 414 (1976).
5. G. Herzberg and J.W.C. Johns. Astrophys. J. 158, 399 (1969).

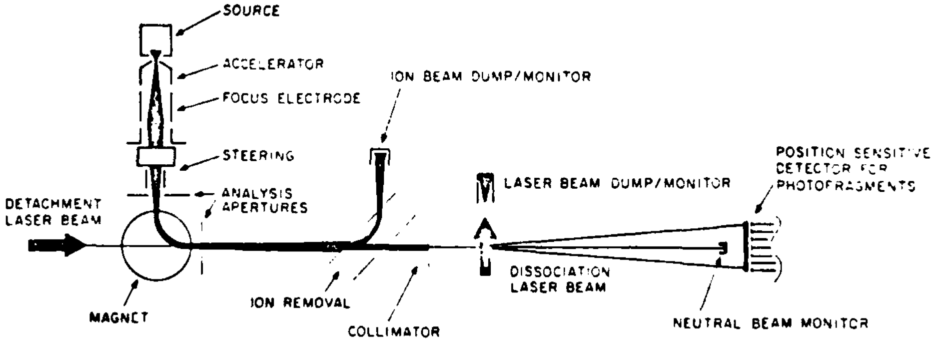

Fig. 1: Schematic of the Experiment.

Attachment B

Observation of Neutral Fragments from the Photodissocation of Fast Molecular Ions

L.D. Gardner, M.M. Graff, and J.L. Kohl

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Abstract Submitted

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Physical Review
Analytic Subject Index
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Bulletin Subject Heading
in which Paper should be placed
Photodissociation

Observation of Neutral Fragments from the Photodissociation of Fast Molecular Ions. L.D. GARDNER, M.M. GRAFF, and J.L. KOHL, Harvard-Smithsonian Center for Astrophysics.*--We are carrying out measurements on the photodissociation of H_2^+ in order to determine the properties of our ion source and to assess the performance of our fast beams apparatus. Our ultimate goal is to make measurements on fast neutral beams produced by photodetaching electrons from fast negative ion beams. The H_2^+ beam is produced by accelerating and mass analyzing ions extracted from a duoplasmatron ion source. A pulsed dye laser beam induces photodissociation of some of the ions. Those fast neutral fragments with significant momentum components perpendicular to the initial beam direction drift out of the beam and strike a position sensitive detector consisting of a channelplate fitted with a multiple anode array. Neutral fragments from the photodissociation of vibrationally excited H_2^+ molecules have been observed.

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*Supported by the Office of Naval Research Contract N00014-83-K-0134 and by the Smithsonian Institution through its Scholarly Studies and Postdoctoral Fellowship Programs.

Submitted by

Signature of APS Member

Larry D. Gardner
Same name typewritten

Harvard-Smithsonian
Center for Astrophysics
Address
60 Garden Street
Cambridge, MA 02138

(x) **Prefer Poster Session**
( ) **Prefer Standard Session**
( ) **No Preference**

Attachment C

Photodissociaton of Neutral Free Radicals of Astrophysical Interest

L.D. Gardner, M.M. Graff, and J.L. Kohl

in Proceedings of the Eighth International Colloquium on Ultraviolet
and X-ray Spectroscopy of Astrophyscial and Laboratory Plasmas,
International Astronomical Union Colloquium No. 86,
27-29 August, 1984

PHOTODISSOCIATION OF NEUTRAL FREE RADICALS OF ASTROPHYSICAL INTEREST

L.D Gardner, M.M. Graff and J.L. Kohl
Harvard-Smithsonian Center for Astrophysics
Cambridge, MA 02138

The necessity for understanding molecular formation and destruction processes occurring in astrophysical environments is well known. Accurate molecular data are of critical importance in formulating models of such diverse regions as interstellar clouds and planetary and stellar atmospheres. With this in mind we have devised an experimental method and constructed an apparatus for the determination of cross sections as well as the kinetics for photodissociation processes in chemically unstable neutral molecules. Similar experimental methods have been independently developed by de Bruijn and co-workers and by Chen et al. (1).

A schematic of our apparatus is shown in Figure 1. We produce the negative ion of the species of interest in a discharge ion source. The ions are extracted and electrostatically accelerated to velocities greater than 10^7 cm/sec. To insure beam purity they are mass analyzed using a magnetic sector which also deflects them onto the primary axis of the apparatus, where they are subsequently collimated. The beam from a pulsed laser is also directed along this axis. The energy of the photons in this beam is chosen to be just sufficient to induce photodetachment of the negative ions, and the intensity is chosen to be high enough to induce the photodetachment of a very large fraction of the ions in the beam. The remaining negative ions are electrostatically swept out of the beam, and the now neutral molecular beam is allowed to pass into the next section of the apparatus. Here ultraviolet light from a second pulsed laser crosses the neutral beam at right angles. Absorption of photons from this laser causes photodissociation of some of the molecules. Part of the energy of the absorbed photon is converted into kinetic energy of the photofragments. The fragments therefore move away from each other and also from the axis as they continue their flight along the beam line. If the collimation angles are small enough, some of the fragments will leave the cone of the parent molecular beam and form a "halo" (not necessarily circular) around it. Since they are moving at high velocity, they may be detected with secondary electron multiplying devices such as channelplates. If the detection system records the fragment impact positions and arrival times relative to the firing of the dissociation laser, then individual fragment kinetic energies can be deduced and angular distributions determined.

We have carried out experiments on the photodissociation of excited states of H_2^+ in order to assess the performance of the apparatus (see Figure 2). Light from a flashlamp-pumped (rhodamine 6G) dye laser was directed along the beam axis, and it induced dissociation from states of vibrational quantum number v' = 7 and above. H^+ fragments were directed onto a channel electron multiplier and H fragments were allowed to strike a channelplate electron multiplier fitted with a coarse annular multianode array. The data we have obtained are shown in Figure 3. Note that the channeltron preferentially detects H^+ ejected along the beam axis, while the channelplate preferentially detects H ejected perpendicular to the beam axis. The number of fragments ejected at a given angle to the axis (i.e., the angular distribution) is related to the laser beam polarization and to details of the initial and final quantum mechanical states (2). For this experiment large angles are expected (3) and observed.

Experiments on the astrophysically important free radical CH have been initiated. The C $^2\Sigma^+$ state can be excited from the X $^2\Pi$ ground state with 3140 Å light from a frequency doubled dye laser. It is inferred from spectroscopic evidence (4) that all vibrational-rotational substates of this electronic state predissociate, and this resonant process is considered to be the primary photodestruction mechanism for interstellar CH (5). We intend to study this predissociation by observing directly the H fragments. The apparatus can also be used to study the dissociation of CH through higher lying repulsive Σ and Π states and the dissociation of OH through predissociating substrates of the A $^2\Sigma^+$ state (6) and through the repulsive 1 $^2\Sigma^-$ state (7). This last process is expected to be a major loss mechanism for interstellar OH (7).

This work was supported by the Office of Naval Research under Contract N00014-84-K-0134 and the Smithsonian Institution through its Scholarly Studies and Postdoctoral Fellowship Programs.

REFERENCES

1. D.P. de Bruijn and J. Los, Rev. Sci. Ins. 53, 1020 (1982); H. Helm, D.P. de Bruijn and J. Los, post deadline paper at the Annual Meeting of the Division of Electron and Atomic Physics of the American Physical Society, Storrs, CT, May 30-June 1, 1984; Y.S. Chen, J.H. Newman, K.A. Smith, and R.F. Stebbings, Bull. Am. Phys. Soc. 29, 801 (1984).

2. R.N. Zare, Ph.D. thesis, Harvard University, 1964.

3. G.H. Dunn, Phys. Rev. 172, 1 (1968); M. Tadjeddine and G. Parlant, Molec. Phys. 33, 1797 (1977).

4. J. Hinze, G.C. Lie, and B. Liu, Ap. J. 196, 621 (1975); J. Brzozowski, P. Bunker, N. Elander, and P. Erman, Ap. J. 207, 414 (1976).

5. A. Dalgarno, in Atomic Processes and Applications, P.G. Burke and B.L. Moiseiwitsch, eds. (North-Holland Publishing Company, 1976) p. 109, and references therein.

6. J.Czarny, P. Felenbok, and H. Lefebvre-Brion, J. Phys. B 4, 124 (1971)

7. E.F. van Dishoeck and A. Dalgarno, J. Chem. Phys. 79, 873 (1983).

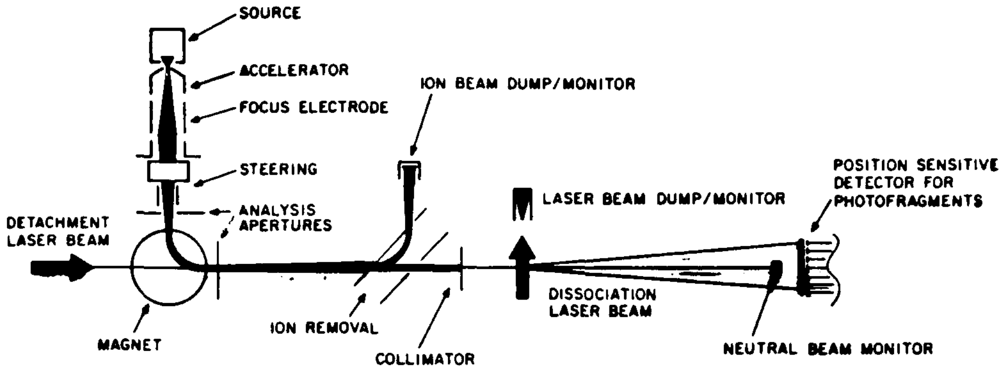

Figure 1

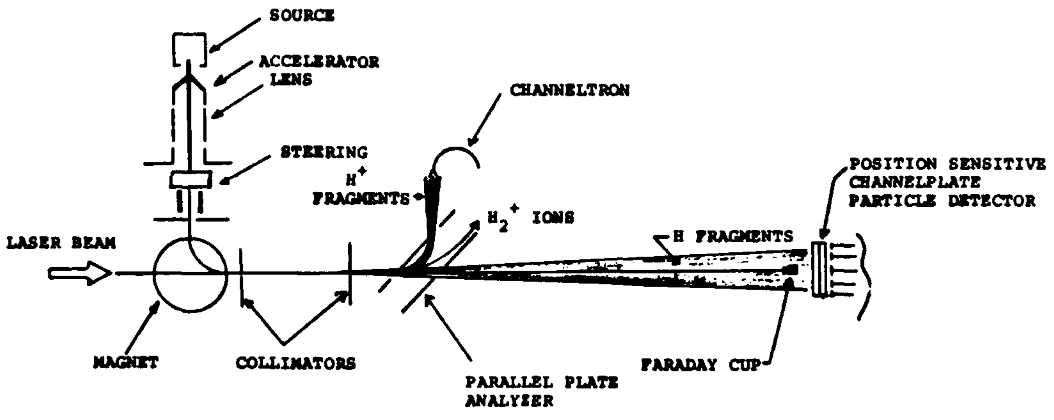

Figure 2

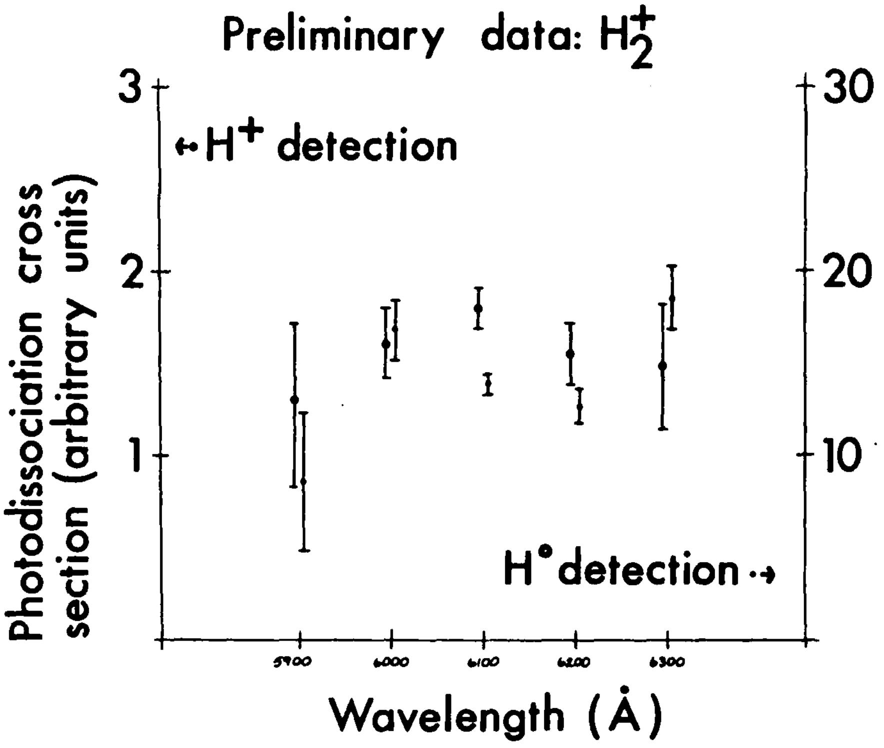
Preliminary data: H_2^+
3
2
1
30
20
10
← H^+ detection
H° detection →
Photodissociation cross section (arbitrary units)
5900
6000
6100
6200
6300
Wavelength (Å)

Figure 3

Attachment D

Fast Beams Apparatus for the Study of Photodissociation Processes

L.D. Gardner, M.M. Graff, and J.L. Kohl

submitted to Review of Scientific Instruments

August 1985

Fast Beams Apparatus for the Study of Photodissociation Processes

L.D. Gardner, M.M. Graff[a), and J.L. Kohl

Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138

Abstract

An apparatus is described for studying the photodissociation of neutral free radicals and positive molecular ions with a fast beam technique. Particular attention is given to studies of diatomics whose constituent atoms have very different masses and to photodissociation of polyatomic systems. Novel features of this design include fast neutral beam generation by photodetachment of negative ions, beam energies sufficiently high to detect neutral products, and a beam filter for reducing noise from background processes. A position-sensitive detector provides the data required to determine separation energies and angular distributions for dissociation studies where only one fragment is detectable.

Introduction

The interactions of molecules with radiation are known to have important effects on the chemical and physical evolutions of planetary and stellar atmospheres, laboratory plasmas, and interstellar clouds. Consequently, there has been a considerable effort devoted to measuring fundamental parameters associated with these interactions. The bulk of the data that has been acquired is for stable molecules, i.e., for molecules that do not undergo rapid chemical changes at standard pressures and temperatures. These data consist primarily of photoabsorption and photoemission line positions and cross sections. In the tenuous environments mentioned above, unstable molecules such as neutral free radicals and molecular ions often play more important physical and chemical roles than do stable molecules. Hence methods must be developed to study these transitory species.

Since the early 1970's there has been a substantial effort devoted to the study of the photodissociation of molecular ions by a variety of methods including the drift tube, the fast beam, the double mass spectrometer, and the selected ion flow tube (SIFT) (see Moseley[1,2] and references therein). Most of these techniques use ion photofragment spectroscopy, the direct detection of fragment ions, to characterize the photodissociation event and thereby deduce molecular parameters such as dissociation energies and potential curves. In the case of fast beam photofragment spectroscopy, the kinetic energies and angular distributions of the fragment ions can also be measured, thereby providing a much more complete determination of the photodissociation process.

Recently an experiment on the photofragment spectroscopy of H_2 has been described by Helm <u>et</u> <u>al</u>.[3] Neutralization of a fast beam of H_2^+ was effected by charge exchange and resulted in a relatively hot beam of H_2. The photodissociation event was evidenced by detecting the two H photofragments in coincidence on a microchannel plate position sensitive detector with concentric ring anodes. Their anode configuration makes use of the fact that both fragments are well removed from the beam axis. It is best suited for photodissociation of molecules with fragments of similar mass.

It is the purpose of this paper to describe an apparatus, initiated and developed independently of the above experiment, that is capable of applying fast beam photofragment spectroscopy to neutral free radicals.[4] In the present case, particular attention is paid to molecules whose photofragments have very different masses, e.g., first row hydrides CH and OH. The experiment is amenable to both diatomic and polyatomic molecules. While intended primarily for the measurement of free radical photodissociation cross sections, the apparatus can also be applied to spectroscopic studies of both ions and neutrals. The design specifically favors detection of photodissociation events resulting in a relatively large separation energy (~1 eV). Traditional on-axis detection techniques are extremely limited in their ability to probe such processes.

I. Description of the Basic Technique

Our experimental approach for the study of molecular ions consists of the production of a fast ion beam, the interaction of this beam with a laser, and the direct detection of the products of dissociation. For studies of neutral free radicals, a fast beam of neutrals can be created by photodetachment of the corresponding negative molecular ion. The fast beam provides a collisionless environment for the photodissociation study, thereby avoiding the complicating effects of collisions and chemical reactions. Furthermore, we choose to use a fast beams technique so that the neutral photofragments may be detected directly with conventional charged particle detectors and without the usual intervening ionization step. In principle, all the fragments from a single dissociation event can be detected in coincidence, thereby making it possible to determine the identity and the kinetic energy of each photofragment.

A diagram of the experimental apparatus is shown in Figure 1. The basic technique relies on the fact that when a molecule dissociates following photon absorption, some of the energy of that photon is converted into kinetic energy of the fragments. For example, consider the photodissociation of molecule AB as shown in Figure 2. At the moment of photon absorption, the molecule is located in space at position $(x,y,z) = (0,0,-\ell)$ and has a net center of mass velocity v_0 along the z-axis. After photon absorption, the molecule breaks up into fragments of mass M_1 and M_2 with center of mass velocities $\vec{v}_1$ and $\vec{v}_2$ as shown. The fragments in general have non-zero velocity components perpendicular to the original direction of v_0. The fragments therefore move away from the z-axis as they travel toward the origin where a position sensitive particle detector is located. The detector with its accompanying electronics provides knowledge of the positions of the fragments and their arrival times relative to the time of photon absorption. The knowledge of the impact positions of the fragments, their arrival times, the mass of the parent molecule, the flight distance, and the photon energy enable the determination of the masses and kinetic energies of each fragment. In order to illustrate this more clearly, we will present in the following paragraphs the kinematics of the above described prototypical dissociation.

A. Dissociation into Two Fragments

Consider the direct dissociation of a diatomic or polyatomic molecule into two fragments A and B as shown in Figure 2. The fragments strike the detector at times t_1 and t_2 after the dissociation and at radial positions R_1 and R_2. These quantities are to be measured. They can be related in a straightforward way to the total axial flight distance ℓ, the velocity of the center of mass v_0, the velocity vectors $\vec{v}_1$ and $\vec{v}_2$ in the center of mass frame, and the angle θ between these vectors and the direction of flight of the center of mass (see Fig. 2):

$$R_1 = |\vec{v}_1| t_1 \sin\theta \tag{1a}$$

$$R_2 = |\vec{v}_2| t_2 \sin\theta \tag{1b}$$

$$t_1 = \frac{\ell}{v_0 + |\vec{v}_1| \cos\theta} \tag{2a}$$

$$t_2 = \frac{\ell}{v_0 - |\vec{v}_2| \cos\theta} \tag{2b}$$

Conservation of momentum forces the relationship between the velocities and masses of the fragments:

$$M_1 \vec{v}_1 + M_2 \vec{v}_2 = 0 \tag{3}$$

Combining Eq. (3) with Eqs. (1) and (2) leads to the independent relationships:

$$\frac{M_1}{M_2} = \frac{R_2}{t_2}\frac{t_1}{R_1} \tag{4}$$

$$\frac{M_1}{M_2} = -\frac{v_0 - \ell/t_2}{v_0 - \ell/t_1} \tag{5}$$

The determination of the ratio of masses, together with the known mass of the parent molecule, provides the mass of each fragment.

1. Dissociation into two fragments of similar mases

For the case where the two photofragments have similar masses ($M_2/M_1 < 5$) quantities R_1, R_2, t_1, and t_2 can be separately measured to determine masses M_1 and M_2. The accurate determination of quantities R_1 and R_2 is limited by the uncertainty in the position of the center of mass due to finite beam collimation. The quantities t_1 and t_2 are uncertain due to the finite duration of the laser pulse. In addition, position and time variables are both subject to finite resolution in measurement. For an uncertainty in the center of mass of the fragments at the detector ΔR and for laser pulse duration Δt, the uncertainty in the determination of M_1/M_2 from Eq. (4) is approximately

$$\frac{\Delta(M_1/M_2)}{(M_1/M_2)} = \Delta R\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \Delta t\left[\frac{1}{t_1} - \frac{1}{t_2}\right] \qquad (6)$$

The uncertainty corresponding to Eq. (5) is

$$\frac{\Delta(M_1/M_2)}{(M_1/M_2)} = \ell\Delta t\left(\frac{1}{t_2^2(v_0-\ell/t_2\ )} - \frac{1}{t_1^2(v_0-\ell/t_1)}\right). \qquad (7)$$

In deriving Eqs. (6) and (7), it has been assumed that uncertainties in the measurement of the detected positions and arrival times are negligible compared to the center of mass and dissociation time uncertainties ΔR and Δt. This assumption is valid for the case of a 1 mm diameter beam of divergence 1 mrad, a laser pulse duration of 10 nsec, and a detection system capable of measuring positions with an accuracy of better than ~0.5 mm and arrival times with an accuracy of 1 nsec.

While Eqs. (4) and (5) are both applicable in all photodissociation events, the method of choice for determining the ratio of fragment masses depends on the direction of fragment ejection. Equation (4) provides best results for large fragment separation $|R_1-R_2|$, corresponding to photodissociation nearly perpendicular to the beam axis. Equation (5) is most accurate for large differences in arrival times t_2-t_1, corresponding to fragment ejection nearly parallel to the beam axis.

The kinetic energy of each fragment may be determined from the fragment masses and velocities. The separation energy is then

$$W = \frac{1}{2}M_1\left(\frac{R_1^2\, v_0^2}{\ell^2} + \left(\frac{\ell}{t_1} - v_0\right)^2\right) + \frac{1}{2}M_2\left(\frac{R_2^2\, v_0^2}{\ell^2} + \left(\frac{\ell}{t_2} - v_0\right)^2\right) \qquad (8)$$

This experimentally determined parameter, together with the known photon energy, can be used to determine the dissociation energy of the parent molecule and/or the degree of internal excitation of the fragments.

The separation energy can be determined relatively accurately due to a cancellation in the uncertainty ΔR of the fragments' center of mass. The energy-uncertainty is

$$\Delta W = \frac{M_1}{2}\left[\frac{2R_1 v_0^2}{\ell^2}\,\delta R - \frac{2\ell^2}{t_1^3}\,\Delta t + \frac{2\ell v_0 \Delta t}{t_1^2}\right] + \frac{M_2}{2}\left[\frac{2R_2 v_0^2}{\ell^2}\,\delta R - \frac{2\ell^2}{t_2^3}\,\Delta t + \frac{2\ell v_0 \Delta t}{t_2^2}\right] \qquad (9)$$

where δR is the uncertainty in the measured positions of the fragments on the detector, Δt is the laser pulse duration, and the uncertainty in arrival times is again neglected.

In the case of photodissociation via an intermediate resonant state (predissociation), the apparent separation energy determined in Eq. (8) will differ from the actual separation energy if the predissociation lifetime is a significant fraction of the time of flight after laser interaction. This will be a consideration only for very slow predissociations, $\tau > 10$ nsec. In principle the spread of apparent separation energies can be related to the predissociation lifetime.

2. Dissociation into two fragments of dissimilar masses

For diatomic molecules whose constituent atoms have very different masses ($M_2/M_1 > 5$), conservation of linear momentum causes the heavy fragment to remain very near the beam axis, while the light partner carries away the greater fraction of the separation energy. Finite beam collimation makes the detection of the heavy fragment impractical, because it remains essentially within the cone of the primary beam itself. The determination of separation energies and angular distributions must therefore be determined by the spatial distribution of only the light fragment on the anode array.

In a given experiment the separation energy is determined from an ensemble of dissociation events by choosing those events which produce maximum values of R_1. The separation energy of the dissociation event is given by

$$W = \frac{M_1 E_0}{M_2} \frac{R_{MAX}}{\ell^2} \qquad (10)$$

where E_0 is the initial laboratory kinetic energy of the parent molecule, and where M_2 and M_1 are the masses of the heavy and light fragments, respectively. The uncertainty in W is determined from finite beam collimation considerations.

3. Angular distribution of photofragments

In general the fragments from photodissociation do not have center of mass velocity vectors uniformly distributed in space. For one-photon electric dipole transitions this is due to the fact that the probability of excitation of a molecule is proportional to the square of the cosine of the angle between the transition dipole and the electric vector of the radiation field. Thus for an ensemble of randomly oriented molecules in a plane polarized radiation field, there will be excitation of molecules with certain preferred spatial orientations. Since the fragment recoil angular distribution is correlated with the original transition dipole, this polarized light induced orientation will be maintained, and a non-isotropic angular distribution of fragments results. The convolution of the transition dipole angular distribution with the fragment recoil angular distribution leads to an expected fragment angular distribution in the center of mass of the form:[5]

$$f(\Theta) = \frac{1}{4\pi} (1 + \beta P_2(\cos \Theta)) \qquad (11)$$

where β is a constant, Θ is the angle between the light polarization vector and the fragment velocity vector, and $P_2(\cos \Theta)$ is the Legendre polynomial of degree two. The constant β is related to the symmetry, configuration, and lifetime of the parent molecule's excited state, and may take on values between -1 and +2. For nonzero values of β, this function is peaked either along the light polarization direction or perpendicular to it. In a given experiment the polarization direction may be chosen so that the peak of the photofragment distribution occurs at θ (see Figure 2) equals 90°, which results in a maximum likelihood of fragment detection. Shown in Figure 3 are expected distributions of radius vectors R_1 and R_2 for the two extreme cases $\beta = -1$ and $\beta = 2$ with laser polarization along the x-axis in Figure 2.

B. Dissociation Into More than Two Fragments

It may be possible to extend the technique outlined above to the study of multiple-fragment dissociations. For the direct dissociation of a molecule of mass M into three fragments

$$ABC + h\nu \rightarrow A + B + C$$

(where A, B, and C may be atomic or molecular), conservation laws of momentum and mass provide the relationship

$$M_A = \left(\frac{x_B y_C - y_B x_C}{x_B y_C - y_B x_C - x_A y_C + y_A x_C + x_A y_B - y_A x_B}\right) M \tag{12}$$

and similar expressions for M_B and M_C. Narrow beam collimation, which enables the accurate determination of fragment positions (x_i, y_i), is more critical than for the two-fragment case. The kinetic energy of each fragment in the center of mass frame is given by

$$E_i = \frac{1}{2} M_i \left(\left(\frac{x_i}{t_i}\right)^2 + \left(\frac{y_i}{t_i}\right)^2 + \left(\frac{\ell}{t_i} - v_0\right)^2\right) \tag{13}$$

The complications of predissociation are more severe for multiple-fragment dissociations than for two-fragment dissociations. The fragment positions and arrival times could be affected not only by predissociation lifetimes of the excited parent complex, but also by predissociation lifetimes of individual fragments:

$$\begin{aligned} ABC + h\nu &\rightarrow ABC^* \\ &\rightarrow A + BC^* \\ &\rightarrow A + B + C \end{aligned}$$

Figure 4 illustrates dissociation into three fragments involving a longlived intermediate state.

It may be possible to determine details of the transition from the temporal and spatial distributions of photofragments, but we are not aware of any current theoretical models that would be useful for interpreting such distributions.

II. DESCRIPTION OF THE APPARATUS

The basic apparatus for studying the photodissociation of neutral free radicals is shown in Figure 1. First, a beam containing the negative ion of the desired neutral is accelerated and mass-selected; second, this beam is photodetached using a high energy pulse of visible or infrared photons; third, the molecules are dissociated by a pulse of ultraviolet photons; and fourth, the photofragments are detected directly with spatial and temporal resolution. For experiments concerning the photodissociation of molecular ions, the neutralization step is eliminated.

The duoplasmatron ion source (General Ionex model 358) produces either positive or negative ions by appropriate choice of acceleration potentials and minor mechanical adjustment of the source itself. This type of source was chosen for its characteristic of producing a nearly thermal (T ~ 1000 K) distribution of negative ions,[6] thereby facilitating eventual measurement of photodissociation cross sections.

The source potential is chosen to provide an energy-to-mass ratio of ~1 keV/amu for the desired ion. This enables final detection of neutral H photofragments.[7] The extracted ions are focused by an Einzel lens immediately following the acceleration column. Source bias and focusing potentials are provided by very well regulated high voltage power supplies (Spellman series RHR and RHSR). After traveling through a region containing an electrostatic quadrupole lens (used, to date, only as a steering element), the beam passes between the 23 cm diameter poles of an electromagnet (Varian model V2501). The magnetic field is adjusted to deflect the molecular ion of interest by 90° into the primary axis of the apparatus, where the beam is collimated by two 2 mm apertures separated by a distance of 100 cm.

The on-axis location of the neutral particle detector presents an inherent source of noise that is more severe than for off-axis or charged-particle detection systems. Collisional dissociation and scattering with the background gas result in neutral fragments in a narrow cone around the beam axis. Most of this noise can be eliminated by improving the vacuum and by combining tight collimation (2 mrad full angle) with a Faraday cup that is large enough to intercept most fast neutrals resulting from background collision processes.

Beam scattering from the second collimating aperture was found to be a more troublesome source of noise. While strongly peaked in the direction of the beam axis, interactions with the second collimator resulted in a significant background on the same area of the detector as the signal. This background was reduced but not eliminated by choosing a thin (.25 mm) collimator. The remaining noise made it necessary to limit the maximum primary beam current to ≤ 1 nA, well below the desired level.

The noise was significantly reduced with the introduction of a beam filter, shown schematically in Figure 5. The first element of this electrostatic filter is the second collimator. Following final collimation, the beam is first steered away from, then returned to, the center line of the apparatus by four pairs of deflection plates. Each pair of deflectors is separated from the next pair by a blinder plate whose aperture height is staggered with the position of the beam and whose width is considerably greater than that of the collimating aperture. The height of the center aperture is chosen just large enough that there exists no optical path between the second collimator and the microchannel plate detector. This assembly greatly diminishes all sources of noise discussed above. The operating voltage of the beam filter is ideally (and, in practice, very nearly)

$$V = \frac{2E_0ab}{c^2} \tag{14}$$

where E_0 is the beam energy, a is the separation of the deflection plates, c is the length of each plate, and b is the maximum displacement of the beam from the center line. To facilitate beam tuning, the blinder plates B1-B4 can be maintained at ground potential with only minor loss of electric field symmetry. It was found that operating in this manner caused no discernible change in the final beam direction and changed the filter operating voltage only slightly.

For studies of molecular ion photodissociation, a single laser beam enters the apparatus through a quartz window and crosses the ion beam at a point just beyond the beam filter. Immediately following this region is a 90° parallel plate electrostatic analyzer, which is tuned either to deflect the parent ions into a Faraday cup for beam monitoring or to deflect product ions onto the 1 cm diameter entrance cone of a channeltron electron multiplier for signal detection. Neutral particles produced by the laser beam travel unhindered through the analyzer and enter a flight tube. After a flight distance of approximately one meter, those fragments with significant velocity components perpendicular to the beam axis strike a position sensitive electron multiplier, and a data acquisition system records the number of events on each anode.

For studies of neutral free radical photodissociation, two laser interaction regions are required--one to prepare the neutrals through photodetachment and one to actually cause the dissociation. This is most cleanly accomplished by using two separate laser systems. The beam from the first enters the apparatus in the same place as the dissociation laser of the molecular ion experiments. The beam from the second laser system enters after the parallel plate analyzer, which is used as a residual negative ion remover and monitoring aid, after a delay appropriate to the flight time of the neutral from the photodetachment region to the phodissociation region. The fragments from photodissociation then enter a flight tube and eventually strike a position sensitive electron multiplier as described above.

In order to avoid the complications entailed with the use of two entirely separate laser systems, we are carrying out neutral free radical photodissociation experiments as shown in Figure 1. Here two laser beams enter the apparatus and cross the beam at essentially the same point at essentially the same time. This is accomplished by using one "pump" laser to drive one or more dye lasers. Visible light is appropriate for the photodetachment of the negative ions of many neutral free radicals[8] and is readily obtainable from dye lasers. The photodissociation light source may be provided by splitting off some of the pump laser beam and using it directly or as a pump for a second dye laser whose output is then frequency doubled into the ultraviolet using nonlinear crystals. An even more simple method is to frequency double the output of a dye laser for the dissociation source and use the "leftover" dye laser light as the detachment source. These methods employing the physical superposition of two laser beams have a potential problem in that there is no clear ion removal region before dissociation takes place. Care must therefore be taken to ensure that observed neutral fragments are from the dissociation of the neutral and not from the direct dissociation of the negative ion.

The signal to noise ratio for all the experiments is greatly enhanced by the use of pulsed laser systems and tightly gated detection electronics that detect pulses only during the short duration that corresponds to possible photodissociation events.

The vacuum system was almost entirely composed of stainless steel chambers pumped by baffled oil vapor diffusion pumps. Pump baffles are cooled to -100 C by a cascade refrigeration system. O-ring seals were employed prior to and immediately after the electromagnet. The magnet chamber was made of aluminum with an inner lining of copper foil.

All chambers after the electromagnet are standard 10 cm nominal OD tube fittings joined by copper gasketed Conflat flanges. Base pressure in the system was below 5×10^{-7} torr in the chamber immediately after the ion source. With the ion source operating, this pressure rose to typically 7×10^{-6} torr. Base pressures elsewhere in the system ranged from 1×10^{-7} torr immediately after the analyzing magnet to 1×10^{-8} torr at the detector. These pressures did not change significantly with operation of the ion source.

The windows used to allow the laser beams to enter and leave the apparatus were made from 3.5 cm diameter by 0.5 cm thick quartz flats, sealed by O-rings to 7 cm diameter conflat flanges. Each window provided a 2.5 cm diameter clear aperture into the apparatus.

A detailed drawing of the detector is shown in Figure 6(a). The detector is a 40 mm diameter matched chevron microchannel plate pair manufactured by Galileo Electro-Optics Corporation. A 90% transmission grid made from 0.1 mm diameter tungsten wire was mounted approximately 5 mm in front of the detector and biased to repel secondary electrons ejected from the channel plate back to its surface. The detector is operated at negative high voltage polarity to avoid noise from background electrons. A double Faraday cup with an inner cup of diameter 4 mm and an outer cup of diameter 7 mm is mounted coaxially with and 2.5

cm in front of the channel plates assembly. The inner cup is used for beam tuning, while the outer cup masks the detector from background fast neutrals. The anode of the detector, mounted 1 mm behind the second channel plate, was made from double sided copper clad epoxy circuit board and contained five distinct regions as shown in Figure 6(b).

A higher resolution anode is shown in Figure 6(c). This anode design is composed of six rings outside the shielded central region. The outer (inner) rings are divided into six (four) distinct angular sections. The anisotropy parameter of a transition determines the distribution in angle, and the separation energy of a transition is primarily responsible for the radial distribution. A computer code has been developed to simulate the distribution of photofragments on the anode array for a given anisotropy parameter, separation energy, and beam spread. This code will be used in comparison with observed distributions to determine transition parameters. Analysis is simplified by adding contributions of different anodes that are, for reasons of geometry, equivalent (Figure 6(c)).

Voltages for the various parts of the detector assembly were provided by a resistor network connected to a well regulated and stable power supply (Hewlett-Packard model 6516A).

The electronics system used with the detector is shown in Figure 7. Pulses from the individual anodes are fed into individual very high bandwidth amplifier/discriminator/counter channels. A logic pulse initiated by laser light striking a photodiode triggers an adjustable delay, after which the gated counters are enabled for a preset period corresponding to the expected arrival time of photofragments. The counters are then read out one digit at a time through a special interface[9] connected to a parallel input port on an LSI 11/2 computer system. Upon completion of the readout cycle, the computer resets the counters and initiates a second firing of the delay/gate circuitry. This background measurement is also read out by the interface. The computer then resets the counters and waits for the next laser pulse. After each 100 pulses, the data accumulated for laser on/off conditions are processed, stored on a floppy disk, and displayed on a video terminal. The computer then either returns to data acquisition or requests further instruction.

Three different laser systems have been used to acquire data with the fast beams apparatus. A Nd:YAG-pumped dye laser system (Quanta-Ray models DCR-1 and PDL-1) was used on some preliminary photodetachment and photodissociation experiments. The photodissociation data presented in the next section were obtained using a flashlamp-pumped dye laser (Chromatix model CMX-4). The laser system currently in use is an excimer-pumped dye laser system (Lambda Physik models EMG 101E and FL 2001). The short pulse duration of the current system greatly enhances the signal-to-noise ratio of the experiment and enables time-resolved measurements.

III. EXPERIMENTAL RESULTS

In order to verify the performance of the apparatus, we have carried out experiments on the molecular ion H_2^+. This molecule was chosen because it has been extensively studied both experimentally[10,11,12,13] and theoretically[14] and is produced in copious quantities in all bound vibrational states by our ion source.[15] Linearly polarized light near 600 nm was directed perpendicular to the ion beam. H_2^+ ions in excited vibrational levels ($6 \leq v'' \leq 9$) of the $1s\sigma_g$ ground state[11] may be dissociated at these photon energies by excitation to the continuum $2p\sigma_u$ state. The parallel transition produces an angular distribution peaked in the direction of the laser polarization, which was aligned perpendicular to the beam axis for maximum detection efficiency.

Shown in Figure 8 are the data we have obtained at several laser wavelengths near 600 nm. Both neutral and charged fragments were detected, and, in the case of the neutrals, the rate integrated over all anodes is plotted. The higher detection rate for neutral H reflects the different detection efficiencies for H and H^+ in the present geometry: the effective area of the charged particle detector is a factor of four smaller than the neutral detector and furthermore, it detects only those few H^+ fragments ejected nearly parallel to the beam axis. The laser-neutral detector distance was chosen such that all neutral fragments are contained within the 4 cm diameter circle described by the microchannel plate. The neutral fragment detection rate was about ten times higher on the outer anode ring than on the inner ring. This is consistent with the parallel nature of the transition and the flight length.

The observed count rates were consistent with the known cross section[14] and experimental measurements[15] of the excited state distribution from a duoplasmatron ion source.

CONCLUSION

We have demonstrated that the apparatus herein described is useful for carrying out photodissociation experiments on transitions in molecular species where the fragments gain a significant amount of kinetic energy. We are proceeding with improvements to the apparatus. Among these are a more powerful laser system (Lambda Physik EMG101E and FL2001) (already installed) and a detector system with more position and temporal resolution. With these improvements it should be possible to study in detail the photodissociation of neutral free radicals as well as large excess energy dissociations in molecular ions.

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[a] Smithsonian Postdoctoral Fellow, 1983-1985. Present address: Physics Department, University of Oregon, Eugene, OR 97403

[1] J.T. Moseley, in <u>Electronic and Atomic Collisions</u>, edited by G. Watel (North Holland: Amsterdam), 1978, pp. 681-697.

[2] J.T. Moseley, in <u>Photodissociation and Photoionization</u>, Adv. Chem.

Phys. Vol 60, edited by K.P. Lawley (London: Wiley), 1985, pp. 245-297.

[3] H. Helm, D.P. de Bruijn, and J. Los, Phys. Rev. Lett. 53, 1642 (1984).

[4] L.D. Gardner, in Abstracts of Contributed Papers to the XII Conference on the Physics of Electronic and Atomic Collisions, edited by S. Datz (Gatlinburg) 1981, p. 52.

[5] R.N. Zare, Ph.D. Thesis, Harvard University (1964); see also C. Pernot, J. Durup, J.-B. Ozenne, J.A. Beswick, P.C. Cosby, and J.T. Moseley, J. Chem. Phys. 71, 2387 (1979).

[6] A. Kasdan, E. Herbst, and W.C. Lineberger, Chem. Phys. Lett. 31, 78 (1975).

[7] J.L. Wiza, Nucl. Instrum. Methods 162, 587 (1979), and references therein.

[8] K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules (New York: Van Nostrand Reinhold Co.) 1979.

[9] L.D. Gardner and G.P. Lafyatis, in preparation.

[10] F. Von Busch and G.H. Dunn, Phys. Rev. A5, 1725 (1972).

[11] N.P.F.B. van Asselt, J.G. Maas, and J. Los, Chem. Phys. 5, 429 (1974).

[12] J.B. Ozenne, J. Durup, R.W. Odom, C. Pernot, A. Tabche-Fouhaille, and M. Tadjeddine, Chem. Phys. 16, 75 (1976).

[13] A.K. Edwards, R. Kutina, N. Cue, D.S. Gemmell, K. Inglis, E.P. Kanter, and B.J. Zabransky, Phys. Rev. A23, 2724 (1981).

[14] G.H. Dunn, Phys. Rev. 172, 1 (1968).

[15] E.P. Kanter, P.J. Cooney, D.S. Gemmell, K.-O. Groeneveld, W.J. Pietsch, A.J. Ratkowski, Z. Vager, and B.J. Zabransky, Phys. Rev. A20, 834 (1979).

Figure Captions

Figure 1 Diagram of the apparatus. Lasers 1 and 2 are used for detachment and dissociation, respectively. Laser 1 is not used for studies of molecular ions.

Figure 2 Diagram of the direct dissociation of a molecule into two fragments.

Figure 3 Photofragment distributions for (a) $\beta=-1$, and (b) $\beta=2$, with laser polarization perpendicular to the beam axis. The distribution is shown for one fragment only. The axis of laser polarization is indicated by a solid line in each case.

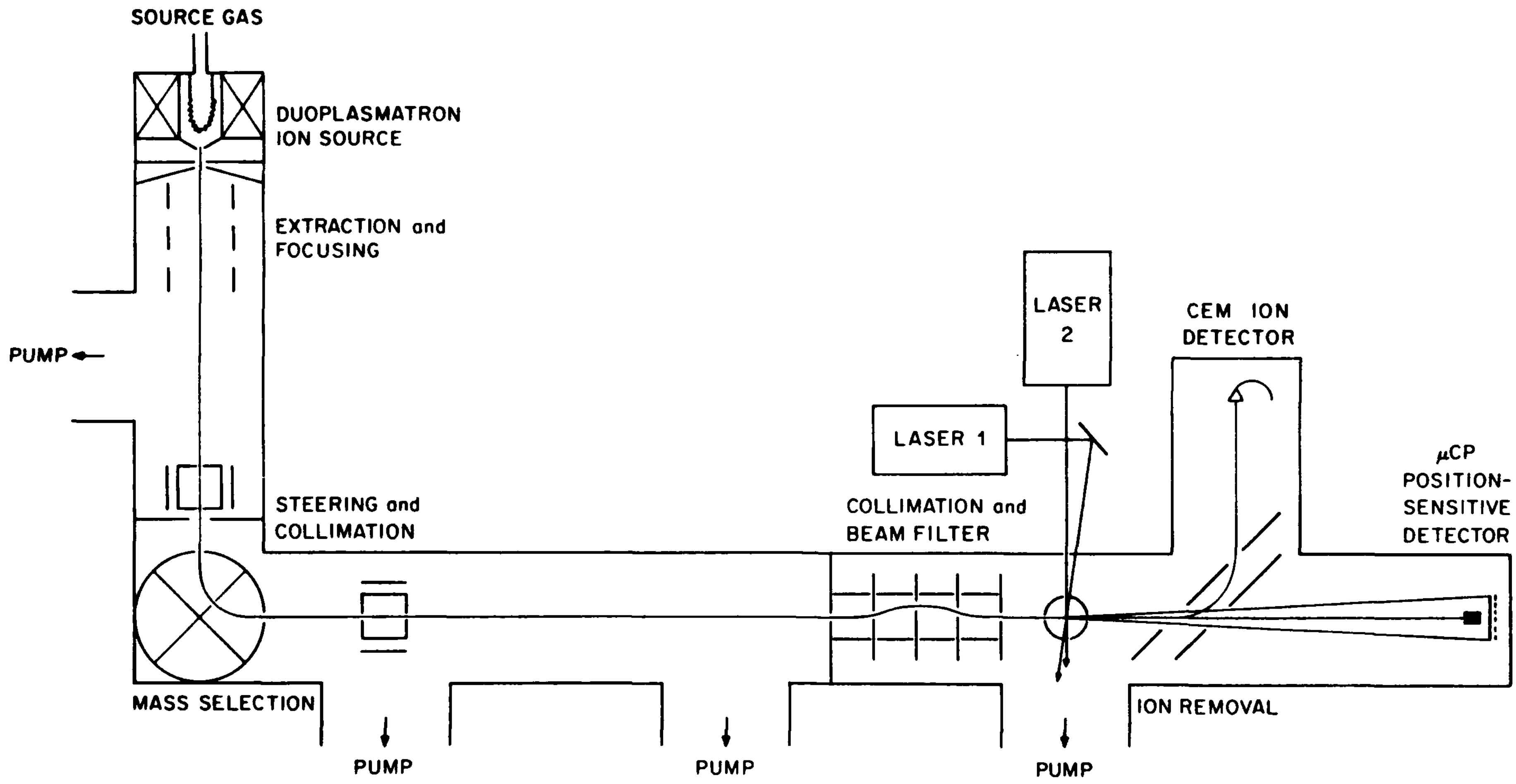
Figure 4 Diagram of the direct dissociation of a polyatomic molecule into two fragments, followed by predissociation of one of the fragments.

Figure 5 Beam filter. After the second collimating aperture, the beam is deflected away from the center line for a short distance. Blinder plates B1-B4 reduce background particles in the beam.

Figure 6 Position-sensitive detectors. (a) Detector configuration, side view. (b) Anode array used in diagnostic experiments. (c) Anode array for studying dissociation of heavy-light diatomics. The center anode of each array is shielded by a Faraday cup (shaded area). In (c), four anodes that are geometrically equivalent areas of the detector are also shaded.

Figure 7 Electronics arrangement for photofragment detection.

Figure 8 H_2^+ photodissociation data.


SOURCE GAS
DUOPLASMATRON ION SOURCE
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PUMP
STEERING and COLLIMATION
MASS SELECTION
PUMP
PUMP
COLLIMATION and BEAM FILTER
LASER 1
LASER 2
PUMP
CEM ION DETECTOR
ION REMOVAL
μCP POSITION-SENSITIVE DETECTOR

Figure 1

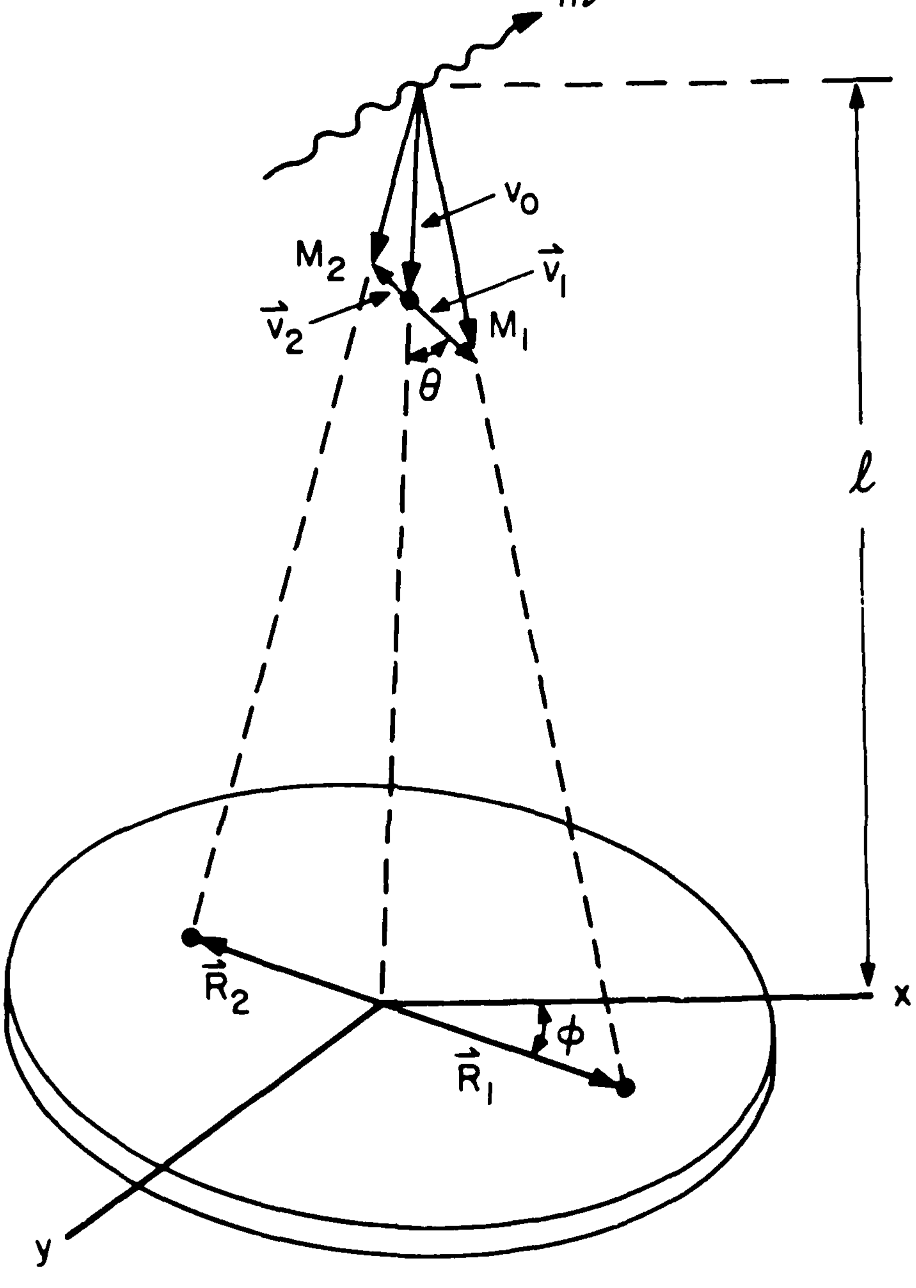
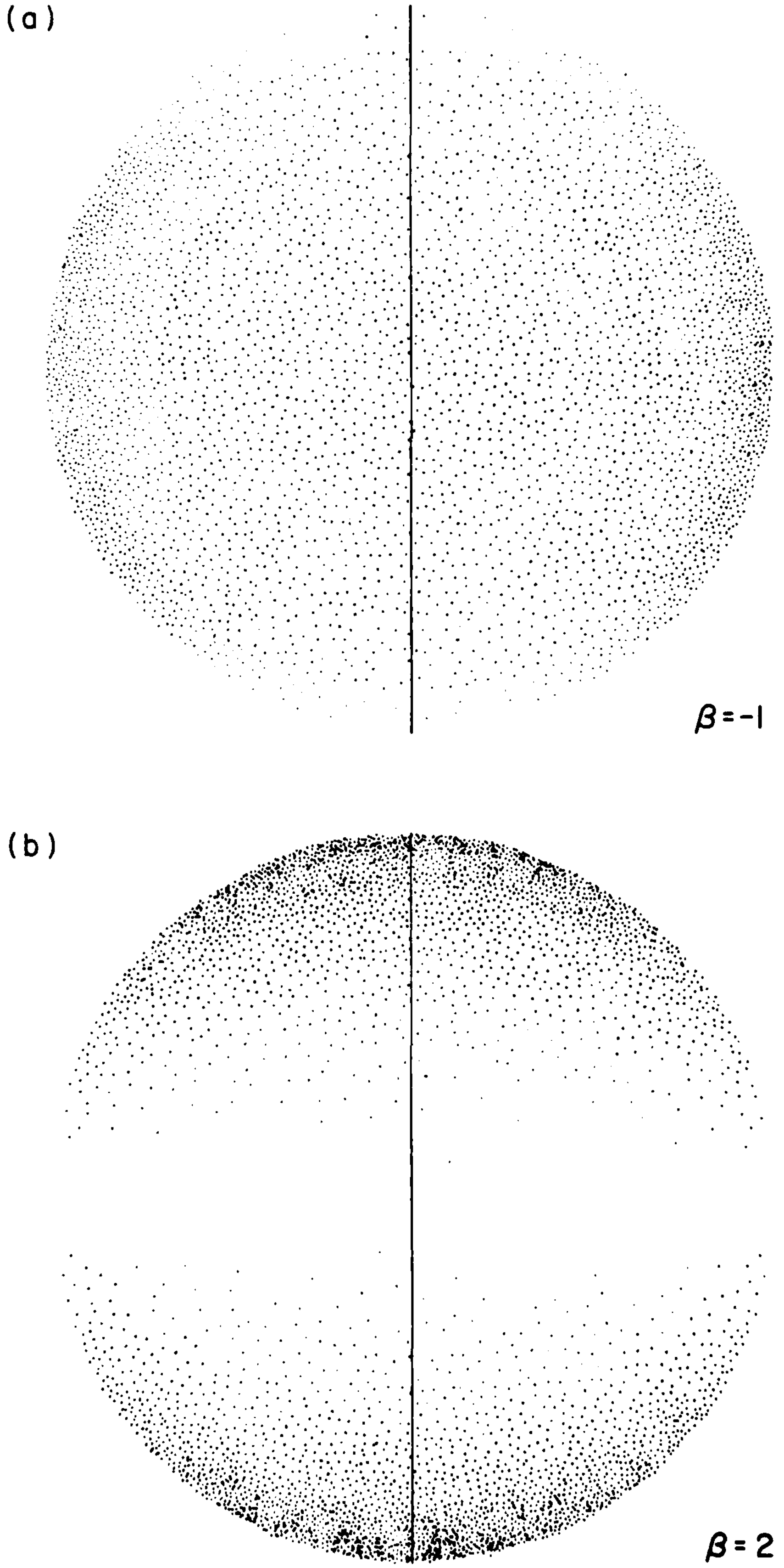


Figure 2



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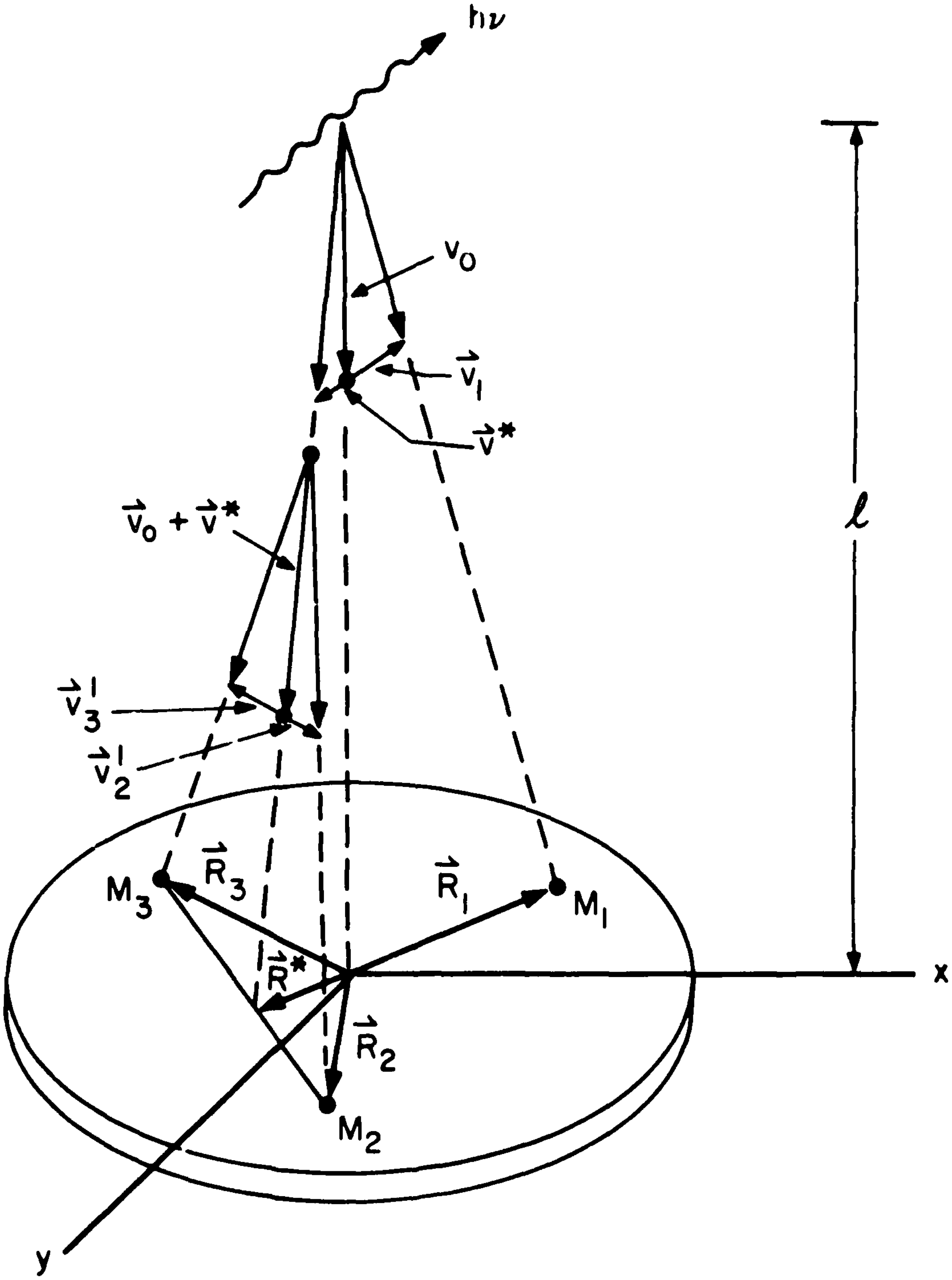

hν
v_0
$\vec{v}_1$
$\vec{v}^*$
$\vec{v}_0 + \vec{v}^*$
$\vec{v}_3^{\,1}$
$\vec{v}_2^{\,1}$
ℓ
M_3
$\vec{R}_3$
$\vec{R}_1$
M_1
$\vec{R}^*$
$\vec{R}_2$
M_2
x
y

Figure 4

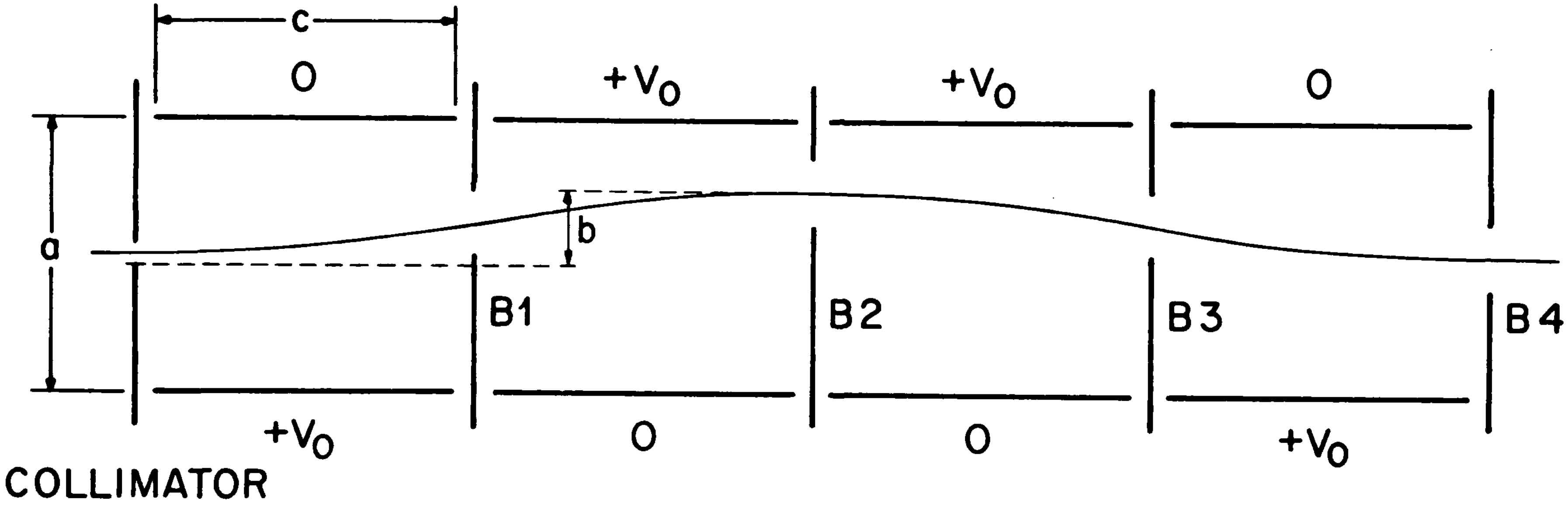

Figure 5

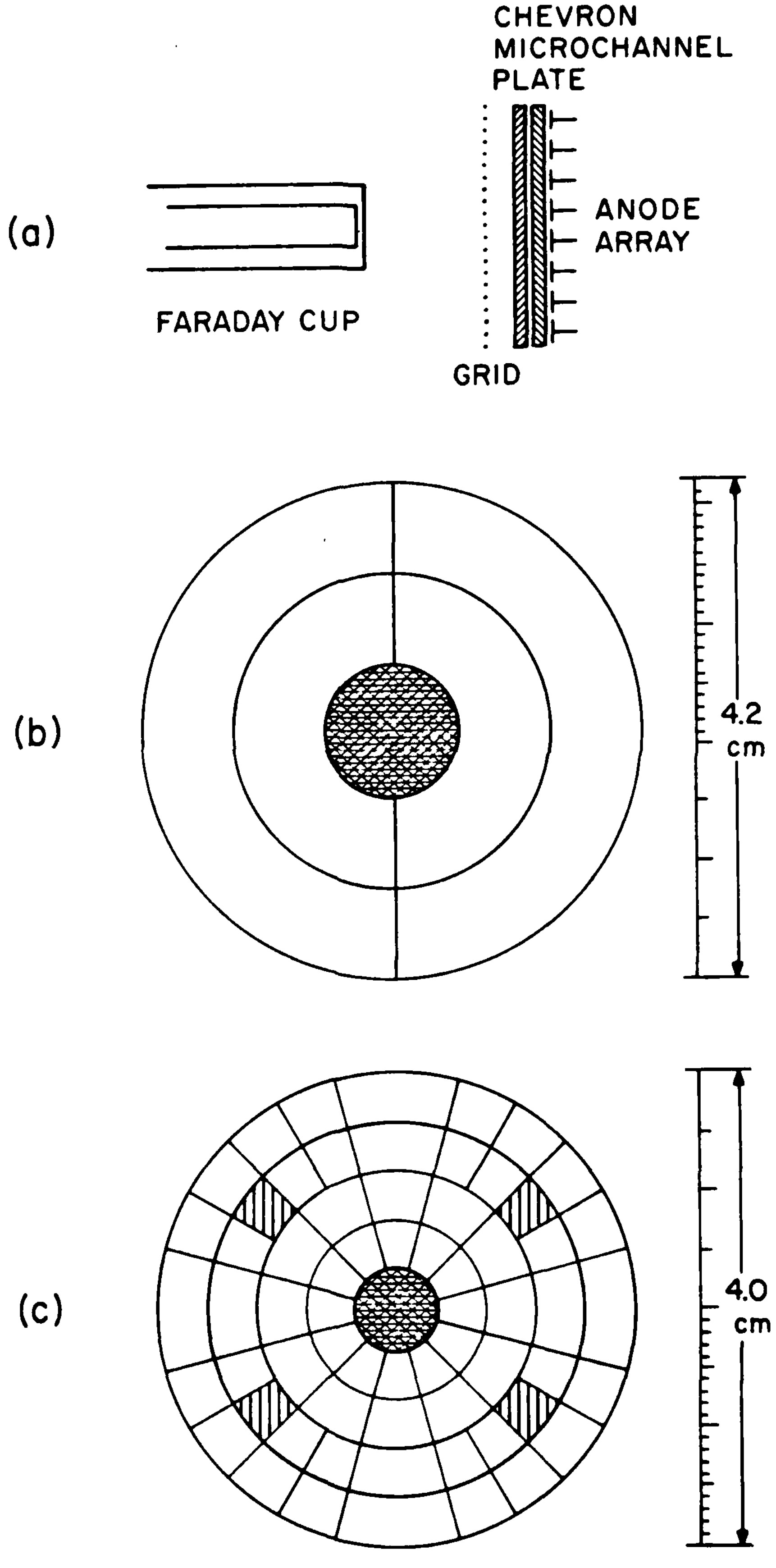
CHEVRON
MICROCHANNEL
PLATE
(a)
ANODE
ARRAY
FARADAY CUP
GRID
(b)
4.2
cm
(c)
4.0
cm

Figure 6

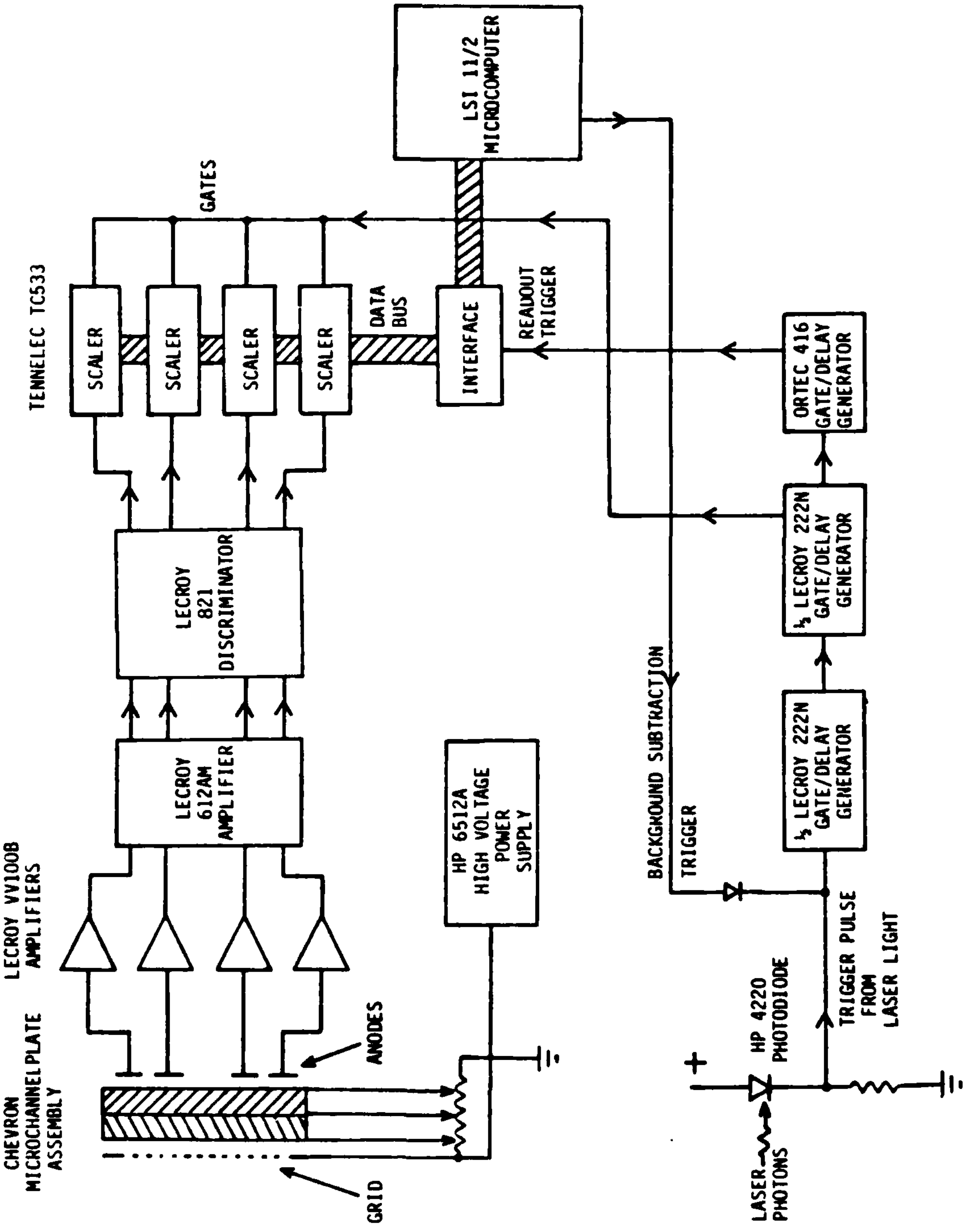
CHEVRON MICROCHANNEL PLATE ASSEMBLY
GRID
ANODES
LECROY VV100B AMPLIFIERS
LECROY 612AM AMPLIFIER
LECROY 821 DISCRIMINATOR
TENNELEC TC533
SCALER
SCALER
SCALER
SCALER
DATA BUS
INTERFACE
GATES
READOUT TRIGGER
LSI 11/2 MICROCOMPUTER
HP 6512A HIGH VOLTAGE POWER SUPPLY
BACKGROUND SUBTRACTION
TRIGGER
½ LECROY 222N GATE/DELAY GENERATOR
½ LECROY 222N GATE/DELAY GENERATOR
ORTEC 416 GATE/DELAY GENERATOR
+
LASER PHOTONS
HP 4220 PHOTODIODE
TRIGGER PULSE FROM LASER LIGHT

Figure 7

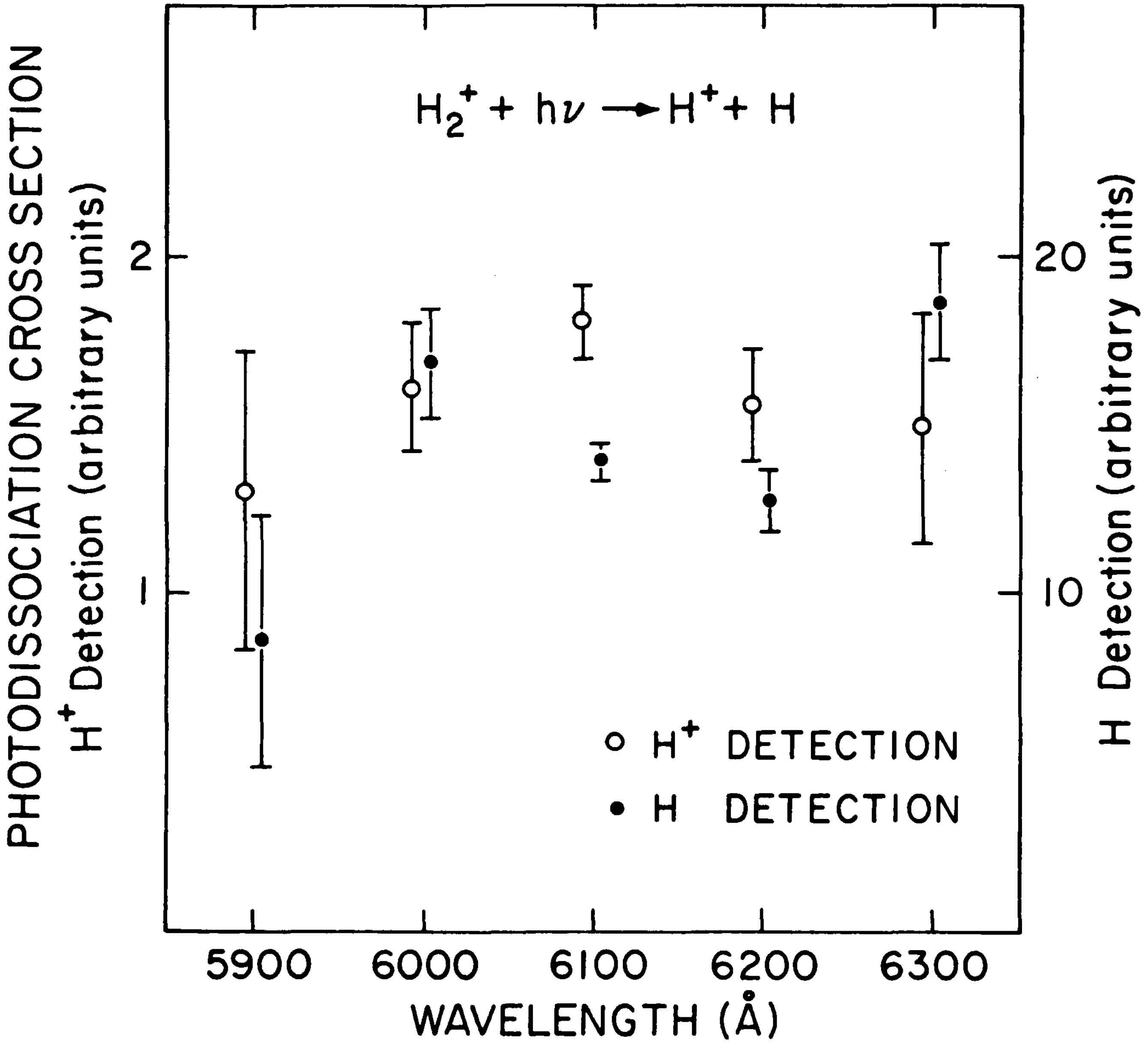
$H_2^+ + h\nu \rightarrow H^+ + H$
PHOTODISSOCIATION CROSS SECTION
H^+ Detection (arbitrary units)
H Detection (arbitrary units)
2
1
20
10
○ H^+ DETECTION
● H DETECTION
5900
6000
6100
6200
6300
WAVELENGTH (Å)

Figure 8

END

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