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**Title:** Time-of-flight Spectroscopy of Ionic and Metastable Fragments from Dissociating Molecules

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**Abstract:**
Progress is reported on research involving dissociation of molecules by electron bombardment. Time-of-flight techniques are used to determine the velocity distribution of metastable and ionic fragments. One recently completed experiment involved detection of proton fragments from dissociation of the hydrogen halides in the electron bombardment energy range of 20-60 electron volts. Threshold bombarding energies were obtained for several features in the proton velocity spectrum, and several of these features were identified as resulting from

(continued)
dissociation of molecular ions with a particular inner electron orbital
hole. Other experiments described are: (1) an unsuccessful attempt to
detect protons from the electron bombardment dissociation of the hydrogen
molecular ion; (2) an ongoing attempt to detect, in coincidence, metastable
and ionic fragments from dissociation of hydrogen; (3) an experiment on
proton fragments from the dissociation of water and hydrogen sulfide.
Annual Technical Report

"Time-of-Flight Spectroscopy of Ionic and Metastable Fragments from Dissociating Molecules"

Principal Investigators

Willis E. Lamb, Jr., Professor of Physics and Optical Sciences

L. C. McIntyre, Jr., Professor of Physics

AFOSR Grant 80-0218

Summary of research June 1983 - June 1984


Department of Physics and Optical Sciences Center

University of Arizona

Tucson, Arizona 85721

September 25, 1984
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I. Research Status

A. Introduction

This report contains a summary of research in molecular physics conducted under AFOSR grant 80-0218 during the period 15 June 1983 to 14 June 1984. The research was done in the Department of Physics at the University of Arizona by faculty and staff of the Department of Physics and Optical Sciences Center.

During the past several years, we have used time-of-flight methods to measure the velocity distribution of metastable and ionic fragments from molecules dissociated by electron impact. We have concentrated on hydrogen-containing molecules and have observed \( \text{H}(2S) \) metastable atoms and \( \text{H}^+, \text{H}_2^+, \) and \( \text{H}_3^+ \) ionic fragments. The \( \text{H}(2S) \) metastable fragments are detected by quenching in an electric field followed by observation of the resulting Lyman-\( \alpha \) radiation. The ions are detected in a large-entrance-aperture lens system which focuses ions onto a channel-electron-multiplier. This ion detector can be used in conjunction with a mass filter,\(^1\) developed in this laboratory, which uses a time-dependent potential barrier to obtain a separate velocity spectrum for each ion mass.

Completed experiments include investigation of both the "slow" peak\(^2\) and the "fast" peak\(^3\) in the kinetic energy spectrum of \( \text{H}(2S) \) fragments from electron bombardment dissociation of \( \text{H}_2 \). Other published experiments include an investigation of ionic fragments from dissociation of \( \text{H}_2, \text{D}_2, \) and \( \text{HD} \),\(^4\) and a study of \( \text{H}^+, \text{H}_2^+, \) and \( \text{H}_3^+ \) fragments from methane, ethane, methanol, and ethanol.\(^5\)

Current research will be described in the following sections.

B. Dissociation fragments from the hydrogen halides

This experiment has been completed and a paper is being prepared for submission to the Journal of Chemical Physics. This experiment was the subject of the Ph.D. dissertation of Bruce Kittams who obtained his degree in July 1984. An abstract for the paper is given below.
Time-of-flight and kinetic energy distributions were obtained for $H^+$ fragments resulting from electron bombardment of HF, HCl, HBr, and HI at electron energies between 21.2 and 51.2 eV. Several distinct features were observed in these spectra for each molecule and the corresponding threshold electron bombarding energies were obtained. Some of those features are proposed to originate from dissociation of $HX^+$ which is excited by removing an inner $\sigma$ shell electron in the corresponding molecule. Results from recent $(e, 2e)$ experiments support this proposal.

C. Dissociation of $H_2^+$

Considerable effort was made in the past year in an attempt to measure the kinetic energy spectrum of protons from the electron bombardment dissociation of the molecular ion $H_2^+$. Although this attempt was ultimately unsuccessful, we will describe here the motivation and the methods used.

The first and only reference to the measurement of the proton kinetic energy spectra from electron impact on $H_2^+$ is that of Caudano and Delfosse in a conference presentation in 1969.\textsuperscript{6} Previously, Dunn and Van Zyl\textsuperscript{7} had calculated the proton kinetic energy distribution assuming the validity of the first Born approximation while Zare\textsuperscript{8} and Peek\textsuperscript{9} had provided the formal theory of electron impact dissociation of $H_2^+$. Some analysis of the Caudano and Delfosse results were given in 1971 by Peek and Green.\textsuperscript{10}\textsuperscript{1}

Since the early 1970's, the proton kinetic energy spectra from electron impact on $H_2^+$ has been virtually ignored in both theory and experiment. However, much progress has been made in measuring cross sections for various electron impact processes with $H_2^+$, notably the series of papers by Peart and Dolder.\textsuperscript{11} Progress has also been made in the field of photodissociation of $H_2^+$ (see, for example, Van Asselt, Maas, and Los\textsuperscript{12}).
A schematic diagram of the experiment is shown in Fig. 1. H$_2^+$ was produced by electron impact ionization of H$_2$ using a 0.1 µsec pulse from an electron gun capable of delivering a direct current of over 10 mA at 100 V. This gun is called the source gun. The unwanted protons from the initial impact of neutral H$_2$ were blocked from the detector by a conical electrode to which a 1 µsec "cleaning" voltage pulse was applied. Since the H$_2^+$ produced by the source gun has a thermal distribution of velocities, in principle, there is enough H$_2^+$ in the interaction region so that following the cleaning pulse, a second electron gun called the "probe" can be pulsed through the interaction region to dissociate the H$_2^+$. Protons from the dissociation of H$_2^+$ then drift through a 12-cm field-free time-of-flight region into a 0.27 steradian collection cone between 17 and 24 degrees in the forward direction. Protons from the dissociation of H$_2^+$ are then focussed into a Channeltron detector by a cylindrical mirror lens. The source gun must be operated at energies well below 18 eV to avoid dissociation of residual neutral H$_2$.

After numerous attempts, this experiment has been abandoned because of extremely low counting rates and background problems.

D. Coincidence detection of H(2S) and H$^+$ from dissociation of H$_2$

We are presently attempting to detect, in coincidence, H$^{}$(2S) and H$^+$ fragments which move in opposite directions from an interaction region where an electron beam crosses an H$_2$ gas target. There are at least two known excited, dissociating states of H$_2^+$ that come apart yielding these two fragments. We hope to eventually be able to measure the kinetic energy distribution of these fragments using our usual time-of-flight method.

We have constructed an experimental arrangement which has oppositely directed flight paths extending from a central interaction region. Preliminary tests are underway.
E. Dissociation of H$_2$O and H$_2$S

We are well underway on a study of proton kinetic energy distributions from dissociation of H$_2$O and H$_2$S at electron energies from 20 to 50 eV. We are using our computer-controlled electron gun to measure threshold bombarding energies for observed features in the kinetic energy spectrum. Examples of preliminary data are shown in Fig. 2.

References

II. Personnel

We list below personnel associated with this research program:

Principal investigators:

W. E. Lamb, Jr.
B.S. (Chemistry) University of California (Berkeley) 1934
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L.H.D. Yeshiva University 1965
D.Sc. Gustavus Adolphus College 1975

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Ph.D. (Physics) University of Wisconsin 1965

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Ph.D. (Physics) University of Chicago 1969

Research Assistants:

Richard Cordaro
B.A. Millersville St. College, Penn. 1973
M.S. (Physics) Lehigh University 1978

Bruce Kittams (left Aug. 1984)
B.S. Oregon State University 1971
M.S. (Physics) University of Arizona 1981

Hyuck Cho
B.S. Sogang University, 1975
M.S. Sogang University, 1977
FIGURE 1

Apparatus For
Electron Impact Dissociation of H$_2^+$

- Guard Rings
- Cylindrical Mirror Electrodes
- Wire Grids
- Spherical Screens
- Faraday Cup
- Cleaning Electrode
- Guide Nozzle
- Detector
- Time of Flight Region
- Diffusion Pump #1
- Diffusion Pump #2

Sample Ion Trajectory (red)
TOF $H^+ / H_2S$ 37.2 cm

JULY 12, 1984 CORDARO

ENERGY (UPPER TO LOWER)
- 45 eV
- 35 eV
- 30 eV
- 25 eV

TOF $H^+ / H_2O$ 37.3 cm

JUNE 27, 1984 CORDARO

INTENSITY (ARB. UNITS)

TOF IN µS