

OPTICAL SIGNATURES OF MOLECULAR PARTICLES VIA
MASS-SELECTED CLUSTER SPECTROSCOPY

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ABSTRACT

A new molecular beam apparatus has been developed to study optical absorption in cold ($< 100\text{K}$) atomic clusters and complexes produced by their condensation with simple molecular gases. In this instrument, ionized clusters produced in a laser vaporization nozzle source are mass selected and studied with photodissociation spectroscopy at visible and ultraviolet wavelengths. This new approach can be applied to synthesize and characterize numerous particulates and weakly bound complexes expected in planetary atmospheres and in comets.

INTRODUCTION

The extreme conditions present in the atmospheres of the inner and outer planets produce an abundance of unusual chemical species, including small molecular radicals and ions, in the presence of more common molecules formed from the lighter elements. At the characteristic low temperatures ($< 100\text{K}$), condensation phenomena produce small elemental molecules (atomic clusters) as well as neutral or ion-molecule complexes. Condensation produces a distribution of particles ranging in size from molecules to dust grains. In a dynamic interaction with condensation there are photon-induced ionization and dissociation processes. The details of these chemical and physical processes are critical to an understanding of the formation and ongoing evolution of the solar system.

Optical spectroscopy is a time honored method to study planetary atmospheres, which can be accomplished from earth-based observatories or from more direct probes such as the Voyagers or Galileo. However, laboratory measurements are essential to aid in the assignment and interpretation of atmospheric spectra. Unless these laboratory measurements reproduce the extreme temperature and pressure conditions in planetary atmospheres, it is impossible to generate the desired molecules in the appropriate quantum levels to replicate observed spectra. Until recently, the required conditions could not be generated in the laboratory. However, new molecular beam experiments, particularly those in the interdisciplinary area of "cluster science," have made it possible to produce a variety of atomic and molecular aggregates at ultracold temperatures. When combined with new laser spectroscopy methods, the optical absorption and photodissociation processes of these complexes can be characterized. We describe here the applications and potential of this new cluster beam technology for the study of molecular aggregates important in planetary atmospheres. For ionized particles, these experiments provide size selected optical spectra.

EXPERIMENTAL

The molecular beam apparatus for these experiments has been described in the literature.^{1,2} It employs laser vaporization of solid samples in a pulsed supersonic expansion to produce a variety of atomic and/or molecular clusters at temperatures of 50-100K. This source produces neutral and/or ionic atomic clusters of virtually any metal, semiconductor, or non-metal material (M_x , where $X = 2-50$). A modified version of the source produces metal/molecular mixed complexes of the form $M R_y$ where M is a metal or semiconductor atom and R is a rare gas atom or small molecule (e.g. $Al^+(CO_2)_7$). In principle, it is now possible to synthesize virtually any atomic or molecular aggregate in this source. These conditions are the closest laboratory approximation to those in outer planetary atmospheres.

Clusters or complexes produced in this source may condense directly as ions or they may be ionized downstream with ultraviolet lasers. For mass selected spectroscopy we use ions produced in the source which have been supersonically expanded and are therefore internally cold. Mass selection occurs in a reflectron time-of-flight spectrometer system developed in our laboratory² and shown in Figure 1. Cold ions are extracted from the molecular beam by pulsed acceleration voltages. They are mass selected by their time-of-flight through an initial drift tube section. Undesired ions are rejected, and the selected size transmitted, with pulsed deflection plates located just before a reflection grid assembly. The reflection assembly decelerates the selected ions with an electric field. At the turning point in the ion trajectory a tunable laser irradiates the ions. Photodissociation may occur if the incident light is resonantly absorbed and if the one-or multiphoton energy exceeds the threshold for dissociation. When dissociation occurs, parent and fragment ions are mass analyzed in a second drift tube section. This process identifies photodissociation products, while the depletion in the parent ion channel provides a measure of the photodissociation cross section. Dissociation spectra are recorded by monitoring the appearance of a selected parent ion as a function of the dissociation laser energy.

Figure 2 shows an example of a new photodissociation spectrum for the diatomic cation Te_2^+ obtained with this instrument.³ The features shown are assigned to the vibrationally resolved $A^2\Pi \leftarrow X^2\Pi_{g,1/2}$ electronic transition, observed near 670 nm. Analysis of this spectrum yields the ground and excited state vibrational frequencies (279 and 199 cm^{-1}) and the excited state anharmonicity (0.5 cm^{-1}) and dissociation energy ($D_e = 2.27$ eV). The cross section for photodissociation is approximately 1×10^{-18} cm^2 . In principle, rotationally resolved spectra could be obtained with this method using narrower bandwidth lasers and lighter molecules. In addition to Te_2^+ , we have recently observed similar spectra, which are not yet completely assigned, for Bi_2^+ , Al_2^+ and S_2^+ . Other experiments in our laboratory have used fixed energy lasers to probe product channels and dissociation cross sections for atomic clusters of carbon, sulfur, silicon, aluminum and silver, and for metal/molecular complexes of aluminum/benzene and aluminum/acetone.

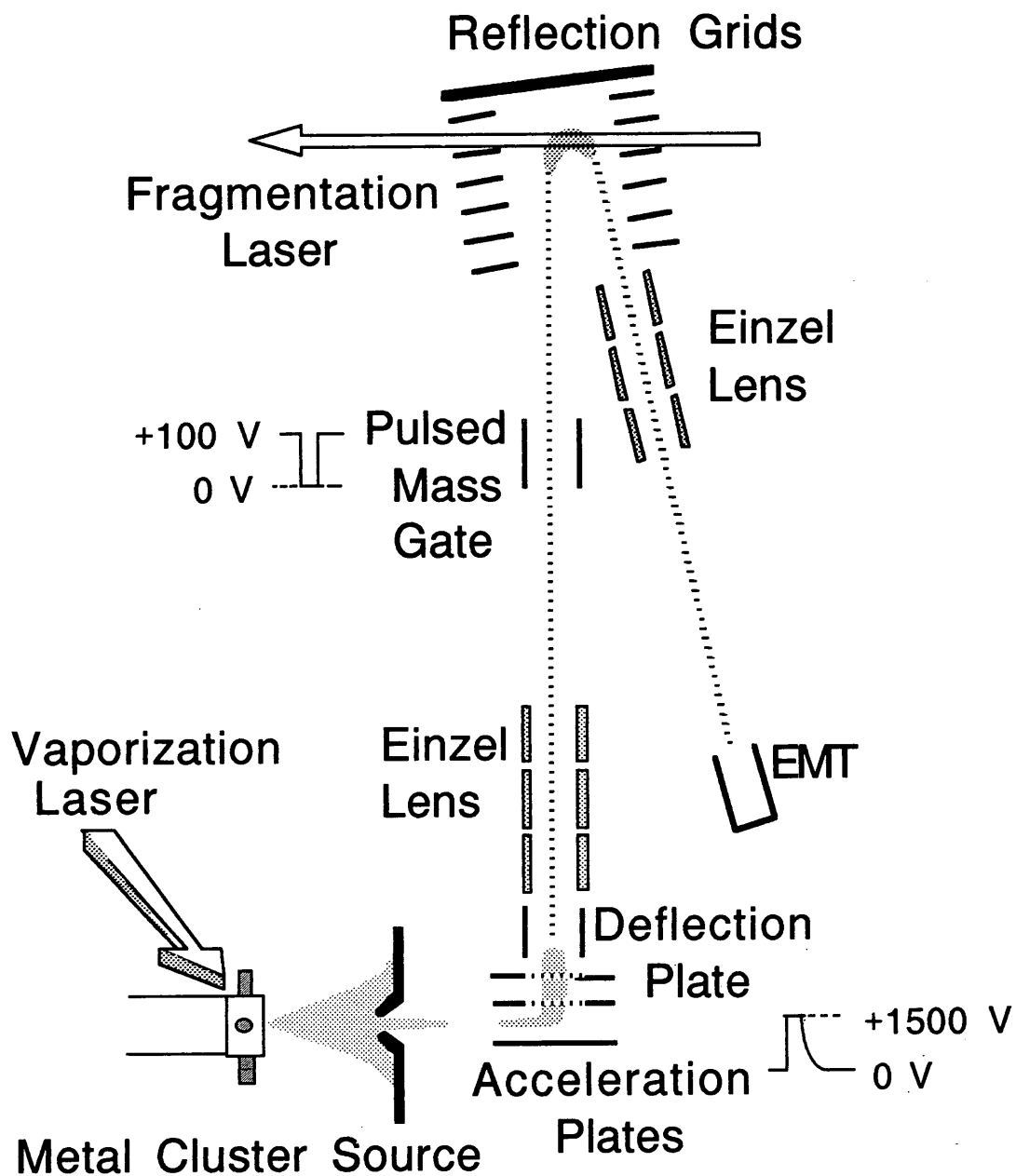


Figure 1. The reflectron mass spectrometer system used for mass selection of cluster particles followed by photodissociation spectroscopy.

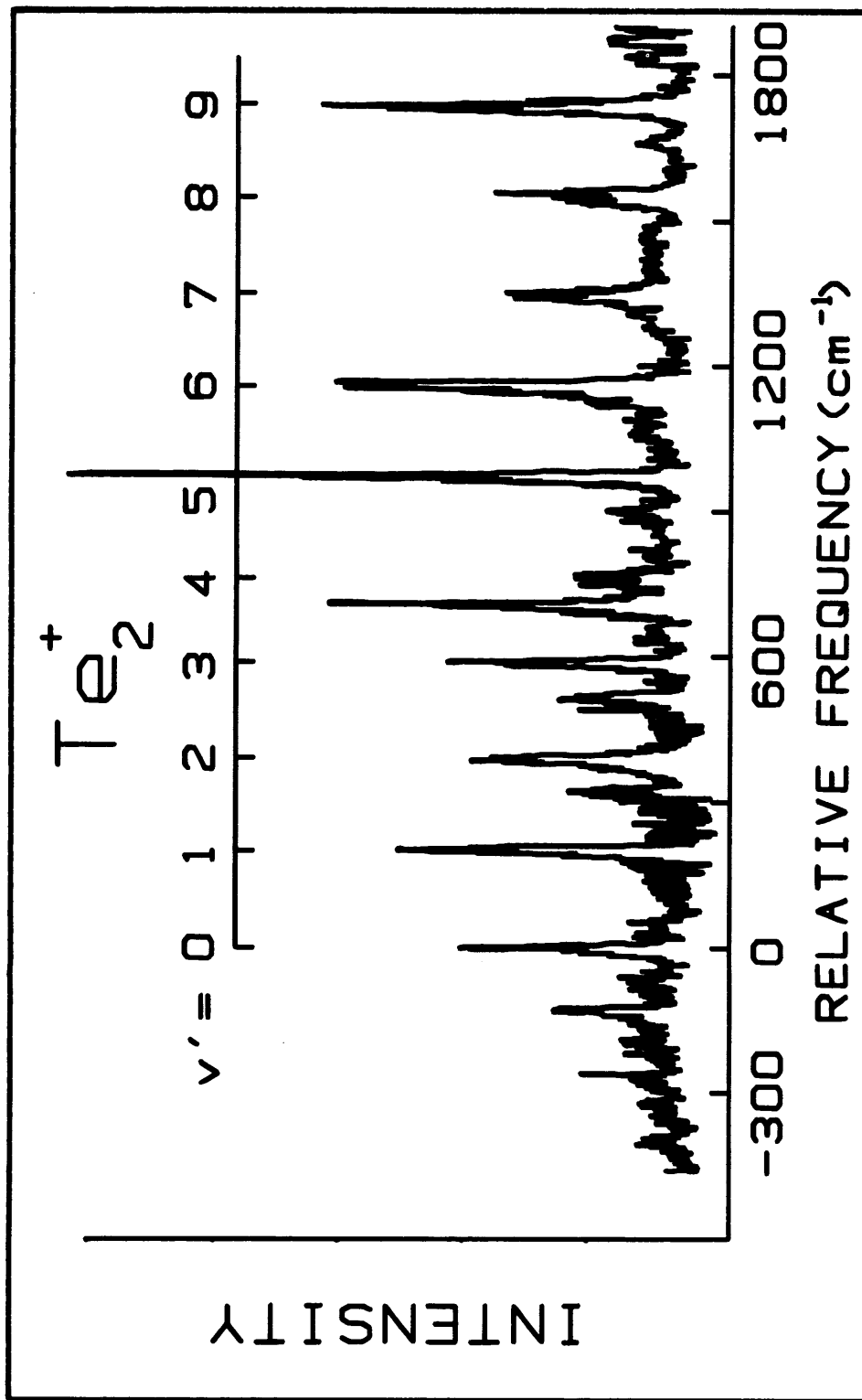


Figure 2. The photodissociation spectrum of Te_2^+ near 670 nm.

FUTURE EXPERIMENTS ON PLANETARY ATMOSPHERIC SPECIES

Ongoing and future experiments in our laboratory will focus on the optical photodissociation spectra of carbon and sulfur atomic cluster cations. There are existing fixed frequency data for carbon cluster cations, but no spectra.⁴ Except for our own recent data, there are no photodissociation data for sulphur. Carbon clusters are expected to be important in the formation of dust particles and ice grains in environments such as cometary comas. Elemental molecules of sulfur are expected in the atmosphere of Venus. Similar experiments will focus on ion-molecule complexes of silicon or aluminum with light molecules (e.g. $Al^+C_2H_2$), with which are also likely constituents of cometary comas.

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