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PHYSICS WITH FAST MOLECULAR IONS*

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ABSTRACT

Argonne's 5-MV Dynamitron accelerator is currently being used to study the interactions of fast (MeV) atomic and molecular ions with matter. The present emphasis of the work is upon the problem of determining the stereochemical structures of molecular-ion projectiles. The technique is based upon the "Coulomb explosion" of these projectiles when they strike a thin-foil target. By making careful determinations of the momenta of all of the fragments emitted from these Coulomb explosions, one can infer the original configuration of the molecular constituents in the projectile and, in favorable cases, their vibrational motions. This technique is particularly useful for those cases where the more traditional spectroscopic approaches cannot be applied. During the past year, new ideas and developments in the Coulomb-explosion technique have come to fruition. Radically new multiparticle detectors have been developed and implemented. Extremely thin film targets have been produced which reduce the "blurring" effect of multiple scattering, and a low-excitation ion source has been installed. These developments have resulted in direct measurements of the complete stereostructures of several small polyatomic molecular ions. In this paper we describe the experimental techniques, discuss some of the difficulties, and present some recent results.

I. INTRODUCTION

Of the many ionic species that normally emerge from the ion source of an electrostatic accelerator, it has traditionally been only the monatomic ions that are considered to provide "useful" beams. The remaining beams of molecular ions (H_2^+ , H_3^+ , HeH^+ , OH^+ , etc.) which frequently constitute most of the total ion-beam current, are seldom exploited for experimental purposes.

In recent years, however, it has been realized that many important phenomena in atomic and molecular physics can be addressed using fast molecular-ion beams. In research with such beams experimenters take advantage of the spatial and temporal correlations of the constituents of the molecular projectiles. These correlations persist during the dissociation process initiated when a molecular ion strikes a target foil. Experiments with fast molecular ions are providing interesting new information, for example, about the charge states of fast ions

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inside and outside solids, the interactions of such ions with a solid medium, and a variety of other atomic-collision phenomena. These studies can also be applied to the often difficult problem of determining the geometrical structures of molecular ions.

In more traditional experimental techniques used to derive the stereochemical structures of molecular ions, the difficulty in obtaining a sufficient column density of the ions to be studied presents a severe limitation. Thus, for example, photon emission or absorption techniques usually involve searching for extremely weak or narrow lines in the presence of intense background radiation. Where such methods have been successfully applied, they result in very precise structure determinations. However, it has so far only proved possible to measure a handful of molecular-ion structures with these "standard" techniques. (This situation contrasts strongly with that for neutral molecules for which the experimental problems are much less severe and for which thousands of structures have been determined.)

We report here on recent research on molecular-ion structures using fast molecular-ion beams provided by Argonne's 5-MV Dynamitron accelerator. The method has become known as the "Coulomb-explosion" technique. Related work is also in progress at other laboratories, notably the Weizmann Institute of Science in Israel and Sichuan University in China.

II. METHOD

When molecular-ion projectiles travelling at velocities of a few percent of the velocity of light strike a foil, the electrons that bind the molecular projectiles are almost always totally stripped off within the first few Angstroms of penetration into the solid target. Thus the stripping time is typically $<10^{-16}$ sec. This leaves a cluster of bare (or nearly bare) nuclei which separate rapidly as a result of their mutual Coulomb repulsion. This violent dissociation process in which the initial electrostatic potential energy is converted into kinetic energy of relative motion in the center-of-mass, has been termed a "Coulomb explosion".

The characteristic time for this explosion is typically on the order of a femtosecond (10^{-15} sec). In comparison, typical periods for molecular vibrations ($\sim 10^{-14}$ sec) and rotations ($\sim 10^{-12}$ sec) are much longer. The explosion time is on the same order of magnitude as the dwell time for the projectile if the foil thickness is approximately 100 Å. (Recent experiments have employed even thinner foils--see below.) As a result, the Coulomb explosion takes place partially inside the foil and then runs to completion in the vacuum downstream after the fragments emerge from the target.

The dissociation fragments emerge from the foil with velocities equal to the original beam velocity combined with components resulting from the Coulomb explosion. These components cause shifts in the laboratory energy and angle for each fragment; the shifts depend on the structure and orientation of the incoming molecule. Because all

orientations are equally populated in the incident beam, joint distributions in energy and angle for the emerging fragments are ring-like in character. The diameter of the ring for a given fragment is determined by the stereochemical structure of the molecular projectile. For diatomic projectiles the ring diameter reflects the bond length for the projectile and the "thickness" of the ring reflects the distribution of internuclear separations and thus the vibrational excitation of the incident molecules. An example¹ of such a ring pattern obtained for 3-MeV HeH^+ ions is shown in Fig. 1. Since the shifts in energy and angle are small, it is essential that experiments of this type be performed with high resolution. At Argonne's Dynamitron accelerator² the relative energy resolution is typically $\Delta E/E = \pm 3 \times 10^{-4}$ and the overall angular resolution is $\Delta\theta = \pm 1.5 \times 10^{-4}$ radian. Data of the type shown in Fig. 1 have been analyzed^{1,3,4,5} to provide the first experimental determination of the bond length of the HeH^+ molecular ion together with information about the spectrum of vibrationally excited states in the incident beam.

In 1978 the Coulomb-explosion technique was expanded to examine the structures of polyatomic molecular ions. A joint study of the simplest such ion, H_3^+ , was undertaken at the University of Lyon, the Weizmann Institute, Argonne National Laboratory, and subsequently at Sichuan University. Each laboratory performed a measurement based on the Coulomb explosion of fast H_3^+ ions. Although somewhat different techniques were used, the four measurements gave results in agreement with one another and it was experimentally demonstrated for the first time that H_3^+ is equilateral triangular in shape.^{6,7} About the same time, studies at Argonne⁸ with 3.5-MeV beams of CO_2^+ and N_2O^+ were able to verify the known linear structures of these ions in their low-lying states and to demonstrate the order in which their constituent atoms lie (O-C-O and N-N-O).

These and other early studies⁴ on the Coulomb explosion of polyatomic molecular ions served not only to demonstrate the power of the technique, but also some of the difficulties. In the remainder of this Section we list some of these problems and the way that they have been attacked in continuing experimental studies at Argonne National Laboratory.

Firstly, there are difficulties associated with the use of a foil target. Foils (rather than gaseous targets) are desirable for inducing the molecular-ion fragmentation since small-impact-parameter collisions dominate, thereby leading to energetic Coulomb explosions which can be measured very precisely. Also, heavy ions take on a well-defined effective charge while inside a solid target. During their traversal of the foil the ionic fragments suffer both energy loss and multiple scattering. This leads to an effective blurring of the resolution in Coulomb-explosion studies. Energy-loss straggling contributes to the loss of precision in the longitudinal direction and multiple scattering in the transverse direction. In addition, there are "wake forces" that influence the motions of the cluster of ionic fragments inside the foil (see, for example Ref. 9). To minimize the impact of these three factors, one uses foils that are as thin as possible and that contain

low-Z elements. It turns out that of the three factors alluded to above, multiple scattering is by far the most damaging. At Argonne a careful study¹⁰ of the foil problem has resulted in the now-routine use of $\sim 0.3\text{-}\mu\text{g}/\text{cm}^2$ Formvar films supported on a nickel mesh. These films are estimated to be about 30 Å thick. In terms of Coulomb-explosion measurements, this thickness means that the multiple-scattering contribution to the angular distributions of the fragments from, for example, 4.5-MeV H_2O^+ ions is about half the width of the distributions due to bond-length variations in the molecular ion because of zero-point vibrations.

Further experimental difficulties occur when one tries to characterize the quantum states of the molecular projectiles incident upon the target foil. Ideally, one would like to have the projectiles in a single, well-defined electronic and ro-vibronic state (e.g., the ground state). In practice this is difficult to achieve and a range of excitations is usually obtained. A few years ago Coulomb-explosion experiments¹¹ demonstrated dramatically that HeH^+ beams produced in an rf ion source were vibrationally much "hotter" than beams produced in a duoplasmatron. Recent work at Argonne on the Coulomb explosion of polyatomic molecular ions¹²⁻¹⁴ has been based upon the use of ion beams produced by low-energy electron impact upon a parent gas. The ionization threshold for the desired molecular ions was determined from measurements of the accelerated molecular-ion beam currents as a function of the electron kinetic energy. The Coulomb-explosion experiments were then performed with the electron energy set ~ 0.5 V above the measured ionization threshold. This procedure provided beams with excitations believed to lie in a narrow band near the ground state. Flight times from the ion source to the dissociation foil are typically 5-10 μs . Work is also under way at Argonne¹⁵ on a state-selective ion source in which molecular ions are produced by photoionization with a UV lamp. The plan here is to extract ions from the source when they occur in coincidence with electrons feeding specific residual states. Thought is also being given to the possibilities of preparing molecular ions in specific states excited by lasers. At the Weizmann Institute fast neutral molecules are produced by threshold photo-detachment from negative ions using a laser beam.

Data of the type shown in Fig. 1 were taken using a set of electrostatic "post-deflector" plates located just downstream from the foil target to disperse the molecular fragments in a horizontal plane. Those fragments entering the small entrance aperture of an electrostatic analyzer located several meters downstream from the target, were analyzed according to their energies and charge states. It was early recognized, however, that to extend the technique, a detection system would be needed that enabled the complete measurement of both longitudinal and transverse components of all fragments emerging from the dissociation of the molecular projectiles. Various "intermediate" solutions to this problem have been implemented including, for example, photographic detection and electronic-imaging techniques^{6,16}. (These provide information on the transverse component of the Coulomb-explosion momenta only). At Argonne we used a system of movable silicon detectors in coincidence with the electrostatic analyzer.⁴ However, none of these

approaches was really satisfactory. A significant step forward was made with the development of a multiparticle avalanche detector¹⁷ that allowed, for the first time, the simultaneous determination of the positions (to an accuracy of ~ 0.1 mm) and times of arrival (to an accuracy of ~ 0.1 nsec) of all of the fragments from molecular-ion projectiles containing up to about six atomic constituents. The apparatus at Argonne has recently undergone modifications to permit the simultaneous use of two large-area (~ 30 cm dia.) position- and time-sensitive multi-particle detectors -- one intended for use with heavy fragments and one for light fragments (usually protons).

The remaining major difficulty with the Coulomb-explosion technique, when applied to more complex molecular ions, lies in the data analysis. For projectiles containing N atoms, each dissociation produces N ionic fragments which are detected in coincidence. The positions and times of arrival of each ionic fragment are converted, on-line, into the "cluster velocity vector". This $3N$ -dimensional velocity is reduced by subtraction of the center-of-mass velocity to give a $(3N-3)$ -dimensional vector for every projectile analyzed. By accumulating data for a large number of projectiles, an ensemble of these $(3N-3)$ -dimensional vectors in velocity space can then be analyzed to provide the mean velocity vector for each fragment and also the associated variances and covariances. Ideally, of course, one would like to derive from the measured data the original spatial positions of the nuclei in the projectile together with the variances and covariances of these positions. In general, this presents a formidable computational problem, even assuming that one can find a reasonable approximation for the interatomic potentials. A considerable amount of effort is currently being invested¹⁸ into the search for suitable analysis techniques to obtain this type of spatial information. However, much can be learned about the spatial structure by contemplating the data in velocity space. This includes certain symmetry properties. Also, if one assumes pure Coulomb forces between atoms represented as point charges, approximate values can be derived for the spatial coordinates and their variances and covariances.

III. SOME RECENT RESULTS

(1) Direct determination of the stereochemical structure of CH_4^+

CH_4^+ has been the subject of numerous theoretical and experimental studies. One of the major reasons for the interest in CH_4^+ is that it is one of the simplest cases in which a Jahn-Teller distortion from symmetry is predicted. Despite this well-known prediction, this ion's structure had not hitherto been established. Coulomb-explosion data measured recently at Argonne¹² (Figs. 2 and 3) clearly demonstrate the C_{2v} symmetry of the molecule, consistent with the recent findings of electron-spin-resonance (ESR) spectroscopy. These data have allowed us to measure not only mean geometries (bond lengths and bond angles), but the deviations within our sample from those averages. The results demonstrate the power of these techniques not only to study mean geometries of polyatomic molecules, but also to measure directly the vibrational motions of the constituent nuclei.

(2) Low-energy stereostructure of $C_2H_3^+$

The problem of determining the low-lying structure of $C_2H_3^+$ has received considerable attention largely because of the important role such protonated hydrocarbons are thought to play in the chemical evolution of interstellar clouds. Unfortunately, laboratory spectroscopy of such molecules has been difficult. Recent Coulomb-explosion results¹³ demonstrate that the nonclassical bridged structure dominates (Fig. 4). Although our analysis techniques are not yet sufficiently refined to discern small admixtures of rare structures, we have been able to place an upper limit of at most 15% of our sample displaying the classical structure (however, this is merely an upper limit and the data are also consistent with none of that structure). This hinted very strongly that earlier theoretical predictions were incorrect and prompted further exploration of the potential surface in higher-order calculations. These now verify that the classical structure is in fact not a potential minimum but rather a saddle point, in agreement with our result.

(3) The Geometrical Structures of C_3^+ , $C_3H_3^+$, and $C_3H_4^+$

Although C_3^+ is considered to be the fundamental building block of larger carbon clusters, the geometry of this molecule is unknown. Several authors have reported results of ab initio calculations in which the optimized geometry of the ion is deduced, assuming a linear configuration,¹⁹ in agreement with the structure of the neutral C_3 molecule. Results¹⁴ on the Coulomb explosion of C_3^+ suggest that, contrary to theoretical expectations, the ground state of this ion forms a rigid ring. This finding has prompted higher-order ab initio calculations that have now borne out this conclusion. Figure 5 shows data obtained in velocity space for the ions C_3^+ , $C_3H_3^+$, and $C_3H_4^+$. To derive the data shown in the figure, the three velocities for the carbon ions in each exploded molecule were first ordered with $v_a < v_b < v_c$ and then the quantity $R_s = (v_a + v_b)/v_c$ derived. Thus R_s lies between 1 (corresponding to linear molecules) and 2 (corresponding to an equilateral geometry). While it is not possible to deduce the spatial geometries directly from the velocity-space data, comparisons of such distributions for different structures provide a rapid and simple means of finding similarities in the stereo-chemistries of such molecules. The data in Fig. 5 suggest that C_3^+ and $C_3H_3^+$ have a ring-like carbon structures whereas $C_3H_4^+$ appears to be linear.

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Figure Captions

- Fig. 1. Joint distribution in energy and angle for protons from the dissociation of 3-MeV HeH^+ ions incident on a 195-Å-thick carbon foil. The diameter of this ring pattern is mainly determined by the bond length in HeH^+ . The width of the "rim" reflects variations in the internuclear distance of the incident molecular ions due to their vibrational motion. The nonuniform distribution of intensity around the ring can be accounted for quantitatively in terms of forces due to the polarization "wakes" generated by the ions as they traverse the foil.
- Fig. 2. A density plot of the projection on the plane of the MUPPATS detector of the images of fragment ions resulting from the Coulomb explosion of CH_4^+ ions. The hexagon denotes the active area of the detector. The protons, and various charge states of carbon ions, have been separated by electrostatic deflection in the x direction.
- Fig. 3. Contour plots of the densities of protons in velocity space (relative to the projectile center of mass) following the event-by-event rotations described in the text. The ensemble mean for the carbon-ion position is marked by (x). The data consist of five-fold coincidences between four protons and one C^{3+} ion for each event. (a) Projection on the X-Z plane as defined in the text. (b) Projection on the Y-Z plane. Contour levels are at 1.5%, 2.5%, 4%, 7%, 11%, and 19% of the peak intensity.
- Fig. 4. Plots of the densities of fragment ions measured in velocity space (relative to the mean carbon-ion velocity) following the foil-induced dissociation of 4.5-MeV C_2H_3^+ . The carbon-ion densities have been artificially reduced by a factor of 5 for display purposes. Above: isometric display of the nuclear density projected onto the plane containing the two carbon nuclei and the bridging proton. Below: contour plot of the same data.
- Fig. 5. Measured distributions for the ratio R_s , as described in the text, for the carbon fragment ions (all C^{2+}) resulting from the dissociation of 4.5-MeV C_3^+ , C_3H_3^+ , and C_3H_4^+ . The ordinate represents the actual number of molecules for the case of C_3^+ . The data for C_3H_4^+ are normalized to yield the same integral as the C_3^+ data while the distribution for C_3H_3^+ has been arbitrarily scaled. Error bars represent the effect of sampling statistics only. The lines are drawn to guide the eye.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5