Coulomb Explosion Imaging of Small Molecules

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Most of our knowledge of the structures of free molecules comes from indirect observations that focus on other properties (for example, energy or mass spectra) that depend on structure. Recently, a new method has been developed that instead yields geometrical images of individual molecules. This method takes advantage of the large Coulomb repulsion of the nuclei within molecules rapidly stripped of their electrons. The first experiments with this new technique have already revealed structural images of several important species, such as positively charged methane ions.

FOR MOST PEOPLE, THE WORDS "MOLECULAR STRUCTURE" are associated with a mental model in which a molecule is pictured as a set of colored balls (representing atoms) and connected at precise angles and distances by rods representing chemical bonds. The theory underlying this "rods and balls" model is well established and based on several crucial physical properties of real molecular systems. Among these properties, the most important is the large difference between the masses of the constituent nuclei compared to those of the binding electrons. The light electrons move at much greater velocities than the heavy nuclei. Therefore, to a good approximation, the positive nuclei are imbedded in an average cloud of negatively charged electrons. Insofar as the slow nuclei are concerned, the cloud of electrons can be represented by an attractive potential that is a function of the nuclear coordinates (*1*). The lowest energy state of the molecule is reached when the nuclei are arranged in the configuration corresponding to the minimum of this potential.

For many molecules, the widths of the potential minima are so narrow that the amplitude of the vibrational motions of the nuclei is small compared to the average internuclear distances. This is the other important ingredient of the simple picture. For such rigid molecules (for example, H_2O or CO_2), there are extremely refined theoretical models that can provide detailed descriptions of these molecules on the basis of measurements of the rotational and vibrational spectra. The success of the theory to verify and predict the experimental results stems from the rigidity of the molecules involved. This rigidity leads to the notion of three different time scales: the short scale of electronic motions, the intermediate range of vibrational motions, and the slow rotations of the whole molecule. Relatively simple models, which incorporate the separation of these different motions, are thus very successful when applied to rigid systems.

However, not all molecules are sufficiently rigid to justify this simple picture. Important practical examples of nonrigidity are highly excited molecules with enough energy for isomerization or dissociation. In general, all molecules at high excitation will display behavior characterized by large amplitude vibrations. In such circumstances, the separation of vibrations and rotations loses its validity. For atomic clusters and van der Waals molecules (such as nitrogen dimers), the floppiness occurs even for low-lying states. These molecules cannot be described by the "rods and balls" models. The structures in these cases need to be defined by mathematical density functions. In quantum mechanical terms, these are simply related to the wave functions. Such descriptions correlate the complex motions of the molecular constituents so that all possible aspects of the motions are contained in the density function.

While spectroscopic studies of such systems can be quite revealing, that information does not yet provide as complete a description as has been achieved for rigid molecules (*2*). In the last several years, however, new experimental methods, being developed jointly in our laboratories at Argonne National Laboratory and the Weizmann Institute of Science, have demonstrated that it is possible to measure the density functions for a broad variety of polyatomic molecules (*3*). Although not as precise as alternative studies of rigid molecules, these new methods provide direct maps of the geometries and thus require no a priori assumptions about the molecule. Hence, these methods are appropriate for studying rigid and nonrigid systems alike. As will be described in the following section, the raw data obtained in these experiments consist of a set of multidimensional vectors. Each vector characterizes the geometry of an individual molecule in a beam. Such measurements provide all of the information, including correlations, necessary to completely describe the structure of the molecule under investigation.

Coulomb Explosion Imaging

To understand the new method, consider the case of CH_4^+ (see Fig. 1). The ensemble of molecular ions to be studied is prepared in a defined environment, the ions are accelerated to a velocity of approximately 2% of the speed of light, and then passed through a thin solid film (in our experiments ~30 Å thick). While in the solid, the probability for Coulomb scattering of the projectile nuclei out of the beam (to angles $>10^{-4}$ radian) is small. However, the projectile electrons will be scattered to very large angles by many encounters with the electrons present in the dense solid target. As a result, these scattered electrons will be separated from the projectile molecule after penetrating a few atomic layers. According to the Bohr criterion (*4*), any electron whose orbital velocity is less than the projectile velocity will be stripped in this way. Thus, except for the

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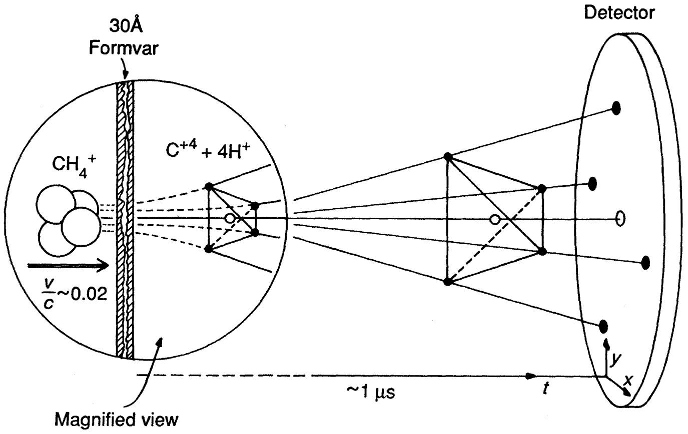

Fig. 1. A schematic view of a Coulomb explosion experiment. When a swift molecule passes through a thin solid film, it loses all of its binding electrons. The remaining positive ions repel each other, thus transforming the microstructure (as seen in the magnified view) into a macrostructure that can be measured precisely with an appropriate detector. The measured traces (x, y, t) of each fragment nucleus for individual molecules are then transformed into the original molecular structure.

tightly bound K-shell electrons of the carbon atom, all of the electrons will be removed. Typically, this stripping process is complete within approximately 10^{-16} s after the projectile enters the solid. This time scale is faster than any characteristic motions of the nuclei, such as vibrations ($>10^{-14}$ s) or rotations ($>10^{-12}$ s) within the molecule.

This fast stripping marks the zero time for a new regime in which the molecule dissociates rapidly (*5*). Because the nuclei are rotating and vibrating, the geometric relationships of the constituent nuclei will be different at time zero (t_0) for each molecule in the beam. In the language of quantum mechanics, the density matrix describing these relationships of the nuclei at t_0 is identical to the stationary density matrix of atoms within the molecules. Thus, the geometric relations of the nuclei at t_0 contain all of the structural information of the initial ensemble of molecules.

After t_0, the resulting aggregate of positive ions explodes owing to their mutual Coulomb repulsion, hence the term Coulomb explosion. The evolution of the distribution in time under the influence of the Coulomb Hamiltonian is well defined. The final density function describes the motions of free ions and can be expressed in terms of the velocity of the center-of-mass of the molecule and the relative velocities of the fragment ions. Therefore, the measurement of all of the velocity components of all of the emerging fragments ions resulting from the Coulomb explosion of each individual molecule in our ensemble provides us with a density distribution that has all of the information necessary to describe the stereostructure of the originally prepared ensemble of bound molecules.

This point can be illustrated by referring to our example of CH_4^+. Consider at t_0 a single molecule with the following five spatial vectors defining the positions of the carbon nucleus and protons respectively: $\mathbf{r}_C$, $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_4$. For simplicity, ignore the proton-proton interactions as compared with the stronger carbon(4+)-proton forces. Under such conditions, the H–C–H angles are preserved in the explosion and the potential of each C–H pair is converted to kinetic energy as follows:

$$\frac{4e^2}{|\mathbf{r}_C - \mathbf{r}_n|} = \frac{\mu\,|\mathbf{V}_C - \mathbf{V}_n|^2}{2} \qquad (1)$$

where μ is a reduced mass and $\mathbf{V}_C$ and $\mathbf{V}_n$ are the measured final velocities of the carbon nucleus and the nth proton, respectively, and e is the electronic charge. The kinetic energy preceding the explosion is negligible compared to the Coulomb energy and thus, a measurement of the final vector velocities completely defines the initial geometry of the molecule. Corrections for the proton-proton interactions can be determined by numerical solution of the equations of motion (*6*).

If we define the 15-dimensional vector $\mathbf{R}(i) = \{\mathbf{r}_C(i), \mathbf{r}_1(i), \mathbf{r}_2(i), \mathbf{r}_3(i), \mathbf{r}_4(i)\}$, representing the geometry of the ith molecule in a sample of N molecules, then the N measured **R**-vectors form an ensemble for estimating any observable quantity that depends on the structure. For example, if the ensemble includes only CH_4^+ ions in their ground states, then the density of the measured **R**-vectors in configuration space is simply the square of the nuclear ground-state wave function. It is important to realize that such data describe not only the three-dimensional densities of finding a single nucleus within the molecule, but also all possible correlations between the constituent nuclei. Such a direct measurement of the square of the multidimensional wave function of a many-body system is a challenge by itself that, as far as we know, has never been achieved in any field of physics.

The symmetry properties of molecules play a crucial role in the theory of molecular structure. When a molecule contains one or more groups of identical atoms, then the structural density function is invariant under permutations of those identical particles. It is important to realize that in a Coulomb explosion experiment, it is possible to select molecules in which the identical fragment ions have the same charge. This selection ensures that the final velocity density distribution preserves the permutation symmetry. Therefore, for many cases, it is possible to identify important structural symmetry features and correlations from the density distributions of the raw experimental data.

Experimental Arrangement

In order to carry out such measurements, there are two major experimental problems: (i) the preparation of the molecular ensemble to be studied and acceleration to sufficiently high velocity and (ii) the detection and identification of the emergent fragment ions, and measurements of their vector velocities, following dissociation in the foil.

In the apparatus in use at Argonne, the molecules are accelerated as positive ions by a 5-million-volt Dynamitron electrostatic accelerator. Most of the experiments to date have used low-energy electron impact on various gases in the high-voltage terminal of the accelerator to produce the molecular ions studied. After acceleration, the fast molecular ions are magnetically analyzed, to select the proper mass/charge ratio, collimated, and then steered toward the stripper film.

While this arrangement has so far been limited to positive ions, the Weizmann Institute work has stressed the study of neutral species. In those experiments, the beam preparation starts with bunches of mass-selected negative ions. These ions are then accelerated from ground potential to the 14-million-volt terminal of a Pelletron tandem accelerator. When a bunch of ions reaches the field-free terminal region, it is struck by a 10-ns pulse from a tunable dye laser. The laser pulse serves to photodetach (and sometimes photodissociate) the negative molecular ions, and this produces swift neutral molecular beams. These fast neutral molecules emerge from the accelerator and, after magnetic deflection of the charged components, are dissociated in a thin stripper film.

The basic principle behind the velocity measurements is as follows. The laboratory velocity of the molecular beam is $V \sim 0.02c$ (where c is the speed of light). In the center-of-mass of the moving molecule, the final velocities of the fragment ions after the Coulomb explosion are typically $u \sim 0.0004c$. The molecular fragments are then restricted to a cone with half-angle $\theta = u/V \sim 0.02$ radian. An accuracy of a few percent in bond lengths requires a similar accuracy in the determination of θ, hence $\delta\theta \sim 0.4 \times 10^{-3}$ radian for all components of **u**. The components of **u** transverse to the beam direction are determined by measuring the position of impact (x,y) on the detector plane, while the longitudinal component is given by the relative time-of-flight (t) of each fragment. In these experiments, the principal limitation on the accuracy of measuring the velocity components is determined by the time resolution. A detector with a time resolution ~0.4 ns then necessitates a flight time of around 1 μs (or a corresponding flight length of 5.5 m). These dimensions correspond to the Argonne apparatus.

Another important requirement for the detector is the ability to detect several ions arriving simultaneously (or at most 10 to 20 ns apart). At Argonne, these requirements have been met with a specially designed low-pressure multiwire proportional counter (*7*). In the Weizmann Institute experiments, a microchannel plate is used with a hybridized anode consisting of both wire planes and video storage technologies (*8*). Because the time resolution of this system is better by a factor of ~2, the corresponding flight path is only 2.5 m.

The application of Coulomb explosion imaging to the study of polyatomic molecules is a recent development. Some of the new aspects of molecular structure revealed by these experiments are described below.

Nonclassical Molecules

One of the most exciting challenges in molecular physics today is the study of nonclassical molecular structures (*2*). As explained before, such molecules do not possess a "structure" in the classical sense, but rather are dynamical systems exhibiting highly fluxional, rapid nuclear motions. Experimentally, such systems produce extremely complex spectra and it is hoped that eventually these will be explained by the very elegant theories incorporating quantal tunneling that are now being developed (*9*). As pointed out previously, large-amplitude motions are particularly simple to observe in Coulomb explosion experiments and thus this technique affords a new perspective on nonclassical systems.

A problem that has deservedly received considerable attention from theorists and experimentalists alike is that of determining the structures of the lowest energy states of the vinyl cation ($C_2H_3^+$). This is particularly interesting because it is the simplest molecule that might exhibit both a classical structure as well as a nonclassical bridged form. The interest in this molecular ion is also driven by the important role such protonated hydrocarbons are thought to play in the chemical evolution of interstellar clouds (*10*). Apart from the problems of interpretation, conventional laboratory spectroscopy of such molecules had been difficult because of the extreme reactivity of these species. Because of the ability to study single isolated molecules, the Coulomb explosion technique is well suited for such cases.

There have been many theoretical investigations of this system to ascertain which of the two structures is more stable. Although early work with limited basis sets predicted the classical form to be more stable by ~20 kcal/mol (*11*), most of the more extensive ab initio calculations now agree that the bridged form lies lower in energy. There remains, however, an important question of the energy difference and barrier height separating these structural isomers. Subsequent work by Pople and co-workers gave a difference of 3.0 kcal/mol (*12*) and later 5.0 kcal/mol and further suggested that the classical structure was probably not a local minimum on the potential energy surface (*13*). These findings were supported by another study (*14*) which found a gap of about 4 kcal/mol.

The Coulomb explosion results (see Fig. 2) clearly demonstrated that the nonclassical bridged structure dominated the sample of molecules studied (*15*). Although experiments performed so far have not been sufficiently refined to discern small admixtures of rare structures, they were able to place an upper limit that corresponds to at most 15% of the sample displaying the classical structure (this is merely an upper limit and the data are also consistent with none of that structure as well). This finding means that it is very improbable that the classical structure exists as a low-lying isomer in our sample of molecules.

Although the infrared spectrum of this molecular ion has now been observed (*16*), the analysis of the spectroscopic data has been extremely difficult. The results indicate that the nonclassical structure dominates (as in the Coulomb explosion experiment), but there are difficulties in fitting the spectra and there are unexplained lines with significant intensity. These observations indicate that the spectrum is not that of a well-behaved asymmetric rotor. A possible explanation of these discrepancies might come from recent theories. As mentioned earlier, in contrast to a rigid model with only two equivalent protons, these theories treat the problem of three equivalent protons tunneling through a barrier and rotating in the plane of the molecule (*17*).

The Coulomb explosion experiments performed so far indicate an extremely floppy proton configuration; however, more refined measurements with more selectivity in the preparation of the molecular ensemble and charge-state separation of the fragment ions need to be carried out. With such data, it should be possible to derive the full density distribution and to firmly establish the nature and extent of the large amplitude motions within this molecule.

Correlations and Dynamics

The final state of the Coulomb explosion experiment involves the measurement, for each molecule in a beam, of the final velocities of all of the fragment ions resulting from the dissociation. For each individual molecule, these final velocities can be transformed into the initial spatial configuration of the nuclei. Each such configuration of an individual molecule is a sample of the probability density of the nuclear coordinates (the wave-function squared integrated over the electronic coordinates) of the particular molecular state being studied. Thus, in addition to information about time-averaged "mean structures" as was demonstrated above, these density distributions contain much deeper information about the correlations as well. To illustrate the quality and characteristics of the information obtained from more detailed analyses of the Coulomb explosion results, we consider the example of the methane cation.

The methane cation has been the subject of numerous theoretical and experimental papers in recent years. While the neutral methane molecule exhibits a highly symmetrical tetrahedral geometry, it has long been known that a quantum mechanical phenomenon known as the Jahn-Teller effect (*18*) would cause its ion (CH_4^+) to be distorted from tetrahedral symmetry. Despite this well-known prediction, its structure had not been definitively established (*19*).

The Coulomb explosion experiments (*20*) have demonstrated an average structure that is consistent with the recent findings of electron spin resonance spectroscopy (*21*). However, such data permit a far more detailed picture of nuclear motions within this molecule. The raw experimental data consist of three coordinates for each of the five nuclei. Because we are uninterested in the trivial center-of-mass motion (three translational degrees of freedom) and rotations about this center-of-mass (three rotational degrees of freedom), the data are reduced to $3 \times 5 - 6 = 9$ structural coordinates. In order to picture the motions of nuclei in nine-dimensional

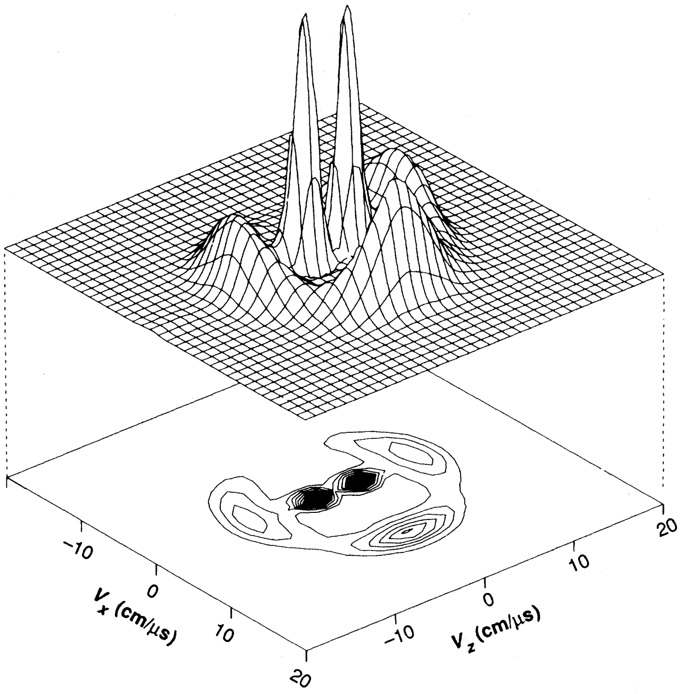

Fig. 2. Plots of the densities of fragment ions measured in a coordinate system defined by the final velocities of each particle (relative to the mean carbon-ion velocity) following the foil-induced dissociation of 4.5-MeV $C_2H_3^+$. The carbon-ion densities have been reduced by a factor of 5 for display 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 [see (*15*) for details].

space, it is important to choose those coordinates judiciously. Although the four protons may or may not occupy equivalent sites in the original molecule, they are identical and hence indistinguishable after the Coulomb explosion. A suitable choice of coordinates has to account for this. The use of symmetry-adapted linear combinations of the internal coordinates (*22*) fulfills these requirements.

As noted above, the Coulomb interaction Hamiltonian is invariant under both rotations in configuration space (*R*-space) and permutations of the identical particles. Therefore, it is expected that the use of symmetry coordinates in *V*-space (the space defined by the final velocity vectors of the fragments) can result in a simplified description of the density of measured events that can later be related to the *R*-space symmetries. In our analysis of CH_4^+, we used appropriate coordinates to represent the distortions of the molecule from a symmetric tetrahedral geometry (*23*).

Four of these coordinates, which describe stretching of the CH bonds, revealed comparatively rigid motions (that is, $\Delta r/r$ is quite small). The angular degrees of freedom, however, appear to be quite floppy. To explore this floppy motion, consider three of those coordinates relating the angular changes:

$$B_x = \tfrac{1}{2}(\alpha_{12} - \alpha_{34}) \tag{2}$$

$$B_y = \tfrac{1}{2}(\alpha_{13} - \alpha_{24}) \tag{3}$$

$$B_z = \tfrac{1}{2}(\alpha_{14} - \alpha_{23}) \tag{4}$$

where α_{kj} is the angle formed in velocity space between the *k*th and *j*th protons at the carbon nucleus (H_kCH_j).

Before further discussion we should look at some Coulomb explosion data of CH_4^+ and NH_4^+ along some of these coordinates. Probably the most informative cut through the distribution is the density on a plane which includes the B_x axis and bisects the angle between the B_y and B_z unit vectors.

As seen in Fig. 3, the "peak" on the positive B_x axis is of a C_{2v} symmetry. It is not really a peak but a saddle point that appears as a peak in this view. An equivalent point is situated at the same distance from the origin but on the negative B_x axis. Its density is lower than the densities of the two equivalent peaks below the $B_y - B_z$ plane that are of a C_s symmetry. The T_d point is at the origin and is of much lower probability. An instructive comparison is shown in Fig. 4. This is exactly the same cut as Fig. 3 but with data resulting from an NH_4^+ Coulomb explosion measurement. The NH_4^+ ion is isoelectronic with the CH_4 molecule. It is expected to manifest a T_d symmetry (*24*). Indeed Fig. 4 shows essentially one peak at the origin corresponding to a tetrahedral structure. Further studies of the B_x-B_y-B_z distribution for CH_4^+ reveal 12 equivalent peaks of the C_s nature that are connected through high-density regions. Thus, the structure of this molecule is highly fluxional. While these data may represent the behavior of the molecule in its ground state, we cannot at present rule out the possibility that the ensemble produced by low-energy electron impact on methane is excited. A small excitation energy, concentrated in these angular coordinates, would induce fluxional behavior. With higher potential barriers near the C_s structures, the lower classical velocities would lead to regions of high densities. With such an ensemble, the true potential minima (possibly, for example, the C_{2v} geometries) would appear less dense because of the increased velocities in these regions imparted by the excitation energy.

This example demonstrates the densities in the nuclear coordinates for a truly dynamical situation. It stresses the quality of information that one would get from the Coulomb explosion experiments if one would more precisely control the production mechanism of the measured species.

Stereostructures of Small Clusters

One of the most exciting frontiers in molecular structure today is the study of atomic clusters. Besides the pedagogic interest in this subject as a way to study the transition from isolated molecules to condensed matter, even small clusters show us new features of molecular structure that simpler ground-state molecules do not exhibit. This is a consequence of the complex nature of vibrations in such many-body systems. Coulomb explosion studies of clusters of identical atoms are more complicated than the experiments discussed above. Practical difficulties arise in the classical trajectory method of mapping data from the "velocity-space" geometries measured after the Coulomb explosion to the configuration space before the explosion. These problems increase with cluster size because of the presence of many identical particles with similar interactions. While point-by-point mapping is not feasible in such cases, these analytical difficulties may eventually be overcome by comparing the full post-explosion distributions with the results of time-dependent quantum mechanical calculations of the fragmentation dynamics (*25*). However, even without such detailed analyses, significant structural information can be gathered about comparative geometries. A recent study of C_3^+ illustrates this point.

Nearly 30 years ago, Hintenberger *et al.* (*26*) reported that the abundances of carbon cluster ions, produced in a graphite spark source, displayed a curious oscillatory dependence on the number of carbon atoms in the cluster. This same behavior was later confirmed for ions produced by laser vaporization of graphite (*27*). More recently, Brown *et al.* (*28*) have reported measurements of the fragmentation energies for the reaction $C_n^+ \rightarrow C_{n-1}^+ + C$. These latter authors have further suggested that these observations could be explained by a similar structural dependence on the cluster size. Their theoretical calculations predict that carbon cluster ions containing an odd number of carbon atoms would be most stable in a linear form whereas even-numbered clusters would form ring structures. In an effort to investigate such effects, we began a study of the structures of small carbon clusters (*29*) and their ions.

In analyzing the Coulomb explosion results for C_3^+, we used a simple comparative method. We have studied the *V*-space geometries of the carbon atoms within the molecules C_3^+, C_3H^+, $C_3H_2^+$, $C_3H_3^+$, and $C_3H_4^+$. Experimental information on the chemical reactivity of $C_3H_3^+$ and $C_3H_4^+$ had previously suggested these species to be predominantly cyclic and linear, respectively (*30*). Based on comparison to these "known" structures, our results (*31*) for C_3^+ showed quite dramatically that the ground state of this ion is not linear, as had been presumed previously. More extensive exploration of the potential surface seems to indicate that the C_3^+ molecule is indeed bent (*32*), in agreement with these observations. Further analysis of our data, incorporating a mapping to spatial configuration space, is under way and should provide more detailed information on these structures.

Future Perspective

As the internal energy of a molecule is raised, spectroscopic information becomes difficult to unravel and statistical arguments are usually employed. Furthermore, spectroscopy provides information predominantly on excited states that emit or absorb electric dipole radiation. These may represent only a subset of the highly excited states that ultimately determine the thermodynamic properties of a molecule (*33*). The Coulomb explosion technique may make it possible to obtain a detailed picture of how specific molecular structures evolve with increasing excitation energy and it is toward that goal that this research is evolving.

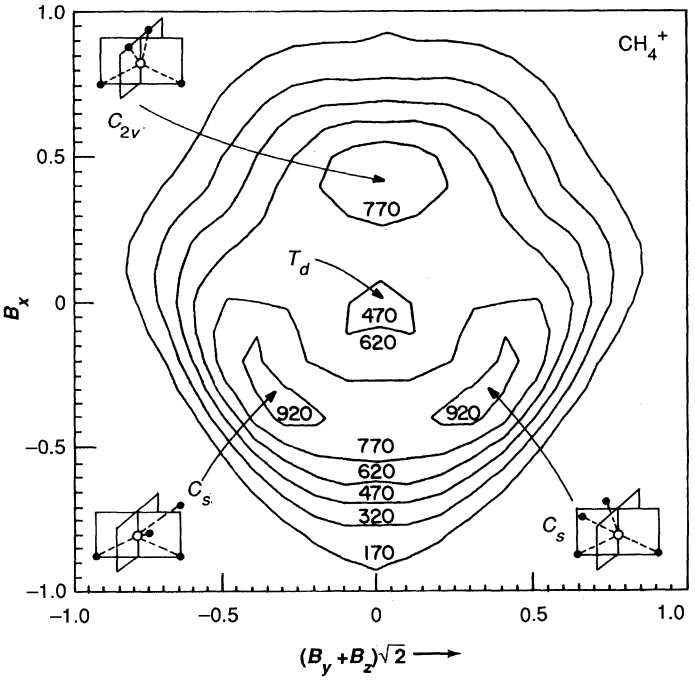

Fig. 3. Density of events in symmetry coordinates (see text) after the Coulomb explosion of $\sim 10^4$ 4.5-MeV CH_4^+ ions. Equations 2 through 4 were used to define the coordinate system. The scales are in radians. The contour levels shown denote the density in arbitrary units. The point denoted by T_d corresponds to a symmetric tetrahedral geometry. These coordinates are chosen to demonstrate deviations from this symmetry. The geometries of molecules represented by the C_{2v} and C_s symmetry point groups are shown.

Detailed Coulomb explosion studies of intramolecular dynamics, however, have not yet been carried out because of the difficulty of providing projectile molecular beams with well-defined internal energies. All of the experiments described above used low-energy electron impact to form molecular ions from parent neutral species. Ionization by this method can lead to cold ion beams for species with potential surfaces similar to the parent neutral molecule (for example, H_2O and H_2O^+) where Franck-Condon excitation approximately preserves the initial thermal distribution. In general this is not the case and other methods must be used. Because of the 100% efficiency of the Coulomb explosion experiments, selectivity does not present a problem for experimental count rates. However, it is a technical challenge to design cold molecular sources to operate in conjunction with conventional nuclear accelerators.

Traditionally the sources used in nuclear accelerators are built to produce high currents of charged atoms. For example, the Pelletron accelerator used at the Weizmann Institute utilizes either a duoplasmatron or a sputtering source to produce copious beams of negative ions. These ions are mass-selected and then accelerated from ground potential to a high positive voltage (≤ 14 million volts) at the terminal of the accelerator. When accelerating atomic ions, a gas or foil stripper is commonly used to produce highly charged positive ions that are then further accelerated down to ground potential. However, when applied to molecules, such collisional stripping is inappropriate. Solid strippers cannot be used because all but a small fraction ($\sim 10^{-11}$ to 10^{-5}) of such fast molecules dissociate in dense media. Collisional stripping in a gas target generates a variety of molecular species in many electronic, vibrational, and rotational states. A number of alternative methods are currently under development for the production of swift molecules with well-defined internal energies.

One approach towards single-state preparation uses electron photodetachment (EPD) for the charge-changing process, instead of the usual collisional stripping. Photodetachment can be selective owing to the fact that a known amount of energy is deposited in the negative ion. In principle, by combining it with electron energy

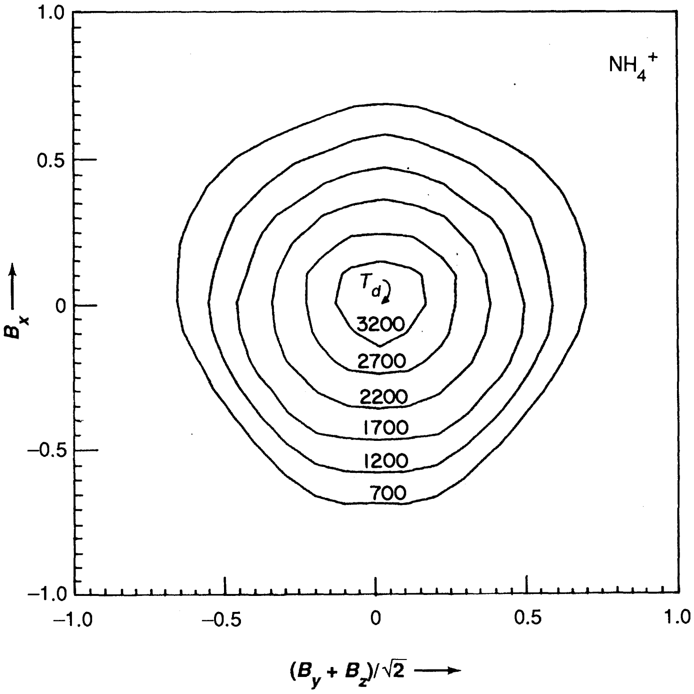

Fig. 4. The same as Fig. 3 but for events resulting from the Coulomb explosion of NH_4^+.

analysis in a coincidence experiment (*34*), one could perform a Coulomb explosion measurement of neutral molecules prepared with a well-defined internal energy. The accuracy of the internal state definition depends on the resolution of the electron energy analyzer. When this method is used in combination with accelerated species, the large velocity of the center-of-mass ensures high resolution combined with high collection efficiency. However, because of the construction of the Weizmann Institute accelerator, collection of the photodetached electrons would entail placing an electron energy analyzer in the high-voltage terminal, where it is difficult to perform this type of measurement. Because of this technical problem, the most straightforward use of the EPD method is to prepare cold negative ions that have vertical transitions to only a few vibrational states in the daughter neutral molecule. Many such systems have been reported (*35*), and the current setup can be used for their investigation by the Coulomb explosion method without further modifications.

The results obtained to date demonstrate the ability to produce neutral species in the accelerator by laser photodetachment; however, unless the method is combined with an electron energy analyzer, it is not possible to use it as a general scheme for preparing molecules in a single state. The method is further restricted to species having similar structures in the negative ion and neutral states. Because detection of detached electrons is difficult owing to the accelerator configuration, it would be interesting to instead detach a fragment and measure its kinetic energy, in coincidence with the corresponding polyatomic species that is studied by the Coulomb explosion method. In other words, if we could detach a light neutral atom from the initially prepared cold negative molecular ion, and then measure the kinetic energy of the detached atom, it would then be possible to determine the structure of polyatomic species with a well-defined energy. This is precisely the scheme for our photodetachment-photodissociation arrangement.

In these experiments, one starts with a species of the form MA^-, where M is a polyatomic molecule and A a light atom. Following laser irradiation, the complex dissociates to produce $M + A^-$. Another photon is then applied to neutralize the anion. A coincidence measurement is performed on the two fragments. The kinetic energy of the dissociation products can be determined by measuring the relative velocities between their centers-of-mass at the detector and thus the internal energy of the polyatomic species is defined. This process is equivalent to measuring the electron energy in electron detachment experiments. Having a spatial resolution of about 1 mm on the detector, and a flight path of about 30 m from the terminal to the detector, we can achieve an excellent resolution of several wavenumbers in the definition of the internal energy of the polyatomic molecule. Such methods are now being used at the Weizmann Institute to study the structures of polyatomic species having well-defined internal energies.

As was mentioned above, the development of Coulomb explosion imaging has required several technological advances to achieve the scientific goals. It seems that the most difficult of these are already behind us and experiments are now concentrating on understanding this new and unique perspective of molecules. As this work matures, we can expect to uncover many new facets of molecular structure.

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