

CONF-8710159--5

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DE88 003086

Invited Talk/12th Intl. Conf.
on Atomic Collisions in Solids
Okayama, Japan, Oct. 12-16, '87

THE STRUCTURE OF SMALL MOLECULES WITH THE COULOMB EXPLOSION METHOD

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Abstract

The content of this paper is divided into two parts: I) Achievements of the last two years in studying molecular ion structure with the aid of the newly developed Coulomb-Explosion (CE) method, and II) the understanding of the modern CE data in terms of an invariant density of nuclear coordinates of the studied molecule.

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*Work supported by the U. S. Department of Energy, Office of Basic Energy Sciences, under Contract W-31-109-ENG-38.

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We have developed a method that ultimately should enable the measurement of the square of wave functions of the nuclear-coordinates of selected states in small molecules. The direct observation of the "nuclear-density" of gas-phase molecules and clusters is of importance in several fields, like astrophysics, plasma-physics, physical-chemistry and theoretical chemistry.

The principle of the method is as follows. The first stage is the preparation of the studied molecules in a unique quantum mechanical state in a beam with a speed of above 2% of the speed of light (~ 200 keV/amu). The second stage is the "minimal multiple scattering" stripping. The molecules impinge upon an extremely thin target of Formvar [1] (~ 30 Å or less) and all the binding electrons and other loose molecular electrons scatter away within a few times 10^{-17} of a second. To a very good approximation, the nuclear part of the wave function does not change at all while the Hamiltonian switches from the original molecular Hamiltonian to an almost pure Coulomb repulsion regime. The next stage is the development of the nuclear wave function through the well-known Coulomb Hamiltonian into the asymptotic region of the final state. This stage (the CE) takes about 10^{-15} of a second. The final state is fully measured in a multiparticle position and time-sensitive (MUPPATS) detector [2] (situated about 6 meters downstream) which yields the final velocities of all of the fragment ions. The final velocities for each individual molecule can be transformed (via "Coulomb-trajectory" calculations) into the initial "R-space" configuration. Each such configuration of an individual molecule is a sample of the probability density (PD) of the nuclear-coordinates (the wave-function squared intergrated over the electronic coordinates) of the studied molecular state.

Up to now we have developed an experimental set-up including these extremely thin Formvar targets which provide efficient electron strippers with

low multiple scattering characteristics and the MUPPATS detector which provides accurate velocity information on multiparticle events. We have also made an effort to prepare beams of selected molecular states. This will be discussed elsewhere [3].

Currently we have information on several molecular ions including: CH_5^+ , CH_4^+ , CH_3^+ , NH_4^+ , NH_3^+ , C_3H_3^+ , C_3H_4^+ , and C_3^+ . The CH_4^+ measurement [4] will serve here as an example.

The CH_4^+ ions were prepared inside the high-voltage terminal of Argonne's 4.5-MV Dynamitron by low-energy electron impact with methane gas at a pressure of about 50 mTorr. The ions were steered toward a foil target composed of $0.3 \mu\text{g}/\text{cm}^2$ Formvar supported on a fine nickel mesh. Measurements on multiple scattering, thickness calibrations [5], and methods of target preparation [1] are published elsewhere.

Downstream from the target, the dissociation fragments were deflected electrostatically in the horizontal (or "X") direction. Figure 1 shows a two-dimensional projection on the plane of the detector, of the images of fragments from the Coulomb explosions of $\sim 10^4$ CH_4^+ ions. One can observe, in order of increasing deflection, the positions of the C^+ , C^{2+} , C^{3+} , and C^{4+} ions and a large disk corresponding to the accompanying protons. For each event analyzed, a five-fold coincidence is recorded with one carbon ion and four protons. The position and time of each ion are converted on-line into the individual ions velocity vectors. This 15-dimensional velocity, v_c, v_1, v_2, v_3, v_4 is reduced further by subtraction of the center-of-mass velocity (which serves as an overall resolution test of the system) and a choice of orientation. Thus, $15-6 = 9$ "body" degrees of freedom are left.

To display the Jahn-Teller effect in the CH_4^+ ion, we project the data in the following manner. For every event, the two protons for which the H-C-H

angle in velocity space (VS) is minimal are selected and indexed as 1 and 2. The VS is rotated such that $v_{x1} = -v_{x2}$, $v_{y1} = v_{y2} = 0$, and $v_{z1} = v_{z2} \geq 0$. Thus, after this transformation, the angle H_1-C-H_2 is in the XZ plane symmetrically around the positive Z axis. A contour plot of the density of all the protons onto the XZ plane in velocity space following this event-by-event rotation is shown in fig. 2(a). The spreads in the two groups with positive v_z are thought to be mainly due to zero-point fluctuations and low vibrational excitation. The average $H_1-(c.m.)-H_2$ angle is approximately 70° . The other two protons (3,4) lie mainly below the XY plane and the groups are not separated in this view. The YZ contour plot of the density of protons, using the same rotation procedure, is shown in fig. 2(b). Now, the proton groups 3 and 4 are well separated below the XY plane with an average $H_3-(c.m.)-H_4$ angle of 120° . The nonequivalence of the 1,2 and 3,4 proton groups is evident. The data clearly demonstrate the C_{2v} symmetry of the measured CH_4^+ molecules. This observation is consistent with the recent findings of electron-spin-resonance spectroscopy which suggest a dynamical Jahn-Teller distortion leads to a C_{2v} structure [6,7].

The special choice of rotations and projections which emphasizes the above qualitative result indicates the power of this technique, but distorts the quantitative results. In effect, the selection of "the smallest angle" above the XY plane introduces a bias among the otherwise equivalent four protons. It is clear that new analysis methods need to be developed for dealing with such enormous amounts of data with so many parameters. This is the subject of the second part of this paper:

The understanding of the Coulomb explosion data [8].

The aim of analyzing CE data is to get a parameterized function describing the probability density of the correlated nuclear coordinates. One is faced with the following problems:

- 1) There is no trivial way to calculate the initial R-space configuration from the final V-space coordinates. We must therefore numerically integrate trajectories from assumed R-space configurations.
- 2) A single Coulomb trajectory calculation, though simple, takes about 2 seconds on an IBM 3081.
- 3) Existing and future CE experiments are expected to have 10^6 - 10^7 events. It is inconceivable to transform each event to its R-space configuration.
- 4) In the above example of CH_4^+ there are 9 structural degrees of freedom. It is absurd to think in terms of computing trajectories for 10 boxes per degree of freedom (10^9 boxes!).
- 5) When the molecules contain some identical atoms then chemists talk about "equivalent" and "non-equivalent" sites of atoms. How does one distinguish such atoms in V-space?

We do believe that the scheme outlined below addresses all these problems.

- 1) Choice of R-space coordinates.

The choice of R-space coordinates is conveniently made to diagonalize the kinetic energy such that

$$2T = \sum_n \dot{q}_n^2$$

This choice allows several physically meaningful estimates to be made. 1) Phase space statistics (energy shell calculations); 2) Simple local approximations to multidimensional harmonic motion. For example, a peak in the probability density can be interpreted as a square of the Gaussian ground state wave function of a local harmonic motion. An orthogonal transformation of q can diagonalize the bilinear form describing the assumed Gaussian peak of the density. The resulting eigenvalues are simply related to the vibrational frequencies of the molecule.

A simple choice of such coordinates are the modified cartesian coordinates:

$$q_{\alpha} = \sqrt{m_p} X_{pa} \quad \begin{array}{l} p = 1, \dots, N \text{ \# of particles} \\ a = 1, 2, 3 \\ \alpha = pa = 1, \dots, 3N, \end{array}$$

though only $3N-6$ coordinates are necessary to describe the structure of the molecules (the relative nuclear positions). The remaining 6 coordinates describe CM translational motion and rotations.

An arbitrary choice of $3N-6$ independent body coordinates can be made. The 9 coordinates chosen in fig. 2 are just one possibility. The same reduction can be made in both v -space and R -space. The density in the pure cartesian coordinates q ($3N$) and the density in the special choice Q ($3N-6$) are related by a transformation Jacobian. Specifically, this Jacobian is the square root of the determinant of the matrix

$$A_{ij} = \sum_{\alpha=1}^{3N} \frac{\partial Q_i}{\partial q_{\alpha}} \frac{\partial Q_j}{\partial q_{\alpha}}$$

The $P(Q) | A |^{-1/2} d^n Q$ probability density (PD) is invariant to the choice of Q and is proportional to the probability density required. The choice of coordinates made in fig. 2 result in a determinant which is INDEPENDENT of the specific configuration. Therefore a peak in the PD with those coordinates is also a peak in the required PD.

2) Equivalent atoms.

When a molecule contains several identical atoms then the PD is invariant under the permutation of those atoms. Thus when an event is measured at a certain point in N dimensional V space then the equivalent points (which one gets by permuting the indices of the equivalent atoms) are as probable as the original event. Figure 2 is misleading in this respect.

3) Strategy

If one defines a volume in R -space and calculates enough CE trajectories to define the corresponding volume in V -space then all that is required in order to find the PD is to count the number of the measured events and their allowed permutation within this volume. The density at the point in R -space is simply the above number of events in the corresponding volume in V -space normalized to the R -space volume.

A rectangular box in 9 dimensions has $2^9 = 512$ corners. It is a formidable amount of calculations to evaluate 2^9 trajectories for each individual sampling box. The solution to that is to define boxes which are generalized tetrahedra (known as simplexes). A simplex volume can be defined by $N+1$ points for an N dimensional space. For example, for the purpose of defining a maximum in 9 dimensions one needs to know at least 55 constants of a bilinear form. Thus, at least 55 "boxes" should be defined in R -space and

correspondingly, at least $55 \times 10 = 550$ trajectories should be calculated for the complete determination of this bilinear form near a peak of the PD. (Adjacent simplexes reduces significantly the number of needed trajectories).

Once volumes in V-space are defined by such a procedure, it is a matter of passing once through the data in order to know how many events (including permutations of equivalent atoms) fall into each volume element which immediately can be converted to density in the desired R-space.

Application of this method to the CH_4^+ data proved several things.

1) The 10^4 event measured is by far too low for reasonable extraction of vibrational frequencies. 2) The average configuration published [4] is very close to the average found in this manner. 3) This average configuration is probably NOT a true maximum of the distribution but a saddle point. The true, very shallow maxima, may lack any symmetry.

Conclusion

We have constructed an experimental set-up which can provide us with highly detailed information on individual states of small molecules. In principle, the data should provide us not only the equilibrium configuration and its symmetry but also the eigenmodes of vibrations and their corresponding frequencies.

We have outlined the method in which the CE data could be processed. This circumvents difficulties we had in the past and opens up the possibility of achieving the above goals.

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Figure Captions

Fig. 1. 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. 2. 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 defines 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.

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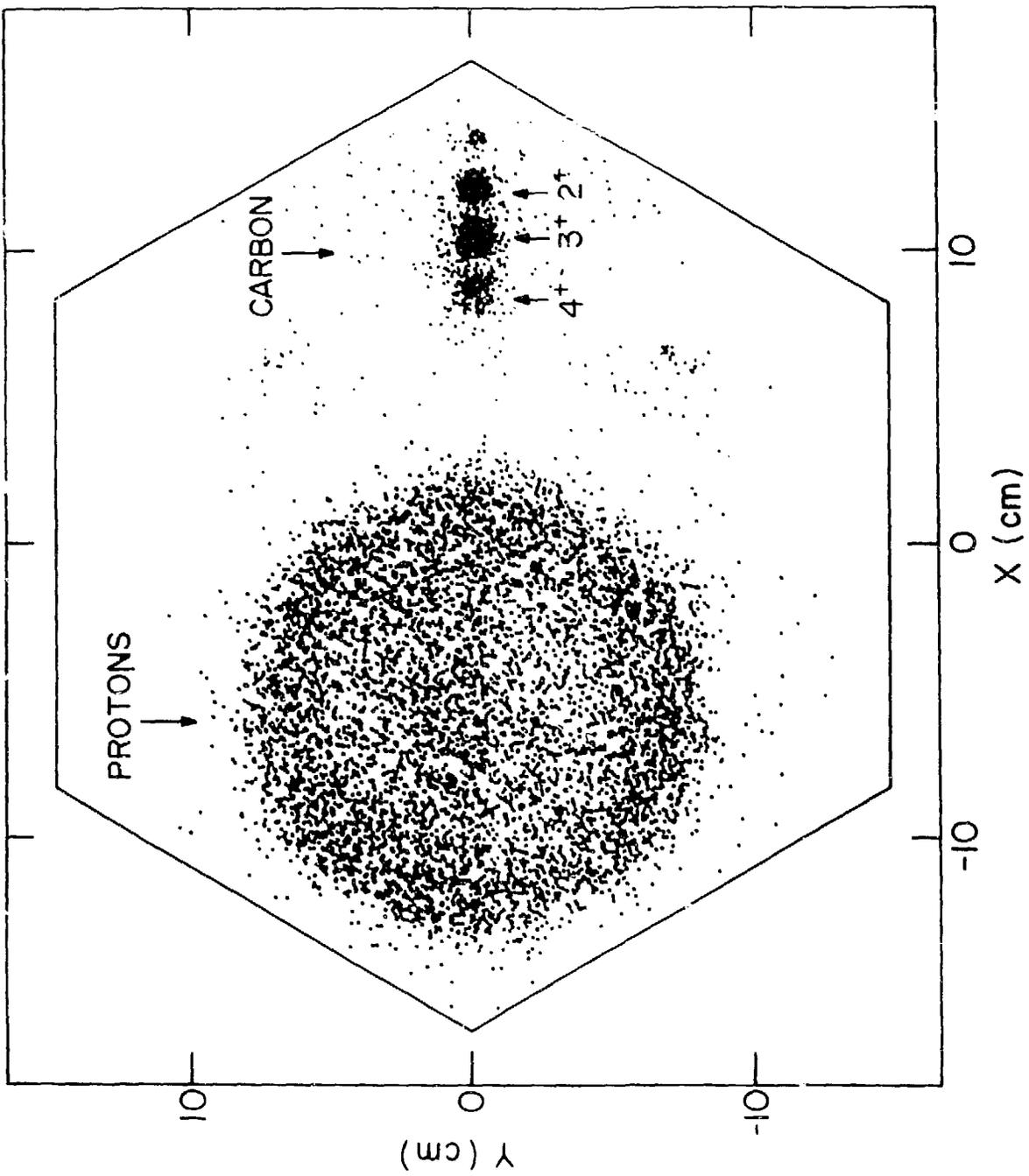


Fig. 1

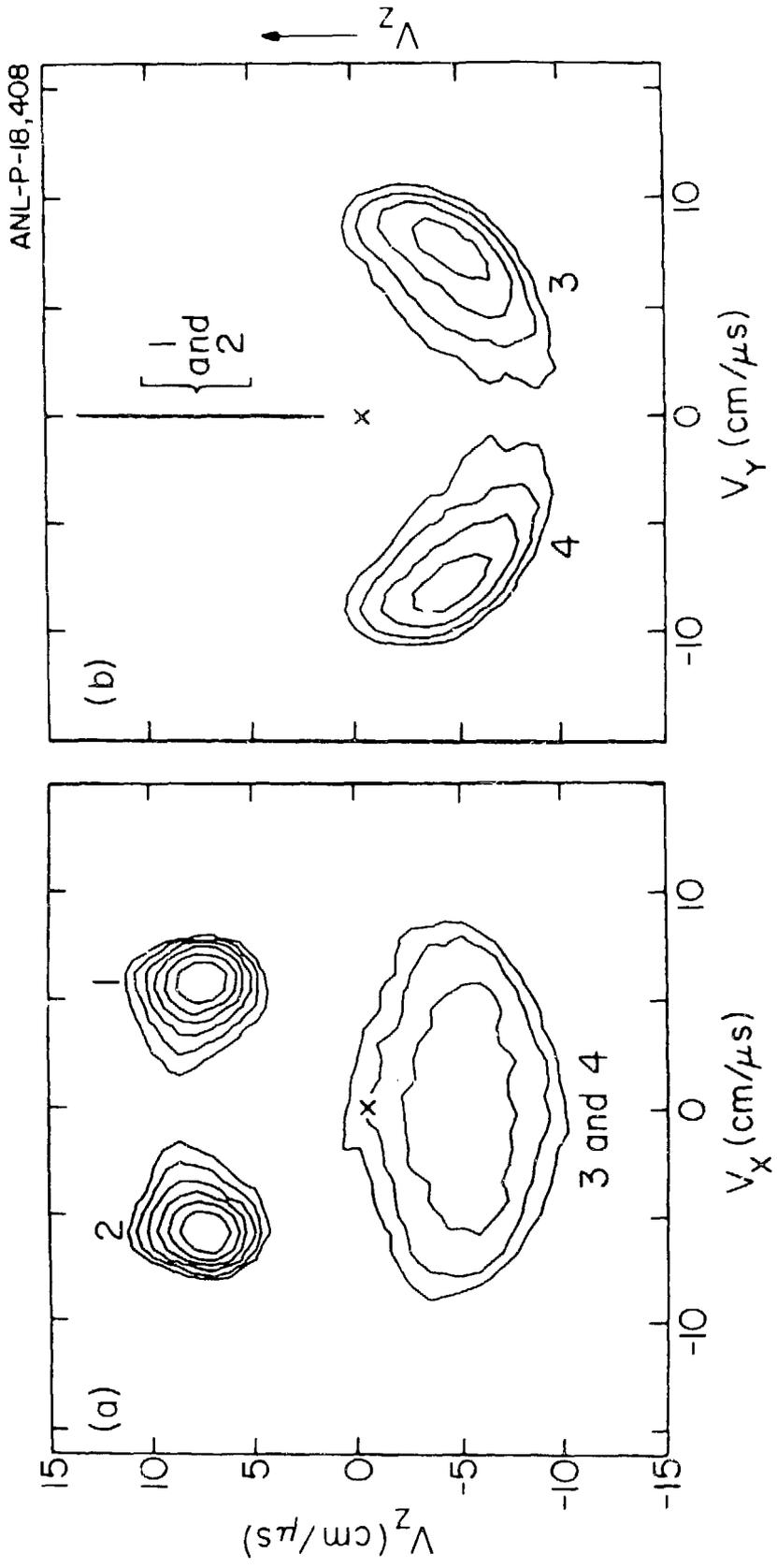


Fig. 2