

Direct Determination of the Stereochemical Structure of CH_4^+

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The use of the Coulomb-explosion technique combined with a new multiparticle detector, extremely thin targets, and low-excitation ion source has enabled a direct measurement of the complete stereochemistry of the CH_4^+ molecular ion. Preliminary analysis of the data gives a structure consistent with predictions of the Jahn-Teller-distorted ground state. We outline the techniques by which this method can be generalized to determine directly complex vibrational motions in polyatomic molecules.

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The structure of CH_4^+ has been the subject of numerous theoretical and experimental papers.¹ It has several aspects of scientific significance. For example, CH_4^+ has been thought to have been abundant in the early atmosphere and considered to be important in the chain of chemical evolution preceding the origin of life.² It is also one of the simplest cases in which a Jahn-Teller deviation from symmetry is predicted.²⁻⁶ It is considered to be a simple molecule and thus provides a tractable challenge for theorists. Yet, its structure has not hitherto been established because of general difficulties in the experimental study of molecular ions, and in particular its high reactivity.

During the last few years, new ideas and developments in the Coulomb-explosion technique for determining molecular structures⁷ have shown promising results.⁸ In particular, the MUPPATS detector⁹ developed at Argonne now allows the simultaneous measurement of the velocity vectors of up to six particles permitting studies of polyatomic molecules. Furthermore, extremely thin targets of Formvar¹⁰ now provide efficient electron strippers with low multiple-scattering characteristics.¹¹ In contrast to earlier experiments, where multiple scattering masked the influence of vibrational motions in the measured bond-length distributions,⁸ such corrections are now small compared to zero-point fluctuations. In the following, we describe our first measurements on CH_4^+ exploiting these new developments. We give our preliminary results demonstrating the power of this technique and comment on the future potential of further analysis of the data.

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. After acceleration to 4.5 MeV, the momentum-analyzed ion rate was measured as a function of the electron kinetic energy. The electron energy was then set ~ 0.5 V above the measured ionization threshold of 12.7 eV (a value in good agreement with that obtained from photoelectron spectra¹²). Because the ionizing electrons were nearly monoenergetic

(13.2 ± 0.3 eV), this procedure provided a beam of CH_4^+ ions with excitations believed to lie in a narrow band near the ground state. After a flight time of ~ 7 μs , the ions were then steered toward a foil target composed of 0.3-g/cm² Formvar supported on a fine nickel mesh. Measurements on multiple scattering, thickness calibrations,¹¹ and methods of target preparation¹⁰ will be published elsewhere.

Passing through the target, the CH_4^+ ions lose several electrons in a time ($\sim 10^{-17}$ s) much shorter than any characteristic molecular rotation or vibration. Almost all the molecular ions decompose rapidly into a cluster of four protons and a carbon ion in a charge state that is experimentally determined (mostly 3^+). Thus, there is a sudden change of the Hamiltonian from that of a bound molecular ion into an almost pure Coulomb repulsion. The internal potential energy (about 200 eV) acquired by this change, is then converted into relative kinetic motion of the five dissociative fragment ions. This "Coulomb-mapping" from the geometric (spatial) structure of the nuclei within the initially bound molecule to the velocity-space (VS) structure following the Coulomb explosion is the essence of the method used here.

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. These data represent roughly twelve hours of data collection. 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 fivefold coincidence is recorded with one carbon ion and four protons. The position and time of each ion are converted on-line into the cluster ("molecule") velocity vector. This 15-dimensional velocity, $\mathbf{v}_c, \mathbf{v}_2, \mathbf{v}_3, \mathbf{v}_4$ 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.

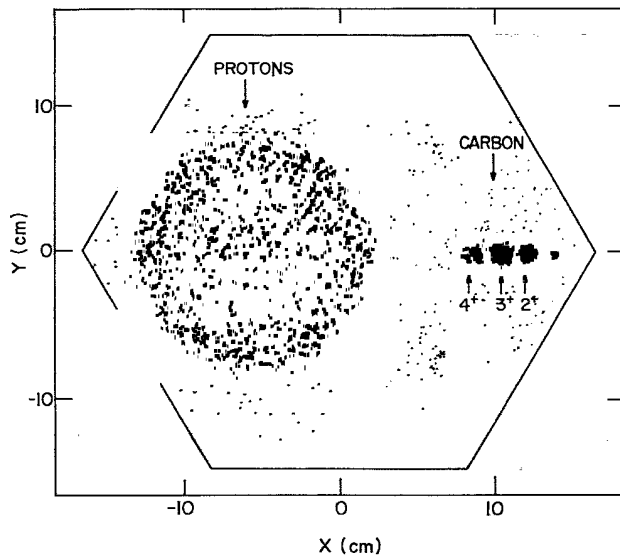


FIG. 1. A density plot of the projection on the plane of the MUPPATS detector of the images of fragment ions resulting from the Coulomb explosion of CH_4^+ ions. The hexagon denotes the active area of the detector. The protons, and various charge states of carbon ions, have been separated by electrostatic deflection in the x direction.

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 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 $\text{H}_1\text{-C-H}_2$ is in the XZ plane symmetrically around the positive Z axis. A contour plot of the density of all the protons projected 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 $\text{H}_1\text{-(c.m.)-H}_2$ 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 $\text{H}_3\text{-(c.m.)-H}_4$ 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.^{13,14}

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. Meanwhile, we present here the preliminary results of an unbiased analysis of our data on CH_4^+ in terms of its equilibrium structure. The data offer further possibilities for deriving eigenmodes and eigenvalues for the nine-dimensional vibrations around equilibrium.

The speeds of the four protons in the center-of-mass system (v_1, v_2, v_3, v_4), and five proton-proton relative velocities ($v_{12}, v_{13}, v_{14}, v_{23}, v_{24}$) were chosen as rotationally invariant independent parameters. These form the vector \mathbf{x}_k representing the k th permutation of the protons. A maximum-likelihood method was used to fit 54 pa-

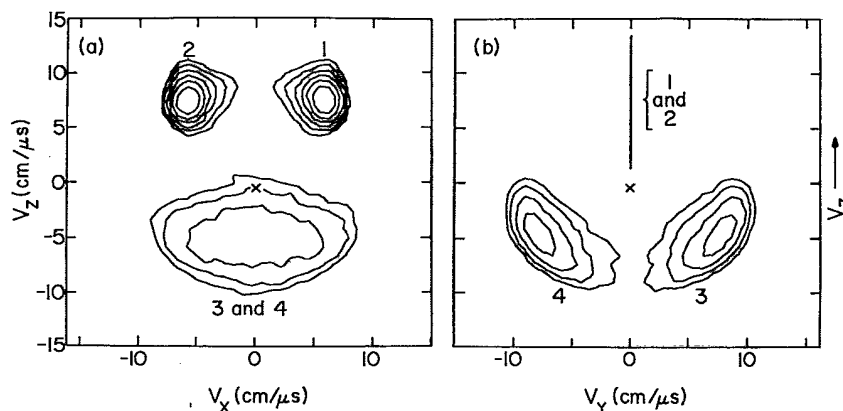


FIG. 2. Contour plots of the densities of protons in velocity space (relative to the projectile center of mass) following the event-by-event rotations described in the text. The ensemble mean for the carbon-ion position is marked by (\times). The data consist of five-fold coincidences between four protons and one C^{3+} ion for each event. (a) Projection on the XZ plane as defined in the text. (b) Projection on the YZ plane. Contour levels are at 1.5%, 2.5%, 4%, 7%, 11%, and 19% of the peak intensity.

TABLE I. Structural parameters of CH_4^+ derived from the fitting procedure described in the text. Bond angles are in degrees and bond lengths are in angstroms. Typical errors are $\sim 0.04 \text{ \AA}$ in bond length (see text).

	Experiment	Theory ^(a)
$\theta(\text{H}_1\text{CH}_2)$	67	59
$\theta(\text{H}_1\text{CH}_3)$	107	114.5
$\theta(\text{H}_1\text{CH}_4)$	118	114.5
$\theta(\text{H}_2\text{CH}_3)$	115	114.5
$\theta(\text{H}_2\text{CH}_4)$	117	114.5
$\theta(\text{H}_3\text{CH}_4)$	122	123
r_1	1.19	1.164
r_2	1.22	1.164
r_3	1.20	1.075
r_4	1.21	1.075
r_{12}	1.33	1.146
r_{13}	1.91	1.884
r_{14}	2.06	1.884
r_{23}	2.04	1.884
r_{24}	2.08	1.884
r_{34}	2.11	1.889

^(a)Reference 14.

rameters to a proton-symmetrized multivariate Gaussian distribution of the form

$$P(\mathbf{x}) = \sum_k \exp\left\{-\frac{1}{2}(\tilde{\mathbf{x}}_k - \tilde{\mathbf{p}})A^{-1}(\tilde{\mathbf{x}}_k - \tilde{\mathbf{p}})\right\} \times (2\pi)^{-9/2} |A|^{-1/2}.$$

Maximizing the joint product probability of all 10^4 events produces the nine-parameter vector \mathbf{p} for the nine-dimensional mean of the Gaussian and the 45 elements of the covariance matrix A (a symmetric 9×9 matrix).

Five-particle Coulomb trajectory computations were carried out for the 3^+ charge state of the carbon and four accompanying protons to produce the equilibrium CH_4^+ spatial geometry corresponding to the mean of the velocity-space Gaussian. Table I shows the spatial parameters resulting from a preliminary attempt to maximize the joint probability function. The principal source of error comes from the fitting procedure used to symmetrize the data. We believe these errors to be up to 3% in the bond lengths and 3° in the angles. The table also shows the predicted geometry of the C_{2v} structure predicted by *ab initio* calculations.¹⁴

The next step, which is out of the scope of this Letter, is to compute the "Coulomb transformation" Jacobian between the spatial nine-dimensional geometry and the corresponding velocity space. This will enable one to transform the covariance matrix A directly into that cor-

responding to the spatial coordinates of the molecule. With the assumption of only zero-point fluctuations, this will ultimately produce the nine-dimensional vibrational wave function of the CH_4^+ molecule.

These results demonstrate the power of this technique not only to study the mean geometries of polyatomic molecular ions, but to observe directly the vibrational motions of the constituent nuclei. With proper analytical tools it should be possible to derive and classify the normal modes of molecular motion. This radically new approach to molecular structure gives results that complement the precise information obtained by spectroscopy, when available.

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