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Molecular Structure Studies by 3D Imaging of Fast Ion Beams

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The use of the Coulomb-explosion technique combined with a radically new multi-particle detector, extremely thin film targets, and low-excitation ion source has enabled, for the first time, direct measurements of the complete stereochemistry of complex polyatomic molecular ions. We outline the methods used and present results for protonated acetylene ($C_2H_3^+$) and the methane cation (CH_4^+) as examples. We demonstrate the techniques by which these methods can be generalized to determine directly vibrational motions in polyatomic molecules.

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The problem of determining the sterochemical structures of molecular ions continues to command the attention of experimentalists and theorists alike [1]. Among the reasons for the great interest in this subject is the role of molecular ions in stereoselective organic reactions [2] which are extremely important in such diverse problems as the ecological impact of "acid rain" [3] and the chain of chemical evolution preceding the origin of life [4]. On the theoretical side, there have been considerable advances over the years in the predictive power of computational quantum chemistry [5] which has been strengthened by coetaneous advances in spectroscopic techniques [6]. Nevertheless, these techniques are not yet generally applicable to a great variety of polyatomic molecular ions. Indeed, to date only a handful of such molecules have been studied.

In contrast to the spectroscopic approaches, it has long been recognized that the so-called "Coulomb explosion" technique offers a potentially powerful method of studying the gross geometric features of a great variety of molecular ions [7]. During the past year, new ideas and developments in these techniques have come to fruition [8-9]. In particular, the MUPPATS detector [9-10] developed at Argonne now allows the simultaneous measurement of the 3-dimensional velocity vectors of up to six fragment particles. Extremely thin films of Formvar [11] provide efficient electron strippers with low multiple-scattering characteristics. In the following, we describe some recent measurements exploiting these developments.

When fast molecular ions (0.1-1.0 Mev/amu) pass through a thin foil, their valence electrons are stripped away initiating a rapid molecular dissociation process which has been termed a Coulomb explosion [12]. The stripping of outer-shell electrons takes place within an extremely short time (10^{-17}s) compared to any characteristic vibrational and rotational motions of the initial molecule. The internal potential energy acquired by this rapid change of the molecular Hamiltonian is then converted into relative kinetic motion of the dissociative fragment ions. This "Coulomb-mapping" from the 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. Measuring the relative momenta of the Coulomb explosion fragment ions thus provides a "snapshot" of the positions of the nuclei in the incident molecular ion [7].

Ideally, one hopes to measure, with high resolution, the relative momenta of all dissociation fragments. To accomplish this task, we have developed a new large-area (34 cm in diameter), low-pressure, multiwire proportional counter which is capable of imaging, in three dimensions, up to ~10 simultaneous dissociation products as might result from the Coulomb explosion of a molecular ion. The MUltiParticle Position- And Time-Sensitive detector is a Breskin-like gas counter [13] with a wide dynamical range. A detailed description of the MUPPATS detector can be found elsewhere [9-10].

In the experiments described here, the molecular ions were formed inside the high-voltage terminal of Argonne's 4.5-MV Dynamitron by low-energy impact with ethylene and methane gases. The energies of the nearly-monoenergetic ionizing electrons in the source were adjusted to lie ~0.5 eV above the measured threshold for the molecular ions of interest in each experiment. It is believed that this procedure produces a beam of molecular ions with excitation energies lying in a narrow band near the ground state. After acceleration to 4.5 MeV the momentum-analyzed molecular-ion beam struck a thin-film target composed of 0.3-μg/cm^2 Formvar supported on a fine nickel mesh (80 lines/mm). Measurements on multiple scattering, thickness-calibration [14], and methods of target preparation can be found elsewhere [11].

Downstream from the target, the dissociation fragments are deflected electrostatically in the horizontal (or "X") direction, and after a flight path of ~ 6 meters, strike the MUPPATS detector. Figure 1 shows a two-dimensional projection on the plane of the detector, of the images of ~10^4 CH_4^+ ions. For each event analyzed, an N-fold coincidence is recorded corresponding to the N fragment ions. In order to deduce structural information, the position and relative arrival time of each fragment ion are converted on-line into a 3N-dimensional cluster velocity vector. This vector is then further reduced by subtraction of the measured center-of-mass velocity, and a choice of orientation, to leave the 3N-6 "body" degrees of freedom representing the VS structure of the molecule. In general, it is necessary to perform extensive N-body Coulomb trajectory computations in order to quantitatively map a given VS structure to the true spatial geometry of a polyatomic molecule. However, for the case of molecules consisting of a heavy ion and several protons, the "Coulomb mapping" described above is symmetry-preserving and hence the VS structure can be quite illuminating. We illustrate this with the case of CH_4^+.

CH_4^+ has been the subject of numerous theoretical and experimental papers in recent years [1]. 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 [4,15-18]. Despite this well-known prediction, its structure had not hitherto been established. To display the Jahn-Teller effect in CH_4^+, we project our data in the following manner. For every event, the two protons for which the HCH angle in VS is minimal are selected and indexed as 1 and 2. The molecule is rotated so that the bisector of that angle lies on the z axis, with the molecular center of mass at the origin, and these two protons lie in the x-z plane. A contour plot of the density of all the protons, projected onto the x-z plane in velocity space following this event-by-event transformation, is shown in Figure 2a. The other two protons (3,4) lie mainly below the x-y plane and the groups are not distinguished in this view. Figure 2b shows the y-z contour plot of the VS proton density using the same rotation procedure. In this view, the proton groups 3 and 4 are well separated and the inequivalence of the (1,2) and (3,4) proton groups is evident. These data clearly demonstrate the C_{2v} symmetry of the molecule and rule out the D_{2d} structure. This observation is consistent with the recent findings of electron spin resonance (ESR) spectroscopy which suggest a dynamical Jahn-Teller distortion leading to the C_{2v} structure [19-20].

A further example of these methods is the case of protonated acetylene ($C_2H_3^+$). The most extensive *ab initio* calculations predict that the nonclassical "bridged" structure lies lower (by only 0.7 kcal/mole) than the classical isomer [21]. The experimental infrared spectra however have proven to be far too complex to resolve this question, or even to ascertain if either of these structural isomers is present [22]. Although our results are still preliminary, the data clearly show the nonclassical bridged structure to dominate our sample of molecules.

To display the bridged proton structure, we project these data in the following manner. For every molecule observed, the origin is chosen to be the mean velocity of the two carbon fragments and the molecule is rotated so that the z-axis lies along the C-C relative velocity vector. The x-axis is determined by the proton that is found to have the maximal velocity component relative to this z-axis. The fragments are then rotated about the z-axis so that this chosen proton lies in the xz plane with a positive x-component. Figure 3 shows contour plots of the proton densities, projected onto the three Cartesian planes, after these rotational transformations are performed. Figure 4 shows a contour plot, as well as an isometric display, of the total particle density (including the carbon fragments) projected onto the xz plane. The five particle groups can be separated easily to give an average "velocity-space" (VS) geometry and a covariance matrix representing the full correlated deviations from this average. The average VS geometry [23] is consistent with a planar molecule and a symmetry plane perpendicular to the C-C axis, i.e. the nonclassical "bridged" geometry [21,24].

The special choice of rotations and projections which emphasizes the above qualitative result indicates the power of this technique, but distorts the quantitative results. It is clear that new analysis methods need to be developed for dealing with such enormous amounts of data with so many parameters in an unbiased way. Preliminary results have been obtained with such techniques for the case of CH_4^+ [25]. The results show that although the detailed structure is somewhat changed as one would expect, the difference in that case was minor and did not affect the symmetry group classification.

So far, we have dealt only with the mean geometries, however it is clear that such data can provide information about dynamics as well. Because the 3N-6 body parameters are measured for each and every molecule, ensemble averages of any operator can be computed from these data. In particular, it is possible to derive eigenmodes and eigenvalues for the 9-dimensional vibrations around equilibrium of the molecules discussed here. The next step, which is beyond the scope of this paper, is to compute the "Coulomb transformation" Jacobian between the spatial 9-dimensional geometry and the corresponding VS. This will enable one to transform the VS covariance matrix (a 9 by 9 real symmetric matrix which has already been extracted from the data) directly into that corresponding to the spatial coordinates of the molecule. Diagonalization of those matrices will ultimately yield the 9-dimensional vibrational wave functions of these two molecular ions. Such an analysis of these data is currently in progress.

These results demonstrate the power of these techniques not only to study mean geometries of polyatomic molecules, but also 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 from spectroscopy, when available.

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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 horizontal 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 transformations described in the text for the CH_4^+ molecule. The ensemble mean for the carbon-ion velocity is marked by (X). The data consist of 5-fold coincidences between 4 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 percent of the peak intensity.

Fig. 3 Contour plots of the densities of protons in velocity space following the Coulomb explosion of $C_2H_3^+$. Each molecule has been oriented as described in the text. (a) Projection on the x-y plane. (b) Projection on the x-z plane. (c) Projection on the y-z plane. Contour levels are at 20, 30, 40, 50, 60, 70, 80, and 90 percent of the peak intensity for each corresponding proton group. The solid contour is the 50 percent level.

Fig. 4 A contour plot as in 3b, but including the carbon ions as well. The carbon-ion densities have been artificially reduced by a factor of 5 for display purposes. Above: isometric display of the same projection.

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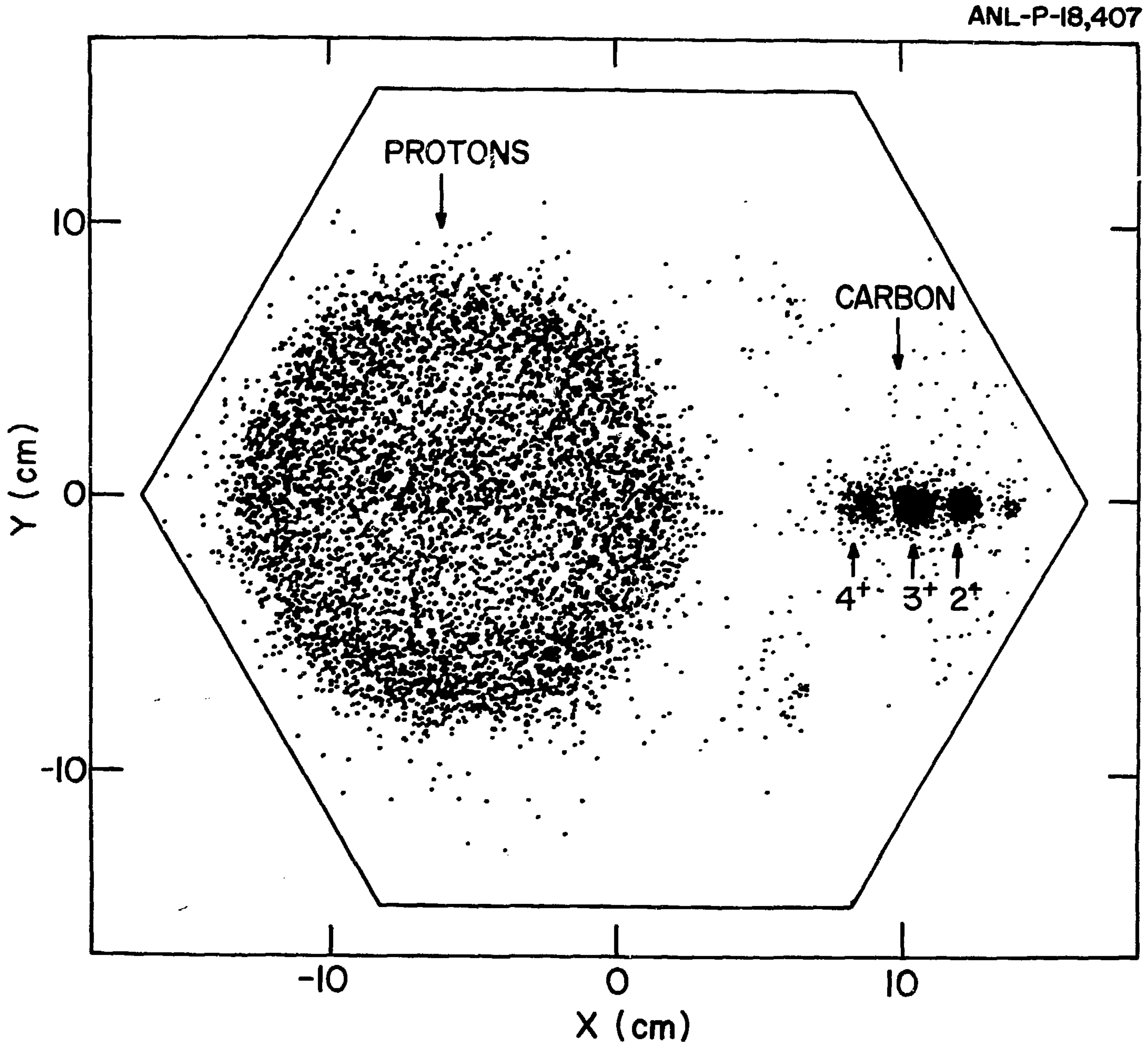
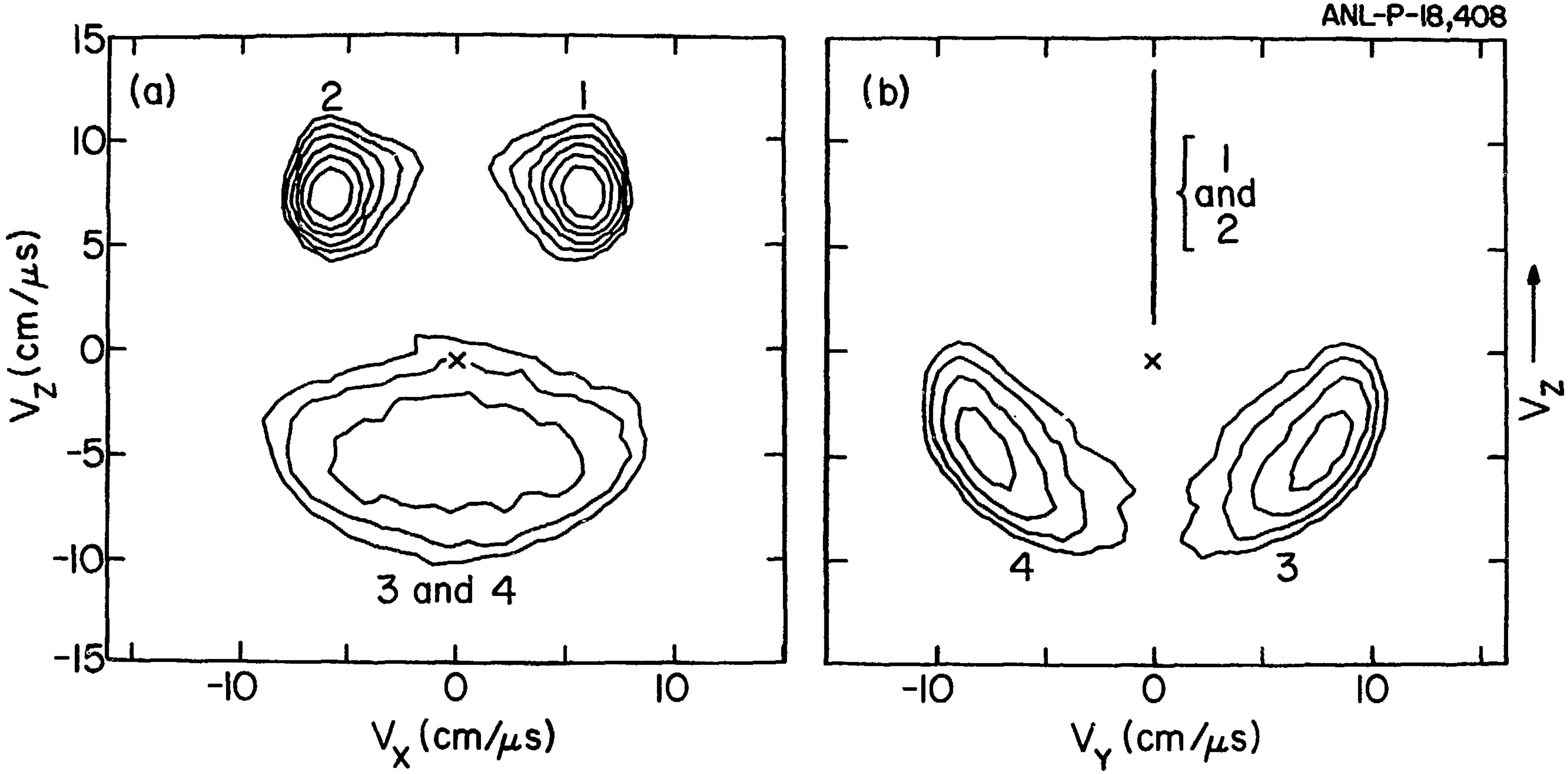


Fig. 1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(a)
2
1
3 and 4
×
15
10
5
0
-5
-10
-15
V_Z (cm/μs)
-10
0
10
V_X (cm/μs)
(b)
1 and 2
×
4
3
V_Z
-10
0
10
V_Y (cm/μs)

Fig. 2

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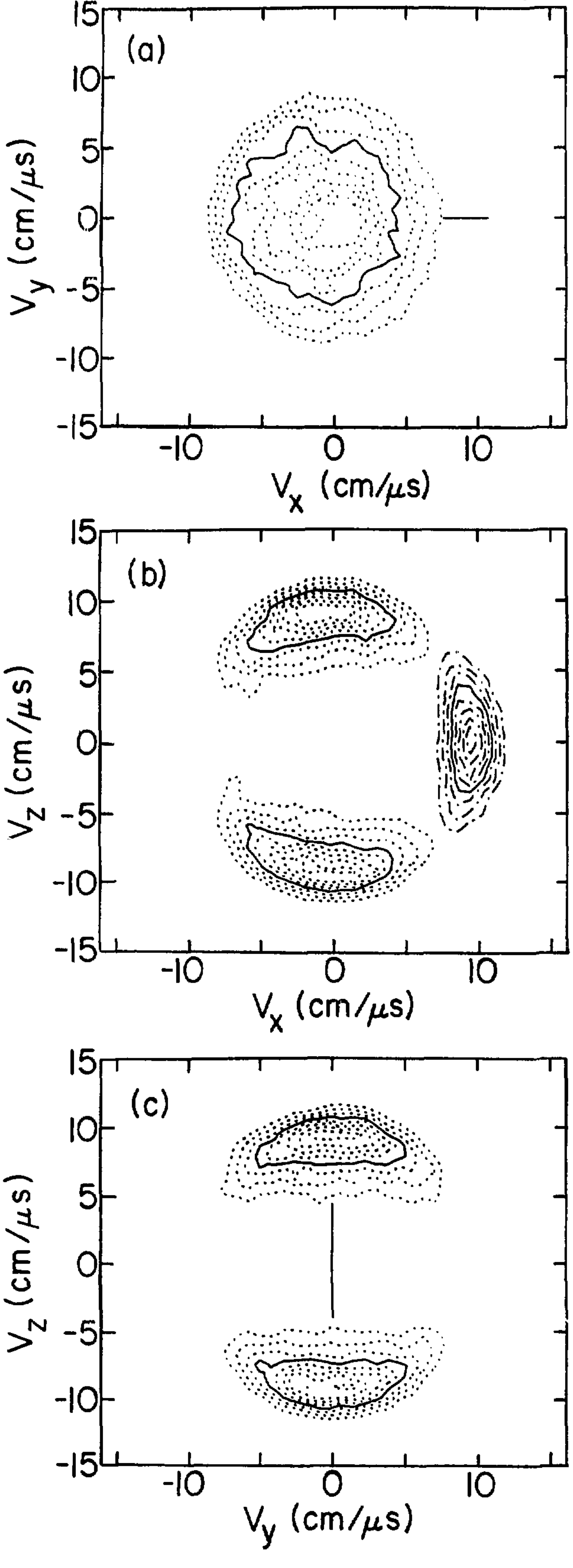

Fig. 3

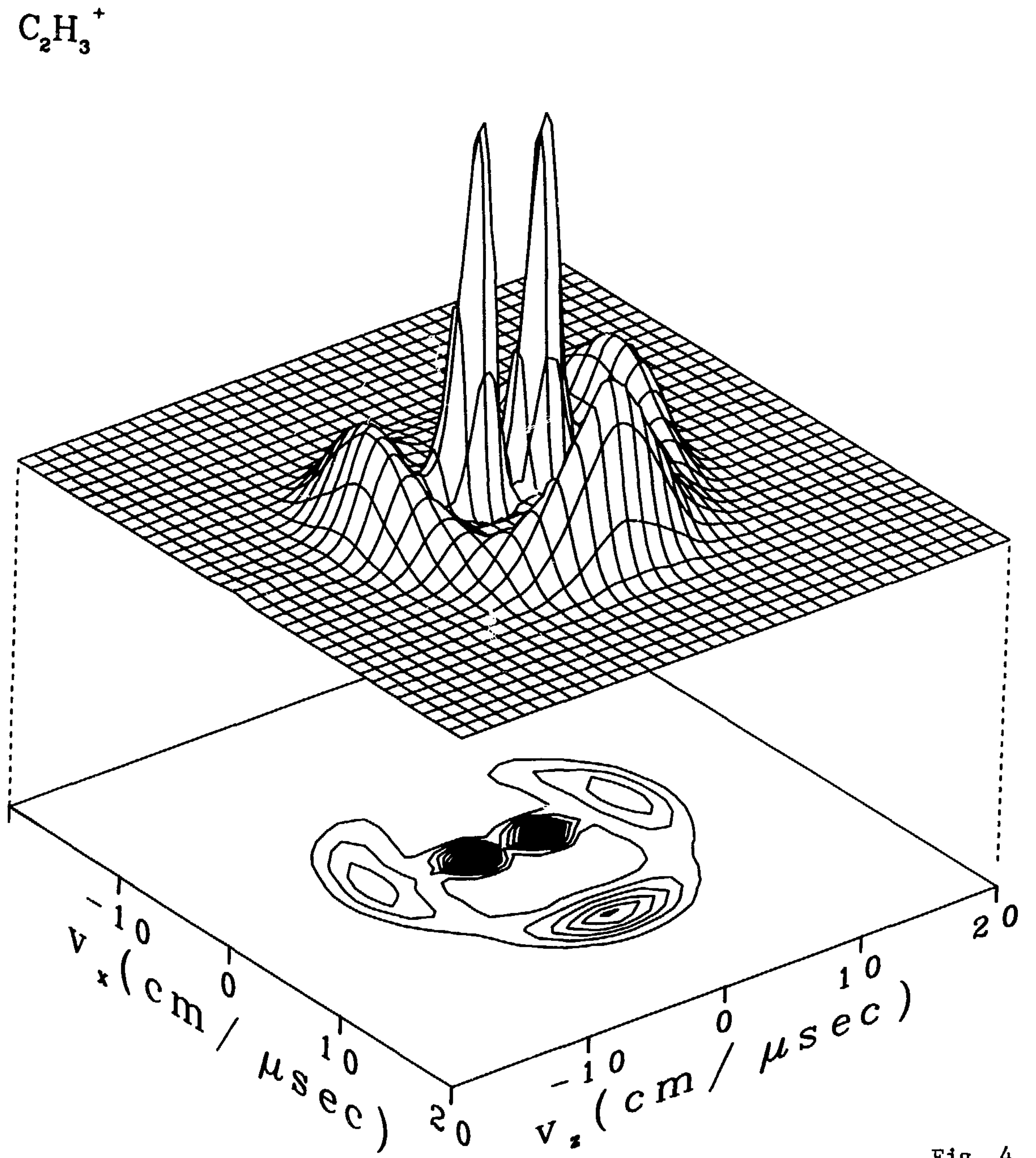

Fig. 4