

Experimental Evidence for Anomalous Nuclear Delocalization in $C_2H_3^+$

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The structure of protonated acetylene ($C_2H_3^+$), including correlations, is measured and analyzed by an advanced Coulomb explosion imaging method. In the data analysis, it is essential to include large-amplitude motions of the nuclei within the molecule and many-body correlation features for revealing the correct structure. We find that the nuclear conformations in this molecule differ markedly from theoretical predictions and previous experimental findings.

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Spectroscopic data, combined with Born-Oppenheimer approximation (BOA) based *ab initio* calculations, are the principal basis for our understanding of molecular structure. One of the main tenets of that picture is the assumption that the atomic nuclei within the molecule are localized to regions near an equilibrium conformation [1]. This assumption allows the use of single separable BOA molecular states near equilibrium and facilitates both the theoretical calculations as well as the interpretation of experiments. The main purpose of this Letter is to show that the localization assumption can be misleading. This will be demonstrated by a specific example, the $C_2H_3^+$ ground state structure. In the last 60 years, a great number of papers, mainly theoretical, have been published on $C_2H_3^+$. The relative stability of the classical [Fig. 1(a)] vs nonclassical bridged [Fig. 1(b)] planar structures has been the main issue in most of these papers. The earliest modern calculations generally predicted the classical structure to be the more stable [2]. More recent calculations, taking into account configuration interactions, reached the opposite conclusion [3–5]. The hydrogen migration problem has been treated by Hougen [6] and Escribano and Bunker [7]. They computed the intramolecular reaction path for the three protons assuming planar tunneling. On the experimental side, Berkowitz, Mayhew, and Ruscic [8] measured the photoionization

spectrum of the vinyl radical and discussed the implications for the cation structure. The infrared spectroscopy of this ion was studied by Oka and co-workers [9,10] and millimeter wave results have been reported by Bogey *et al.* [11]. The spectroscopic results have been interpreted to favor the bridged, nonclassical structures as being the most stable ones. However, the assignment of the lines in the infrared spectrum was not perfect and the observed spectral pattern was anomalous in several respects which are detailed by Oka [9]. Furthermore, the millimeter wave spectroscopy [11], although apparently consistent with the supposed bridged geometry, failed to observe the line splittings predicted by the planar tunneling model [7]. In a previous publication [12], the average structure of $C_2H_3^+$ was measured using the Coulomb explosion imaging (CEI) method. There, a preliminary analysis consisting of two-dimensional projection from the 9 nuclear internal degrees of freedom was shown, with the conclusion that the nonclassical “bridged” structure dominated the data sample. The interesting possibility of looking at correlations between the various degrees of freedom was brought up merely as a suggestion for further improved analysis.

In the present work, we have remeasured the structure of $C_2H_3^+$ using the CEI method with an improved experimental procedure and treated the full correlation between the angular degrees of freedom in the analysis. The surprising result is that the ground state structure found in this way differs markedly from the anticipated planar bridged and “classical” geometries of past predictions. It will be shown that the use of the assumption of a localized conformation in the previous CEI analysis [12] led to a bridged structure, the same erroneous result found in the spectroscopic studies.

The CEI [13] method is a model-independent technique for molecular structure determination which directly samples the fully correlated many-body nuclear density for both rigid and floppy systems. In the present experiment, $C_2H_3^+$ ions were produced by electron-impact ionization followed by supersonic expansion in the terminal of the Argonne 5-MV Dynamitron accelerator. This

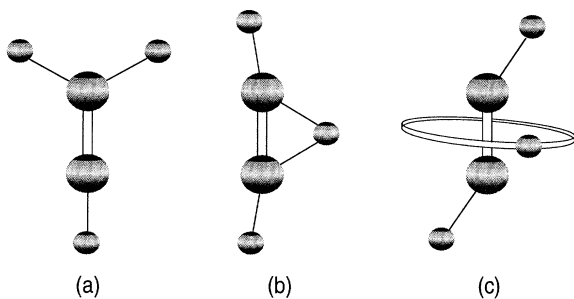


FIG. 1. Schematic views of (a) the classical structure, (b) the bridged structure, and (c) the nonplanar configuration.

serves to cool the internal nuclear motions in the molecular ion. Details concerning this ion source can be found in a previous publication [14]. After the free expansion, the molecular ions were extracted and accelerated to 4.5 MeV, magnetically analyzed, and stripped of their valence electrons by a 60-Å Formvar target [15]. The stripping process occurs in about 10^{-16} s and the resulting atomic ions start Coulomb exploding. For about 30% of all impinging molecular ions, three protons and two carbon ions with charge +2 were collected in coincidence using two multiparticle detectors [16,17]. From the information provided by these detectors, the values of all velocity components may be deduced for all fragments of each molecule (i.e., a total of fifteen components) producing a set of "velocity space" coordinates [13]. Further details of the experimental procedure may be found in Refs. [16,18]. In the previous CEI experiment [12], the charge states of the carbon ions could not be resolved nor was the beam cooled by supersonic expansion. These experimental enhancements now permit a far more detailed analysis.

When the new data are treated with the same restricted analysis performed on the previous CEI data [12], the results are nearly identical. Although we now find somewhat sharper distributions than seen in the old data, this two-dimensional analysis again yields three distinct proton groups. By taking the average coordinates of each group over the measured ensemble, one would again conclude that the equilibrium structure is of the planar bridged type. It is stressed here that the averaging procedure for each proton group is equivalent to the standard hypothesis that molecular states have a localized structure. Abandoning this hypothesis we arrive at a significantly different result.

To what extent can one abandon any *a priori* assumption in data analysis? Clearly, if there had been a measurement which determined positions of all constituents within individual noninteracting systems from an ensemble prepared in a unique quantum state, then there is no need for any assumption. The quantum mechanical observables are completely determined by such an ideal measurement. The CEI method is not such a measurement. Although all nuclear coordinates are measured in the "Coulomb-transformed" space, there is no information on the electronic coordinates. The localization assumption may now be removed; however, the characteristics of the total wave function are only partially known. Nevertheless, there is substantial structure information available in the subspace of the nuclear coordinate density which we discuss below.

To extract the correlated many-body nuclear density in velocity space, the z axis is chosen for each measured molecule parallel to the C-C vector and passing through the origin at the center of mass of the molecule. The Cartesian velocity components of each measured molecule were converted to polar angular coordinates. For

each permutation of the three protons and the two carbons, five orthogonal angular coordinates were determined, namely, $\cos\theta_1, \cos\theta_2, \cos\theta_3, \phi_{12}, \phi_{13}$, where θ_i is the polar angle of the i th proton and ϕ_{ij} are the azimuthal angles between protons i and j around the z axis. All other coordinates (i.e., the four stretching modes) were assumed to be fixed at their average values. The three cosine coordinates were transformed to permutational symmetry coordinates [19] including the totally symmetric coordinate

$$S = \sum_{i=1}^3 \cos\theta_i \quad (1)$$

and the two-dimensional representation

$$E_1 = (2\cos\theta_1 - \cos\theta_2 - \cos\theta_3)/\sqrt{6}, \quad (2)$$

$$E_2 = (\cos\theta_2 - \cos\theta_3)/\sqrt{2}. \quad (3)$$

A procedure for smoothing [20] the statistical fluctuations of the density was used [21]. Projecting the data on the E_1 - E_2 plane, we find six equivalent prominent peaks connected by saddle points at about half the peak height. These peaks are located at $(E_1, E_2) = (0, \pm 1.20)$ and $(\pm 1.04, \pm 0.60)$. This is yet another two-dimensional projection from the complete 5D angular space and is therefore still an incomplete description. For a complete description, we choose one of these peaks and explore the distribution in the full 5D density space. For example, we display in Fig. 2(a) the density on the ϕ_{21} - ϕ_{13} plane

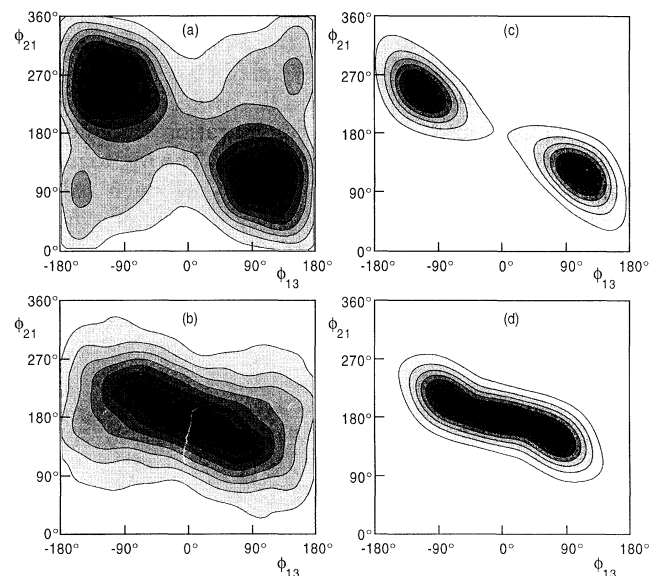


FIG. 2. (a) Contour plot for the densities of the three protons in the ϕ_{21} - ϕ_{13} plane for $S=0$, $E_1=0$, and $E_2=1.2$. (b) Same plot for the planar configuration near the point 0 (or 2π) in the path (see Fig. 3). (c) Simulated contour plot for the same coordinate cuts as in (a). (d) Simulated contour plot with the same cuts as in (b).

when the other three coordinates are $S=0$, $E_1=0$, and $E_2=1.2$. This corresponds to $\theta_1 \approx 90^\circ$, $\theta_2 \approx 30^\circ$, and $\theta_3 \approx 150^\circ$. The two peaks shown in Fig. 2(a) represent nonplanar structures with a definite chirality at $(\phi_{21}, \phi_{13}) = (110^\circ, 110^\circ)$ and $(250^\circ, -110^\circ)$.

To explore the proton migration path, an accurate tracing of the ridges of the 5D density is needed. A computer search was made along the ridges of the smoothed measured 5D density [20]. The result of that search is shown in Fig. 3, where the various θ_i and ϕ_{ij} coordinates are plotted along the most probable measured path. There is almost no change in density along this closed loop. Figure 1(c) shows a simplified schematic view of the geometric evolution along this path. In addition to this gross feature, the path described in Fig. 3 also shows a significant flexing of the acetylene core. Although the continuous change of conformations passes through a planar structure, it is neither the bridged nor the classical geometry. For example, the density in the (ϕ_{21}, ϕ_{13}) plane is plotted for the near-planar case (corresponding to the path in the region of 0 and 2π in Fig. 3) in Fig. 2(b).

To investigate the "r"-space structure represented by this v -space analysis, a simulation of the CEI process [22] was carried out. This simulation included all known foil effects and assumed an initial distribution which uniformly populated a path in r space similar to the v -space path described in Fig. 3. The spread of the wave function

transverse to this path was neglected in this simulation so that the smearing of the final velocities is due mainly to the simulated multiple scattering of the nuclei in the foil and folding effects of the Coulomb trajectories. The results of this simulation, plotted in the same coordinates, are shown in Figs. 2(c) and 2(d) for the same cuts as in Figs. 2(a) and 2(b), respectively. As can be seen, the general behavior of the simulation is similar to these data. This is also true for the other subspace cuts which were investigated but not shown here. The assumed path which was used to generate the simulation is slightly modified from the 5D v -space path of Fig. 3 due to Coulomb distortions. Again, Fig. 1(c) represents a good approximation to the path in r space. This dynamical structure is very different from past predictions and findings of alternative experimental techniques.

Is this discrepancy between *ab initio* structure calculations and experiment an isolated case or a symptom which can be discovered in a variety of other molecules? At this time, the answer is unknown. It is important to realize that experimentally, the $C_2H_3^+$ CEI measurement is comparable to the previously reported CEI measurement of $C_2H_2^+$ [23] with respect to ion-solid interactions, atomic ion excitation, detector resolutions, etc. That earlier measurement agrees with the *ab initio* theory in both the equilibrium structure and the spatial extent of the angular modes (i.e., bending frequencies). This substantially reduces the likelihood that the present findings could be flawed by unforeseen systematic effects.

In conclusion, the correlated density of nuclei within the ground state of $C_2H_3^+$ was determined with the CEI method. It is substantially different from past theoretical predictions and experimental results. For fluxional molecules, such a complex many-body density cannot be obtained without a fully correlated data set such as that given by the CEI method. We believe that the large-amplitude motion away from a definite localized structure challenges the validity of the BOA in the *ab initio* treatment of this molecule. It will be interesting to see whether this new information about the structure of $C_2H_3^+$ might help to clarify the interpretation of the spectroscopic anomalies [10].

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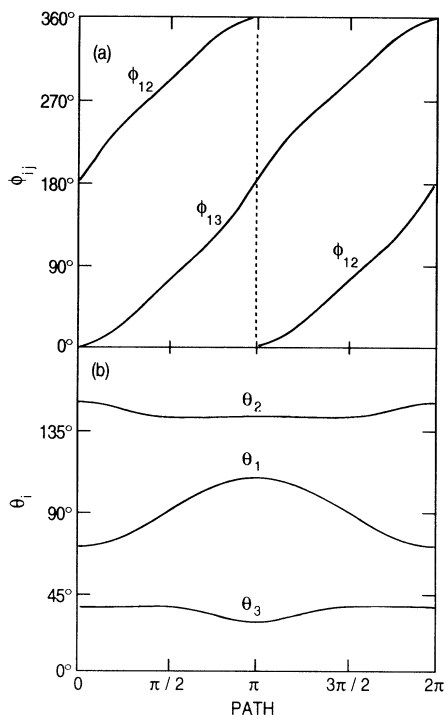


FIG. 3. (a) The ϕ_{12} and ϕ_{13} angles and (b) the θ_1 , θ_2 , and θ_3 angles along the most probable path in the measured density. The abscissa represents a phase angle along the path.

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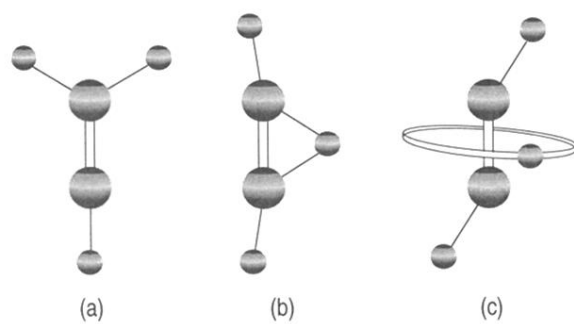


FIG. 1. Schematic views of (a) the classical structure, (b) the bridged structure, and (c) the nonplanar configuration.

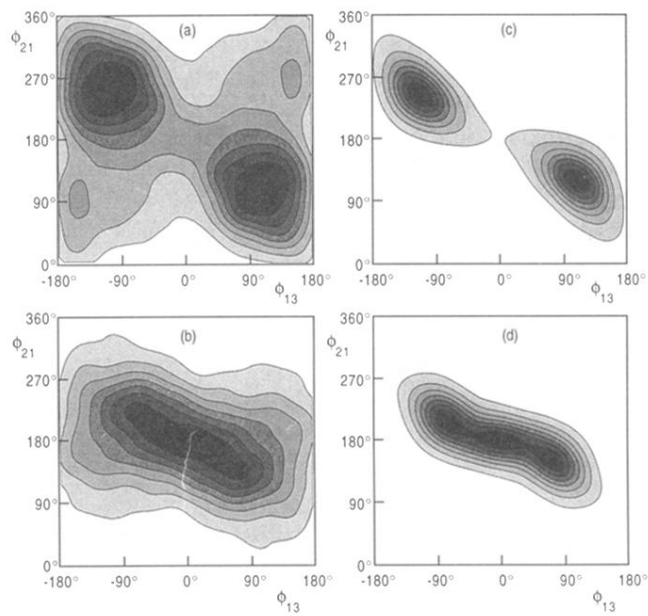


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