The Effect of Quantum and Thermal Fluctuations on the Structure of the Floppy Molecule $C_2H_3^+$

Dominik Marx* and Michele Parrinello

The structure of protonated acetylene $C_2H_3^+$ was investigated through a series of ab initio simulations that treat all nuclei as either classical or quantum particles. This makes it possible to probe separately the effects of quantum and thermal fluctuations on the molecular structure of this floppy molecule. The simulations show that the quantum ground state of $C_2H_3^+$ is best pictured as a quasi-planar bridged structure with anisotropic delocalization of the protons due to zero-point quantum effects. Comparison with high-temperature simulations suggests that recent Coulomb explosion imaging data that led to a different conclusion did not probe the ground state of the fluxional molecule $C_2H_3^+$.

Many molecules can be associated with a rigid structure for which the atomic motions within the molecule can be understood as small vibrations around this well-defined molecular structure. Important exceptions to this rule are the so-called fluxional or floppy molecules. In these cases the amplitudes of the intramolecular motion are so large that nuclear positions can become ill-defined. Such large-amplitude motions can be activated by temperature or by quantum effects. The study of such molecules poses severe experimental and theoretical challenges (*1*). An important example where there is considerable controversy is the case of protonated acetylene, $C_2H_3^+$. Recent Coulomb explosion imaging (CEI) experiments (*2*) have suggested a different ground-state structure from that found in spectroscopic (*3*–*5*) and quantum chemical studies (*6*–*8*), and a Car-Parrinello ab initio simulation (*9*) with classical nuclei suggested a high degree of proton mobility at room temperature.

The quantum chemical calculations (*6*–*8*) based on high-level theory have led to the conclusion that the global minimum on the potential energy surface of $C_2H_3^+$ corresponds to a bridged structure, also termed the "nonclassical" carbonium structure (*10*). It is characterized by an essentially linear H–C–C–H backbone, with the third (bridging) proton forming a nearly equilateral triangle with the two carbon atoms [a three-center bond (*10*)]. Another low-energy structure has a Y-shaped "classical" vinyl cation structure (*10*), with a linear H–C–C fragment and two protons forming a triangle with the remaining carbon. Both structures possess C_{2v} symmetry and are planar. The best available estimate (*6*) for the energy difference between these structures is 4.2 kcal/mol (≈0.18 eV), with an estimated overall uncertainty of at most ±1 kcal/mol due to the approximate treatment of electron correlation and the use of finite one-particle basis sets. Advanced infrared (*3*) and millimeter (*4*, *5*) spectroscopy clearly favor a bridged structure subject to proton tunneling, and the deduced rotational constants (*3*, *4*) as well as the barrier height (*5*) agree with theoretical predictions for the bridged structure.

The CEI experiment (*2*) has strongly challenged this established picture. In CEI (*11*), valence electrons get stripped off a molecule rapidly when it passes through a thin film. This initiates an "explosion" of the molecular constituents, which is mainly driven by unscreened internuclear Coulomb forces. The instantaneous molecular configuration at the moment of the explosion has to be inferred indirectly from the detected velocities. Nevertheless, CEI is the most direct experimental technique to determine molecular structures (*11*). In the case of floppy molecules, one can argue (*12*) that ro-vibrational excitations might effectively average over several distinct structures; however, the reliable assessment of such effects proves difficult (*13*). The most recent CEI data (*2*) indicated that the ground-state structure of $C_2H_3^+$ differs markedly from the traditional planar bridged and Y-shaped geometries. Instead, a trans-bend nonplanar structure with a "proton orbiting on a cyclic migration path around the C–C axis" was proposed. On the other hand, room temperature ab initio simulations (*9*) with classical nuclei indicated that $C_2H_3^+$ is floppy, with the protons permutating cyclically among the axial and bridging positions by means of Y-like structures, but they did not support the CEI picture (*2*) of a proton orbiting around the C–C bond.

Stimulated by this controversy, we undertook a quantum simulation study of $C_2H_3^+$. Our research differs in several important ways from the earlier standard Car-Parrinello simulations (*14*, *15*) of floppy molecules (*9*, *16*), where the nuclei were approximated as classical particles subject to thermal fluctuations only. First, the crucial energy difference between the bridged and Y-shaped structures is close to the best quantum chemical estimate (*6*), whereas the value 1.2 kcal/mol of (*9*) is clearly outside the theoretical bounds (*6*). Second, at low temperatures, which are relevant if the question of the ground-state structure of $C_2H_3^+$ is to be addressed, zero-point quantum motion and proton tunneling are likely to become decisive phenomena and cannot be neglected. This regime is now accessible by ab initio path integral molecular dynamics (*17*, *18*), where the interactions between quantum nuclei are simultaneously determined from electronic structure calculations for each configuration in the Born-Oppenheimer approximation. The nuclei of $C_2H_3^+$ are treated as distinguishable quantum particles within Feynman's path integral formulation of quantum statistical mechanics, which leads to efficient numerical schemes (*19*, *20*). In our approach (*17*) such effects as tunneling on the Born-Oppenheimer surface and ro-vibrational coupling are automatically included. However, symmetry restrictions on the population of rotational levels and nonadiabatic electronic effects are not taken into account. In addition to the simulations with quantum nuclei, we investigated systematically the exclusive influence of thermal fluctuations with classical (standard) ab initio simulations (*14*, *15*) at temperatures ranging from 5 to 5000 K.

We have used a cubic simulation box (with a box length of 18 atomic units) without periodic boundary conditions to avoid artifacts in the charged system. Norm-conserving pseudopotentials replaced the core electrons, and the valence orbitals were expanded in plane waves up to 35 rydberg. Using the local density approximation of the Kohn-Sham density functional theory (*15*), we obtained $C_2H_3^+$ geometries (*21*) in good agreement with quantum chemical data (*6*, *8*). Most importantly, the energy difference (3.6 kcal/mol) was within the bounds of the best theoretical estimate (*6*) (4.2 ± 1 kcal/mol). Two independent ab initio path integral simulations [see (*17*) for methodological details], starting from topologically different configurations, were conducted at 5 K for 10,600 and 31,200 steps with a 32-bead discretization as the usual approximation to the continuum limit of the path integral, which is expected to represent essentially the quantum ground state of the molecule (*18*). Both runs yielded nearly indistinguishable results when analyzed separately, which indicates that we have sampled the configuration space exhaustively. Consequently, we have taken into account both runs for obtaining the presented quantum statistical averages.

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany.

*To whom correspondence should be addressed.

The most extensive standard Car-Parrinello simulations (*14*, *15*) with classical nuclei were performed at 5, 200, 1000, and 3000 K with 45,000 (6.5 ps), 160,000 (23.2 ps), 180,000 (26.1 ps), and 270,000 (39.2 ps) configurations, respectively.

In Fig. 1 the nuclear density is projected onto the plane spanned by the carbon atoms and the most distant proton. In the classical simulation at 5 K (Fig. 1A), the protons are highly localized around the equilibrium positions of the bridged structure, and even at 200 K we did not observe thermally activated proton exchange. The introduction of quantum effects at 5 K (Fig. 1B) induces tunneling and proton exchange among the preferred sites. These effects, however, only lead to an anisotropic broadening of the projection, and the nuclear density pattern still shows well-separated peaks at the axial and bridging sites. This is in contrast with the CEI data (*2*, *22*) reported in velocity-space, where the distribution at the bridging site was smeared out considerably and was connected to the axial sites by two well-developed ridges. We were able to obtain such a pattern directly in real space by increasing the temperature considerably in the simulation (see Fig. 1C for a classical simulation at 3000 K). From this projection alone one would again deduce that the structure is also bridged; however, we will show below that this is not the case and that strongly distorted nonplanar configurations are responsible for the significant broadening.

We performed a detailed analysis of the nuclear distribution in terms of the special set of angular coordinates used in the CEI analysis (*2*), namely, the generalized coordinates (S, E_1, E_2) [defined as the symmetrized combinations $S = \Sigma_{i=1}^{3} \cos \theta_i$, $E_1 = (2 \cos \theta_1 - \cos \theta_2 - \cos \theta_3)/\sqrt{6}$, and $E_2 = (\cos \theta_2 - \cos \theta_3)/\sqrt{2}$ based on the $i = 1, \ldots, 3$ polar angles (θ_1, θ_2, θ_3)] and the two azimuthal angles ϕ_{ij} between protons i and j around the C–C axis; for each molecular configuration the z axis is chosen to be parallel to the C–C axis and passes through the origin at the molecular center of mass. To each molecular configuration corresponds then a point in the five-dimensional space (S, E_1, E_2, ϕ_{21}, ϕ_{13}). Following the data analysis in the CEI experiment (*2*), we took account of the permutation symmetry and applied the same Gaussian convolution to our raw data to smooth down statistical fluctuations.

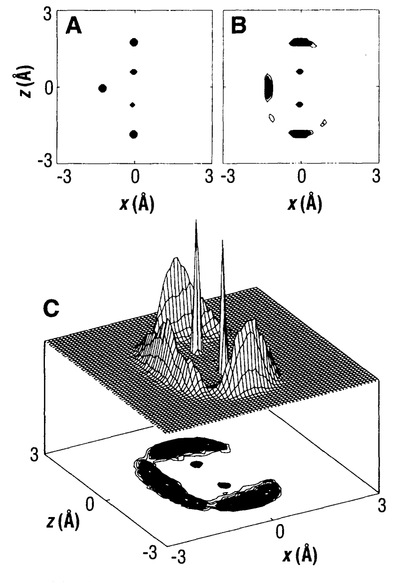

Fig. 1. Nuclear density projected onto the z-x plane spanned by the carbon atoms and the most distant proton, which defines the negative x direction: The center of mass of the C–C fragment is the origin, the z axis coincides with the C–C axis, and the carbon density is reduced by a factor of 5 as in (*22*). (**A**) 5 K, classical nuclei; (**B**) 5 K, quantum nuclei; and (**C**) 3000 K, classical nuclei.

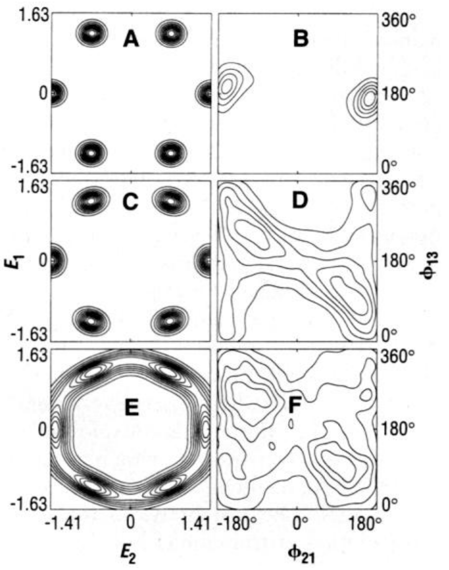

Fig. 2. Contour plot of the proton densities in the E_1-E_2 plane (left side) and in the ϕ_{21}-ϕ_{13} plane (right side) at fixed values (S, E_1, E_2). (**A** and **B**) 5 K, classical nuclei [(B): at (0, 0, 1.414)]; (**C** and **D**) 5 K, quantum nuclei [(D): at (0, 0, 1.414)]; and (**E** and **F**) 3000 K, classical nuclei [(F): at (0, 0, 1.33)]. Note that the z axis of this coordinate system is, in general, not identical to the C–C axis.

Visualizing such a multidimensional distribution is very difficult. Following the experimental strategy (*2*), we first project the full distribution onto the E_1-E_2 plane. At the position of one of the equivalent maxima of this reduced distribution, which selects the most important configurations, we also present the complete angular resolution in the ϕ_{21}-ϕ_{13} plane. In this representation, the planar bridged minimum structure subject to small amplitude (thermally activated) vibrations leads to the patterns of Fig. 2, A and B, obtained at 5 K with classical nuclei. In particular, the maximum at (S, E_1, E_2) ≈ (0, 0, $\sqrt{2}$) reflects the angular arrangement (θ_1, θ_2, θ_3) ≈ (90°, 0°, 180°) characteristic of the bridged minimum. Quantum effects (Fig. 2C) do not alter the E_1-E_2 projection substantially, but they do change the shape of the ϕ_{21}-ϕ_{13} distribution (Fig. 2D). This could result from large amplitude out-of-plane trans distortions of the two axial protons. However, their magnitude can be determined directly: the root-mean-square (rms) fluctuations of the axial protons relative to the plane defined by the carbon atoms and the bridging proton are only $\Delta y \approx \pm 0.06$ Å. Also, the average polar angular deviation from the C–C axis is very small, $\Delta\theta \approx 5°$. This is consistent with the presence of a well-defined maximum at (S, E_1, E_2) ≈ (0, 0, $\sqrt{2}$) with an essentially linear H–C–C–H backbone and the third proton located perpendicular to the C–C axis (*23*). We thus conclude that our quantum simulations at 5 K, which reflect the properties of the vibrational quantum ground state of $C_2H_3^+$, correspond to a quasi-planar bridged structure, and that the average as well as the most probable geometries (*24*) are very close to the bridged minimum (*21*), subject to an-

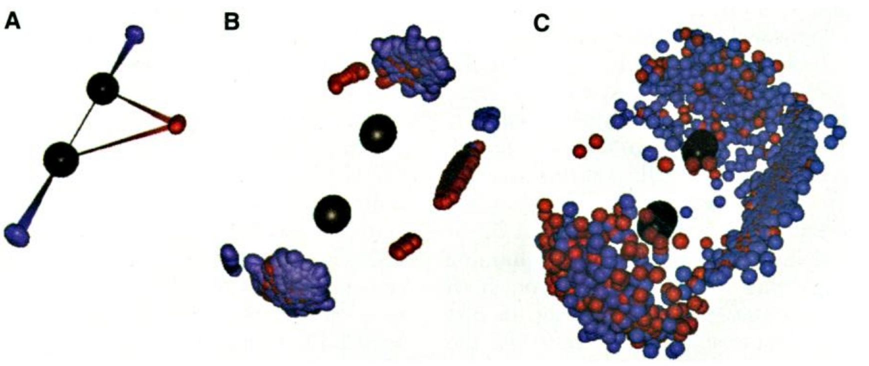

Fig. 3. Superimposed configurations obtained from the trajectories in three spatial dimensions; the reference frame is as defined in Fig. 1. For clarity, we show only a set of representative configurations, and including more does not alter the pictures qualitatively. Two protons are colored blue and the third one is red. (**A**) 5 K, classical nuclei; (**B**) 5 K, quantum nuclei; and (**C**) 3000 K, classical nuclei. Note the complete localization of the protons in (A), the small fraction of planar Y-shaped structures and tunneling in (B), and the thermal spread in (C).

harmonicity. Note that this is a conservative statement, because our energy difference between the bridged and the Y-shaped structures is somewhat smaller than the best theoretical estimate (*6*).

The qualitative features of the ϕ_{21}-ϕ_{13} distribution at 3000 K (Fig. 2F) resemble those obtained for the ground state (Fig. 2D). However, the magnitude of the out-of-plane trans distortion has increased considerably at 3000 K to $\Delta y \approx \pm 0.23$ Å and $\Delta\theta \approx 23°$. This is consistent with the qualitative change of the E_1-E_2 projection with increasing temperature: The maximum at $(S, E_1, E_2) \approx (0, 0, \sqrt{2})$ is shifted to about (0, 0, 1.33) at 3000 K (Fig. 2E). This corresponds neither to the bridged nor to the Y-shaped structure, but rather to a distorted one with $(\theta_1, \theta_2, \theta_3) \approx (90°, 20°, 160°)$. Ignoring the important differences between our real space and the velocity space of CEI, which is smeared by multiple scattering, this is very close to the values (90°, 30°, 150°) inferred from CEI (*2*). In addition, the features of Fig. 2E, with the six peaks connected by saddle points at about half the peak height and the (S, E_1, E_2) peaks shifted away from $(0, 0, \pm\sqrt{2})$, resemble those obtained from CEI (*2*). Thus, we observe only at quite high temperatures the behavior attributed to the ground state of $C_2H_3^+$ by CEI (*2*). Again, note that for a quantitative comparison of our real space distributions with CEI data reported only in velocity space, a simulation (*11*, *13*) of the Coulomb scattering process itself has to be carried out.

We summarize our main points pictorially by superimposing in Fig. 3 representative configurations obtained from the trajectories of $C_2H_3^+$. The resulting smearing is induced either by thermal or by quantum fluctuations of the molecular structure. As expected, the classical distribution at 5 K (Fig. 3A) is nearly indistinguishable from the planar bridged minimum structure. In the quantum ground state (Fig. 3B) the protons are mainly localized around the bridged configuration in Fig. 3A and exchange sites through tunneling. Thus, the quantum ground-state structure of $C_2H_3^+$ is best described as a quasi-planar bridged structure broadened significantly by anisotropic delocalization of the protons due to zero point motion. Rovibrational excitations at higher temperatures lead only to a broad distribution of nonplanar structures, including bridged and Y-shaped ones (Fig. 3C).

How does the scenario predicted by ab initio simulations compare with the CEI data? As demonstrated, the quantum ground-state structure is clearly different from what was deduced from CEI (*2*). We obtain, however, good agreement with the CEI data at high temperatures. This strongly suggests that CEI (*2*) did not probe the quantum ground state of the floppy molecule $C_2H_3^+$, but an ensemble of ro-vibrationally excited molecules. This aspect calls for further clarifications in view of the extraordinary prospects of CEI to probe nonrigid molecular structures (*11*).

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21. For the bridged structure, $r_{CC} = 1.233$ Å, $r_{CH1} = 1.304$ Å, $r_{CH2} = 1.101$ Å (where r_{ij} is the distance between the i and j atoms), and the angle formed by H1–C–H2 ($\angle_{H1CH2}$) is 117.8°; here, H1 and H2 denote the bridging and terminal protons, respectively. For the Y-shaped structure, $r_{CC} = 1.255$ Å, $r_{CH1} = 1.104$ Å, $r_{CH2} = 1.123$ Å, and $\angle_{H2CH2} = 115.8°$; here, H1 denotes the proton that forms the linear H1–C–C bond, and H2 denotes the other two equivalent protons. For notation and structures, see also (*8*).
22. E. P. Kanter, Z. Vager, G. Both, D. Zajfman, *J. Chem. Phys.* **85**, 7487 (1986).
23. A search for the maximum directly in $(S, E_1, E_2, \phi_{21}, \phi_{13})$ real space for the quantum nuclei at 5 K yielded approximately (0, 0, 1.414, 100°, 120°), and the other equivalent maxima are related by symmetry. The uncertainty of the ϕ_{ij} coordinates is estimated to amount to at least ±10°.
24. For the average structure with rms fluctuations, $r_{CC} = 1.235 \pm 0.013$ Å, $r_{CH1} = 1.320 \pm 0.090$ Å, $r_{CH2} = 1.103 \pm 0.016$ Å, and $\angle_{H1CH2} = 118.1 \pm 5°$; for the most probable structure, $r_{CC} = 1.234$ Å, $r_{CH1} = 1.290$ Å, $r_{CH2} = 1.104$ Å, and $\angle_{H1CH2} = 117.7$. Both structures were obtained with quantum nuclei at 5 K with the notation defined in (*21*).
25. A substantial part of the computations was carried out on the SP1 at the IBM Thomas J. Watson Research Center.

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Controlled Room-Temperature Positioning of Individual Molecules: Molecular Flexure and Motion

T. A. Jung, R. R. Schlittler, J. K. Gimzewski,
H. Tang, C. Joachim

Two-dimensional positioning of intact individual molecules was achieved at room temperature by a controlled lateral "pushing" action of the tip of a scanning tunneling microscope. To facilitate this process, four bulky hydrocarbon groups were attached to a rigid molecule. These groups maintained sufficiently strong interactions with the surface to prevent thermally activated diffusional motion, but nevertheless allowed controllable translation. Simulations demonstrated the crucial role of flexure during the positioning process. These results outline the key role of molecular mechanics in the engineering of predefined properties on a molecular scale.

Nanofabrication combines physical and chemical processes to assemble structures on the molecular scale. Important elements of engineering at this level, such as the controlled assembly of molecular arrays (supramolecular chemistry), require the positioning and interlocking of intact molecules without disruption of their internal atomic structure. Scanned probe microscopy (SPM) (*1*) combines the capability for manipulation of individual atoms and molecules with high-resolution imaging for determination of structure and orientation. Typically, manipulation has involved the breaking of atomic bonds through the use of voltage pulses,

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T. A. Jung, R. R. Schlittler, J. K. Gimzewski, IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland.

H. Tang and C. Joachim, Centre d'Elaboration de Materiaux et d'Etudes Structurales–Centre National de la Recherche Scientifique, 29 rue J. Marvig, Post Office Box 4347, F-31055 Toulouse Cedex, France.