

Study of Unimolecular Reactions by Coulomb Explosion Imaging: The Nondecaying Vinylidene

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Isomerization of a highly excited vibrational state of acetylene was studied using the Coulomb explosion imaging technique. A vinylidene isomer was prepared by electron photodetachment of the negative molecular ion and the corresponding distribution function of the nuclear configurations of the molecule was sampled after a time period of $3.5 \mu\text{s}$. The population of the vinylidene isomer was found to be significantly high ($\sim 50\%$), in contrast to the commonly accepted notion of vinylidene as a short-lived isomer. [S0031-9007(98)07417-1]

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The general situation of a bound system interacting with a system of much higher density of states appears in different fields of physics. Some well known examples are doorway state reactions, giant resonances [1], radiationless transitions [2], and isomerization. Often the production of "doorway states" is enabled by transitions which obey selection rules to proceed through a single resonant channel. In the particular case of molecular isomerization, the process is sometimes described as follows. A single state of an unstable (or metastable) isomer is created due to Franck-Condon overlap with an initial state. Within a short time this state interacts with the vibrationally excited levels of the stable isomer, and the molecule undergoes internal radiationless rearrangement into the stable isomeric states. This description is exact only at the limit of infinitely dense manifold of levels of the final states such as the dissociation into a continuum. For many practical cases, the high density of the stable isomer states is approximated as such a continuum.

It is the purpose of this Letter to show how the Coulomb explosion imaging (CEI) method can be used to study such molecular isomerization by measuring the full nuclear density function of a molecule at a doorway energy state. The structure and relative population of the isomers provides information on the nature of the isomeric interaction.

The equilibrium of the acetylene in the $^1\Sigma_g^+$ ground electronic state has a linear ($\text{H}-\text{C}\equiv\text{C}-\text{H}$) geometry and a rigid structure [3]. Numerous theoretical studies of the potential energy surface [4–9] predicted a local minimum at the "vinylidene" conformation ($:\text{C}=\text{CH}_2$). The energy of the vinylidene isomer is about 2 eV higher than the acetylene ground state, and the estimations of the isomerization barrier range from 0 to 0.26 eV. Recent experimental evidence including this Letter support the existence of the vinylidene isomer. Yet, the time dependent picture found in the literature is of an initially prepared vinylidene isomer which decays within a few picoseconds through a low barrier to acetylenic configurations. Carrington *et al.* [6] studied the vinylidene-acetylene isomerization dynamics by a semiclassical reaction path and analyzed

it in terms of the vinylidene decay lifetime. Their calculation yields a lifetime of 0.24 to 4.6 ps. The vinylidene isomer can be accessed directly by photodetachment from the ground state of the negative ion which also possesses the vinylidene structure [10,11]. This process has been investigated experimentally by Ervin and co-workers [12] who measured the corresponding photoelectron spectrum. Pronounced peaks were resolved and assigned to the vinylidene normal mode vibrations. Chen *et al.* [13] measured a high resolution spectrum of acetylene in the energy region that corresponds to the predicted isomerization. They were not able to assign the measured spectrum levels and used statistical analysis to attribute certain perturbations of the spectrum to the presence of the vinylidene isomer.

The experimental apparatus at the Weizmann Institute in Rehovot is designed for CEI measurements of neutral molecules. The reader is referred to Ref. [14] (and references therein) for a detailed description of the experimental setup and the principle of the CEI technique. In the experiment reported here, C_2H_2^- anions were produced by a reaction of O^- with ethylene [12] in a supersonically expanding jet. The anions were accelerated to 11.5 MeV by a 14UD Pelletron accelerator and subsequently interacted with a beam from a Nd-YAG laser (1064 nm). Part of the anions were neutralized by electron photodetachment in a process similar to the one described in Ref. [12]. Therefore, the C_2H_2 molecules produced at this stage possessed the vinylidene conformation due to the Franck Condon overlap with the low lying states of the negative ion. The neutral molecules continued in a free drift towards the CEI target chamber while all the charged particles were deflected away by a magnetic field. The target was an ultrathin foil ($1 \mu\text{g}/\text{cm}^2$) made of Formvar [15]. The collision with the target induced instant electron stripping and dissociation of the C_2H_2 molecules by Coulomb repulsion between the ionic fragments. Each molecule disintegrated into two protons and two carbon ions, mostly C^{+3} and C^{+4} . Fragments of each molecule were separated by a magnetic field and detected simultaneously. The detection system measured the position and time of

arrival for each ion fragment and its asymptotic velocity vector was derived. A $3N$ dimensional distribution was created by recording data in “ V space” from a large number of molecules. This space was defined by the directly registered velocities of the N atomic ion fragments for each molecule. The V space distribution is directly related to the distribution of the nuclear conformations in the measured molecular ensemble. We denote the nuclear conformation space as R space. The relation between R space and V space and inversion methods that allow one to reconstruct the R space density are treated in previous publications [16,17].

We emphasize two important features of the reported experiment.

(a) The energy of the detachment photons (1.17 eV) was too small to populate the excited electronic states of C_2H_2 [12].

(b) The time of flight between the region where neutral C_2H_2 molecules were created and the CEI target is 3.5 μsec .

The goal of the present Letter is to exhibit and discuss the main feature observed in the data, namely, the relative population of the vinylidene and acetylene isomers. For this purpose it is enough to show some of the data features in the directly measured V space. We, therefore, postpone the detailed structural analysis in the space of molecular conformations (R space) to a future publication.

About 10^4 measured molecules with both carbons ending up in C^{+4} charge state, after passing through the foil, were used to generate a V space distribution. This distribution is expressed as a parametrized analytic function with estimated error limits according to the method derived in Ref. [16]. It is expanded via functions of the bending coordinates $\cos \theta_1$, $\cos \theta_2$, and ϕ which are defined in Fig. 1.

$$\mathcal{D}(\cos \theta_1, \cos \theta_2, \phi) = \sum a_i f^{(i)}(\cos \theta_1, \cos \theta_2, \phi), \quad (1)$$

$f^{(i)}$ being orthonormal functions constructed from linear combinations of the form

$$f^{(i)}(\cos \theta_1, \cos \theta_2, \phi) = \sum \xi_{j,k,l}^i P^j(\cos \theta_1) \times P^k(\cos \theta_2) \cos(l\phi), \quad (2)$$

where $P^i(\cos \theta)$ are Legendre polynomials of degree i . The coefficients a_i and their errors σ_{a_i} were directly derived from the data. The linear combinations in (2) were chosen such that the representation (1) had uncorrelated errors, namely, that all nondiagonal covariance terms of the coefficients a_i vanished. Only statistically significant coefficients were used ($a_i > \sigma_{a_i}$) giving altogether 250 terms in Eq. (1). The expansion in Eq. (2) involved Legendre polynomials of order $k = 0, 1, \dots, 8$ and cosine terms with $l = 0, 1, \dots, 9$ (for a detailed description of the data analysis method see Refs. [18] and [16]). Assuming that the distribution is given by the functions defined

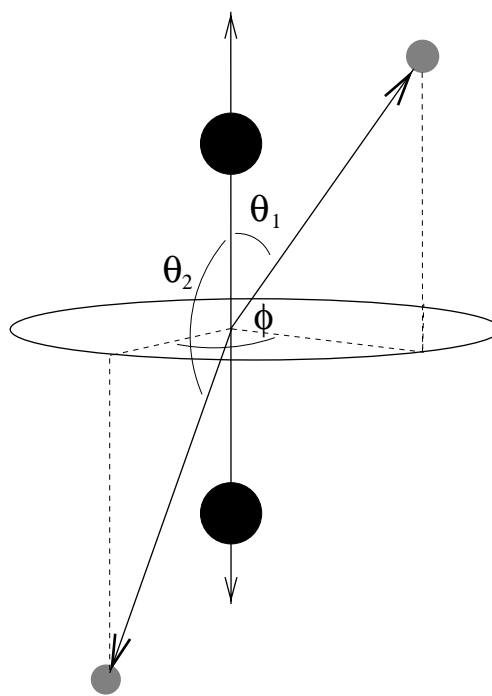


FIG. 1. The bending coordinates of C_2H_2 . The center of the CC vector is chosen as the axes origin. The polar angles of the two protons relative to the CC axis are θ_1 and θ_2 , and ϕ is the relative azimuthal angle between the protons.

in Eq. (2), the derived density function \mathcal{D} is a faithful representative of the measured data and its associated statistical errors.

Two dimensional cuts of the function \mathcal{D} are shown in Fig. 2. Contours on the plane defined by $\cos \theta_1$ versus $\cos \theta_2$ are plotted for five different azimuthal angles ϕ . One dimensional plots of the density function within $\pm \sigma$ error limits along the diagonal axes x and y (see figure) are added beneath each contour plot. CEI simulations show that the local peak in the density centered at $\cos \theta_1 = \cos \theta_2 = \pm 0.6$ and $\phi = 180^\circ$ corresponds to the theoretical vinylidene geometry ($\angle HCH = 120^\circ$ in R space) [6]. This peak disappears for $\phi < 120^\circ$ indicating a planar geometry with a vibrational out-of-plane extension. The peaks at the corners, $\cos \theta_1 = -\cos \theta_2 = \pm 1$, correspond to the linear acetylene conformation. These peaks represent 2 eV excited acetylenic structures and show preferences to asymmetric bending of a single proton.

To quantify the isomeric population ratio we defined a one dimensional path connecting the vinylidene and acetylene peaks, constrained to pass on the ridge of the density function in the three dimensional space of the bending coordinates. The density along this path is plotted in Fig. 3 within $\pm \sigma$ error limits. The point along the path where the function reaches a minimum could be used to split the distribution into two parts by inserting a boundary surface perpendicular to the path at this point. Measured molecules which correspond to data points on one side of the boundary were counted as vinylidene while those which correspond to the other side were

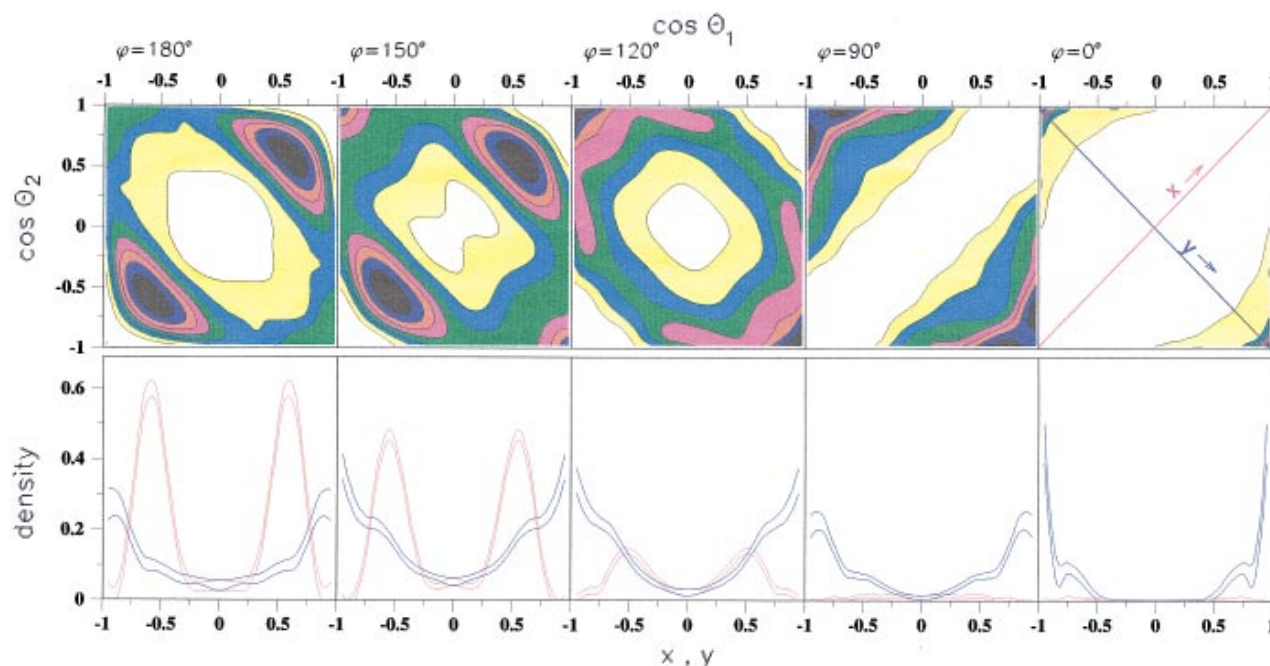


FIG. 2(color). Cuts in the measured density function $\mathcal{D}(\cos \theta_1, \cos \theta_2, \phi)$ through planes defined by $\cos \theta_2$ vs $\cos \theta_1$ for five different values of ϕ are shown as contour plots. The contour levels are equally spaced, ascending from white to black. Beneath each contour plot, the corresponding density is plotted along the diagonal axes $x = (\cos \theta_1 + \cos \theta_2)/2$ (red) and $y = (\cos \theta_1 - \cos \theta_2)/2$ (blue). The density is shown within $\pm\sigma$ error limits.

attributed to the acetylene isomer. The resulting fraction of vinylidene population given by this approximate division procedure is $\mathcal{T} \sim 50\%$. The conformation at this point was found to be close to the theoretical transition point (see, e.g., [6]).

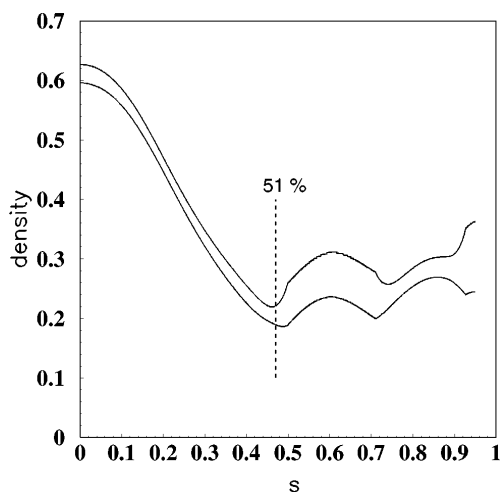


FIG. 3. A path is defined that connects the vinylidene ($s = 0$) and the acetylene ($s = 1$) peaks by following the ridge of the density function. The density along the path is shown within $\pm\sigma$ error limits. The path length s is in arbitrary units. When a boundary surface, perpendicular to the path, is defined at the minimum denoted by the dashed line, the relative population of the vinylidene isomer is 51% (see text).

The data analysis given here shows unambiguously that a large part ($\sim 50\%$) of the molecules measured $3.5 \mu\text{s}$ after their production as vinylidene isomers retains the vinylidene geometry. This is inconsistent with the generally accepted concept of the vinylidene being a short-lived isomer which decays into the linear isomer within a few picoseconds.

The interpretation of this result should be given within a nonlocalized picture that considers the eigenstates of the total molecular Hamiltonian. To formulate this define the Feshbach operators P and Q such that $P = 1 - Q$ and Q is the projection on a single vinylidene resonant state $Q = |V\rangle\langle V|$. Then, an exact eigenstate of the total molecular Hamiltonian corresponding to an eigenenergy E_k can be expressed as

$$\Psi^{(k)} = Q\Psi^{(k)} + P\Psi^{(k)} = \sqrt{p_k}|V\rangle + \sqrt{1-p_k}\Psi_P^{(k)}, \quad (3)$$

where $\Psi_P^{(k)}$ is the normalized $P\Psi^{(k)}$. The coefficient p_k ($\sum p_k = 1$) measures the vinylidene weight of each exact state. If one assumes that at the time of the photodetachment a pure vinylidene state was created, then according to Eq. (3) it can be expressed as

$$\Psi(t=0) = |V\rangle = \sum_k \sqrt{p_k} \Psi^{(k)}. \quad (4)$$

At later times, considered to be shorter than the radiative times, this wave packet develops such that each term in the sum oscillates with its characteristic energy E_k

and the initial vinylidene “coherence” disappears. Define $\{\Psi, \Phi\} = \int \Psi^* \Phi dr$ (r —electronic degrees of freedom), then the density measured by CEI is simply related to

$$\{\Psi(t), \Psi(t)\} = \sum_k p_k \{\Psi^{(k)}, \Psi^{(k)}\} + \text{time dependent terms.} \quad (5)$$

For time-insensitive measurements such as the one reported here, the last terms are smeared out. The terms in the sum can be expressed, by substituting (3), as

$$p_k \{\Psi^{(k)}, \Psi^{(k)}\} = p_k^2 \{V, V\} + p_k(1 - p_k) \{\Psi_P^{(k)}, \Psi_P^{(k)}\} + 2p_k \sqrt{p_k(1 - p_k)} \Re\{V | \Psi_P^{(k)}\}. \quad (6)$$

The last term in Eq. (6) is a fluctuative interference term which is small for distinct isomers since the corresponding electronic functions are defined on different configuration spaces. To a good approximation the measured density is

$$\begin{aligned} \rho &= \{V, V\} \sum_k p_k^2 + \sum_k p_k(1 - p_k) \{\Psi_P^{(k)}, \Psi_P^{(k)}\} \\ &= \mathcal{T} \rho_v + (1 - \mathcal{T}) \rho_p, \end{aligned} \quad (7)$$

where ρ_v is the density of the vinylidene isomer and ρ_p is a weighted average density of the acetylenic configurations that interact with the vinylidene state. The quantity $\mathcal{T} \equiv \sum p_k^2$ measures the relative population of the vinylidene isomer. Yet, since $\sum p_k = 1$, it is also related to the effective number of exact states with significant vinylidene contribution (the number of coefficients p_k in the sum which are significantly larger than zero). Therefore, \mathcal{T} defines the spreading of the resonant vinylidene state, created by the Franck Condon selective photodetachment channel. This point is elaborated below.

The extreme conditions are as follows:

- (1) $\mathcal{T} = 1$, the vinylidene isomer is a metastable state.
- (2) $\mathcal{T} \ll 1$, the vinylidene state $|V\rangle$ spreads on a large number of quasicontinuum exact states. The population of each state is small and can be approximated by a resonance behavior. The initially created vinylidene wave packet will decay, and the corresponding spectral strength of the vinylidene structure will have a Lorentzian shape.

The properties of isomerization discussed so far in the literature [6], in terms of “the lifetime of the vinylidene,” correspond to the second case, when the final distribution contains a negligible contribution of the initially created vinylidene. The data show, however, that $\mathcal{T} \sim 0.5$. This means that only a small number of exact levels contribute to the vinylidene resonant state. This rules out the simple “lifetime” interpretation. For example, imagine a two state model with $p_1 = p_2 = 1/2$. This matches the experimental findings with $\mathcal{T} = 1/2$ and a time dependent wave packet which goes back and forth between the prepared vinylidene structure and some acetylenic structure given by the CEI data. Eventually,

this wave packet will decay by radiative processes. Future time-sensitive experiments might demonstrate such recurrence phenomena of this system.

It is instructive to compare this result to the lifetime broadening of the vinylidene state calculated by Carrington *et al.* [6]. The number of participating levels is given approximately by $N \sim 1/\mathcal{T} = 2$ and the spreading in energy is $\Gamma \approx N\varepsilon$ where ε is the average spacing of the participating states. If the experimental value $\varepsilon = 2 \text{ cm}^{-1}$ is used [13], then $\Gamma \sim 4 \text{ cm}^{-1}$ corresponding to a fictitious lifetime $\tau = 2\hbar/\Gamma = 2.6 \text{ ps}$ which is in fair agreement with the calculation in Ref. [6].

To summarize, it was shown by measurements of the density function of nuclear conformations that the vinylidene isomer of C_2H_2 , which was believed to be very short lived, survives for a period of at least $3.5 \mu\text{s}$. A simple theoretical framework was introduced in order to clear up a misconception in the literature. In this framework the observed vinylidene structure corresponds to 2–3 exact states, each is given by a coherent superposition of both vinylidene and acetylene amplitudes.

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