

## Photoelectron-Photoion Momentum Spectroscopy as a Clock for Chemical Rearrangements: Isomerization of the Di-Cation of Acetylene to the Vinylidene Configuration

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We have used complete correlated momentum mapping of the photoelectron and heavy ion products from the dissociation of the di-cation of acetylene, induced by photoionizing the carbon *K* shell of one of the atoms, to map out the angular correlation between the electron and the axis of the target molecule. The (quasi-) symmetric decay is found to proceed through both acetylene and vinylidene configurations. By using the strongly peaked photoelectron emission to “start a clock,” an upper limit of 60 fs is placed on the isomerization time from the acetylene to the vinylidene configuration.

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The importance of the vinylidene configuration of  $C_2H_2$  as an intermediate in combustion and other organic reaction pathways has been heavily studied and discussed in the literature for more than two decades since the discovery of this molecule (see Refs. [1–6] for an entry to the literature). The isomerization between the acetylene and vinylidene configurations of  $C_2H_2$  has been heavily studied in both neutral [2–6] and ionic species [7] and for numerous excitation/ionization entrance channels. Experiments which provide direct measurements of the time scale for the rearrangement are rare [7].

The species under investigation in this Letter is the di-cation of acetylene/vinylidene, which has been comprehensively investigated through various means [8–14]. In particular, the photo fragmentation of acetylene in the UV region by Thissen *et al.* [14], who studied photo-double ionization of acetylene near threshold (35–65 eV), showed a significant population of the  $CH_2^+—C^+$  dissociation channel, indicating that the excited molecular ion can rearrange to the vinylidene configuration following photoionization but prior to dissociation. An accompanying theoretical study in that work, and a following comprehensive *ab initio* study of the  $C_2H_2^{2+}$  molecular ion by Dufлот *et al.* [15] provided a very detailed interpretation of the experimental data and description of the decay pathways for this isomerization as well as for other photo dissociation channels. Gadea *et al.* [16] suggested that a core-excited acetylene molecule, produced via x-ray excitation, would be unstable toward the vinylidene configuration, and might change its configuration on a time scale comparable to that for the decay of the *K* hole, and thus possibly provide a natural clock for studying the speed with which the rearrangement occurs.

The present Letter deals with the double ionization of acetylene through photoionization of the molecule just

above the carbon *K* edge (photoelectron energy 20 eV). The molecule so ionized then populates the di-cation via Auger electron emission and subsequently fragments into two charged pieces. We measure the momentum vectors of the photoelectron and the emitted fragments. The usual approach [17–19] is to use the molecular breakup in the radial dissociation approximation to *a posteriori* align or orient the molecule, and use this to measure the photoelectron angular distribution relative to the molecular axis. In this Letter we approximately turn this idea around: we use the photoelectron distribution to indicate the alignment of the target molecular axis at the time of photoionization, and then ask to what extent the molecule decays along this axis. For the acetylene configuration (*A*), we find that the symmetric dissociation into the  $CH^+—CH^+$  channel is along the line of the target. For the vinylidene final configuration (*V*), indicated by decay into the  $CH_2^+—C^+$  channel, considerable rotation of the  $C=C$  bond prior to dissociation is seen. From the quantitative analysis of the data, we deduce the rotation angle and are able to place an approximate upper limit on the time taken by the molecular ion to rearrange from the *A* to the *V* configuration.

The experimental arrangement is similar to that described in Refs. [17–19], where more detail can be found. Linearly polarized (polarization: *x* axis; propagation: *z* axis) 310 eV photons from the Advanced Light Source (ALS) (beam lines 9.3.2 and 4.0) were incident on a supersonic jet (*y* axis) of acetylene gas and ionized the *K* shell of one of the carbon atoms of the molecule, ejecting a photoelectron of 20 eV. The singly charged ion subsequently Auger decays to the di-cation and dissociates, usually emitting two singly charged ions. The two ions and the electrons were collected by a static electric field of 10 V/cm, oriented perpendicular to the photon beam (*z* axis), and projected onto the faces of

position- and time-sensitive channelplate detectors equipped with delayline anodes. From the times and positions with which the particles hit the detectors, the vector momenta of all three particles were reconstructed on an event-by-event basis.

The emission of the photoelectron is a fast process: a 20 eV electron will traverse a typical molecular distance of 2 a.u. in a time of  $4 \times 10^{-17}$  sec, during which the atomic constituents of the molecule cannot move nor can the molecule Auger decay. Thus the photoelectron is prompt, and the angular distribution of the photoelectrons with respect to axis of the target molecule is determined before the breakup occurs. The molecular ion then undergoes an Auger decay in approximately 7 fs, somewhat faster than either the dissociation or rearrangement times, and finally dissociates. (In further discussion we will make the simplifying assumption that the Auger decay precedes the dissociation and the rearrangement, an assumption supported by the results of Bøvre *et al.* [20], although this assumption is not essential to the final conclusions of the Letter.)

The photoion-photoion (PIPICO) spectrum, in which the flight time of the first heavy fragment is plotted versus that of the second one, shows a clearly defined line (sharp line in Fig. 1) corresponding to decays of a mass-26-amu molecular ion into nearly symmetric pairs (13/13 or 12/14). This spectrum does not, however, allow the separation of these two possibilities. The presence of both of these channels appears when the fragment momenta in the  $xz$  plane are calculated under the (incorrect) assumption that only the 13/13 channel (hereafter referred to as the *A* or acetylene channel, yielding  $\text{CH}^+$  and  $\text{CH}^+$ ) is present (upper panel of Fig. 2). If a single kinetic energy release (KER) for the *A* channel were populated, all events would lie on the solid black curve superimposed on the data. The presence of events on the other two (distorted) circles is due to the 12/14 breakup of the molecule into  $\text{C}^+$  and  $\text{CH}_2^+$  (hereafter referred to as the *V* or vinylidene channel). The dashed circles show the calculated positions we would expect to see if the fragmen-

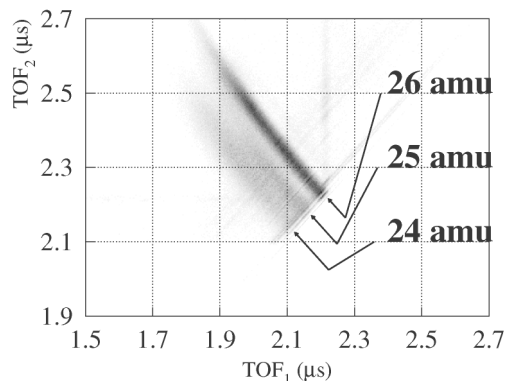


FIG. 1. PIPICO spectrum of acetylene: time of flight of first fragment versus time of flight of second, in  $\mu\text{sec}$ .

tation were really into mass 12/14 and we mistakenly calculated  $p_x$  and  $p_z$  assuming only mass 13 were present. It is clear that this is exactly what is occurring. The KER values used in calculating the curves, 5 and 4.5 eV for the *A* and *V* channels, respectively, are our observed experimental values.

By using the fact that the vector sum of the momenta of the two ions must be zero, we are able to place conditions on the data of Fig. 2 which separate the *V* and *A* channels. This works if the molecular axis is within  $45^\circ$  of the  $x$  axis, and in further analysis we use only data in this angular range. The population of the *V* channel is roughly 30% of that of the *A* channel. For comparison, we show in the lower panel of Fig. 2 what the  $xz$  momentum spectrum looks like when the complication of the two breakup paths is not present. This panel shows the corresponding data for an ethylene target, where only the fully symmetric  $\text{CH}_2^+/\text{CH}_2^+$  channel is observed.

In Fig. 3(a) we show the angular distribution of *photoelectrons* measured relative to the molecular dissociation axis, for the *A* decay channel. For this figure, we have plotted only data for which the fragments exit within  $10^\circ$  of the polarization ( $x$ ) direction. The strongly peaked and characteristic structure due to an enhanced *f*-wave strength is typical of that seen near the shape resonance in  $\text{N}_2$  and  $\text{CO}$ , and also appears here. The sharpness of the

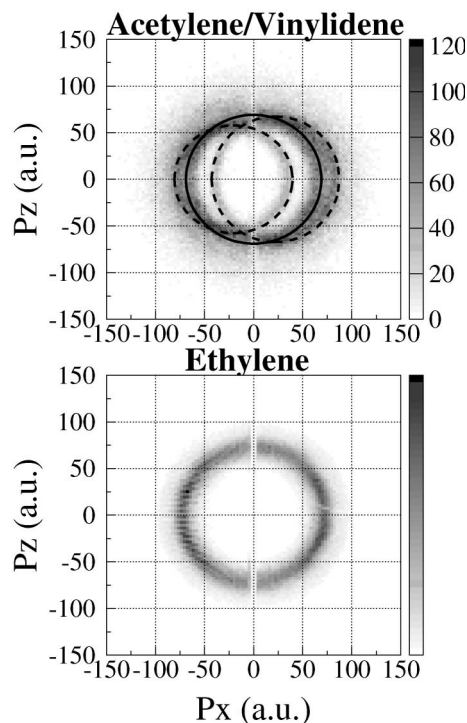


FIG. 2. Upper panel:  $p_x$ - $p_z$  spectrum for the breakup of mass 26 molecules from an acetylene target, calculated on the (incorrect) assumption that only the 13/13 channel is present. See text for details. Lower panel: corresponding spectrum for an ethylene target.

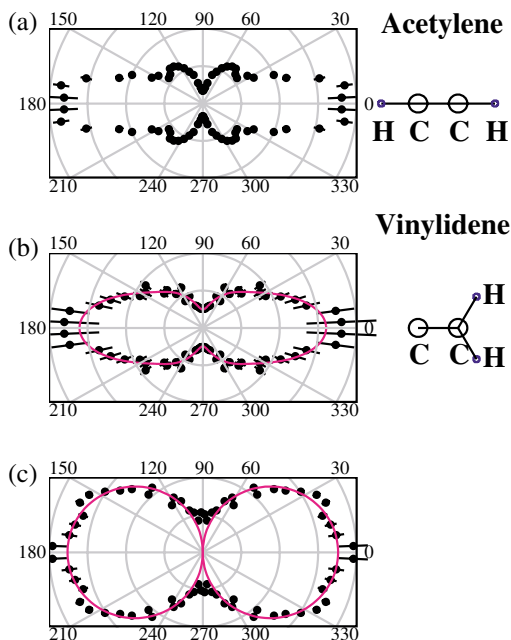


FIG. 3 (color online). (a) Polar plot of photoelectrons in the body-fixed frame for the *A* channel. (b) Same as (a) but for the *V* channel. (c) Polar plot of photoelectrons accompanying mass 26 breakup in the laboratory frame, with the polarization vector horizontal. See text for further details.

structure around  $45^\circ$  indicates that the molecule has decayed promptly so that the axis of the decay fragments coincides quite accurately with that of the target. For example, a molecule dissociating into two symmetric fragments along a Coulomb potential curve, starting at an internuclear separation distance of 1.4 a.u. would rotate only  $1.4^\circ$  if the rotational temperature of the target were 80 K. If the dissociation were slow (lifetime more than a hundred fs or so) so that the molecule could rotate appreciably before it came apart, the correlation between photoelectron and photofragment decay axis would become progressively lost. This effect was seen for the CO molecule in Ref. [18].

Figure 3(b) shows the corresponding photoelectron angular distribution for the *V* channel. The angular distribution is now considerably washed out, a result which we attribute to rotation of the molecular ion prior to dissociation. In Fig. 3(c) we show for comparison the laboratory angular distribution of all photoelectrons which accompany mass 26 breakup, with no condition on the molecular axis. This spectrum is nearly the same as that which would be obtained if the molecular ion rotated for a very long time before it came apart. (We note that this statement is not in general true, but we verified that it holds in this case by tests done with the ethylene target data.) Figure 3(b) is clearly intermediate between Figs. 3(a) and 3(c), indicating some but not complete washout. (The distributions of Fig. 3 have been forced to be symmetric about the horizontal and

vertical axes, as is required by the experimental geometry for the situations of Figs. 3(a) and 3(c). For Fig. 3(b), symmetry about the vertical axis is not required in principle, but is expected on physical grounds [19] and was observed to hold within experimental error, so we chose to symmetrize this distribution as well.)

We have deduced an experimental “rotation angle” from the data of Fig. 3(b) in the following way. It was assumed that the molecular ion produced the photoelectron distribution of Fig. 3(a), but before it emitted the heavy fragments it rotated by an angle  $\theta$ . Using the *A* channel data, the angles of all particles were calculated in the usual way, but, before plotting, a randomization angle, of a magnitude reflecting a Gaussian distribution centered at  $\theta_0$ , was added to the angle between the photoelectron and the molecular axis. The direction of the rotation axis was taken to be random with respect to the molecular axis. This is approximately what the molecular ion itself does in the decay process. The width of the Gaussian was taken to be 25% of  $\theta_0$ ; the results were found to be very insensitive to this percentage. The parameter  $\theta_0$  was then varied until the distribution of Fig. 3(b) was produced from the data of Fig. 3(a). The result is shown as a solid curve in Fig. 3(b). A plot of the chi-squared of the resulting fit to the data of Fig. 3(b) is shown in Fig. 4 as a function of  $\theta_0$ . A clear minimum is seen near  $\theta_0 = 0.35$  rad.

It is tempting to directly interpret this angle as being due to the product of the initial angular velocity of the molecule, caused by the finite rotational velocity of the target, and the time taken by the di-cation to reach the *V* configuration. However, it is important to remember that some rotation of the angle of the CC bond inevitably accompanies the rearrangement from the *A* to the *V* configuration, even for an instantaneous rearrangement.

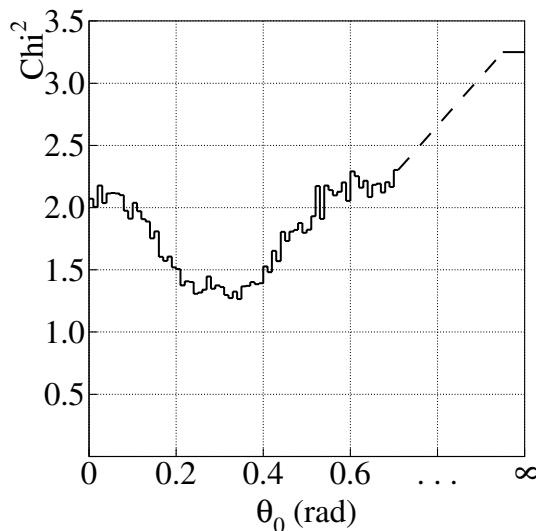


FIG. 4.  $\text{Chi}^2$  of fit versus  $\theta_0$ .

The minimum rotation consistent with the mass rearrangement depends on the path the H atom follows in proceeding from its initial position on one end of the di-cation to its final home at the other end. If it goes straight down the C—C axis, no rotation is required; however, this is a very unlikely path. The details of the transition states through which the di-cation is expected to isomerize are described by Duflo *et al.* [15], and resemble more closely a tangential path around the center of mass of the system. Taking a constant radius path around the center as a model, one can deduce that the minimum rotation of the CC bond consistent with the mass rearrangement is 0.38 rad, essentially equal to the experimentally observed angle. Thus the data are consistent with an instantaneous rearrangement from the *A* to the *V* configuration. We conservatively estimate that an additional angle of no more than 0.2 rad due to rotation prior to decay would be consistent with the data. The Auger decay of the *K* hole emits an electron with a momentum of 4.6 a.u., which, on a lever arm of 0.7 a.u., would impart to the molecule a maximum angular momentum of 3 a.u., with an average value near 2 a.u.. If the di-cation had 2 a.u. of rotational angular momentum, it would require only about 60 fs to rotate by 0.2 rad. We thus believe that an isomerization time greater than about 60 fs is inconsistent with our data. If an additional contribution to the target rotational velocity due to its rotational temperature were introduced, an even lower time would be deduced. An isomerization time at least this small is consistent with the expected [15] bending frequencies for the molecule, of order  $10^{14}$  Hz. We therefore conclude that the H atom makes a very prompt trip around the periphery of the molecule following ionization.

In conclusion, we have observed that the acetylene molecular ion formed by removing a single carbon *K* electron often rearranges from the acetylene (*A*) to the vinylidene (*V*) configuration before dissociating into the (quasi)symmetric mass-conserving channels of the doubly charged molecule. We have used the very peaked angular structure of the photoelectron angular distribution to deduce that this isomerization process must be a prompt one, with no more than about 60 fs delay between photoelectron emission and final dissociation into the *V* channel. We suggest that the quantitative use of such photoelectron distributions as a clock for measuring characteristic times for chemical rearrangements could prove of quite general usefulness.

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