

Probing Instantaneous Single-Molecule Chirality in the Planar Ground State of Formic Acid

D. Tsitsonis,¹ M. Kircher¹, N. M. Novikovskiy², F. Trinter³, J. B. Williams,⁴ K. Fehre,¹ L. Kaiser¹, S. Eckart¹, O. Kreuz⁵, A. Senftleben,² Ph. V. Demekhin^{2,*}, R. Berger^{5,†}, T. Jahnke^{6,7,‡}, M. S. Schöffler^{1,§}, and R. Dörner^{1,||}

¹*Institut für Kernphysik, Goethe-Universität Frankfurt, Max-von-Laue-Straße 1, 60438 Frankfurt am Main, Germany*

²*Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany*


³*Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

⁴*Department of Physics, University of Nevada, Reno, Nevada 89557, USA*

⁵*Department of Chemistry, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany*

⁶*Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany*

⁷*European XFEL, Holzkoppel 4, 22869 Schenefeld, Germany*

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We experimentally demonstrate that individual molecules of formic acid are chiral even when they are in the vibronic ground state, which has a planar equilibrium structure. We ionize the C 1s shell of the molecule and record the photoelectron in coincidence with positively charged fragments. This provides two consecutive measurements of the structure of one molecule, the first by photoelectron diffraction imaging and the second by Coulomb explosion imaging. We find that both measurements show the same handedness of the specific molecule. The phenomenon of being achiral on average but chiral at the level of individual molecules is general to prochiral molecules and is a consequence of the three-dimensional zero-point delocalization of the nuclei in the vibrational ground state.

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Structures of rigid molecules are often represented using ball-and-stick models, which convey the classical perspective that atomic nuclei occupy fixed positions with well-defined arrangements, distances, and angles. However, even within the Born-Oppenheimer approximation, the vibrational wave function possesses a finite spatial extent, challenging the notion of nuclei as particles with precise locations. The quantum nature of atomic nuclei implies that if their positions in isolated molecules were measured, one would find a distribution of positions with probabilities given by the square of the vibrational wave function. For molecules with at least four atoms and a planar equilibrium structure, this quantum feature has an important consequence: due to the statistical interpretation of the squared norm of the wave function almost every snapshot generated using any experimental technique that is sensitive to the instantaneous position of all atoms in an individual molecule would show a three-dimensional rather than a two-dimensional molecular arrangement as the nuclei will be found slightly out of the equilibrium plane. Extruding an object from two to three spatial dimensions can lead to the

emergence of a new property absent in planar objects embedded in three-dimensional space: chirality. A notable molecular example is formic acid, which has a planar equilibrium structure in the electronic ground state. Because of quantum delocalization and zero-point motion of the nuclei, practically all measurements of an individual formic acid molecule will find a chiral structure with R and S enantiomers appearing, neglecting the effect of parity violation due to the fundamental weak interaction [1,2], with equal probability.

The established terms “dynamical chirality” [1,3,4] and “transient chirality” [5] (for further discussions of the terms, see also Refs. [6,7]) do not fully capture the quantum nature of this phenomenon. Instantaneous chirality is present in the time-independent, stationary ground state of a molecule—even in the absence of nuclear motion—and therefore does not require dynamics. In contrast to transient chirality, it is not induced by interactions and does not arise, evolve, or decay during a reaction. In the pioneering work of Kitamura *et al.* [4] on ion-impact-induced Coulomb explosion of CD₄, four distinguishable momentum vectors of the D⁺ ions were observed upon complete fragmentation, revealing chirality in the fragmentation pattern. The authors attributed this effect to zero-point vibrations, in the same spirit as the interpretation adopted in the present Letter. However, they referred to it as dynamical chirality, whereas we propose the term “instantaneous chirality.” It is one of the puzzling aspects of

*Contact author: demekhin@physik.uni-kassel.de

†Contact author: robert.berger@uni-marburg.de

‡Contact author: jahnke@atom.uni-frankfurt.de

§Contact author: schoeffler@atom.uni-frankfurt.de

||Contact author: doerner@atom.uni-frankfurt.de

quantum theory that for a stationary state, instantaneous chirality does not already exist as a realistic property of the prochiral molecule before it is measured (see Ref. [8]). It first emerges due to spontaneous symmetry breaking during the measurement process. For simplicity and readability, this Letter will, however, adopt the not entirely accurate “realistic” terminology, setting aside these complex quantum theoretical nuances.

The purpose of the present Letter is to report on an experiment in which we measure the handedness of individual formic acid molecules in the gas phase twice, in two consecutive measurements on the same molecule, exploiting inner-shell photoionization. The first measurement is done by photoelectron diffraction and the second one follows shortly after by imaging the Coulomb explosion as the molecule rapidly fragments. In photoelectron diffraction, a photoelectron wave is emitted from a localized K shell “illuminating the molecule from within” [9]. This creates a diffraction pattern in the molecular frame of reference. The power of this technique for structure determination has been shown in many works (see Ref. [10] for a review).

Historically, the Coulomb explosion was first ignited by passing swift molecular ions through a thin foil, consequently stripping many electrons [11]. Today, mostly neutral molecules are multiply charged by a strong femto-second laser pulse [12,13], a photon pulse from a FEL [14], or by single-photon ionization of an inner-shell electron followed by Auger cascades [15–18]. In Coulomb explosion imaging, one measures the linear momentum vectors of ionic fragments that carry the desired information on the structure in coordinate space. In cases where the ionic potential surface is known exactly [19], with some constraints, even an inversion from the measured linear momenta into the initial coordinate space is possible [20–23]. The technique is well-suited for measuring deviations from the equilibrium structure. Examples include the precise determination of the helium dimer bond length [24] and the helium trimer geometry, where the notion of a well-defined triangular structure was shown to fail completely [25]. The sensitivity of this technique to ground-state fluctuations, i.e., to correlations between positions of atoms in the ground state of larger molecules, has recently been shown in Ref. [26].

The experiment was performed at beamline P04 of the synchrotron radiation facility PETRA III at DESY (Hamburg, Germany) in 40-bunch mode [27]. The pulsed photon beam was crossed with a supersonic molecular beam in a COLTRIMS reaction microscope [28–30], such that on average less than one molecule Coulomb-explodes per photon pulse. Electrons and ions were guided by an electric field of 160 V/cm onto microchannel-plate detectors with hexagonal delay-line position readout [31]. From the measured times of flight and positions of impact of the ions, the mass-over-charge ratios and the three-dimensional

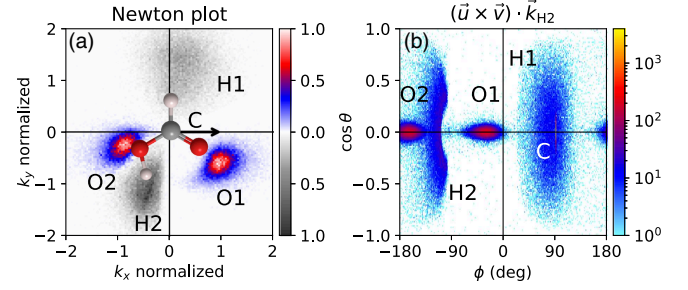


FIG. 1. Coulomb explosion imaging of formic acid (HCOOH) following C 1s photoionization at a photon energy of 305.5 eV. Four charged particles (C^+ , O^+ , O^+ , and H^+) are detected, and the linear momentum vector of the fifth particle (H) is obtained using linear momentum conservation. Panel (a) shows the distribution of momenta in the plane of the molecule; the carbon ion is emitted upward (as indicated by the arrow; see text for definition of coordinates). The magnitudes of the momenta of the particles i are scaled by $1/\sqrt{m_i}$, where m_i is the mass of each fragment. The color bar represents the normalized relative intensity of the data. Superimposed in this plot is the equilibrium structure of formic acid with C in gray, O in red, and H in white. (b) Polar representation of a side view onto the plane shown in panel (a). The plane is located at $\cos \theta = 0$, where θ is the polar angle with respect to the normal of the plane in panel (a). $\phi = 90^\circ$ is selected to be the direction of the carbon ion and is visible as a sharp, vertical line.

momentum vectors were calculated. To distinguish the two O and two H atoms, we followed the procedure described in the “Methods” section of Ref. [32].

Figure 1 shows the measured linear momentum vectors for the case where we detected four charged particles: C^+ , O^+ , O^+ , and H^+ . The momentum vector of the undetected H was obtained by exploiting linear momentum conservation. We find that the momentum vectors of the three heavy particles are almost coplanar, and we use them to define a coordinate frame as follows: the momenta of the heavy particles span the x - y plane, and the carbon ion momentum is fixed within the plane, which is defined by the z and the positive- x direction. In this frame, the unit vectors \hat{x} , \hat{y} , \hat{z} are defined as follows:

$$\hat{z} = \frac{\vec{u} \times \vec{v}}{|\vec{u} \times \vec{v}|}, \quad \hat{x} = \frac{\hat{z} \times \vec{w}}{|\hat{z} \times \vec{w}|}, \quad \hat{y} = \hat{z} \times \hat{x}, \quad (1)$$

with

$$\vec{u} = \vec{k}_{\text{O2}} - \vec{k}_{\text{C}}, \quad \vec{v} = \vec{k}_{\text{O1}} - \vec{k}_{\text{C}}, \quad \vec{w} = \vec{k}_{\text{C}} \times (\vec{u} \times \vec{v}). \quad (2)$$

Figure 1(a) shows a Newton-plot-type top view of this molecular plane with the carbon ion momentum pointing upward along positive y , as indicated by the arrow in the panel (which corresponds to the projection of the carbon ion momentum onto \hat{y}). The magnitude of the normalized momenta of particle i shown in Fig. 1(a) has first been

scaled by $1/\sqrt{m_i}$ (with m_i being the mass of the respective particle) to account for the mass differences, and has then been normalized to the carbon $k_{\text{norm},i} = (k_i/\sqrt{m_i})/(k_C/\sqrt{m_C})$. In Fig. 1(b), we show a “side view” of the x - y plane, choosing polar coordinates with respect to the z axis, that is, the polar angle is $\theta_i = \arccos(k_{i,z}/k_i)$ and the azimuthal angle is $\phi_i = \arctan2(k_{i,y}, k_{i,x})$. In these coordinates, the x - y plane is located at $\cos \theta = 0$ and the carbon ion momentum defines $\phi = 90^\circ$. This representation, indeed, shows the linear momenta of the heavy nuclei to be narrowly confined to the plane at $\cos \theta = 0$. The momenta of the two protons are bending broadly out of the molecular plane. The angles shown in the figure are angles between the measured linear momentum vectors, and the mapping from angles in position space to momentum space is highly nonlinear. Coulomb explosion, as a tool for sensing this out-of-plane extrusion of light particles, profits from a magnification upon changing from coordinate to final-state momenta (see, e.g., Supplemental Material of Refs. [32] and [26]). To give an example, a wagging of H1 of 6° out of the plane results in an out-of-plane angle of 15° for the H1 linear momentum after the Coulomb explosion.

In Fig. 2, we show the structure of the vibronic ground state of formic acid. There are nine vibrational normal modes: seven in-plane and two out-of-plane deformations. When considering small amplitude displacements in the vibrational ground state of formic acid, only the latter two are of interest in the current context, while for larger displacements, nonlinearities will kick in. Panels (a) and (b) show the molecule’s structure at the classical turning points of the respective torsional and wagging normal modes. In the harmonic approximation, the ground-state

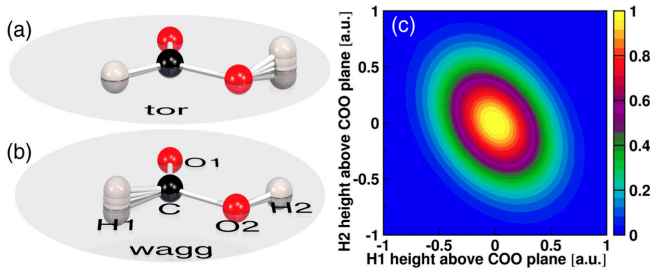


FIG. 2. Formic acid vibronic ground state. (a),(b) Structures between the classical turning points of the two out-of-plane normal modes of the formic acid electronic ground state as computed in the harmonic approximation on the explicitly correlated coupled-cluster levels with iterative single, double, and perturbative triple amplitudes [CCSD(T)-F12] with a triple-zeta basis set (aug-cc-pVTZ-F12) using MOLPRO [33,34]. (a) OH torsional mode (669.67 cm^{-1}). (b) CH wagging mode (1054.68 cm^{-1}). (c) Computed correlation between the two H atoms in the vibrational ground state based on the reduced two-mode harmonic model. The horizontal and vertical axes show the height of H1 and H2 above the COO plane, respectively.

wave function as a function of the generalized coordinates of the normal modes is a product of two Gaussian functions. Coulomb explosion does not sense the normal-mode coordinates but the position coordinates of the individual atoms. The transformation of the ground state to these experimentally accessible coordinates is shown in Fig. 2(c). This shows that, within the ground state, the position of the two H atoms with respect to the plane spanned by the heavy atoms is highly anticorrelated. Such ground-state correlations have recently been experimentally confirmed, as well, for a larger molecule [26].

The broad distribution of the out-of-plane angle of the proton momenta suggests the use of $\cos \theta_{k_{\text{H2}}}$ as an indicator of the chirality. It is given by the triple product (see Refs. [32,35])

$$\cos \theta_{k_{\text{H2}}} = \frac{(\vec{u} \times \vec{v}) \cdot \vec{k}_{\text{H2}}}{|\vec{u} \times \vec{v}| \cdot |\vec{k}_{\text{H2}}|}. \quad (3)$$

Here, $\cos \theta_{k_{\text{H2}}} > 0$ corresponds to the R enantiomer and $\cos \theta_{k_{\text{H2}}} < 0$ to the S enantiomer. This allows unambiguously to split detected molecular fragmentation events into left- or right-handed enantiomers, even though they all arise from the planar ground state of formic acid. In Fig. 3, we select two subsets from our data corresponding to R [panels (a) and (c)] and S [panels (b) and (d)] enantiomers, respectively, choosing $\cos \theta_{k_{\text{H2}}} > 0.25 (< -0.25)$ [i.e., H2 being emitted upward or downward in Fig. 1(b)]. Figures 3(a) and 3(b) show an anticorrelated wagging of the H1 fragment. This is caused, in part, by the anticorrelation in coordinate space (Fig. 2), and to a larger extent by the choice of the coordinates, as the \vec{u} and \vec{v} vectors [Eq. (2)] include the recoil of the hydrogen atoms by linear momentum conservation. Furthermore, anticorrelation between the two protons’ linear momenta is also built up during the fragmentation by the Coulomb repulsion.

The chirality in the momentum pattern that we have discussed so far is measured after fragmentation. While we have argued that the observed *momentum* asymmetry reflects symmetry breaking in the *spatial* structure of the initial ground state, this is not the only possible explanation. Previous studies of multiple ionization of formic acid in a strong laser pulse concluded the opposite. They argued that symmetry breaking might occur during the dynamics on a potential energy surface of an electronically excited state after the promotion of an electron to an unoccupied π^* orbital. This excited state is known to have a double-well potential with minima for R and S pyramidalized geometries [39–41].

Along this question, for single-photon excitation, it has recently been shown and explained, in detail, how the light polarization can be used to drive this excited state preferentially into the R or S geometry [42]. However, an alternative scenario—dynamical symmetry breaking on an excited-state surface—must be excluded. To do so,

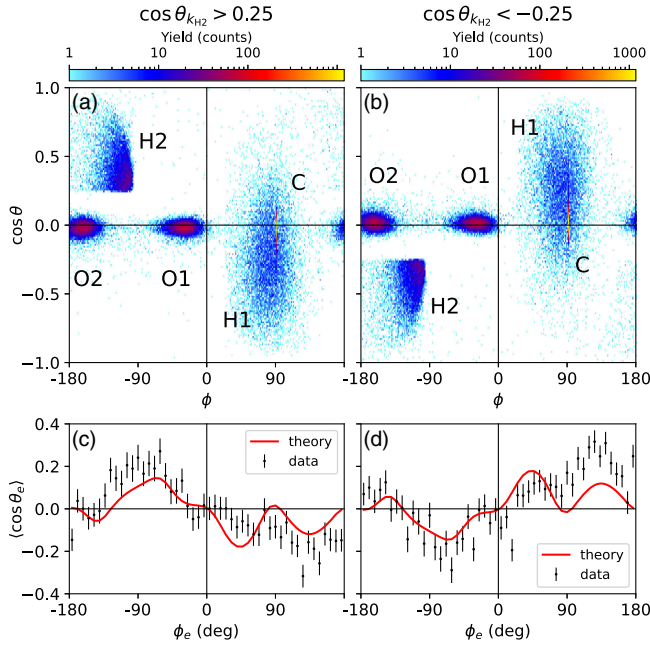


FIG. 3. Combined Coulomb explosion and photoelectron diffraction imaging of instantaneous chirality. (a),(b) Side view of the molecular frame as in Fig. 1(b). Note that the carbon is located exactly at $\phi = 90^\circ$ and is visible as a sharp, vertical line. (a) [(b)] shows a subset of data, where the H2 atom is emitted to upward [downward], $\cos \theta_{k_{H2}} > 0.25$ (R enantiomer) [$\cos \theta_{k_{H2}} < -0.25$ (S enantiomer)]. (c),(d) Photoelectron diffraction imaging of the molecules selected as in (a) and (b). The photoelectron energy ranges from 7 to 11 eV. The vertical axis shows the mean out-of-plane angle of the photoelectrons. Histogram: experimental data. Full lines: result of single-center calculation [36–38] after convolving with an estimated experimental resolution of 20° . For the experimental data in (c) and (d), the three-body breakup channel $H2^+$, C^+ , and $O2^+$ was used.

we now turn to the angular emission pattern of the photoelectrons. Photoelectron diffraction takes a snapshot of the molecular structure at time $t = 0$, the instant of photoabsorption. It captures the structure of the initial molecular arrangement before the nuclei could move and before the fragmentation has set in. The time between this snapshot and the start of the fragmentation is given by the Auger lifetime of the carbon K -shell hole, which is of the order of 7 fs [43]. To avoid the influence of the photon's polarization on the electron angular distribution we inspect polarization-averaged molecular-frame photoelectron angular distributions, which have been shown to capture the three-dimensional molecular structures quite well [44–48] and allow for chiral sensing independent of the light polarization [49]. They can be displayed in the same polar coordinate system as used in Figs. 3(a) and 3(b) with θ_e being the angle of the photoelectron to the normal of the molecular plane [see Fig. 1(a)] and ϕ_e being the respective azimuthal electron emission angle where $\phi_e = 90^\circ$ is defined by the carbon momentum. For a planar

molecular structure, these polarization-averaged photoelectron angular distributions are, by definition, symmetric upon reflection at the molecular plane, i.e., they depend only on the modulus of $\cos \theta_e$, and not on its sign. A robust measure of the out-of-plane torsion is thus the mean value $\langle \cos \theta_e \rangle$. For a planar molecular structure or an equal amount of R and S enantiomeric forms, i.e., an equal amount of upward and downward torsion structures, one obtains $\langle \cos \theta_e \rangle = 0$. Figures 3(c) and 3(d) show the asymmetry $\langle \cos \theta_e \rangle$ as a function of the azimuthal angle ϕ_e of the electron in the molecular frame for the two subsets of fragmentation events, as indicated in panels (a) and (b). We observe a clear out-of-plane symmetry breaking ($\langle \cos \theta_e \rangle \neq 0$) of the electron emission. The electrons follow the correlated upward and downward torsion and wagging of the H1 and H2 fragments. The full red lines in Figs. 3(c) and 3(d) show our calculated results of the photoelectron angular distributions after taking into account an angular resolution of $\Delta \phi_e = 20^\circ$. The calculations were carried out in the frozen-core Hartree-Fock approximation using the stationary single center method [36–38] that allows for an accurate description of angle-resolved molecular photoionization. Similarly to our previous work on this molecule [42], we set the torsion angle $\theta_{k_{H2}}$ to be $\pm 20^\circ$ out of the molecular plane. The calculations show good agreement with the observations. If the symmetry breaking we have observed in the ion fragments would have been the result of a dynamic deformation of an originally planar structure, then we would have found $\langle \cos \theta_e \rangle = 0$ for all ϕ_e . Thus, the observed out-of-the-plane emission of the electrons, i.e., $\langle \cos \theta_e \rangle \neq 0$, unambiguously demonstrates that our experiment senses the instantaneous chirality of individual ground-state molecules. This chirality is present already at $t = 0$ when the photon is absorbed and does not emerge only later during the dissociation.

To conclude, we have shown that upon measurement, formic acid in its planar vibronic ground state is on the single-molecule level found to consist of chiral structures of R or S enantiomers. Formic acid molecules (as well as other prochiral planar species) are instantaneously chiral in their ground state, after the photoabsorption. Two consecutive measurements of the same molecule find the same handedness of the molecule. While this may sound contradictory, the effect is a straightforward consequence of the quantum delocalization of the nuclear wave function. In one dimension, this manifests in the often close-to-Gaussian distribution of bond lengths [21,50] and the spontaneous breaking of the symmetry in photoionization of the CO_2 molecule [51,52]. In two dimensions, it leads to the fact that linear triatomic molecules such as CO_2 extrude into two dimensions and are bent at the single-molecule level [53]. In three dimensions, it leads, as we have shown, to a three-dimensionality and in prochiral cases can trigger instantaneous chirality and spontaneous symmetry breaking of planar molecules upon measurement.

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Data availability—The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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