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Adiabatic ionization potential of acetic acid and torsional dynamics of its cation

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Pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopy and supersonic cooling are used to investigate the CH₃ torsional dynamics of the acetic acid cation and to determine an accurate value for the first adiabatic ionization potential of acetic acid ($\text{IP}=85\,912\pm5\text{ cm}^{-1}$), which has been the subject of debates for more than 40 yr. A doubling of the torsional barrier upon ionization is due to a significant shortening of the C–C bond and reduces the tunneling efficiency by an order of magnitude. © 2009 American Institute of Physics. [DOI: [10.1063/1.3149802](https://doi.org/10.1063/1.3149802)]

The interest in acetic acid (AA) (CH₃COOH) and acetic acid cation (AAC) (CH₃COOH⁺) in astrobiology arises from indications that AA is one of the building blocks of life.¹ Glycine, e.g., is known to be formed from ammonia and AA. Since AA is found in the interstellar medium and in meteorites, it could have been brought to Earth by asteroids, comets, or meteorites. In unscreened regions of space, it is exposed to ultraviolet radiation, which in the extreme ultraviolet (XUV) region leads to ionization and fragmentation. While the spectroscopic properties of carboxylic acids have been investigated extensively,^{2–5} studies on the spectroscopy and photochemistry of their cations are comparatively limited^{6–10} in spite of their essential role in understanding astrochemistry and thus the origin of life. The value of the first adiabatic ionization potential (IP) of AA has been debated for more than 40 yr. Reported values scatter between 10.35 and 10.70 eV, i.e., over a range of more than 2500 cm^{−1} (see Refs. 6, 8, and 10, and references therein). Other important issues with implications for the reaction kinetics of AAC concern the dynamics of its low frequency modes, especially the CH₃ torsion with its unknown potential barrier (H) and tunneling efficiency (Fig. 1). In the present contribution we employ pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy (see Refs. 11–14 and references therein) in combination with supersonic cooling to address these open questions.

The determination of the IP of AA and the torsional dynamics of AAC has turned out to be an experimental challenge. Photoelectron spectroscopy is the method of choice, but the resolution of spectrometers is often limited, while the extraordinary stability of the AA dimer further complicates the situation. The monomer is the dominant species only at high temperatures and low pressures, which can be realized in low pressure cells or effusive beams. Under such conditions, however, hot bands and thermally broadened rotational contours make the accurate determination of the IP and the torsional dynamics impossible. Figure 2(a) shows a simulation of the photoelectron spectrum of AA with the highest resolution yet reported.⁶ The bands are structureless and

broad due to hot bands and broad rotational structure. No torsional structure is observed and the position of the IP remains unclear.

To tackle this problem, we combine a custom-built PFI-ZEKE photoelectron spectrometer with a supersonic expansion of 1.7% AA seeded in helium at a total pressure of 1 bar.^{13–15} This approach allows us to measure the photoelectron spectra of cold AA monomers selectively, very sensitively, and with high resolution (0.5 cm^{−1}). The selectivity in PFI-ZEKE spectroscopy is achieved by laser excitation of very high lying Rydberg states that converge to a rovibrational level of AAC, which are field ionized (0.19 V/cm) after a time delay (2 μs). The time delay, together with a weak discrimination field (0.09 V/cm), ensures that prompt ions and electrons (from AA and its oligomers) leave the ionization region before the Rydberg states are ionized and their electrons are detected. The excitation is effected in a single step by a custom-built ns-XUV laser (resolution of 0.5 cm^{−1}), which is based on resonant four-wave mixing in a rare gas beam. Supersonic cooling of the sample is a prerequisite to reduce the contributions from hot bands and to narrow the rotational structure. Cooling, however, leads to the predominant formation of dimers and larger oligomers with only traces of monomer left in the sample, as illustrated in the time of flight spectrum in Fig. 3. Note that the mass resolution is limited as our setup is optimized for sensitive electron detection (defocused laser beam and short flight tube). The arrow indicates the very small AAC monomer peak, while all other peaks are fragments of oligomers. With only about 100 ppm AA monomer in the supersonic beam, demands on the selectivity and sensitivity of the electron detection are very high.

The PFI-ZEKE photoelectron spectrum in the region of the first adiabatic IP is shown in Fig. 2(b) together with a calculated spectrum for a vibrational temperature of 100 K in trace C. Photoionization spectra (ion signal not shown here) of AA and its oligomers confirm that the ZEKE spectrum arises solely from AA because only AA shows a threshold in this region. The main band at 85 912 cm^{−1} is the transition between the vibrational ground states of the neutral ($v=0$) and the ion ($v^+=0$) (Fig. 1). Our simulation of the rotational

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FIG. 1. Calculated potentials for the CH_3 torsion (ν_{18}) of AA and AAC with corresponding energy levels (labels v and v^+ , respectively, and C_{3v} tunneling symmetry labels in order of increasing energy).

structure shows that the width of this band is determined by the rotational structure with a rotational temperature of 10 K. The A, E torsional tunneling splitting as well as the rotational structure cannot be resolved with our laser. The calculated tunneling splitting is 0.35 cm^{-1} in AA and 0.06 cm^{-1} in AAC. The simulation of the rotational structure reveals a high average density of more than 100 transitions per cm^{-1} . The bands on the high frequency side at $85\,937$ and $85\,976 \text{ cm}^{-1}$ are torsional transitions between states as labeled in Fig. 1. The second band system at $86\,269 \text{ cm}^{-1}$ is the excitation of one quantum of the CCO deformation motion ν_{12} of AAC. This transition is also accompanied by CH_3 -torsional transitions on the high frequency side. The signal of this band system is about a factor of 3 less than for the first band system because the light intensity in this region drops by a factor of 3 due to the four-wave mixing efficiency. This band is scaled accordingly in Fig. 2.

The IP of AA, the torsional barrier height H of AAC, and the corresponding tunneling splittings are derived from an analysis of the torsional structure observed in the ZEKE spectrum. We assume separability between rotational $|r\rangle$, CH_3 torsional $|\tau\rangle$, vibrational $|v\rangle$, and electronic degrees of freedom with nonseparable interactions minimized by im-

FIG. 2. (a) Calculated photoelectron spectrum of AA monomer at a temperature of 298 K and a resolution as reported in Ref. 6. (b) Experimental PFI-ZEKE photoelectron spectrum. (c) Calculated photoelectron spectrum at a vibrational temperature of 100 K.

FIG. 3. Time of flight spectrum recorded at a laser photon energy of $85\,974 \text{ cm}^{-1}$. The AAC monomer is labeled with an arrow. The spectrum is dominated by fragments of the dimer (Di), the trimer (Tr), the tetramer (Te), and the pentamer (Pe). Mass to charge ratio is given in u/e .

posing orthogonality between infinitesimal vibrations, rotations, and torsions. Vibrations are treated as harmonic, except for the torsion, whose eigenfunctions are calculated explicitly in a discrete variable representation.¹⁶ Spectra were simulated within the Franck–Condon (FC) approximation for transition probabilities

$$P(r^+ \tau^+ v^+ \leftarrow r \tau v) \propto \left(\sum_{\ell} f_{\ell}(r, r^+) \right) \cdot |\langle \tau | \tau^+ \rangle|^2 \cdot |\langle v | v^+ \rangle|^2,$$

where (+) indicates ionic functions. The rotational contributions f_{ℓ} , which depend on the photoelectron's orbital angular momentum ℓ , are not known explicitly and therefore replaced with a phenomenological Gaussian band shape. The vibrational FC factors account for geometry change and Dushinsky rotation.¹⁷ The spectrum is given by the convolution of rotational, torsional, and vibrational factors. All equilibrium geometries, harmonic force fields, and torsional potentials were calculated within density functional theory (B3LYP/6-31+G*).¹⁸ At this level of theory the bare potential barriers (without zero point effects) along the minimum energy torsional path amount to 111 and 270 cm^{-1} for the neutral and the ion, respectively. In our calculations we employ these potential functions directly on the equidistant grid that defines the discrete variable representation for the solution of the torsional eigenvalue problem.¹⁶ The torsional potential of the neutral was scaled linearly by a factor of 1.53 to match the experimental barrier height of 170 cm^{-1} .¹⁹ The analogous scaling factor for the torsional potential of the ion as well as the adiabatic IP and the torsional temperature were varied to match the ZEKE spectrum, resulting in an IP of $85\,912 \pm 5 \text{ cm}^{-1}$, a torsional barrier of $H = 316 \pm 10 \text{ cm}^{-1}$, and a torsional temperature of 100 K. In addition, the distance of $357 \pm 5 \text{ cm}^{-1}$ between the two strongest transitions at $85\,912$ and $86\,269 \text{ cm}^{-1}$ is a direct measure of the CCO deformation mode of the AAC. The doubling of the torsional barrier height upon ionization hints at a significant shortening of the C–C bond. B3LYP calculations predict a shortening of the C–C bond by about 1 pm largely independent of the basis set employed (1.6 pm for the PBE0 functional⁶), but the effect is more pronounced at the MP2/aug-cc-pVTZ level, which yields a bond length reduction by 2.1 pm. It may be instructive to note that even CCSD(T)/aug-cc-pVTZ (geometry optimized at the MP2 level) underestimates the

torsional barrier by about 20% (145 and 264 cm^{-1} for neutral and ion, respectively). The increase in the torsional barrier upon ionization drastically reduces the tunneling efficiency by almost one order of magnitude. The accompanying increase in the spacing of torsional energy levels produces corresponding changes in the partition function of AAC which will be most relevant at low temperatures.

In summary, we have shown that the combination of PFI-ZEKE photoelectron spectroscopy with supersonic cooling of an AA/helium mixture allows the determination of an accurate adiabatic IP of AA, thus ending a 40 yr long debate. Supersonic cooling is essential to avoid the congestion caused by hot bands and broad rotational contours, while only a very sensitive and selective spectroscopic method can cope with the exceedingly small AA monomer concentrations in the supersonic expansion. Our experiments have enabled the analysis of the low frequency torsional dynamics of the cation, which will be important for statistical theories of the chemical reaction kinetics of AAC, especially at the low temperatures prevalent in space. Finally we would like to emphasize two more general aspects of this investigation. Our results illustrate the importance of detailed modeling for a reliable quantitative analysis of experimental photoelectron spectra, a point that has not always been appreciated as exemplified in occasionally exaggerated claims of accuracy. Second, this study demonstrates that with due attention to detail and optimization PFI-ZEKE photoelectron spectroscopy can achieve sufficiently high sensitivity to study molecules present only in trace amounts.

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