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Short note

Ultrafast formation of an intramolecular cation–pi bond

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ABSTRACT

Ultrafast conformeric dynamics in N,N-dimethylphenethylamine is initiated by photo-excitation to the 3p Rydberg level. On the ion-like potential energy surface of the Rydberg state, the formation of an intramolecular cation–pi bond between the positively charged amine ion core and the aromatic ring is observed in real time using Rydberg fingerprint spectroscopy. The structural dynamics of the cation–pi bond formation proceeds with a 5.3 ps time constant at an internal temperature of 760 K.

1. Introduction

Cation–pi interactions are prevalent in myriad of chemical systems as a driving force behind structure and dynamics [1,2]. They have been found to be integral to protein structure [3], ion channel regulation [4], biochemical recognition [5,6] and material design [7,8]. Much like the hydrogen bond, the cation–pi interaction is a fundamental chemical interaction that may continue to reveal its significance, as it becomes better understood. We report here on the ultrafast conformational dynamics that leads to the formation of an intramolecular cation–pi interaction in N,N-dimethylphenethylamine (PENNA, Fig. 1) using time-resolved Rydberg fingerprint spectroscopy (RFS), a recently developed technique with outstanding ability to probe structural dynamics.

2. Experimental

2.1. General

RFS uses photoelectron spectroscopy to measure the binding energy of an electron in a Rydberg orbital belonging to a positively charged molecular ion core [9]. The binding energy depends on the molecular structure because the orbiting electron senses the charge distributions within the ion core. After a supersonic expansion in He into the interaction region of the spectrometer, PENNA is excited (208 nm) to a Rydberg state by an ultrashort laser pulse and subsequently ionized (417 nm) in a TOF energy analyzer. The photoelectron and mass spectra are monitored over varying delay times between the excitation and ionization laser pulses. The structural rearrangement of the ion core, which closely resembles that of a free ion, is observed as a time-dependent shift of the Rydberg electron binding energy.

2.2. Materials

PENNA provides a convenient system to study cation–pi interactions as it has two photophysically distinct chromophores, separated by an ethyl spacer [10,11]. N,N-dimethylcyclohexylethylamine (CENNA) (Fig. 1) was chosen as a control system because of its structural similarity yet lacking the pi electron system. CENNA was synthesized according to an adapted method [12] of catalytic hydrogenation. PENNA (7 g, 47 mmol, Sigma–Aldrich) was added to glacial acetic acid (100 mL) with Adam's catalyst (PtO_2, 1 g, 4.4 mmol). The solution was shaken under H_2 (50 psi, 14 h), filtered and condensed. The residual was dried in ether over KOH and condensed to give the pure product as confirmed by ^1H NMR and MS.

Abbreviations: RFS, Rydberg fingerprint spectra; PENNA, N,N-dimethylphenethylamine; CENNA, N,N-dimethylcyclohexylamine; TOF, time of flight.

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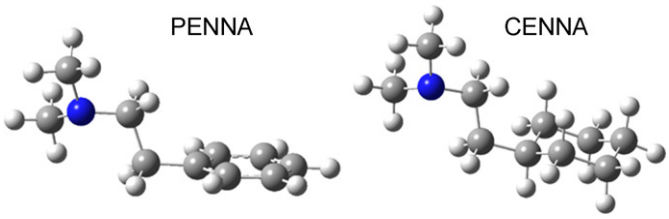

Fig. 1. PENNA and CENNA neutral ground state structures by DFT 6-31g.

3. Results and discussion

Upon laser excitation, an electron from the non-bonding lone pair of the nitrogen is selectively excited to the 3p Rydberg state. It rapidly (163 fs in PENNA and 913 fs in CENNA) decays into the 3s orbit, which serves as a sensitive reporter of the molecular dynamics. The molecular core evolves conformationally on an ion-like potential energy surface, which includes a minimum energy structure arising from the interaction between the positively charged amine group and the phenyl ring of PENNA. By varying the time delay of the ionizing laser pulse with respect to the excitation pulse, we are able to watch the time evolution of the Rydberg electron binding energy that results from the transition of the original anti-structure to the cation–pi bonded structure with the amine group positioned gauche to the ring.

The time-dependent Rydberg electron binding energy spectra of the 3s states of PENNA and CENNA are shown in Fig. 2. After the initial onset, the CENNA binding energy essentially stays flat at 2.815 eV. The 3s of PENNA, in contrast, starts initially broad, undergoes a shift in center position and narrows. We attribute this trend to the conformer dynamics on the ion-like surface of the Rydberg state.

The 3s center positions of PENNA and CENNA, as fit by a single Gaussian, are shown in Fig. 3. For PENNA the Rydberg electron binding energy decreases from 2.88 eV to 2.86 eV after an initial rise that results from the planarization of the amine group. To first order, the binding energy spectra of Rydberg states are blind to vibrational motions: typical vibrational binding energy shifts are less than 0.001 eV [13]. The widths of the PENNA and CENNA spectra are due to structural dispersion of the molecules [14,15], which arises from rotations about the single bonds of the aliphatic chains, and the deformation of the ring in CENNA. The reduction of the line width and the movement of PENNA's center position reveals that the molecule condenses the distribution of conformeric structures with a time constant of 5.3 ps.

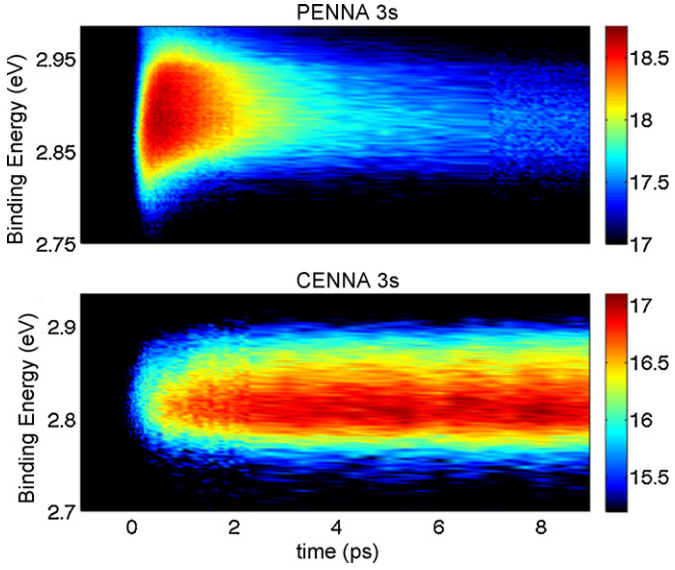

Fig. 2. Time-dependent 3s RFS spectra of PENNA (top) and CENNA (bottom), taken with 208 nm excitation followed by 416 nm ionization. The color indicates the intensity on a logarithmic scale. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

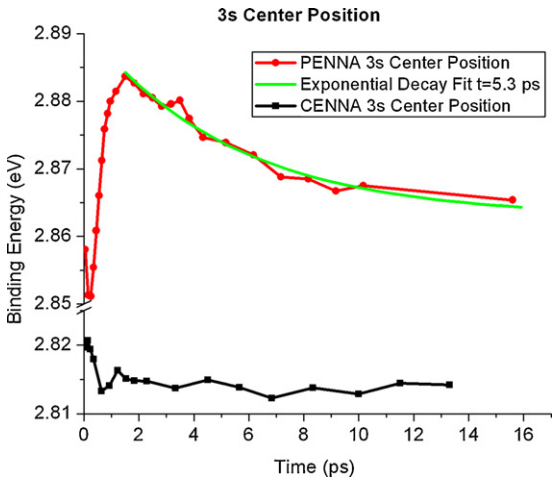

Fig. 3. 3s center positions of PENNA and CENNA as a function of time. The PENNA peak shifts with a 5.3 ps time constant.

Weinkauf et al. have calculated the stable conformer distribution of PENNA in both the molecular ground state and the cation radical [16]. In the ground state, PENNA was found to have five stable structures, four of which are expected to be populated at room temperature. The anti-conformation, with the amine group pointing away from the phenyl ring, has the lowest energy. The large line width of the PENNA binding energy spectrum at time zero (Fig. 2) is an apparent reflection of this structural dispersion.

For the cation radical, Weinkauf et al. found that PENNA has only two energy minima, reflecting geometries that have the N-methyl group anti and gauche with respect to the pi system of the phenyl ring. According to Weinkauf's MP2 (6-31+G(d)) calculation, which we have reproduced [17], the gauche structure is lower in energy by 126 meV on account of the cation–pi interaction. The barrier between the anti and the gauche structures is about 145 meV. We attribute the observed condensation of the PENNA ion core structures into the new minimum to the transition from a distribution of primarily anti-conformer structures to the formation of the gauche structure with the cation–pi bond. The corresponding narrowing of the 3s line width reflects a reduction in the number of stable conformers present in the distribution.

In the experiment, the molecules start near room temperature but are rapidly vibrationally excited by the laser pulse and the subsequent transition from 3p to 3s. This leaves the molecules ion core with about 1.55 eV of energy in vibrations. Upon projection to the Rydberg surfaces, the molecular ion core at an internal vibrational temperature of 760 K reacts across a barrier to form intramolecularly cation–pi bonded conformeric structures with a time constant of 5.3 ps.

4. Conclusion

The formation of an intramolecular cation–pi bond is observed in real time using Rydberg fingerprint spectroscopy. At an internal energy of 1.55 eV, the molecule is able to cross the barrier to the conformational motion and rotate the nitrogen ion core into a position that enables the cation–pi bond formation. This conformeric transition requires motions about several of the skeleton single bond

and takes 5.3 ps. Some structural dispersion about the pi-bonded structure remains.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.05.001.

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