Structural Dynamics and Charge Transfer in Electronically Excited N,N′-Dimethylpiperazine

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S *Supporting Information*

ABSTRACT: Two identical ionization centers, one on each nitrogen atom, make N,N′-dimethylpiperazine an important model to explore how the transfer of a (partial) charge is linked to the structural deformations of the molecular skeleton. Time-resolved photoelectron spectroscopy uncovered that upon excitation to the 3p Rydberg level at 207 nm only one of the initially symmetry-equivalent nitrogen atoms acquires the charge, creating an asymmetric molecular structure with a localized charge. Rapid internal conversion to 3s leads to a multitude of conformeric structures with the charge localized on one nitrogen atom (230 fs time constant) and a rigid structure with the charge delocalized over both nitrogen atoms (480 fs time constant). Structural motions continue while the molecule samples the 3s potential energy landscape, leading to an equilibrium between charge-localized and charge-delocalized conformeric structures that is approached with a 2.65 ps time constant.
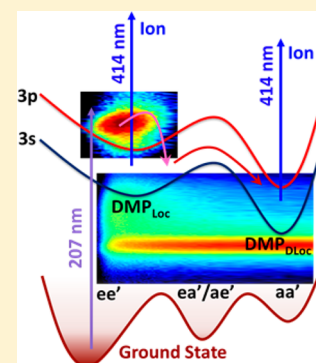
SECTION: Kinetics and Dynamics

Its relevance to both biological[1−3] and chemical[3−5] systems makes charge transfer between two (or more) charge centers an important field of study. N,N′-dimethylpiperazine (DMP, Figure 1a) and its derivatives have been studied theoretically
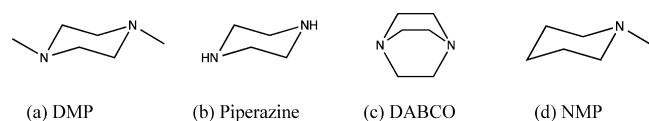

(a) DMP (b) Piperazine (c) DABCO (d) NMP

Figure 1. Structures of (a) DMP, (b) Piperazine, (c) DABCO, and (d) NMP.

and experimentally as prototypes to explore through-bond interaction (TBI) and through-space interaction (TSI) and the charge transfer between two nitrogen atoms.[6−9] In its molecular ground state, DMP has a chair conformation with both N-methyl groups in equatorial positions,[10−13] a structure that is not favorable for interaction between the nitrogen lone pair electrons. In the ground state of the cation, however, DMP can assume a symmetric geometry with both nitrogen atoms in a pseudopyramidal form that supports the delocalization of the positive charge between the two nitrogen atoms.[9] This is evident from photoelectron spectra, which show an absence of splitting of the nonbonding orbitals in DMP, in contrast with piperazine (Figure 1b), where the splitting is 0.55 eV[14] and diazabicyclo[2.2.2]octane (DABCO, Figure 1c), where the well-known TBI gives it a splitting of 2.1 eV.[6] Further evidence comes from the ionization energy of DMP, 8.41 eV,[6] which is quite similar to the 8.35 eV of N-methylpiperidine (NMP, Figure 1d),[15] which has only one nitrogen atom and consequently no charge delocalization.

DMP then presents an interesting molecular model to study charge delocalization upon ionization. In its ground state there is a lack of coupling, and the sp^3 hybridization of the nitrogen atom gives it a pyramidal local structure. In general, cation states of amines have sp^2 hybridization, giving them a planar structure. A DFT computational study of the DMP radical cation by Brouwer et al.[9] showed that when the charge is localized on one of the amine groups, the amine moiety is planar, whereas the other uncharged amine group remains pyramidal. However, the lowest energy structure of the DMP cation has the charge delocalized between the two nitrogen atoms. In that structure, each nitrogen atom formally has half a charge, and they assume a pseudopyramidal structure.[9] Consequently, the transfer of a partial charge between the nitrogen atoms should be associated with a change in the geometrical structure of the DMP cation. It is this interplay between charge transfer and the structural change that we have set out to observe.

Structure-sensitive Rydberg fingerprint spectroscopy (RFS)[16] takes advantage of the discovery that the binding energy (BE) of electrons in Rydberg states is very sensitive to both the geometrical structure of the molecular ion core[17] and the distribution of charges in the molecular system.[16] While we cannot yet invert the spectra to derive molecular structures, the spectral observations serve as fingerprints that allow us to deduce the main structural features. To explore how molecular structures evolve in time, we implement the method using a

time-resolved pump–probe technique. RFS has proven to be an effective tool to observe structural molecular dynamics and has, for example, been applied to explore the charge-transfer dynamics in a bifunctional model system,[18] the conformeric dynamics in flexible molecules,[19] and the collective motions of ligands in large van der Waals clusters.[20] In flexible molecules, different conformeric structures give rise to separate spectral peaks, or, for closely related structures, a broadened peak whose width reflects the structural dispersion of the molecules in the Rydberg state.[21] In the present investigation of structural motions associated with charge transfer, we investigate the dynamics of DMP in its Rydberg states. Because the Rydberg electrons are only weakly bound to the ion core, their contribution to the chemical bonding is small, so that the dynamics in the Rydberg states should closely resemble that of the ground-state ion.

DMP was excited from its ground state to the 3p Rydberg state using a 207 nm (5.99 eV) pulse. The time-dependent dynamics, including the internal conversion from 3p to 3s, was followed by ionizing with 414 nm (2.99 eV) probe pulses. The ejected photoelectrons were analyzed for their energies, which revealed the BE of the Rydberg levels. Figure 2 shows the time
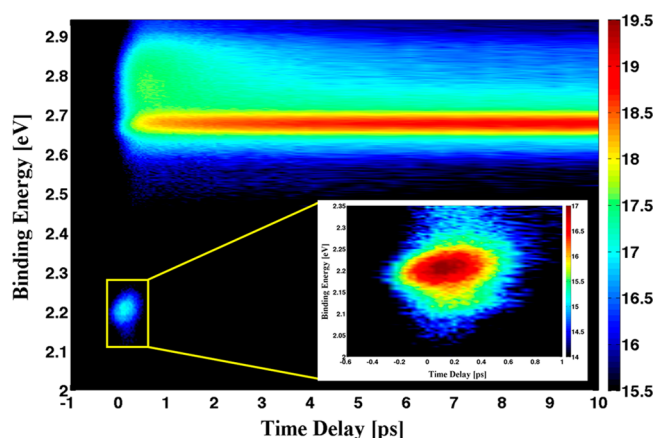
dependence of the BE spectrum. On the basis of our previous work on other amines,[21,22] we assign the short-lived feature at 2.2 eV as the 3p peak. Both the long-lived peak at 2.68 eV and the broad band between 2.60 and 2.91 eV are within the range where the 3s Rydberg state is typically found. DFT calculations[23] show that in DMP, 3s is the first excited state (S₁) and that no other state, in particular, no valence state, exists nearby. We note that for each molecular structure, and ignoring triplet and core-excited states, there can be only one 3s level. Consequently, the presence of the broad band and the narrow peak indicates that multiple structures exist on the 3s Rydberg surface, each with a different BE.

To analyze the spectrally overlapping components of the 3s peak, we fitted the spectra at each time point with two Lorentzian components, as shown in Figure 3a. This yields fractional intensities in the broad and the sharp peaks, with a time dependence, as shown in Figure 3b. A movie showing the time evolution of these peaks is provided in the Supporting Information. The time-dependent intensities were fitted using the kinetics model shown in Scheme 1. The model assumes that only one conformer is present in the ground state and excited to the 3p state. This assumption is rationalized by our observation of a single 3p peak (inset of Figure 2) and further discussed below. The kinetics model lets the 3p state decay to both the broad (2.60 to 2.91 eV) and the sharp 3s (2.68 eV) states with independent time constants, which our fit determines to be 230 and 480 fs, respectively. The transition to 3s yields an initial intensity distribution of ∼70% for the broad, high BE peak and ∼30% for the sharp, low BE peak and implies that the 3p peak initially decays mostly to the broad component of the 3s peak. After the internal conversion, we observe that the broad peak decays in intensity while the sharp peak increases. The model, Scheme 1, assumes molecular structures that interconvert following first-order kinetics, allowing for both forward and backward reactions. The fit gives time constants of 3.4 and 12.0 ps for the forward and backward reactions, respectively, implying that at long delay times the sharp, low BE peak dominates. The kinetics parameters of this fit are listed in Table 1.

Even though the model provides an excellent fit to the spectral and temporal data and can therefore be expected to capture the essence of the dynamics, we do observe evidence that the broad peak itself is composed of several individual
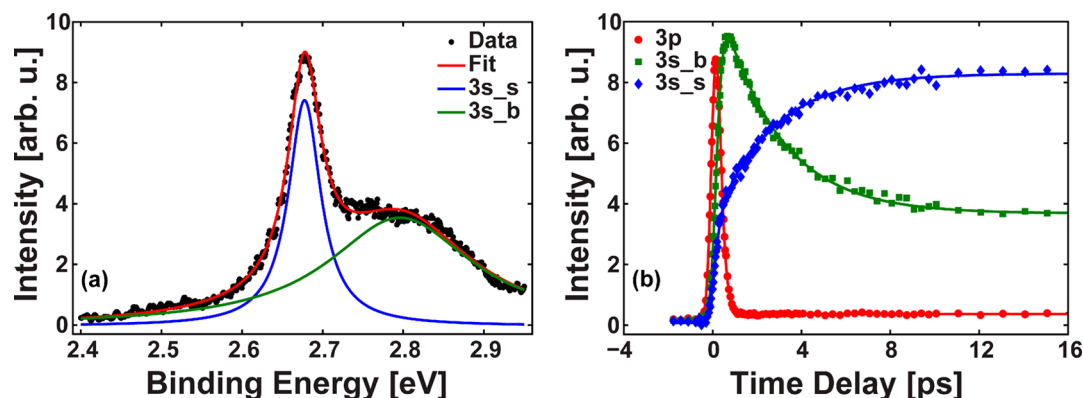

Figure 2. Time-dependent Rydberg electron binding energy spectrum of DMP. The colors represent the intensity (in arbitrary units) on a logarithmic scale as given by the color bar. The inset shows the 3p region in more detail.

Figure 3. (a) Example fit of the spectrum for the time point t = 1.13 ps using two Lorentzian component peaks. The individual intensities are calculated by integrating each component curve. (b) Time-dependent intensities of the 3p peak as well as the broad (3s_b) and the sharp (3s_s) peak components. The experimental data (symbols) were fitted to the kinetics model of Scheme 1 and a convolution with an instrument function, solid lines, which yielded the kinetics parameters listed in Table 1.

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dx.doi.org/10.1021/jz401499q | J. Phys. Chem. Lett. 2013, 4, 2780–2784

Scheme 1. Kinetics Model to Analyze the Data[a]
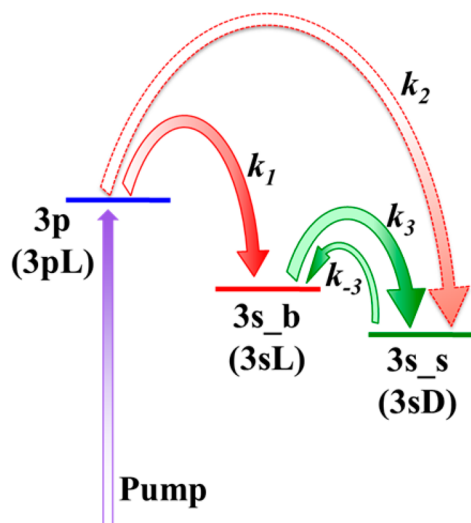
[a]Pump represents the one-photon excitation pulse to the 3p Rydberg state, which we identify as belonging to the localized charge state (3pL). This level decays to 3s_b, the broad 3s peak, and 3s_s, the sharp 3s peak, with rate constants k_1 and k_2, respectively. Those states are identified as the localized 3s state (3sL) and the delocalized 3s state (3sD), respectively. The different 3s state structures transform into each other with rate constants k_3 and k_{-3}.

components. These components, which have previously been observed in a higher resolution experiment,[21] most likely reflect different conformeric structures. While the contour plot of Figure 2 shows that these underlying structures have roughly the same decay dynamics and the quality of the fit of Figure 3b supports this notion, we can detect variations in their decay. Figure 4 plots the time dependence of just the broad peak component, derived by subtracting the fit of the sharp component from the total 3s signal. It is apparent that with increasing delay time spectral features at lower BE receive more intensity. Unfortunately, the peaks are not sufficiently succinct to allow a more detailed kinetics analysis.

To identify the different spectral features of the DMP spectrum, we first note that the 3p peak has a narrow width that is limited by the spectral resolution of the femtosecond laser, suggesting that it represents only one dominant structure. From the discussion above it followed that in the ground state of DMP the nitrogen atoms do not interact. We note further that the excitation of DMP to the 3p state has an absorption maximum at 205 nm, which is very close to that of NMP (207 nm)[6] and that the absorption cross section of DMP is about twice that of trimethylamine.[6] We conclude that excitation of DMP is localized to one nitrogen atom, leading to a 3p Rydberg state with an ion core that has the charge localized at one of the nitrogen atoms (DMP_L).

The sharp BE peak at 2.68 eV is easily identified as belonging to a charge-delocalized molecular structure because the
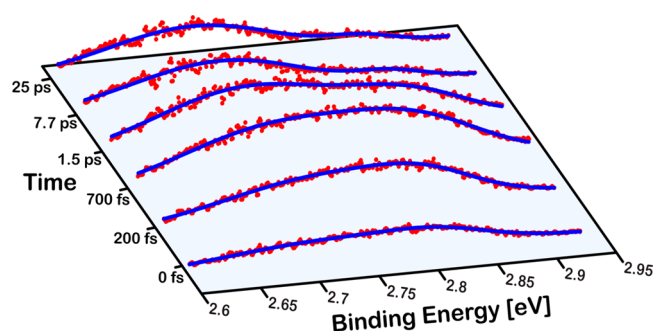

Figure 4. Temporal evolution of the broad peak component of 3s, obtained by subtracting the fit of the sharp peak component from the total 3s signal at each time point.

equivalent spectra of NMP show no corresponding peak (not shown) and because it belongs to the lowest energy structure on the 3s surface. The latter point is supported by the observation that the approach to equilibrium shifts intensity into this peak and by the computations of Brouwer et al.,[9] who found the delocalized structure to be the lowest energy structure of the ion. Our own DFT calculations,[23] using a higher level of theory (B3LYP/6-311++g(2df,2p)), gave similar results. The narrow width of the 2.68 eV peak indicates a rigid structure of the delocalized form, which is consistent with the requirements for charge delocalization.

The broadness of the band from 2.60 to 2.91 eV and the observation (Figure 4) that the different peak components have distinct time evolutions, suggests that many underlying structural features contribute to this peak. In the DMP radical cation, different structures arise from conformeric forms of the ring with different equatorial or axial alignment of the methyl groups. We suggest that the broad peak arises from a multitude of geometrical structures that we cannot further assign here, but because charge delocalization requires specific structures that enable orbital overlap, these structures have to belong to charge-localized states. This identification is also supported by the high BE of those levels, which typically is a sign of tighter charges,[20] and by the similarity to NMP spectra. We conclude that most likely the broad peak at higher BE corresponds to conformeric structures that have the charge localized at one of the nitrogen atoms.

On the basis of these assignments, the story of the structural motions associated with DMP's charge transfer comes into focus. Excitation from the ground state to the 3p Rydberg state initially places a positive charge on only one of the nitrogen atoms. The system undergoes a fast internal conversion from 3p to 3s, which generates both a delocalized structure with both nitrogen atoms in pseudopyramidal, pseudoaxial geometry and a multitude of localized structures where the charged amine is planar while the other is pyramidal. On the 3s surface, there is sufficient internal energy to convert between these structures on a picosecond time scale. The most dramatic effect is that even though the molecules initially are preferentially in the

Table 1. Time Constants Obtained in a Global Fit of All Time-Dependent Data, Together with Uncertainties (3σ)

processes	fit parameters (3σ)
electronic transition 3p (3pL) → 3s_b (3sL)	τ_1 = 230 (30) fs
electronic transition 3p (3pL) → 3s_s (3sD)	τ_2 = 480 (70) fs
structural dynamics and charge transfer 3s_b (3sL) → 3s_s (3sD)	τ_3 = 3.4 (0.1) ps
structural dynamics and charge transfer 3s_s (3sD) → 3s_b (3sL)	τ_{-3} = 12.0 (0.8) ps

charge-localized structures, over the course of several picoseconds they explore the conformational landscape of the 3s surface and find the geometry that suits charge delocalization. The time constant for this charge delocalization is 3.4 ps, while that of the reverse relocalization is 12.0 ps, making for an overall approach of the equilibrium with a 2.65 ps time constant. (Details are described in the Supporting Information.) Of course, electron motions are typically some three orders of magnitude faster, implying that the rate of charge transfer is not limited by the motion of electrons but rather by the rate at which the system explores the landscape of conformeric molecular structures on the 3s electronic surface. We conclude further that charge delocalization does not occur while the molecule is still in 3p, presumably because the internal conversion (230 and 480 fs) is much faster than the charge delocalization or relocalization (3.4 and 12.0 ps) on a single Rydberg surface.

The present studies on DMP provided insights into the fascinating world of the photochemistry of bridged diamines. Ongoing studies continue to explore the intricate interplay between conformeric molecular structures, energy flow between electronic surfaces, and the delocalization of charge-related diamines with varying flexibility of the carbon-skeleton bridges.

■ EXPERIMENTAL DETAILS

The experimental apparatus has been previously described.[24,25] A regenerative amplifier operating at 5 kHz produces subpicosecond pulses at 828 nm, which are upconverted to the second and fourth harmonics to provide the probe and the pump pulses, respectively. The laser beams are focused perpendicularly onto a molecular beam, which was generated by entraining DMP at 0 °C in a stream of helium carrier gas and expanding through a 100 μm nozzle and a 150 μm skimmer. Photoelectrons were recorded using a linear time-of-flight spectrometer. The time zero of the laser pulse overlap was determined by monitoring the cross-correlation between the pulses using the molecular response of DABCO, giving a cross-correlation time of 230 fs.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Movie of the time evolution of the decomposed peaks and details of the kinetics modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Moser, C. C.; Keske, J. M.; Warncke, K.; Farid, R. S.; Dutton, P. L. Nature of Biological Electron-Transfer. *Nature* **1992**, *355*, 796−802.

(2) Wasielewski, M. R. Energy, Charge, and Spin Transport in Molecules and Self-Assembled Nanostructures Inspired By Photosynthesis. *J. Org. Chem.* **2006**, *71*, 5051−5066.

(3) Zewail, A. H. Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond. *J. Phys. Chem. A* **2000**, *104*, 5660−5694.

(4) Halls, J. J. M.; Cornil, J.; dos Santos, D. A.; Silbey, R.; Hwang, D. H.; Holmes, A. B.; Bredas, J. L.; Friend, R. H. Charge- and Energy-Transfer Processes at Polymer/Polymer Interfaces: A Joint Experimental and Theoretical Study. *Phys. Rev. B* **1999**, *60*, 5721−5727.

(5) Newton, M. D. Quantum Chemical Probes of Electron-Transfer Kinetics - the Nature of Donor-Acceptor Interactions. *Chem. Rev.* **1991**, *91*, 767−792.

(6) Halpern, A. M.; Gartman, T. Structural Effects on Photophysical Processes in Saturated Amines 0.2. *J. Am. Chem. Soc.* **1974**, *96*, 1393−1398.

(7) Halpern, A. M.; Ramachandran, B. R.; Sharma, S. Structural Effects on Photophysical Processes in Saturated Amines 0.6. Excited-State Interactions in Piperazine Derivatives. *J. Phys. Chem.* **1982**, *86*, 2049−2052.

(8) Brouwer, A. M.; Mout, R. D.; van den Brink, P. H. M.; van Ramesdonk, H. J.; Verhoeven, J. W.; Warman, J. M.; Jonker, S. A. Charge Separation in the Excited State Electron Donor − Acceptor Compounds Containing the Piperazine Moiety. *Chem. Phys. Lett.* **1991**, *180*, 556−562.

(9) Brouwer, A. M.; Zwier, J. M.; Svendsen, C.; Mortensen, O. S.; Langkilde, F. W.; Wilbrandt, R. Radical Cation of N,N′-Dimethylpiperazine: Dramatic Structural Effects of Orbital Interactions Through Bonds. *J. Am. Chem. Soc.* **1998**, *120*, 3748−3757.

(10) Verevkin, S. P. Thermochemistry of Amines: Strain in Six-Membered Rings from Experimental Standard Molar Enthalpies of Formation of Morpholines and Piperazines. *J. Chem. Thermodyn.* **1998**, *30*, 1069−1079.

(11) Anet, F. A. L.; Yavari, I. Conformational Equilibrium in N,N′-Dimethylpiperazine. *Tetrahedron Lett.* **1976**, *17*, 2093−2096.

(12) Lett, R. G.; Petrakis, L.; Ellis, A. F.; Jensen, R. K. Nuclear Magnetic Resonance Spectral Parameters and Ring Interconversion of a Series of Piperazines. *J. Phys. Chem.* **1970**, *74*, 2816−2822.

(13) Davis, M.; Hassel, O. Electron Diffraction Investigation of Molecules Containing a Cyclohexane Type 6-Membered Ring. *Acta Chem. Scand.* **1963**, *17*, 1181.

(14) Nelsen, S. F.; Buschek, J. M. Photoelectron-Spectra of Some Cyclic Diamines and Polyamines - Lone Pair-Lone Pair Interaction in 1,3-Diamines and 1,4-Diamines. *J. Am. Chem. Soc.* **1974**, *96*, 7930−7934.

(15) Spanka, G.; Rademacher, P. Transannular Interactions in Difunctional Medium Rings. 1. The n/.pi. Interactions in Cyclic Amino Ketones and Amino Alkenes Studied by Photoelectron Spectroscopy. *J. Org. Chem.* **1986**, *51*, 592−596.

(16) Gosselin, J. L.; Weber, P. M. Rydberg Fingerprint Spectroscopy: A New Spectroscopic Tool with Local and Global Structural Sensitivity. *J. Phys. Chem. A* **2005**, *109*, 4899−4904.

(17) Kuthirummal, N.; Weber, P. M. Rydberg States: Sensitive Probes of Molecular Structure. *Chem. Phys. Lett.* **2003**, *378*, 647−653.

(18) Bush, J. C.; Minitti, M. P.; Weber, P. M. Dissociative Energy Flow, Vibrational Energy Redistribution, and Conformeric Structural Dynamics in Bifunctional Amine Model Systems. *J. Phys. Chem. A* **2010**, *114*, 11078−11084.

(19) Minitti, M. P.; Weber, P. M. Time-Resolved Conformational Dynamics in Hydrocarbon Chains. *Phys. Rev. Lett.* **2007**, *98*, 253004.

(20) Deb, S.; Minitti, M. P.; Weber, P. M. Structural Dynamics and Energy Flow in Rydberg-Excited Clusters of N,N-Dimethylisopropyl-amine. *J. Chem. Phys.* **2011**, *135*, 044319.

(21) Minitti, M. P.; Cardoza, J. D.; Weber, P. M. Rydberg Fingerprint Spectroscopy of Hot Molecules: Structural Dispersion in Flexible Hydrocarbons. *J. Phys. Chem. A* **2006**, *110*, 10212−10218.

(22) Gosselin, J. L.; Minitti, M. P.; Rudakov, F. M.; Solling, T. I.; Weber, P. M. Energy flow and Fragmentation Dynamics of N,N-Dimethylisopropylamine. *J. Phys. Chem. A* **2006**, *110*, 4251−4255.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. et al. *Gaussian 09*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2009.

(24) Kim, B. J.; Thantu, N.; Weber, P. M. High-Resolution Photoelectron-Spectroscopy − the Vibrational-Spectrum of the 2-Aminopyridine Cation. *J. Chem. Phys.* **1992**, *97*, 5384−5391.

(25) Cheng, W.; Kuthirummal, N.; Gosselin, J. L.; Solling, T. I.; Weinkauf, R.; Weber, P. M. Control of Local Ionization and Charge Transfer in the Bifunctional Molecule 2-Phenylethyl-N,N-Dimethyl-amine Using Rydberg Fingerprint Spectroscopy. *J. Phys. Chem. A* **2005**, *109*, 1920−1925.

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dx.doi.org/10.1021/jz401499q | *J. Phys. Chem. Lett.* 2013, 4, 2780−2784