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[18] This result provides preliminary evidence against a mechanism that maintains a palladium(II) oxidation state throughout the reaction (see ref. [10b]); dba = dibenzylideneacetone.

[19] Step III should exhibit a first-order dependence on [Pd], whereas catalyst inactivation should exhibit a bimolecular or higher order dependence on [Pd]. Consequently, enhanced turnover numbers and frequencies are expected at lower catalyst concentrations. For recent mechanistic characterization of the beneficial effect of reduced catalyst loading in aerobic oxidation reactions, see ref. [9]. See also, T. Rosner, J. Le Bars, A. Pfaltz, D. G. Blackmond, *J. Am. Chem. Soc.* **2001**, *123*, 1848–1855.

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ZEKE Photoelectron Spectroscopy of the *cis* and *trans* Isomers of Formanilide[**]

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Cationic states are involved in long-range charge transfer in polypeptides,[1] an area of intense chemical interest.[2] While a number of theoretical and time-resolved studies have contributed to our mechanistic understanding of this problem,[1] there is currently little spectroscopic information available for cationic amides.[3, 4] Basic questions regard the preference for *cis* or *trans* conformations and barrier heights for interconversion. Here we present initial results that indicate that zero electron kinetic energy (ZEKE) spectroscopy,[5, 6] a high-resolution variant of photoelectron spectroscopy, may represent a powerful technique for obtaining vibrationally resolved spectra of cationic amides and model peptides. Spectra are presented for both the *cis* and *trans* isomers of formanilide, an aromatic molecule with an amide side chain. The aromatic group provides a convenient chromophore, while significant charge delocalization occurs from the aromatic ring to the functional group in the cation, so that formanilide is a useful model system for studying the properties of cationic amides.

Local-minimum geometric structures of the neutral (S$_0$) and cationic (D$_0$) isomers of formanilide obtained from MP2(fc)/6-31G* ab initio calculations are presented in Figure 1.[7] For *trans*-formanilide, the calculations predict that the molecule

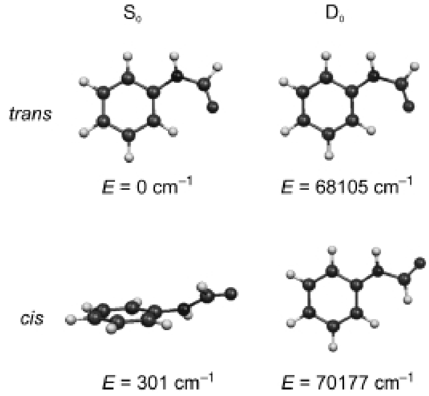

Figure 1. Optimized structures of the neutral (S$_0$) and cationic (D$_0$) isomers of formanilide at the MP2(fc)/6-31G* level of theory illustrating the ionization-induced geometry changes. Total energies are given relative to the energy of the S$_0$ state of *trans*-formanilide (−399.693829 Hartree).

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adopts a planar, C_s-symmetry structure in both the S_0 and D_0 states. The primary ionization-induced structural change for *trans*-formanilide is centered on the N–C_{amide} bond, which contracts from 1.4352 to 1.4286 Å. In addition, the amide oxygen atom moves towards the aromatic ring, whereby the C_1-N-C_{amide} bond decreases by 1.5°. *cis*-Formanilide also adopts a planar, C_s-symmetric structure in the D_0 state, although the neutral molecule corresponds to a nonplanar, C_1 structure in which the amide side chain is twisted relative to the phenyl ring ($\tau_{C2\text{-}C1\text{-}N\text{-}C} = 42°$). The conformational preference for planar cationic structures suggests that both isomers are stabilized by resonance structures involving the nitrogen lone pair. A natural population analysis of partial charge distribution revealed that about 20% of the excess positive charge is delocalized to the side chain in the cation.[8, 9]

Figure 2 presents the ZEKE spectrum of *trans*-formanilide recorded via the $S_1 0^0$ origin transition at 36004.3 ± 0.1 cm^{-1}, the dominant peak in the resonance-enhanced multiphoton ionization (REMPI) spectrum of formanilide.[10–12] The lowest energy feature in the ZEKE spectrum occurs at 67408 ± 5 cm^{-1}, and is assigned as the adiabatic ionization energy (IE), since no additional features were evident in scans to lower energy. The IE measured here is consistent with the vertical ionization energy of 8.6 eV (69359 cm^{-1}) reported for a low-resolution photoelectron spectrum, which contains contributions from both isomers,[4] and improves on the value obtained by Mons et al. (67430 ± 20 cm^{-1}) using threshold photoionization.[13]

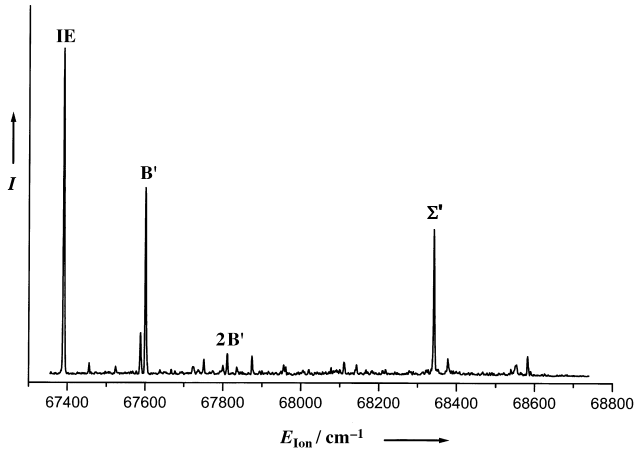

Figure 2. Two-color (1 + 1′) ZEKE spectrum of *trans*-formanilide recorded via the $S_1 0^0$ origin. B′ represents the in-plane bend of the side arm, and Σ′ a mode containing a high proportion of amide stretch.

Two prominent vibrational features appear in the spectrum of *trans*-formanilide at ion internal energies of 211 and 952 cm^{-1}. For C_s-symmetry molecules, vibrational modes are classified according to whether they transform as a′ or a″ through the plane of symmetry. Since the S_0, S_1,[11] and D_0 states of *trans*-formanilide all have planar geometries, we expect that only a′ modes will appear as strong single-quanta features in the ZEKE spectra. We therefore assign the features at 211 and 952 cm^{-1} to an in-plane side-arm bend (B′) and a mode involving a significant proportion of amide stretch (Σ′), by comparison with the ab initio results,[9] which predict harmonic frequencies for these modes at 223 and 1023 cm^{-1}, respectively. Excitation of the Σ′ mode is particularly notable since it indicates that an ionization-induced geometry change occurs at the amide bond, consistent with significant delocalization of excess charge from the aromatic chromophore to the amide side chain in the cation.

Three small features are evident in the ZEKE spectrum in the region below the B′ mode at 65, 135, and 195 cm^{-1}. They appear to correspond to double-quantum excitation of the C_1–N torsion, the out-of-plane side-arm bending modes, and a combination mode thereof.[9] A detailed analysis of these lower intensity features is beyond the scope of this communication. Nonetheless, their observation suggests that ZEKE spectra of related molecules such as *N*-benzylformamide may also involve torsional excitation and hence facilitate the characterization of torsional potential energy surfaces of cationic amides and peptides.

Weak excitation of the torsional modes of *trans*-formanilide is unsurprising given that the molecule adopts a planar geometry in the S_0, S_1,[11] and D_0 states. The ZEKE spectra of *cis*-formanilide, however, should include torsional vibrational features since the ground-state neutral molecule corresponds to a nonplanar, C_1-symmetry structure,[11] but the cation is planar (Figure 1). While resonant two-color spectroscopy of *cis*-formanilide is a formidable task due to the low intensity of this isomer in the molecular beam,[10] it was possible to obtain two-color ZEKE spectra of *cis*-formanilide, and this indicates that strong FC factors exist for $D_0 \leftarrow S_1$ excitation.

Figure 3a displays the ZEKE spectrum of *cis*-formanilide obtained via the $S_1 0^0$ origin at 34904 ± 0.1 cm^{-1}. The single feature at 67710 ± 5 cm^{-1} was assigned as the IE since

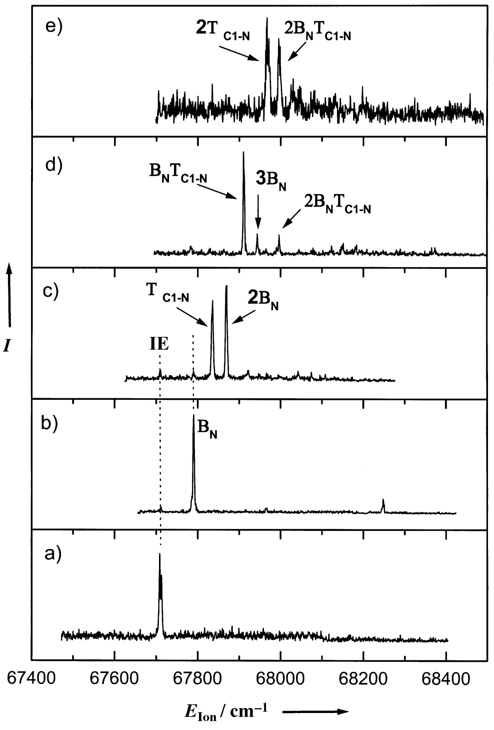

Figure 3. Two-color (1 + 1′) ZEKE spectra of *cis*-formanilide recorded via the a) $S_1 0^0$(s), b) A_0^1(a), c) A_0^2(s) + B_0^1(a), d) A_0^3(a) + $A_0^1 B_0^1$(s), and e) A_0^4(s) + $A_0^2 B_0^1$(a) + B_0^2(s) levels of the S_1 state.[11] B_N represents the out-of-plane side-arm bend, and $T_{C1\text{-}N}$ the C_1–N torsional mode.

additional scans to lower energy revealed the presence of no additional features. We note that IE_{cis} is about 300 cm^{-1} higher than IE_{trans}. Since the ab initio results (Figure 1) predict that the *trans* isomer is the lower energy structure in the S_0 state, this indicates that the *cis* conformation is also the higher energy structure in the D_0 state.

Figures 3b–e present ZEKE spectra of *cis*-formanilide recorded via different vibrational levels of the S_1 state. The very limited vibrational structure in all spectra suggests that the FC windows for $D_0 \leftarrow S_1$ excitation are extremely narrow. However, consideration of the parities of vibrational levels in the S_0, S_1, and D_0 states provides an alternative explanation for the limited vibrational structure evident in these ZEKE spectra. In the nonplanar S_0 state, each torsional level is split into symmetric (s) and antisymmetric (a) components by tunneling through the coplanar potential barrier.[11] Both the S_1 and D_0 states have planar equilibrium geometries, and successive torsional levels therefore alternate between s and a parity. Excitation to the D_0 state via an S_1 state with s or a parity should therefore lead to the appearance of s- or a-parity vibrational features, respectively, in the ZEKE spectra.

The $\Delta\nu = 0$ propensity rule[5] and parity considerations were employed to assign each of the strong vibrational features in the ZEKE spectra of *cis*-formanilide (Table 1). Several of the ZEKE spectra display excitation of features with both s and a parity due to the cation being accessed via S_1 bands corresponding to overlapping $S_1 \leftarrow S_0$ transitions with different parities.[13] The ZEKE spectra reveal overtone and combination bands corresponding to excitation of the out-of-plane side-arm bend centered on the N atom (B_N 80 cm^{-1}) and the C_1–N torsion ($T_{C1\text{-}N}$ 126 cm^{-1}), consistent with the nonplanar to planar $D_0 \leftarrow S_0$ geometry change predicted by the calculations. The out-of-plane bend and C_1–N torsion are predicted to occur at 52 and 96 cm^{-1} at the MP2/6-31G* level of theory, in reasonable agreement with the experimental values. Finally, it is of interest to note that unexpected parity transitions are evident as low-intensity features in the spectra (e.g., the IE feature in Figure 3b).

In summary, spectra of *cis*- and *trans*-formanilide demonstrate that the system is amenable to study by ZEKE spectroscopy. The spectrum of *trans*-formanilide is dominated by excitation of the in-plane side-arm bend (211 cm^{-1}) and amide stretch (952 cm^{-1}), while the spectra of the *cis* isomer contain overtones and combinations of the out-of-plane side-arm bend (80 cm^{-1}) and the C_1–N torsion (126 cm^{-1}). The observation of these modes is in line with planar geometries for both isomers in the D_0 state. Accurate ionization energies were obtained and allowed us to assign the *trans* isomer as the lower energy conformation of the cation. While some of the results presented above are characteristic of the direct attachment of the amide group to the phenyl ring in formanilide (e.g., excitation of B′ in the *trans*-formanilide cation), they demonstrate that ZEKE spectroscopy can productively be applied to obtain vibrationally resolved, conformationally selective spectra of amides and model peptides, and should be a highly useful tool for future studies of these systems.

Table 1. Frequencies [cm^{-1}] of vibrational features observed in the ZEKE spectra of *cis*-formanilide via different intermediate S_1 states.[a]

S_10^0(s)	A_0^1(a)	A_0^2(s) + B_0^1(a)	A_0^3(a) + $A_0^1B_0^1$(s)	A_0^4(s) + $A_0^2B_0^1$(a) + B_0^2(s)	Assignment
0	0	0	–	–	IE (s)
–	80	80	80	–	B_N (a)
–	–	126	–	–	$T_{C1\text{-}N}$ (a)
–	–	158	–	–	$2B_N$(s)
–	–	213	208	–	$B_NT_{C1\text{-}N}$ (s)
–	–	–	241	–	$3B_N$ (a)
–	–	–	262	262	$2T_{C1\text{-}N}$ (s)
–	–	–	294	294	$2B_NT_{C1\text{-}N}$ (a)

[a] Frequencies are given relative to the IE, and parities are denoted as s (symmetric) and a (antisymmetric). S_1 state assignments and notation follow ref. [11]. B_N represents the out-of-plane side-arm bending mode, and T_{C_1-N} the C_1–N torsion.

Experimental Section

The experimental apparatus and techniques employed in this work have been described in detail previously.[5, 6, 14] Formanilide (Aldrich, 99% purity) was heated to 140 °C and seeded in Ne carrier gas at 2 bar from a sample holder located immediately behind the valve (0.8-mm nozzle).

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