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- [15] Allylic C–H activation followed by amination of the resulting  $\pi$ -allyl palladium(II) species cannot be ruled out. However, we disfavor this mechanism because several related substrates that react with similar rates cannot proceed through this pathway (Table 1).
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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,<sup>[1]</sup> an area of intense chemical interest.<sup>[2]</sup> While a number of theoretical and time-resolved studies have contributed to our mechanistic understanding of this problem,<sup>[1]</sup> there is currently little spectroscopic information available for cationic amides.<sup>[3, 4]</sup> 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,<sup>[5, 6]</sup> 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<sub>0</sub>) and cationic (D<sub>0</sub>) isomers of formanilide obtained from MP2(fc)/6-31G\* ab initio calculations are presented in Figure 1.<sup>[7]</sup> For *trans*-formanilide, the calculations predict that the molecule

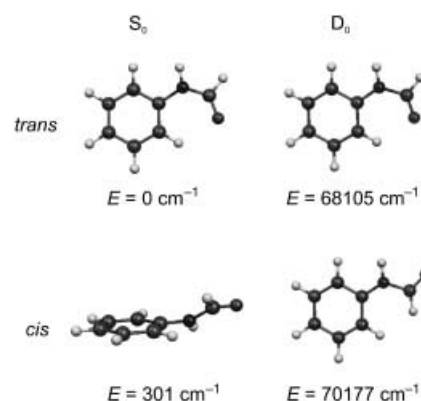


Figure 1. Optimized structures of the neutral (S<sub>0</sub>) and cationic (D<sub>0</sub>) isomers of formanilide at the MP2(fc)/6-31G\* level of theory illustrating the ionization-induced geometry changes. Total energies are given relative to the energy of the S<sub>0</sub> state of *trans*-formanilide (–399.693829 Hartree).

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[\*\*] This work was supported by the EPSRC (grant No. GR/L27770). C.E.H.D. thanks the Royal Society for support from a Royal Society University Research Fellowship and Prof. J. P. Simons for useful discussions. S.U. acknowledges support from the Fonds des Verbands der Chemischen Industrie and DAAD, and G.T. acknowledges support from the Hungarian Ministry of Education and the Peregrinatio II Foundation.

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<sub>amide</sub> bond, which contracts from 1.4352 to 1.4286 Å. In addition, the amide oxygen atom moves towards the aromatic ring, whereby the C<sub>1</sub>–N–C<sub>amide</sub> 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 ( $\tau_{C_2-C_1-N-C} = 42^\circ$ ). 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.<sup>[8, 9]</sup>

Figure 2 presents the ZEKE spectrum of *trans*-formanilide recorded via the  $S_10^0$  origin transition at  $36004.3 \pm 0.1 \text{ cm}^{-1}$ , the dominant peak in the resonance-enhanced multiphoton ionization (REMPI) spectrum of formanilide.<sup>[10–12]</sup> The lowest

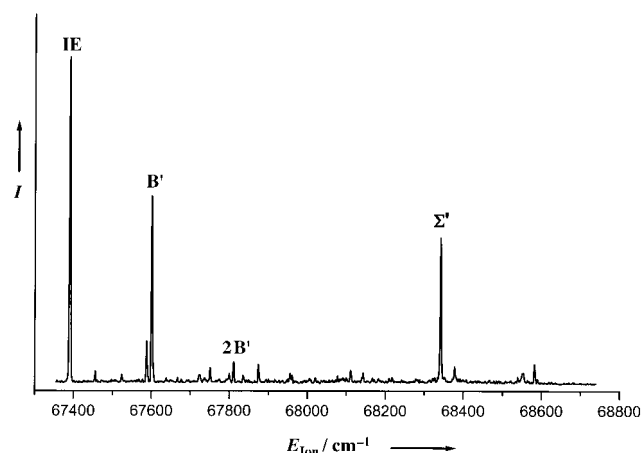


Figure 2. Two-color (1 + 1) ZEKE spectrum of *trans*-formanilide recorded via the  $S_10^0$  origin. B' represents the in-plane bend of the side arm, and  $\Sigma'$  a mode containing a high proportion of amide stretch.

energy feature in the ZEKE spectrum occurs at  $67408 \pm 5 \text{ cm}^{-1}$ , 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 ( $69359 \text{ cm}^{-1}$ ) reported for a low-resolution photoelectron spectrum, which contains contributions from both isomers,<sup>[4]</sup> and improves on the value obtained by Mons et al. ( $67430 \pm 20 \text{ cm}^{-1}$ ) using threshold photoionization.<sup>[13]</sup>

Two prominent vibrational features appear in the spectrum of *trans*-formanilide at ion internal energies of 211 and  $952 \text{ cm}^{-1}$ . 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  $S_0$ ,  $S_1$ ,<sup>[11]</sup> 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  $952 \text{ cm}^{-1}$  to an in-plane side-arm bend (B') and a mode involving a significant proportion of amide stretch ( $\Sigma'$ ), by comparison with the ab initio results,<sup>[9]</sup> which

predict harmonic frequencies for these modes at 223 and  $1023 \text{ cm}^{-1}$ , respectively. Excitation of the  $\Sigma'$  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  $195 \text{ cm}^{-1}$ . They appear to correspond to double-quantum excitation of the C<sub>1</sub>–N torsion, the out-of-plane side-arm bending modes, and a combination mode thereof.<sup>[9]</sup> 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  $S_0$ ,  $S_1$ ,<sup>[11]</sup> 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,<sup>[11]</sup> 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,<sup>[10]</sup> 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  $S_10^0$  origin at  $34904 \pm 0.1 \text{ cm}^{-1}$ . The single feature at  $67710 \pm 5 \text{ cm}^{-1}$  was assigned as the IE since

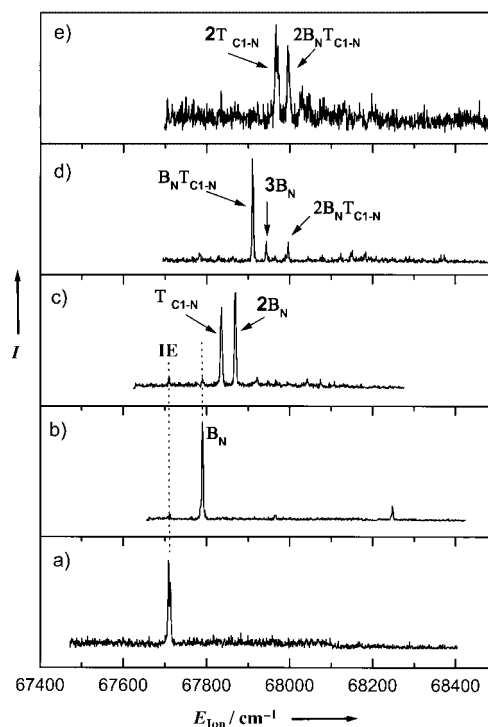


Figure 3. Two-color (1 + 1) ZEKE spectra of *cis*-formanilide recorded via the a)  $S_10^0$ (s), b)  $A_0^1$ (a), c)  $A_0^2$ (s) +  $B_0^1$ (a), d)  $A_0^3$ (a) +  $A_0^1B_0^1$ (s), and e)  $A_0^4$ (s) +  $A_0^2B_0^1$ (a) +  $B_0^2$ (s) levels of the  $S_1$  state.<sup>[11]</sup> B<sub>N</sub> represents the out-of-plane side-arm bend, and T<sub>C1-N</sub> the C<sub>1</sub>–N torsional mode.

additional scans to lower energy revealed the presence of no additional features. We note that  $IE_{cis}$  is about  $300\text{ cm}^{-1}$  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.<sup>[11]</sup> 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<sup>[5]</sup> 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.<sup>[13]</sup> The ZEKE spectra reveal overtone and combination bands corresponding to excitation of the out-of-plane side-arm bend centered on the N atom ( $B_N$   $80\text{ cm}^{-1}$ ) and the  $C_1$ –N torsion ( $T_{C_1-N}$   $126\text{ cm}^{-1}$ ), 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  $96\text{ cm}^{-1}$  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 ( $211\text{ cm}^{-1}$ ) and amide stretch ( $952\text{ cm}^{-1}$ ), while the spectra of the *cis* isomer contain overtones and combinations of the out-of-plane side-

arm bend ( $80\text{ cm}^{-1}$ ) and the  $C_1$ –N torsion ( $126\text{ cm}^{-1}$ ). 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.

### Experimental Section

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

Received: August 10, 2001 [Z17708]

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

$S_1 0^0(s)$	$A_0^1(a)$	$A_0^2(s) + B_0^1(a)$	$A_0^3(a) + A_0^1 B_0^1(s)$	$A_0^4(s) + A_0^2 B_0^1(a) + B_0^2(s)$	Assignment
0	0	0	–	–	IE (s)
–	80	80	80	–	$B_N$ (a)
–	–	126	–	–	$T_{C_1-N}$ (a)
–	–	158	–	–	$2B_N(s)$
–	–	213	208	–	$B_N T_{C_1-N}$ (s)
–	–	–	241	–	$3B_N$ (a)
–	–	–	262	262	$2T_{C_1-N}$ (s)
–	–	–	294	294	$2B_N T_{C_1-N}$ (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.