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# Reactive Pathways in the Chlorobenzene– Ammonia Dimer Cation Radical: New Insights from Experiment and Theory

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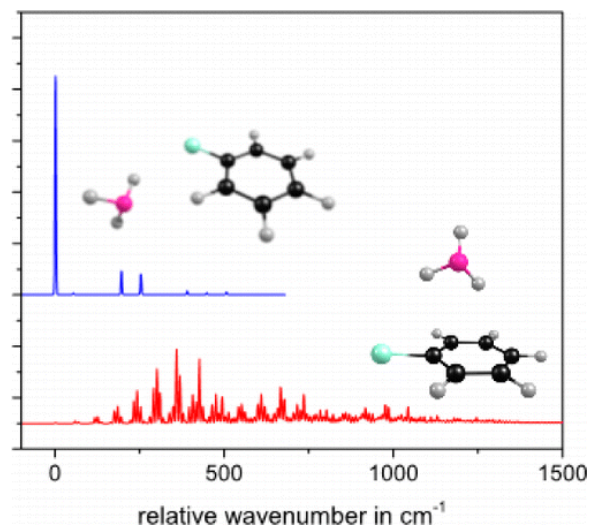
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## Abstract



Building upon our recent studies of noncovalent interactions in chlorobenzene and bromobenzene clusters, in this work we focus on interactions of chlorobenzene (PhCl) with a prototypical N atom donor, ammonia (NH<sub>3</sub>). Thus, we have obtained electronic spectra of PhCl·(NH<sub>3</sub>)<sub>n</sub> ( $n = 1-3$ ) complexes in the region of the PhCl monomer  $S_0-S_1$  ( $\pi\pi^*$ ) transition using resonant 2-photon ionization (R2PI) methods combined with time-of-flight mass analysis. Consistent with previous studies, we find that upon ionization the PhCl·NH<sub>3</sub> dimer cation radical reacts primarily via Cl atom loss. A second channel, HCl loss, is identified for the first time in R2PI studies of the 1:1 complex, and a third channel, H atom loss, is identified for the first time. While prior studies have assumed the dominance of a  $\pi$ -type complex, we find that the reactive complex corresponds instead to an in-plane  $\sigma$ -type complex. This is supported by electronic structure calculations using density functional theory and post-Hartree–Fock methods and Franck–Condon analysis. The reactive pathways in this system were extensively characterized computationally, and consistent with results from previous calculations, we find two nearly isoenergetic arenium ions (Wheland intermediates; denoted WH1, WH2), which lie energetically below the initially formed dimer cation radical complex. At the energy of our experiment, intermediate WH1, produced from *ipso*-addition, is not stable with respect to Cl or HCl loss, and the relative branching between these channels observed in our experiment is well reproduced by microcanonical transition state theory calculations based upon the calculated parameters. Intermediate WH2, where NH<sub>3</sub> adds ortho to the halogen, decomposes over a large barrier via H atom loss to form protonated *o*-chloroaniline. This channel is not open at the (2-photon) energy of our experiments, and it is suggested that photodissociation of a long-lived (i.e., several ns) WH2 intermediate leads to the observed products.

## I Introduction

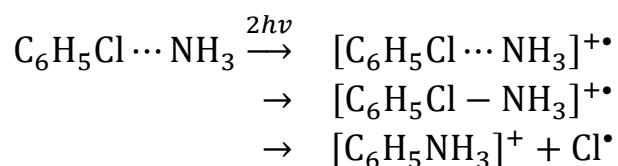
The study of molecular clusters offers valuable insight into important noncovalent interactions including hydrogen bonding,  $\pi$ – $\pi$  stacking, CH/ $\pi$  interactions, and halogen bonding. These fall into a general class of donor–acceptor interactions and are important in many chemical and biological processes. For example, such interactions play an important role in controlling chemical reactivity and molecular structure,(1-10) are central to processes of molecular recognition and binding,(11-16) and contribute to the structure and function of biomolecules.(17-22) Increasingly, halogen-bonding has been recognized as an important noncovalent interaction in systems featuring halogen atoms.(3, 15, 23-30) The halogen bond, which involves a halogen (X) atom as electron acceptor, arises from the polarized electron distribution around the halogen, which gives rise to a region of positive electrostatic potential on the axis of the C–X bond referred to as the “ $\sigma$ -hole”.(31-33) The

magnitude of this hole depends both on the halogen, increasing from F to I, and electron withdrawing power of substituent groups.(34)

Because of the presence of a convenient chromophore, which allows the application of one-color resonant 2-photon ionization (R2PI) spectroscopy with mass-selective detection, clusters of aromatics have long been used as model systems for probing noncovalent interactions of various types.(35, 36) In early studies by Zwier and co-workers,(37, 38) the water–benzene complex was detected using R2PI spectroscopy in concert with resonant ion dip infrared spectroscopy. The data supported a  $\pi$ -type structure for the complex, which, however, was determined in model calculations to be extremely floppy. In the ensuing years, ionization based methods have been extensively applied to the study of molecular complexes.(39-81)

The dimers of halobenzenes with ammonia are model systems for understanding the effects of complex formation on bimolecular reactions, as found initially by Brutschy and co-workers.(82, 83) In a 1988 communication and a later report in 1990, Maeyama and Mikami showed that ionization of the PhCl $\cdots$ NH<sub>3</sub> complex resulted in Cl atom loss to yield protonated aniline (anilinium ion), through an intracuster S<sub>N</sub>2 reaction from the ionized complex.(76) The origin band of the S<sub>0</sub>–S<sub>1</sub> spectrum of the complex was blue-shifted from the monomer (PhCl) origin by  $\sim 76$  cm<sup>-1</sup>, and while no information on the structure of the complex was obtained, the following reaction scheme was postulated:

(1)



Brutschy and co-workers conducted similar R2PI studies on fluorobenzene, chlorobenzene, and *p*-chlorofluorobenzene complexes with methanol and ammonia.(77-83) In the case of the PhF $\cdots$ NH<sub>3</sub> dimer, a blue-shifted ( $\sim 58$  cm<sup>-1</sup>) feature was observed in the S<sub>0</sub>–S<sub>1</sub> spectrum, but the dimer was found to be unreactive upon ionization. This was consistent with earlier biomolecular reactions of halobenzene cations with ammonia, where PhX (X = Cl, Br, I) radical cations were found to react with ammonia to yield anilinium ions, but PhF radical cations did not.(84) However, the PhF $\cdots$ (NH<sub>3</sub>)<sub>2</sub> complex did react upon ionization, decaying via either HF loss, to give the aniline cation radical, or dissociative electron transfer. A band observed  $\sim 47$  cm<sup>-1</sup> above the S<sub>1</sub> origin of the 1:1 dimer was initially assigned to the 1:2 dimer; however, this assignment was later questioned, and this band attributed to a second conformer of the 1:1 dimer.(85) In a more recent study by Cockett and co-workers, which employed multidimensional Franck–Condon simulations,(86) it was shown that the structure in the S<sub>0</sub>–S<sub>1</sub> spectrum can be attributed solely to an in-plane four-center  $\sigma_{\text{ortho}}$  complex, bound by C–H $\cdots$ N and N–H $\cdots$ F interactions.

In 2006, Brutschy and co-workers published IR-depletion spectroscopy in the N–H stretching region of NH<sub>3</sub> clusters with benzene, toluene, fluorobenzene, chlorobenzene, and *p*-difluorobenzene;(87) the spectra were complemented by theoretical studies at the MP2 level. For the halobenzenes, MP2 calculations identified three isomers of the 1:1 complex with ammonia; (a) a structure bound solely by N–H/ $\pi$  interaction with one N–H group pointing into the  $\pi$ -cloud of the halobenzene ( $\pi_{\text{out}}$ ), (b) a structure bound by both N–H/ $\pi$  interaction and a N–H $\cdots$ Cl hydrogen bond ( $\pi_{\text{bridge}}$ ); and (c) an in-plane, four-center structure bound by N $\cdots$ H–C and N–H $\cdots$ Cl hydrogen bonds ( $\sigma_{\text{ortho}}$ ). By comparing the experimental shifts from the free NH<sub>3</sub> absorptions, the authors concluded that the observed structure of the PhF $\cdots$ NH<sub>3</sub> and PhCl $\cdots$ NH<sub>3</sub> clusters corresponded to the out-of-plane ( $\pi_{\text{bridge}}$ ) structure. This stands in contrast with the findings of Cockett and co-workers for PhF $\cdots$ NH<sub>3</sub>.(86) While an above plane ( $\pi$ -type) complex could be envisioned to easily react upon ionization, does the reactive dimer for

PhCl $\cdots$ NH $_3$  correspond to an in-plane structure? This is one of the questions we seek to address in the present study.

Information on the binding energy of PhCl $\cdots$ (NH $_3$ ) $_n$  clusters comes from the study of Garvey and co-workers, who used tunable VUV radiation to effect single-photon ionization.(88) The ionization potentials of the PhCl $\cdots$ (NH $_3$ ) $_n$  clusters with  $n = 1-3$  were measured, and from the appearance potentials, the dissociation energy of the PhCl $\cdots$ NH $_3$  dimer was determined to be  $12.2 \pm 2.2$  kJ/mol, while that of the [PhCl $\cdots$ NH $_3$ ] $^{+\bullet}$  cation radical was found to be  $43.5 \pm 2.9$  kJ/mol. Importantly, this study identified a second loss channel for the ionized dimer, HCl loss giving rise to the aniline cation radical, which was suggested to come from the ionized dimer and not from secondary processes. To date this channel has not been seen in R2PI studies; however, it is noteworthy that a molecular elimination channel forming HCl was observed in R2PI studies of PhClF $\cdots$ NH $_3$  clusters by Brutschy and co-workers.(80, 89)

The prototypical PhCl + NH $_3$  system has also been the subject of theoretical investigation. Early MNDO calculations predicted a triple-well energy profile, with reaction from the initial ionized complex leading through *ipso*-substitution to a chlorocyclohexadienyl radical ion, or Wheland intermediate, the loss of Cl from which proceeded without a barrier to give the Cl + protonated aniline products.(84) At this level of theory, the intermediate was calculated to lie 34 kJ/mol below the ionized complex. Such intermediates in related systems have been the focus of recent experimental studies.(90-92) More recently, Tachikawa examined ionization processes in the PhCl $\cdots$ NH $_3$  complex using direct ab initio molecular dynamics.(93) In this work, the complex was presumed to adopt a  $\pi_{\text{out}}$  structure, and two Wheland intermediates were found, which computationally were formed in nearly equal yield following a vertical photoionization. The first resulted from *ipso*-substitution (we denote this WH1 throughout this work), the second from substitution ortho to the halogen (WH2). At energies corresponding to a vertical ionization, WH1 was formed within  $\sim 0.5$  ps following ionization, and Cl atom loss followed on a  $\sim 1$  ps time scale. In contrast, while WH2 was formed on a similar time scale, it exhibited a longer lifetime ( $>2$  ps) due to the high barrier for C–H bond fission. There has to date been no experimental evidence for the formation of WH2.

Despite the many studies on this prototypical system, it is clear that significant open questions remain, particularly concerning the structure of the reactive complex. Moreover, to date, halogen bonded structures have not been considered. Building upon previous studies of noncovalent interactions in chlorobenzene clusters, the present work highlights the study of clusters of chlorobenzene with ammonia. Experimental studies using R2PI spectroscopy are supported by electronic structure calculations based upon density functional theory (DFT) and post-Hartree–Fock (MP2) methods in concert with correlation consistent basis sets, which have characterized the important stationary points and reactive pathways in this prototypical system. While prior studies have assumed the dominance of a  $\pi$ -type complex, we find that the reactive complex corresponds instead to an in-plane  $\sigma$ -type complex. The reactive pathways in this system were extensively characterized computationally, and consistent with results from previous calculations, we find two nearly isoenergetic arenium ions (Wheland intermediates; denoted WH1, WH2), which lie energetically below the initially formed dimer cation radical. At the energy of our experiment, intermediate WH1, produced from *ipso*-addition, is not stable with respect to Cl or HCl loss, and the relative branching between these channels observed in our experiment is well reproduced by microcanonical transition state theory calculations based upon the calculated parameters.

## II Experimental and Computational Methods

Our experiments utilized a linear time-of-flight mass spectrometer (TOFMS) coupled with a supersonic molecular beam source. A 1:5:100 mixture of chlorobenzene/NH $_3$ /He was generated by passing a premix of NH $_3$ /He over a sample of chlorobenzene held in a temperature controlled bath. This mixture was expanded at a total pressure

of typically  $\sim 1\text{--}2$  bar from the 1.0 mm diameter nozzle of a solenoid-activated pulsed valve (General Valve), and the resulting gas pulse, of  $\sim 1$  ms duration, passed through a 1.0 mm diameter skimmer into the differentially pumped flight tube of a one-meter linear TOFMS. The flight tube vacuum was maintained by a 250 L/s turbomolecular pump, and a gate valve used to isolate the detector, which was kept under vacuum at all times. The main chamber was evacuated with a water-baffled diffusion pump (Varian VHS-4). With the nozzle on, typical pressures were  $\sim 5 \times 10^{-5}$  mbar (main chamber) and  $\sim 1 \times 10^{-6}$  mbar (flight tube). The background pressure in the flight tube could be lowered further by liquid nitrogen cooling of the vacuum shroud; however, this was not required in the present experiments.

Ionization was initiated by a 1 + 1 R2PI scheme, with laser light near 270 nm generated from frequency doubling in a BBO crystal the output of a dye laser (Lambda-Physik, Scanmate 2E), pumped by the third harmonic of an Nd:YAG laser (Continuum NY-61). The laser was operated on a C540A dye, giving typical output pulse energies of  $\sim 1$  mJ in the doubled beam, which was loosely focused with a 1.0 m plano-convex lens into the chamber.

Ions were extracted and accelerated using a conventional three-plate stack, with the repeller plate typically held at +2100 V, the extractor plate at +1950 V, and the third plate at ground potential.<sup>(91)</sup> The ions traversed a path of 1 m prior to striking a dual chevron Microchannel Plate (MCP) detector. The detector signal was amplified ( $\times 25$ ) using a fast preamplifier (Stanford Research SRS445A), and integrated using a boxcar system (Stanford Research SRS250) interfaced to a personal computer. An in-house LABVIEW program controlled data acquisition and stepped the laser wavelength; typically, the signal from 20 laser shots was averaged at each step in wavelength.

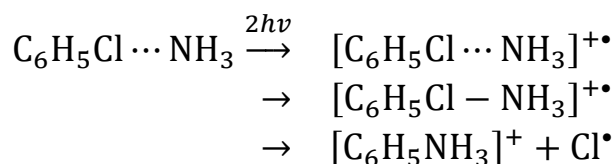
To support our experimental findings, electronic structure calculations were performed using the Gaussian 09 software package on the MU Pere high speed cluster.<sup>(94)</sup> Full geometry optimizations were carried out using DFT (M06-2X) with an aug-cc-pVDZ basis set, with single-point CCSD(T) energies obtained for selected structures. Prior computational studies on related systems<sup>(17, 95, 96)</sup> have extensively benchmarked the performance of DFT methods against high level post-Hartree-Fock ab initio single reference methods. The Minnesota meta-GGA (generalized gradient approximation) hybrid functional M06-2X, among other methods, provides a good cost to performance ratio,<sup>(97)</sup> and the aug-cc-pVDZ basis set performs well in calculating the counterpoise correction.<sup>(95)</sup> Our calculated binding energies were corrected for zero-point energy (ZPE), with the counterpoise method used to correct for basis set superposition error (BSSE).

Time-dependent DFT (TDDFT) methods based on range-separated hybrid and meta-GGA hybrid functionals were used to calculate the electronic spectra of the clusters and the optimized geometry of the  $S_1$  states. Methods employed included the meta-GGA hybrid functionals M06 and M06-2X,<sup>(97)</sup> and CAM-B3LYP,<sup>(98, 99)</sup> all with an aug-cc-pVDZ basis set. The performance of M06-2X for electronic excitations, including Rydberg and Charge Transfer excitations, has recently been benchmarked.<sup>(100)</sup>

### III Results and Discussion

Previous R2PI studies have shown that the  $\text{PhCl}\cdots\text{NH}_3$  complex displays an origin band, which is shifted  $\sim 76$   $\text{cm}^{-1}$  to the blue of the  $S_0\text{--}S_1$  ( $\pi\pi^*$ ) origin band of the PhCl monomer. With the laser tuned to this position, a representative mass spectrum was obtained and is shown in the lower panel of Figure 1. The upper panel displays an expanded view in the region of the  $\text{PhCl}\cdots\text{NH}_3$  dimer. Note the small intensity of the parent dimer peak with respect to the higher order clusters, and the strong intensity of daughter peaks corresponding to aniline (An) and protonated aniline (AnH). This is evidence that the dimer, upon ionization, reacts via the following pathways, in addition to the previously mentioned Cl atom loss (1):

(1)



(2)



(3)



Channels 1 and 2 have previously been examined in detail; however, the nature of the intermediate has not been well determined. For example, it is not known whether the Cl and HCl products arise from the same or different intermediates. To our knowledge, no previous reports have identified a channel for H atom loss.

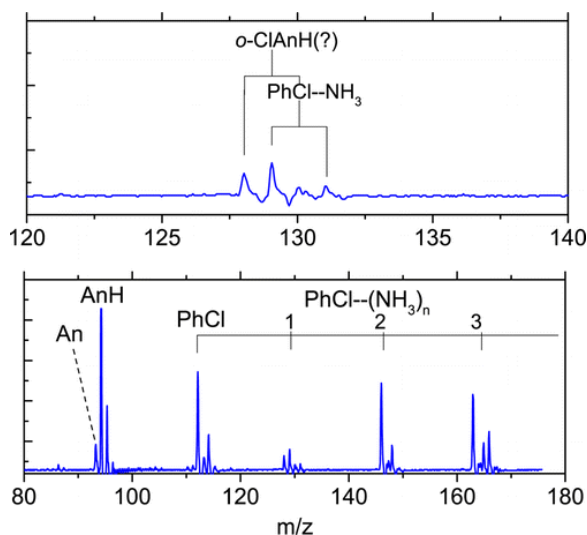


Figure 1. Time-of-flight mass spectrum resulting from resonant 2-photon ionization (R2PI) at a wavelength coincident with the origin band of the  $\text{PhCl} \cdots \text{NH}_3$  dimer. The small signal at the parent wavelength reflects an intracuster reaction upon ionization, leading to (a) Cl atom loss, producing protonated aniline; (b) HCl loss, producing aniline cation radical; and (c) H atom loss, producing *o*-chloroaniline cation radical.

The R2PI spectrum obtained in the  $\text{AnH}^+$  channel, corresponding to Cl atom loss, is compared in the upper panel of Figure 2 with the monomer spectrum. As previously reported, the origin of the complex is shifted  $\sim 76 \text{ cm}^{-1}$  to the blue of the monomer origin, and the spectrum is origin dominated. These points will be discussed further below. The spectrum in Figure 2 is very similar to those measured in the mass channels associated with aniline and the parent complex, as shown in Figure S1 in the Supporting Information,<sup>(101)</sup> indicating that these share a common precursor. Our spectra indicate that the 1:1 complex is responsible for this feature, as the R2PI spectra of the 1:2 and 1:3 complexes display very broad, unresolved bands that are most likely indicative of multiple conformers, as shown in Figure S2 in the Supporting Information.

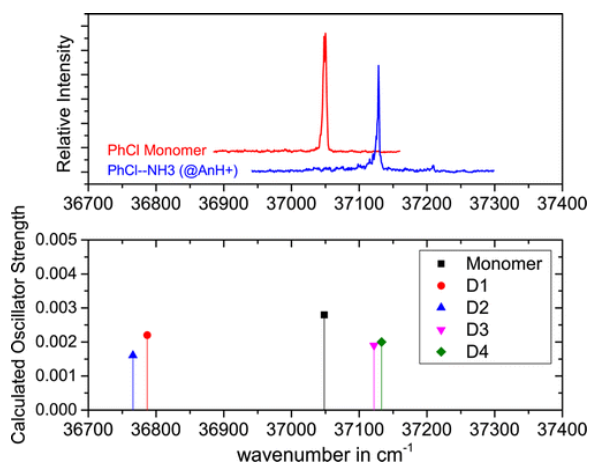


Figure 2. Upper panel: R2PI spectra of the PhCl monomer (red) and PhCl $\cdots$ NH $_3$  dimer (blue). The latter was measured in the protonated aniline mass channel. Lower panel: Calculated adiabatic transition energies of the PhCl monomer and four minimum energy dimer structures (D1–D4) from TDM06-2X/aug-cc-pVTZ optimizations of the  $S_0$  and  $S_1$  states, scaled to match the experimental value of the monomer absorption.

The prior theoretical (MP2) study of Brutschy and co-workers identified three isomers of the 1:1 complex;  $\pi_{\text{out}}$ ,  $\pi_{\text{bridge}}$ , and  $\sigma_{\text{ortho}}$ .<sup>(87)</sup> To further characterize this complex, we employed DFT calculations at the M06-2X/aug-cc-pVXZ (X = D,T) level, with geometry optimizations initiated from a variety of starting geometries. Our choice of functional stems from the extensive benchmarking reported by Sherrill and co-workers on similar types of complexes.<sup>(95)</sup> Four minimum energy structures (D1–D4) were found, and these are shown in Figure 3; noted are the calculated binding energies, counterpoise and ZPE corrected, which are similar at this level of theory. Dimers D1, D2, and D3 correspond to previously identified  $\pi_{\text{out}}$ ,  $\pi_{\text{bridge}}$ , and  $\sigma_{\text{ortho}}$  structures, while D4 is a second  $\sigma$  complex where the NH $_3$  group has rotated to afford two N–H $\cdots$ Cl hydrogen bonds. No minimum associated with a halogen-bonded (i.e., C–Cl $\cdots$ N) structure was found at this level of theory. We subsequently carried out single-point counterpoise-corrected CCSD(T)//M06-2X/aug-cc-pVTZ calculations, and these energies are given in Table 1. At this level of theory, D3 is the global minimum energy structure, with a binding energy of –8.0 kJ/mol. This may be compared with the experimental value of  $-12.0 \pm 2.2$  kJ/mol.<sup>(88)</sup>

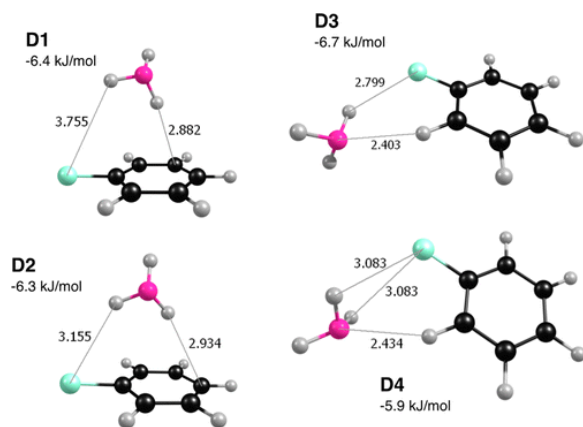


Figure 3. Optimized structures and binding energies of four minimum energy PhCl $\cdots$ NH $_3$  dimer structures (D1–D4) at the M06-2X/aug-cc-pVTZ level.

Table 1. Calculated Binding Energies of PhCl $\cdots$ NH $_3$  Dimer Structures

	calculated binding energies (kJ/mol)	
dimer	M06-2X/aug-cc-pVTZ	CCSD(T)//M06-2X/aug-cc-pVTZ



D1	-6.4	-5.6
D2	-6.7	-4.2
D3	-6.3	-8.0
D4	-5.9	-7.3

Given the range of possible dimer structure(s), which are responsible for the observed electronic spectrum? To answer this question, we carried our TDDFT calculations of the vertical excitation energies, and TDDFT optimizations of  $S_1$  excited states, at the TDCAM-B3LYP and TDM06-2X level of theory, with aug-cc-pVXZ (X = D,T) basis sets. Then, multidimensional Franck–Condon calculations were employed to simulate the vibronic structure in the electronic spectrum, based on the calculated parameters. The adiabatic transition energies obtained from TDM06-2X/aug-cc-pVTZ calculations are shown in the lower panel of Figure 2, where the calculated energies have been scaled to match the experimental energy of the monomer origin.

These calculations predict a red shift for dimers D1 and D2, which involve significant N–H/ $\pi$  interactions, and a blue shift for D3 and D4. The calculated shifts for D3 and D4 are of similar magnitude, and within  $10\text{ cm}^{-1}$  of the experimentally observed shift. Thus, while the electronic spectra cannot distinguish between D3 and D4, our results strongly suggest that the observed electronic absorption is associated with a  $\sigma$ -type neutral complex.

Additional evidence in support of this assignment comes from multidimensional Franck–Condon simulations based upon the calculated equilibrium geometries and mass-weighted normal mode displacements, where the effects of Duschinsky mixing were incorporated. The simulations included the lowest frequency intermolecular modes, and representative spectra were calculated for dimers D2 ( $\pi$ -type) and D3 ( $\sigma$ -type). For D3, our calculations find little geometry change between  $S_0$  and  $S_1$ , giving rise to origin dominated spectra, as shown in Figure 4, where transitions involving the five lowest frequency intermolecular modes were included. In contrast, D2 undergoes a significant geometry change in the electronic transition, where the N–H $\cdots$ Cl interaction is largely broken in the excited state and a bidentate interaction with the  $\pi$ -system is the preferred binding motif. As a result, extensive FC activity is predicted in the low-frequency intermolecular vibrations (Figure 4), a result inconsistent with the experimental spectrum (Figure 2). Thus, FC simulations also support the assignment of the observed spectrum to a  $\sigma$ -type complex.

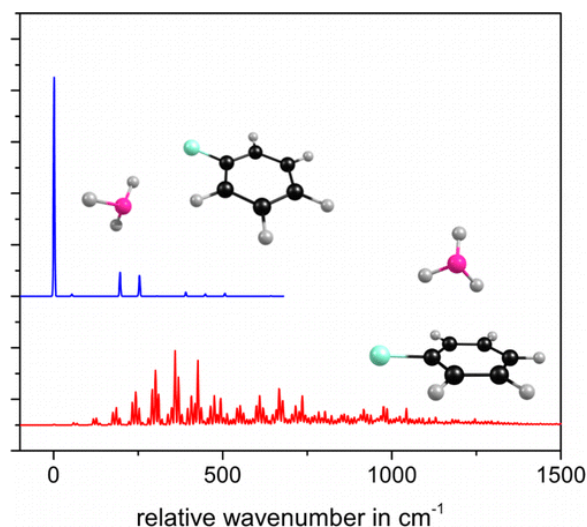


Figure 4. Franck–Condon simulations of the electronic absorptions of the PhCl $\cdots$ NH $_3$  dimers D2 (lower) and D3. The simulations account for the effects of Dushinsky mixing; details are provided in the text.

Having established through electronic structure calculations and Franck–Condon simulations that a  $\sigma$ -type complex is responsible for the experimental R2PI spectra, we carried out additional calculations on the ionized complex to chart the reaction pathways leading to the observed products. In these calculations we considered two types of Wheland intermediates: one derived from *ipso*-substitution (WH1), the other from substitution at a position ortho to the halogen atom (WH2). The rationale for considering substitution at the ortho as opposed to meta or para positions is the expectation that the structure of D3 should favor the former (Figure 3).

Considering the Wheland intermediate derived from *ipso*-substitution, calculations at the M06-2X/aug-cc-pVDZ level show that WH1 lies 30 kJ/mol lower than the ionized complex (D3), as shown in Figure 5a. While a transition state between D3 and WH1 was not identified computationally, Garvey and co-workers used tunable VUV photoionization to determine the ionization potential of the PhCl $\cdots$ NH<sub>3</sub> dimer as  $8.744 \pm 0.022$  eV, and the appearance potential of protonated aniline (formed coincidentally with Cl atom) as  $8.935 \pm 0.004$  eV,<sup>(88)</sup> implying a barrier to reaction of  $\sim 14$  kJ/mol. A transition state connecting WH1 to the products associated with Cl atom loss (i.e., Cl + protonated aniline) was found computationally and verified by intrinsic reaction coordinate calculations (Figure S3 in Supporting Information). This transition state lies  $\sim 15$  kJ/mol above WH1 (Figure 5a). Thus, upon ionization of the complex, *ipso*-substitution leading to WH1 affords C–Cl bond scission to yield protonated aniline.

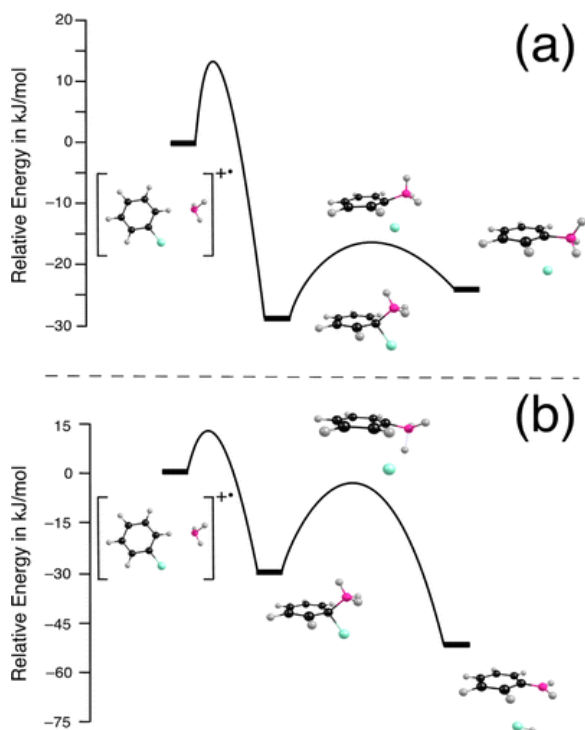


Figure 5. Calculated (M06-2X/aug-cc-pVDZ) stationary points on the potential energy surface of the ionized PhCl $\cdots$ NH<sub>3</sub> complex, reflecting *ipso*-substitution leading to Wheland intermediate WH1. (a) Stationary points associated with the reaction path to Cl atom loss. (b) Stationary points associated with the reaction path to HCl elimination.

Does the HCl elimination channel derive from the same (WH1) intermediate? Theory suggests that it does. As shown in Figure 5b, a four-center transition state leading to the products associated with HCl loss (i.e., HCl + aniline cation radical) was found, as verified by intrinsic reaction coordinate calculations (Figure S4 in Supporting Information). The nature of the reaction path suggests that HCl elimination reflects a frustrated Cl loss from WH1 (Figure 4). It is therefore not surprising that this transition state lies energetically higher than that for Cl loss,  $\sim 25$  kJ/mol above WH1 (Figure 5b), yet still lower than the energy of the ionized complex (D3). Thus, *ipso*-

substitution leading to WH1 will afford HCl elimination to yield the aniline cation radical, as is observed (Figure 1).

Theory suggests that the HCl elimination and Cl atom loss channels occur competitively from WH1, yet due to the lower barrier the latter channel should predominate (Figure 5). To quantify the relative branching, we used microcanonical transition state theory as implemented in the CHEMRATE program.<sup>(102)</sup> On the basis of the transition state structures, vibrational frequencies, and stationary point energies determined from our computational studies, these calculations predict that at the excess energy of our experiment the ratio of Cl to HCl loss is  $\sim 5.6:1$ . This is in very good agreement with our experimental finding of 5.4:1, determined from the integrated intensities in the TOF mass spectrum shown in Figure 1. The calculated rates for the Cl and HCl channels as a function of energy are shown in Figure S5 in the Supporting Information, while the parameters used in the rate calculations are listed in Table S1.

We now turn to intermediate WH2 and the pathway for H atom loss. As shown in Figure 6, a transition state was found computationally [M06-2X/aug-cc-pVDZ level], which is consistent with addition to form WH2 from ionized dimer D3. This transition state lies  $\sim 4$  kJ/mol above the energy of the ionized dimer. Our calculations confirm that WH2 is a minimum, which lies  $\sim 40$  kJ/mol below ionized dimer D3. A second transition state was found computationally, connecting WH2 with the products H + protonated *ortho*-chloroaniline (Figure 6). The IRC calculation for this transition state is shown in Figure S6 in the Supporting Information. Our calculations show that H atom loss occurs over a sizable barrier, and neither the energy of this barrier nor the product asymptote is energetically available at the (2-photon) energy of our experiment. On the basis of the energetics shown in Figure 6, in our experiment WH2, once formed, can only decay back to the ionized complex. Microcanonical transition state calculations based upon the calculated parameters (listed in Table S2, Supporting Information) of WH2 and the transition state for back-isomerization predict that the lifetime of the WH2 intermediate is  $\sim 2.5$  ns at the 2-photon energy accessed in our experiment. This lifetime is comparable to our laser pulsewidth, and thus, subsequent photodissociation of the initially formed WH2 intermediate is the probable explanation for our observation of a H-atom loss channel. However, because of the small signals associated with this channel, it was not possible to conduct measurements of the fluence dependence of the ion yield, which might confirm this hypothesis. It would be highly desirable to probe this channel using ion-imaging methods.

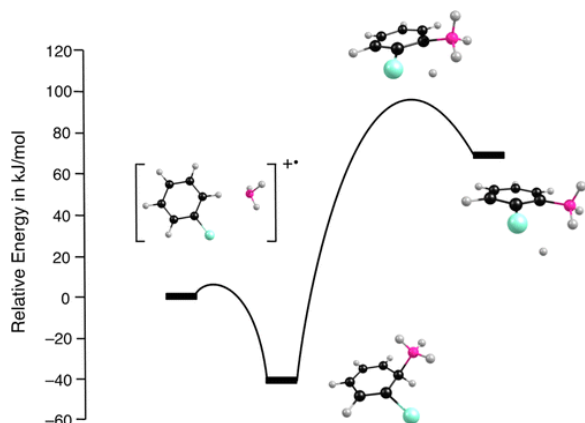


Figure 6. Calculated (M06-2X/aug-cc-pVDZ) stationary points on the potential energy surface of the ionized PhCl $\cdots$ NH $_3$  complex, reflecting substitution *ortho* to the halogen, leading to Wheland intermediate WH2. Stationary points associated with the reaction path to H atom loss are shown.

## IV Conclusions

In this work, we have examined reactive pathways in a prototypical and well-studied system, the cation radical derived from ionization of chlorobenzene (PhCl) complexed with ammonia (NH<sub>3</sub>). R2PI spectra of PhCl⋯(NH<sub>3</sub>)<sub>n</sub> (*n* = 1–3) complexes in the region of the PhCl monomer S<sub>0</sub>–S<sub>1</sub> (ππ\*) transition find, consistent with earlier studies, that the PhCl⋯NH<sub>3</sub> dimer cation radical reacts primarily via Cl atom loss, to give protonated aniline. A second channel, HCl loss to give aniline cation radical, is identified for the first time in R2PI studies of the 1:1 complex, and we have also identified a third channel, H atom loss, for the first time. We have shown, both through electronic structure calculations based upon density functional theory and post-Hartree–Fock methods and Franck–Condon analysis, that the reactive complex corresponds to an in-plane σ-type complex. This stands in contrast to previous reports, which have assumed that the neutral dimer structure corresponded to a π-type complex.

In this work, the reactive pathways following photoionization of the complex were extensively characterized computationally. Consistent with a prior direct ab initio molecular dynamics study, two nearly isoenergetic Wheland intermediates were found (WH1 and WH2), which lie significantly lower in energy than the initially formed dimer cation radical. At the energy of our experiment, intermediate WH1, produced from *ipso*-addition, is not stable with respect to Cl or HCl loss, and the branching between these channels is well reproduced by microcanonical transition state theory calculations based on the computed parameters. In contrast, intermediate WH2, where the NH<sub>3</sub> adds ortho to the halogen, decomposes over a large barrier via H atom loss to form protonated *o*-chloroaniline. This channel is not open at the (2-photon) energy of our experiments, and it is suggested that photodissociation of a long-lived WH2 intermediate leads to the observed product.

## Supporting Information

Figures S1–S2 show additional R2PI spectra in distinct mass channels for the dimer and higher order complexes. Additional computational data includes intrinsic reaction coordinate calculations for the optimized transition states in this work (Figures S3, S4, and S6). Finally, we include tables of calculated data (Tables S1 and S2) that were used as input into the rate calculations, and a figure displaying the output of those calculations (Figure S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## References

- 1 Yamakawa, M.; Yamada, I.; Noyori, R. C–H/ $\pi$  Attraction: The Origin of Enantioselectivity in Transfer Hydrogenation of Aromatic Carbonyl Compounds Catalyzed by Chiral Eta(6)-Arene-Ruthenium(II) Complexes *Angew. Chem., Int. Ed.* **2001**, 40, 2818– 2821
- 2 Nishio, M. C–H/ $\pi$  Hydrogen Bonds in Organic Reactions *Tetrahedron* **2005**, 61, 6923– 6950
- 3 Bertani, R.; Sgarbossa, P.; Venzo, A.; Lelj, F.; Amati, M.; Resnati, G.; Pilati, T.; Metrangolo, P.; Terraneo, G. Halogen Bonding in Metal–Organic-Supramolecular Networks *Coord. Chem. Rev.* **2010**, 254, 677– 695
- 4 Nishio, M. The C–H/ $\pi$  Hydrogen Bond: Implication in Chemistry *J. Mol. Struct.* **2012**, 1018, 2– 7
- 5 Grabowski, S. J. What Is the Covalency of Hydrogen Bonding? *Chem. Rev.* **2011**, 111, 2597– 2625
- 6 Legon, A. C.; Millen, D. J. The Nature of the Hydrogen-Bond to Water in the Gas-Phase *Chem. Soc. Rev.* **1992**, 21, 71– 78
- 7 Del Bene, J. E.; Jordan, M. J. T. Vibrational Spectroscopy of the Hydrogen Bond: An ab Initio Quantum-Chemical Perspective *Int. Rev. Phys. Chem.* **1999**, 18, 119– 162
- 8 Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W.H. Freeman; New York, 1960.
- 9 Schuster, P.; Zundel, G.; Sandorfy, C. *The Hydrogen Bond: Recent Developments in Theory and Experiments*; North-Holland Publishing Company: Amsterdam, The Netherlands, 1976.
- 10 Smith, D. A. Division of Computers in Chemistry. In *Modeling the Hydrogen Bond*; 206th Meeting of the American Chemical Society, Chicago IL; American Chemical Society: Washington, DC, 1994.
- 11 Muraki, M. The Importance of C–H/ $\pi$  Interactions to the Function of Carbohydrate Binding Proteins *Protein Peptide Lett.* **2002**, 9, 195– 209
- 12 Nakagawa, Y.; Irie, K.; Yanagita, R. C.; Ohigashi, H.; Tsuda, K. Indolactam-V Is Involved in the C–H/ $\pi$  Interaction with Pro-11 of the Pkc Delta C1b Domain: Application for the Structural Optimization of the Pkc Delta Ligand *J. Am. Chem. Soc.* **2005**, 127, 5746– 5747
- 13 Ramirez-Gualito, K.; Alonso-Rios, R.; Quiroz-Garcia, B.; Rojas-Aguilar, A.; Diaz, D.; Jimenez-Barbero, J.; Cuevas, G. Enthalpic Nature of the C–H/ $\pi$  Interaction Involved in the Recognition of Carbohydrates by Aromatic Compounds, Confirmed by a Novel Interplay of NMR, Calorimetry, and Theoretical Calculations *J. Am. Chem. Soc.* **2009**, 131, 18129– 18138
- 14 Nishio, M. The CH/ $\pi$  Hydrogen Bond in Chemistry. Conformation, Supramolecules, Optical Resolution and Interactions Involving Carbohydrates *Phys. Chem. Chem. Phys.* **2011**, 13, 13873– 13900
- 15 Cavallo, G.; Metrangolo, P.; Pilati, T.; Resnati, G.; Sansotera, M.; Terraneo, G. Halogen Bonding: A General Route in Anion Recognition and Coordination *Chem. Soc. Rev.* **2010**, 39, 3772– 3783
- 16 Amendola, V.; Fabbrizzi, L.; Mosca, L. Anion Recognition by Hydrogen Bonding: Urea-Based Receptors *Chem. Soc. Rev.* **2010**, 39, 3889– 3915
- 17 Thanthiriwatte, K. S.; Hohenstein, E. G.; Burns, L. A.; Sherrill, C. D. Assessment of the Performance of DFT and DFT-D Methods for Describing Distance Dependence of Hydrogen-Bonded Interactions *J. Chem. Theory Comput.* **2011**, 7, 88– 96
- 18 Nishio, M.; Umezawa, Y.; Hirota, M. The C–H/ $\pi$  Interaction. Implications in Molecular Recognition *J. Syn. Org. Chem. Jpn.* **1997**, 55, 2– 12
- 19 Auffinger, P.; Hays, F. A.; Westhof, E.; Ho, P. S. Halogen Bonds in Biological Molecules *Proc. Natl. Acad. Sci. U.S.A.* **2004**, 101, 16789– 16794
- 20 Voth, A. R.; Hays, F. A.; Ho, P. S. Directing Macromolecular Conformation through Halogen Bonds *Proc. Natl. Acad. Sci. U.S.A.* **2007**, 104, 6188– 6193
- 21 Nishio, M.; Hirota, M.; Umezawa, Y. *The CH– $\pi$  Interaction: Evidence, Nature, and Consequences*; Wiley: New York, 1998.
- 22 Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond: In Structural Chemistry and Biology*; Oxford University Press: Oxford, U.K., 1999.
- 23 Cheng, L.; Wang, M. Y.; Wu, Z. J.; Su, Z. M. Electronic Structures and Chemical Bonding in 4d Transition Metal Monohalides *J. Comput. Chem.* **2007**, 28, 2190– 2202

- 24** Lu, Y. X.; Zou, J. W.; Wang, Y. H.; Jiang, Y. J.; Yu, Q. S. Ab Initio Investigation of the Complexes between Bromobenzene and Several Electron Donors: Some Insights into the Magnitude and Nature of Halogen Bonding Interactions *J. Phys. Chem. A* **2007**, *111*, 10781– 10788
- 25** Lu, Y. X.; Zou, J. W.; Wang, Y. H.; Yu, Q. S. Theoretical Investigations of the C–X/ $\pi$  Interactions between Benzene and Some Model Halocarbons *Chem. Phys.* **2007**, *334*, 1– 7
- 26** Metrangolo, P.; Meyer, F.; Pilati, T.; Resnati, G.; Terraneo, G. Halogen Bonding in Supramolecular Chemistry *Angew. Chem., Int. Ed.* **2008**, *47*, 6114– 6127
- 27** Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. Halogen Bonding Based Recognition Processes: A World Parallel to Hydrogen Bonding *Acc. Chem. Res.* **2005**, *38*, 386– 395
- 28** Parisini, E.; Metrangolo, P.; Pilati, T.; Resnati, G.; Terraneo, G. Halogen Bonding in Halocarbon-Protein Complexes: A Structural Survey *Chem. Soc. Rev.* **2011**, *40*, 2267– 2278
- 29** Politzer, P.; Murray, J. S.; Clark, T. Halogen Bonding: An Electrostatically-Driven Highly Directional Noncovalent Interaction *Phys. Chem. Chem. Phys.* **2010**, *12*, 7748– 7757
- 30** Liu, B. K.; Wang, B. X.; Wang, Y. Q.; Wang, L. Ultrafast Dynamics of Chlorobenzene Clusters *Chem. Phys. Lett.* **2009**, *477*, 266– 270
- 31** Clark, T.; Hennemann, M.; Murray, J. S.; Politzer, P. Halogen Bonding: The  $\sigma$ -Hole *J. Mol. Model.* **2007**, *13*, 291– 296
- 32** Politzer, P.; Lane, P.; Concha, M. C.; Ma, Y.; Murray, J. S. An Overview of Halogen Bonding *J. Mol. Model.* **2007**, *13*, 305– 311
- 33** Politzer, P.; Murray, J. S.; Concha, M. C. Halogen Bonding and the Design of New Materials: Organic Bromides, Chlorides and Perhaps Even Fluorides as Donors *J. Mol. Model.* **2007**, *13*, 643– 650
- 34** Peralta-Inga, Z.; Murray, J. S.; Politzer, P. Computational Exploration of the Relationship between Interaction Energies, Angles of Interaction and Electrostatic Potentials in a Series of Hydrogen- and Halogen-Bonded Complexes. Abstracts of Papers, 239th ACS National Meeting, San Francisco, CA, March 21– 25, 2010; COMP-49.
- 35** Chipot, C.; Jaffe, R.; Mairret, B.; Pearlman, D. A.; Kollman, P. A. Benzene Dimer: A Good Model for  $\pi$ – $\pi$  Interactions in Proteins? A Comparison between the Benzene and the Toluene Dimers in the Gas Phase and in an Aqueous Solution *J. Am. Chem. Soc.* **1996**, *118*, 11217– 11224
- 36** Di Palma, T. M.; Bende, A.; Borghese, A. Photoionisation and Structures of Jet-Formed Toluene Clusters *Chem. Phys. Lett.* **2010**, *495*, 17– 23
- 37** Augspurger, J. D.; Dykstra, C. E.; Zwier, T. S. Hydrogen-Bond Swapping in the Benzene Water Complex: a Model Study of the Interaction Potential *J. Phys. Chem.* **1992**, *96*, 7252– 7257
- 38** Pribble, R. N.; Zwier, T. S. Probing Hydrogen-Bonding in Benzene–(Water)(*N*) Clusters Using Resonant Ion-Dip Ir Spectroscopy *Faraday Discuss.* **1994**, *97*, 229– 241
- 39** Roithova, J. Characterization of Reaction Intermediates by Ion Spectroscopy *Chem. Soc. Rev.* **2012**, *41*, 547– 559
- 40** Troxler, T.; Leutwyler, S. Molecular-Dynamics and Semiclassical Electronic-Spectra of Naphthalene- $Ar_n$  Clusters ( $n \leq 4$ ) *J. Chem. Phys.* **1993**, *99*, 4363– 4378
- 41** Furlan, A.; Leutwyler, S.; Riley, M. J. Intermolecular Perturbation of a Jahn–Teller System: the Triptycene·Ne(*n*) ( $n = 1–3$ ) Van-Der-Waals Clusters *J. Chem. Phys.* **1994**, *100*, 840– 855
- 42** Mandziuk, M.; Bacic, Z.; Droz, T.; Leutwyler, S. Intermolecular Vibrations of the 2,3-Dimethylnaphthalene–Ar Van-Der-Waals Complex: Experiment and Quantum 3-Dimensional Calculations *J. Chem. Phys.* **1994**, *100*, 52– 62
- 43** Droz, T.; Burgi, T.; Leutwyler, S. State-Selective Analysis of Ground-State Vibrational Predissociation Product of an Aromatic Van-Der-Waals Complex *Ber. Bunsen. Phys. Chem.* **1995**, *99*, 429– 433
- 44** Pribble, R. N.; Gruenloh, C.; Zwier, T. S. The Ultraviolet and Infrared Spectroscopy of (Benzene)<sub>2</sub>–(CH<sub>3</sub>OH)<sub>3</sub> Isomeric Clusters *Chem. Phys. Lett.* **1996**, *262*, 627– 632
- 45** Yeh, J. H.; Shen, T. L.; Nocera, D. G.; Leroi, G. E.; Suzuka, I.; Ozawa, H.; Namuta, Y. Resonance Two-Photon Ionization Spectroscopy of the Aniline Dimer *J. Phys. Chem.* **1996**, *100*, 4385– 4389

- 46 Wallimann, F.; Frey, H. M.; Leutwyler, S.; Riley, M. Isotopically Resolved (B)–(X) Electronic Spectrum of  $\text{Ag}_3$  and Calculation of Its Jahn–Teller Effects *Z. Phys. D* **1997**, 40, 30–35
- 47 Furlan, A.; Leutwyler, S.; Riley, M. J. Coupling of a Jahn–Teller Pseudorotation with a Hindered Internal Rotation in an Isolated Molecule: 9-Hydroxytryptene *J. Chem. Phys.* **1998**, 109, 10767–10780
- 48 Gruenloh, C. J.; Carney, J. R.; Hagemester, F. C.; Arrington, C. A.; Zwier, T. S.; Fredericks, S. Y.; Wood, J. T.; Jordan, K. D. Resonant Ion–Dip Infrared Spectroscopy of the S-4 and D-2d Wafer Octamers in Benzene-(Water)<sub>8</sub> and Benzene<sub>2</sub>-(Water)<sub>8</sub> *J. Chem. Phys.* **1998**, 109, 6601–6614
- 49 Knochenmuss, R.; Karbach, V.; Wickleder, C.; Graf, S.; Leutwyler, S. Vibrational-Energy Redistribution and Vibronic Coupling in 1-Naphthol·Water Complexes *J. Phys. Chem. A* **1998**, 102, 1935–1944
- 50 Carney, J. R.; Zwier, T. S. Infrared and Ultraviolet Spectroscopy of Water-Containing Clusters of Indole, 1-Methylindole, and 3-Methylindole *J. Phys. Chem. A* **1999**, 103, 9943–9957
- 51 Bach, A.; Leutwyler, S. Proton Transfer in 7-Hydroxyquinoline-(NH<sub>3</sub>)(N) Solvent Clusters *J. Chem. Phys.* **2000**, 112, 560–565
- 52 Gruenloh, C. J.; Carney, J. R.; Hagemester, F. C.; Zwier, T. S.; Wood, J. T.; Jordan, K. D. Resonant Ion–Dip Infrared Spectroscopy of Benzene-(Water)<sub>9</sub>: Expanding the Cube *J. Chem. Phys.* **2000**, 113, 2290–2303
- 53 Bach, A.; Tanner, C.; Manca, C.; Frey, H. M.; Leutwyler, S. Ground- and Excited State Proton Transfer and Tautomerization in 7-Hydroxyquinoline-(NH<sub>3</sub>)(N) Clusters: Spectroscopic and Time Resolved Investigations *J. Chem. Phys.* **2003**, 119, 5933–5942
- 54 Stearns, J. A.; Zwier, T. S. Infrared and Ultraviolet Spectroscopy of Jet-Cooled *ortho*-, *meta*-, and *para*-Diethynylbenzene *J. Phys. Chem. A* **2003**, 107, 10717–10724
- 55 Tanner, C.; Henseler, D.; Leutwyler, S.; Connell, L. L.; Felker, P. M. Structural Study of the Hydrogen-Bonded 1-Naphthol-(NH<sub>3</sub>)<sub>2</sub> Cluster *J. Chem. Phys.* **2003**, 118, 9157–9166
- 56 Muller, A.; Frey, J. A.; Leutwyler, S. Probing the Watson–Crick, Wobble, and Sugar-Edge Hydrogen Bond Sites of Uracil and Thymine *J. Phys. Chem. A* **2005**, 109, 5055–5063
- 57 Selby, T. M.; Clarkson, J. R.; Mitchell, D.; Fitzpatrick, J. A. J.; Lee, H. D.; Pratt, D. W.; Zwier, T. S. Isomer-Specific Spectroscopy and Conformational Isomerization Energetics of *o*-, *m*-, and *p*-Ethynylstyrenes *J. Phys. Chem. A* **2005**, 109, 4484–4496
- 58 Frey, J. A.; Leist, R.; Muller, A.; Leutwyler, S. Gas-Phase Watson-Crick and Hoogsteen Isomers of the Nucleobase Mimic 9-Methyladenine-2-pyridone *ChemPhysChem* **2006**, 7, 1494–1499
- 59 Tanner, C.; Thut, M.; Steinlin, A.; Manca, C.; Leutwyler, S. Excited-State Hydrogen-Atom Transfer Along Solvent Wires: Water Molecules Stop the Transfer *J. Phys. Chem. A* **2006**, 110, 1758–1766
- 60 Shubert, V. A.; Baquero, E. E.; Clarkson, J. R.; James, W. H.; Turk, J. A.; Hare, A. A.; Worrel, K.; Lipton, M. A.; Schofield, D. P.; Jordan, K. D. Entropy-Driven Population Distributions in a Prototypical Molecule with Two Flexible Side Chains: *O*-(2-Acetamidoethyl)-*N*-acetyltyramine *J. Chem. Phys.* **2007**, 127, 234315
- 61 Baquero, E. E.; James, W. H.; Choi, T. H.; Jordan, K. D.; Zwier, T. S. Single Conformation Spectroscopy of a Flexible Bichromophore: 3-(4-Hydroxyphenyl)-*N*-Benzylpropionamide *J. Phys. Chem. A* **2008**, 112, 11115–11123
- 62 James, W. H.; Baquero, E. E.; Shubert, V. A.; Choi, S. H.; Gellman, S. H.; Zwier, T. S. Single-Conformation and Diastereomer Specific Ultraviolet and Infrared Spectroscopy of Model Synthetic Foldamers: Alpha/Beta-Peptides *J. Am. Chem. Soc.* **2009**, 131, 6574–6590
- 63 LeGreve, T. A.; James, W. H.; Zwier, T. S. Solvent Effects on the Conformational Preferences of Serotonin: Serotonin-(H<sub>2</sub>O)<sub>*n*</sub>, *n*=1,2 *J. Phys. Chem. A* **2009**, 113, 399–410
- 64 Ottiger, P.; Frey, J. A.; Frey, H. M.; Leutwyler, S. Jet-Cooled 2-Aminopyridine Dimer: Conformers and Infrared Vibrational Spectra *J. Phys. Chem. A* **2009**, 113, 5280–5288
- 65 Shubert, V. A.; Muller, C. W.; Zwier, T. S. Water’s Role in Reshaping a Macrocycle’s Binding Pocket: Infrared and Ultraviolet Spectroscopy of Benzo-15-crown-5-(H<sub>2</sub>O)<sub>*n*</sub> and 4’-Aminobenzo-15-crown-5-(H<sub>2</sub>O)<sub>*n*</sub>, *n* = 1, 2 *J. Phys. Chem. A* **2009**, 113, 8067–8079
- 66 Lobsiger, S.; Frey, H. M.; Leutwyler, S. Supersonic Jet UV Spectrum and Nonradiative Processes of the Thymine Analogue 5-Methyl-2-Hydroxypyrimidine *Phys. Chem. Chem. Phys.* **2010**, 12, 5032–5040

- 67 Dean, J. C.; Buchanan, E. G.; James, W. H.; Gutberlet, A.; Biswas, B.; Ramachandran, P. V.; Zwier, T. S. Conformation-Specific Spectroscopy and Populations of Diastereomers of a Model Monolignol Derivative: Chiral Effects in a Triol Chain *J. Phys. Chem. A* **2011**, *115*, 8464– 8478
- 68 Heid, C. G.; Ottiger, P.; Leist, R.; Leutwyler, S. The  $S_1/S_2$  Exciton Interaction in 2-Pyridone-6-Methyl-2-pyridone: Davydov Splitting, Vibronic Coupling, and Vibronic Quenching. *J. Chem. Phys.* **2011**, *135*.
- 69 James, W. H. Evolution of Amide Stacking in Larger Gamma-Peptides: Triamide H-Bonded Cycles *J. Phys. Chem. A* **2011**, *115*, 13783– 13798
- 70 Kumar, S.; Biswas, P.; Kaul, I.; Das, A. Competition between Hydrogen Bonding and Dispersion Interactions in the Indole-Pyridine Dimer and (Indole)(2)-Pyridine Trimer Studied in a Supersonic Jet *J. Phys. Chem. A* **2011**, *115*, 7461– 7472
- 71 Kumar, S.; Kaul, I.; Biswas, P.; Das, A. Structure of 7-Azaindole-2-Fluoropyridine Dimer in a Supersonic Jet: Competition between N-H--N and N-H--F Interactions *J. Phys. Chem. A* **2011**, *115*, 10299– 10308
- 72 Lobsiger, S.; Frey, H. M.; Leutwyler, S.; Morgan, P.; Pratt, D.  $S_0$  and  $S_1$  State Structure, Methyl Torsional Barrier Heights, and Fast Intersystem Crossing Dynamics of 5-Methyl-2-hydroxypyrimidine *J. Phys. Chem. A* **2011**, *115*, 13281– 13290
- 73 Sinha, R. K.; Lobsiger, S.; Trachsel, M.; Leutwyler, S. Vibronic Spectra of Jet-Cooled 2-Aminopurine--H<sub>2</sub>O Clusters Studied by UV Resonant Two-Photon Ionization Spectroscopy and Quantum Chemical Calculations *J. Phys. Chem. A* **2011**, *115*, 6208– 6217
- 74 Kumar, S.; Mukherjee, A.; Das, A. Structure of Indole--Imidazole Heterodimer in a Supersonic Jet: A Gas Phase Study on the Interaction between the Aromatic Side Chains of Tryptophan and Histidine Residues in Proteins *J. Phys. Chem. A* **2012**, *116*, 11573– 11580
- 75 Trachsel, M. A.; Lobsiger, S.; Leutwyler, S. Out-of-Plane Low-Frequency Vibrations and Nonradiative Decay in the (1)Pi--Pi\* State of Jet-Cooled 5-Methylcytosine *J. Phys. Chem. B* **2012**, *116*, 11081– 11091
- 76 Maeyama, T.; Mikami, N. Nucleophilic-Substitution within the Photoionized Vanderwaals Complex- Generation of C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup> from C<sub>6</sub>H<sub>5</sub>Cl<sup>-</sup>NH<sub>3</sub> *J. Am. Chem. Soc.* **1988**, *110*, 7238– 7239
- 77 Brutschy, B. Reactions in Molecular Clusters Following Photoionization *J. Phys. Chem.* **1990**, *94*, 8637– 8647
- 78 Eggert, J.; Janes, C.; Wassermann, B.; Brutschy, B.; Baumgartel, H. Nucleophilic-Substitution Reactions in Mixed Organic Clusters after Resonant 2-Photon Ionization *Ber. Bunsen. Phys. Chem.* **1990**, *94*, 1282– 1287
- 79 Brutschy, B.; Eggert, J.; Janes, C.; Baumgartel, H. Nucleophilic-Substitution Reactions in Molecular Clusters Following Photoionization *J. Phys. Chem.* **1991**, *95*, 5041– 5050
- 80 Brutschy, B. Ion Molecule Reactions within Molecular Clusters *Chem. Rev.* **1992**, *92*, 1567– 1587
- 81 Brutschy, B. Chemical-Reactions in Mixed Molecular Clusters, Studied by Resonant 2-Photon Ionization *Ber. Bunsen. Phys. Chem.* **1992**, *96*, 1154– 1161
- 82 Dimopoulourademann, U.; Rademann, K.; Bisling, P.; Brutschy, B.; Baumgartel, H. A Chemical-Reaction and Charge-Transfer in Heteroclusters of Fluorobenzene *Ber. Bunsen. Phys. Chem.* **1984**, *88*, 215– 217
- 83 Brutschy, B.; Janes, C.; Eggert, J. Selective Intracluster Ion-Chemistry Studied by Resonant 2-Photon Ionization Spectroscopy *Ber. Bunsen. Phys. Chem.* **1988**, *92*, 435– 437
- 84 Tholmann, D.; Grutzmacher, H. F. Aromatic-Substitution of Halobenzenes in the Gas-Phase: a Kinetic-Study by FT-ICR Spectrometry *Chem. Phys. Lett.* **1989**, *163*, 225– 229
- 85 Maeyama, T.; Mikami, N. Intracluster Ion Molecule Reactions within the Photoionized Vanderwaals Complexes of C<sub>6</sub>H<sub>5</sub>F and NH<sub>3</sub> and with H<sub>2</sub>O *J. Phys. Chem.* **1991**, *95*, 7197– 7204
- 86 Tonge, N. M.; MacMahon, E. C.; Pugliesi, I.; Cockett, M. C. R. The Weak Hydrogen Bond in the Fluorobenzene--Ammonia Van Der Waals Complex: Insights into the Effects of Electron Withdrawing Substituents on Pi Versus in-Plane Bonding *J. Chem. Phys.* **2007**, *126*, 154319
- 87 Vaupel, S.; Brutschy, B.; Tarakeshwar, P.; Kim, K. S. Characterization of Weak NH--pi Intermolecular Interactions of Ammonia with Various Substituted Pi-Systems *J. Am. Chem. Soc.* **2006**, *128*, 5416– 5426
- 88 Grover, J. R.; Cheng, B. M.; Herron, W. J.; Coolbaugh, M. T.; Peifer, W. R.; Garvey, J. F. Photoionization-Induced Intracluster Reactions of Chlorobenzene/Ammonia Mixed Complexes *J. Phys. Chem.* **1994**, *98*, 7479– 7487



- 89** Riehn, C.; Lahmann, C.; Brutschy, B. Role of Charge-Transfer in Nucleophilic-Substitution Reactions in Clusters of 1-Fluoro-*N*-chlorobenzene Cations with Ammonia Molecules J. Phys. Chem. **1992**, 96, 3626– 3632
- 90** Mizuse, K.; Fujii, A.; Mikami, N. Infrared and Electronic Spectroscopy of a Model System for the Nucleophilic Substitution Intermediate in the Gas Phase: The C–N Valence Bond Formation in the Benzene-Ammonia Cluster Cation J. Phys. Chem. A **2006**, 110, 6387– 6390
- 91** Hasegawa, H.; Mizuse, K.; Hachiya, M.; Matsuda, Y.; Mikami, N.; Fujii, A. Observation of an Isolated Intermediate of the Nucleophilic Aromatic Substitution Reaction by Infrared Spectroscopy Angew. Chem., Int. Ed. **2008**, 47, 6008– 6010
- 92** Mizuse, K.; Suzuki, Y.; Mikami, N.; Fujii, A. Solvation-Induced Sigma-Complex Structure Formation in the Gas Phase: A Revisit to the Infrared Spectroscopy of  $[C_6H_6-(CH_3OH)_2]^+$  J. Phys. Chem. A **2011**, 115, 11156– 11161
- 93** Tachikawa, H. Intramolecular  $S_N2$  Reaction Caused by Photoionization of Benzene Chloride– $NH_3$  Complex: Direct ab Initio Molecular Dynamics Study J. Phys. Chem. A **2006**, 110, 153– 159
- 94** 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.; Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.
- 95** Burns, L. A.; Vazquez-Mayagoitia, A.; Sumpter, B. G.; Sherrill, C. D. Density-Functional Approaches to Noncovalent Interactions: A Comparison of Dispersion Corrections (DFT-D), Exchange-Hole Dipole Moment (XDM) Theory, and Specialized Functionals J. Chem. Phys. **2011**, 134, 084107
- 96** Sinnokrot, M. O.; Sherrill, C. D. Highly Accurate Coupled Cluster Potential Energy Curves for the Benzene Dimer: Sandwich, T-Shaped, and Parallel-Displaced Configurations J. Phys. Chem. A **2004**, 108, 10200– 10207
- 97** Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals Theor. Chem. Acc. **2008**, 120, 215– 241
- 98** Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange-Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP) Chem. Phys. Lett. **2004**, 393, 51– 57
- 99** Peach, M. J. G.; Helgaker, T.; Salek, P.; Keal, T. W.; Lutnaes, O. B.; Tozer, D. J.; Handy, N. C. Assessment of a Coulomb-Attenuated Exchange-Correlation Energy Functional Phys. Chem. Chem. Phys. **2006**, 8, 558– 562
- 100** Mardirossian, N.; Parkhill, J. A.; Head-Gordon, M. Benchmark Results for Empirical Post-GGA Functionals: Difficult Exchange Problems and Independent Tests Phys. Chem. Chem. Phys. **2011**, 13, 19325– 19337
- 101** See Supplementary Material Document No. \_\_\_\_\_ for six figures and two tables of additional data. For information on Supplementary Material, see <http://www.aip.org/pubservs/epaps.html>.
- 102** Mokrushin, V.; Tsang, W. ChemRate, version 1.5.8; 2009.