

Vibrational predissociation of aniline-Inert gas cluster cations



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ABSTRACT

The molecular structures and predissociation dynamics of aniline (Phenylamine, PhNH₂)-inert gas cluster cations PhNH₂X⁺ (X=Ne, Ar, and Kr) were investigated by infrared (IR) spectroscopy coupled with density functional theory (DFT) calculations and IR photofragmentation studies. The ring isomer was the minimum energy structure for PhNH₂Ne⁺ and PhNH₂Ar⁺ whereas the N–H isomer was more stable in PhNH₂Kr⁺. The decay constants of PhNH₂X⁺ for ejection of X excited with IR depended strongly on the structure of PhNH₂X⁺, presumably because the rate of intramolecular vibrational energy redistribution (IVR) was governed by the structure. As a result, the dissociation was faster for the larger PhNH₂X⁺ clusters, because the rate of IVR was faster for the N–H type structure than the ring type. The decay constants deviate from those expected from the Rice–Ramsperger–Kassel–Marcus (RRKM) theory calculation by the factors of 10⁴ or larger, manifesting that the dissociation occurred mainly via nonstatistical pathways.

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1. Introduction

The research on the structural and dynamical features on van der Waals (vdW) molecules have provided fundamental information required to decode the nature of the weak chemical forces, prevailing in diverse chemical and biological systems. In this regard, extensive work has been carried out to elucidate the physico-chemical nature of the clusters consisting of rare gas and aromatic compounds such as pristine benzene complex with one or more homo or hetero inert gas atoms and clusters containing substituted aromatic compounds as model systems of vdW molecules [1–6]. Most of the research in this area has been focused on the electronic, vibrational, and/or rotational spectroscopic analysis by resonance enhanced multiphoton ionization, mass analyzed threshold ionization (MATI), or zero electron kinetic energy (ZEKE) spectroscopy. A classic review article on infrared (IR) photodissociation and spectroscopy of vdW molecules has been reported by Miller et al. [7].

Among many vdW clusters, aniline-rare gas complexes, PhNH₂Xs, have unique advantages, because aniline provides two distinct primary binding moieties: phenyl ring and amino group and several secondary binding sites. These structural features attribute them as ideal systems to explore not only spectroscopic but also the dynamical features in vibrational predissociation of simple rare gas and aromatic compound clusters, where rare gas

atoms may also act as the structural probes of the intermolecular potential energy surfaces.

However, in spite of extensive spectroscopic studies of aniline itself and its clusters, the dynamical features in the intramolecular vibrational energy redistribution (IVR) and vibrational predissociation (VP) are still not clear yet [8–15]. When vdW clusters are vibrationally excited, dissociation is to be mediated by both IVR and VP. The IVR and VP also compete with internal conversion, radiative process, and intersystem crossing, where IVR and VP may occur either in parallel or in serial modes [16]. While previous studies on vdW molecules have been mainly based on the parallel mechanism [17–20], the serial mechanism has also been modeled [21,22] with the help of Fermi's golden rule [23,24] and restricted Rice–Ramsperger–Kassel–Marcus (RRKM) [25] theory implementation of unimolecular rate constants considering only the vdW modes. The Kelley group, in particular, suggested that many different systems such as benzene, tetrazine, and aniline cluster with argon, nitrogen, methane, water, and ammonia and aromatic dimers follow the serial mechanism rather than the parallel mechanism [16].

Herein, we suggest that the vibrational dissociation of PhNH₂X⁺ clusters occurs via a serial pathway, where the IVR is so slow to result in a very long decay time. Interestingly, the dissociation rates were found to be strongly depending on the structures of PhNH₂X⁺ clusters, explaining the mode-dependence of vibrational predissociation. To support our argument, the molecular structures of PhNH₂X⁺ clusters were investigated by IR spectroscopy and high-level density functional theory (DFT) calculations, and

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the dissociation dynamics was explored by photodissociation (PD) spectroscopy in the IR region. The neutral PhNH_2X cluster with various experimental and theoretical methods has been extensively studied [26–34]; however, literatures on aniline inert gas cluster cations are limited [27,28,35] and cannot be applied to the structure-dependent dynamical features of the VP.

2. Experimental

2.1. Instrumentation

The details of the experimental setup were explained elsewhere [36]. Herein, only a brief description is provided. The experiment was performed with a linear tandem time of flight mass spectrometer consisting of two stages: ionization and dissociation stages apart by 99.3 cm. PhNH_2 vapor was carried to the source chamber with the carrier gas using a pulse valve (General Valve, Series 9) with an orifice diameter of 0.2 mm. Jet-cooled neutral clusters were ionized in the first stage through excitation of the 0–0 transition of $S_1 \leftarrow S_0$ by absorption of two UV photons, which were generated by doubling the output of a dye laser (Quantel, TDL 90) pumped by the second harmonic (532 nm) of a Nd-YAG laser (Quantel, YG 981C-10). The UV power kept low enough to assure two-photon ionization, confirmed by the power-dependence experiment. Mass-selected parent ions were dissociated in the second stage by the absorption of an IR photon generated from a lithium niobate optical parametric oscillator (OPO, Euroscan) pumped by 1064 nm radiation from an injection-seeded Nd:YAG laser (Continuum, SL III-10). To record PD action spectra, the fragment ion intensity was monitored as a function of the IR frequency. For decay time analysis, a specific mode of vibration of the cluster ion was excited by IR, and the fragment ion signal was averaged using a digital storage oscilloscope (Lecroy, Wave surfer 454, 500 MHz, 2GS/s). Care has been taken to make sure single photon absorption of IR, and this was clearly confirmed from the powder-dependence results.

2.2. Theoretical details

Several isomers representing the typical structures of the PhNH_2X^+ clusters were calculated by the Gaussian 09 program package at M06-2X/cc-pVTZ, M06-2X/6-311G++(2d), and B3LYP/cc-pVDZ levels. The discussion is based on M06-2X/cc-pVTZ, and the rest of the calculation results are detailed in the supporting information. The energies of the isomers were estimated after correcting the zero-point vibrational energy from the frequency calculation. The calculated IR frequencies were multiplied by numbers in the range 0.95–0.96 for different clusters and methods to provide the best matching with the experimental spectra. The relative energies of the isomers were calculated with respect to the minimum energy structure. The basis set superposition error (BSSE) corrected binding energies (BE) of the optimized structures were derived with counterpoise=2 calculation using the same method and basis set. Mass selected PhNH_2X^+ clusters were dissociated by exciting the symmetric NH_2 stretching mode vibration assigned from the IR spectra. The RRKM calculation performed using the frequency values obtained from M06-2X/cc-pVTZ and multiplied by 0.9717. The frequency for the transition state was calculated assuming the change in the entropy values of ~ 13 and $35 \text{ J mol}^{-1} \text{ K}^{-1}$ for the tight and loose transition states, respectively, and only the tight transition state results are discussed here. The BSSE corrected BE for PhNH_2X^+ by the same method and basis set taken as the critical energy for dissociation.

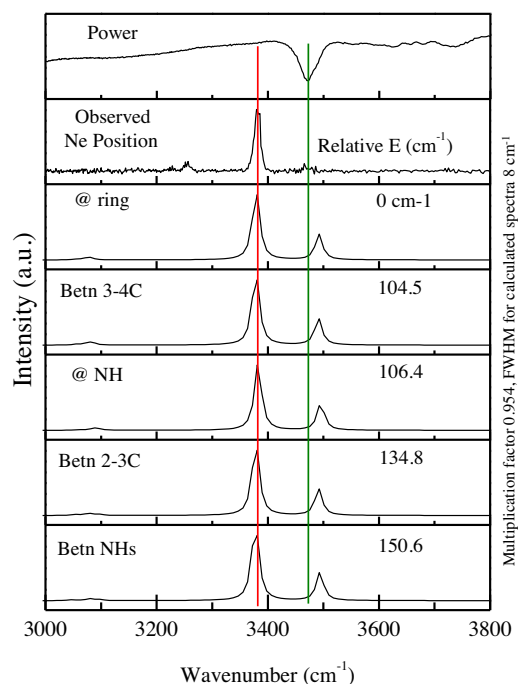


Fig. 1. The observed and calculated IR spectra of PhNH_2Ne^+ ion with M06-2X/cc-pVTZ.

Table 1

The observed and calculated vibrational modes assignment for PhNH_2Ne^+ , PhNH_2Ar^+ , and PhNH_2Kr^+ clusters with M06-2X/cc-pVTZ.

Cluster	Symmetric NH_2 mode	Anti-symmetric NH_2 mode	Structure
PhNH_2Ne^+	3379	>3482	Observed
	3379	3492	Ne above Ring (Structure I)
	3378	3491	Ne Betwn 3–4C (Structure II)
	3382	3495	Ne at N–H (Structure III)
	3378	3491	Ne Betwn 2–3C (Structure IV)
PhNH_2Ar^+	3377	3494	Betw N–H (Structure V)
	3380	3493	Observed
	3380	3493	Ar above Ring (Structure I)
	3362	3478	Ar at N–H (Structure II)
	3380	3493	Ar Betw N–H (Structure III)
PhNH_2Kr^+	3377	3493	Ar Betwn 2–3C (Structure IV)
	3378	3490	Ar Betwn 3–4C (Structure V)
	3379	3504	Observed
	3379	3504	Kr at N–H (Structure I)
	3413	3528	Kr above Ring (Structure II)
3412	3526	Kr Betw N–H (Structure III)	
3405	3521	Kr Betwn 2–3C (Structure IV)	
3419	3534	Kr Betwn 3–4C (Structure V)	

3. Results and discussion

3.1. Structural stability of PhNH_2X^+

Determining the most stable structure among the isomers of PhNH_2X^+ clusters from their IR spectra by the comparison with their theoretical spectra is very tricky, as the isomers show nearly identical theoretical spectra. Therefore, it is indispensable and highly appropriate not only to consider their relative stability but also to count on their BSSE corrected binding energies. Moreover, the relative peak intensities in the IR absorption region may provide a clue on the most stable structure.

Figs. 1 and 2 show the experimental and calculated IR spectra of PhNH_2Ne^+ and PhNH_2Ar^+ cluster cations, respectively. The experimental spectra were obtained by monitoring PhNH_2^+ as the daughter ion after one-photon absorption of IR

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