Slow-electron velocity-map imaging study of aniline via resonance-enhanced two-photon ionization method

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ABSTRACT

Slow electron velocity-map imaging (SEVI) of aniline has been investigated via two-color resonant-enhanced two-photo $(1 + 1')$ ionization (2C-R2PI) method. A number of vibrational frequencies in the first excited state of neutral (S_1) and $^2B_1$ ground electronic state of cation (D_0) have been accurately determined. In addition, photoelectron angular distributions (PADs) in the two-step transitions are presented and reveal a near threshold shape resonance in the ionization of aniline. The SEVI spectra taken via various S_1 intermediate states provide the detailed vibrational structures of D_0 state and directly deduce the accurate adiabatic ionization potential (IP) of $62,271 \pm 6$ cm^{-1}. *Ab initio* calculations excellently reproduce the experimental IP value (Theo. 62,242 cm^{-1}). For most vibrational modes, good agreement between theoretical and experimental frequencies in the S_0 and D_0 states of aniline is obtained to aid us to clearly assign vibrational modes. Especially, the vibrational frequencies calculated at the CASSCF level are much better consistent with experimental data than that obtained using the TDDFT and CIS methods.

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1. Introduction

Aniline and its derivatives have been widely studied and its geometric and electronic structures are very important for understanding the property and the mechanism of electronic relaxation as a self-protection process of living organism from short wavelength radiation [1–3]. The radical cations of aniline and its derivatives also play an essential role in photoinduced electron transfer phenomena [4] and in the oxidation poly-condensation [5].

The aniline neutral and singlet excited states and cationic ground state have extensively been investigated via different spectroscopic and theoretical methods. Excellent agreement between experimental results and theoretical results of vibrational frequencies confirmed the non-planarity of aniline in S_0 state with a pyramidal geometry of the amino group (C_S symmetry) [6–8]. The first excited state is confirmed as $1^1\pi\pi^*$ state (mainly π-π* nature) (S_1) [9–13]. Although, many of spectroscopic experiments have revealed mainly low-frequency vibrational modes, there has still been some controversy over the equilibrium geometry of the $1^1\pi\pi^*$ excited state (S_1). Planar or quasi-planar geometries are predicted using configuration-interaction with single excitations (CIS) calculations [14–16]. Nevertheless, recently, multi-configuration excited state calculations predicted non-planar equilibrium feature to support these experimental investigations of the

photochemistry and photophysics of aniline following excitation of the $1^1\pi\pi^*$ excited state [12,17,18]. Howbeit, they mainly focused on intersystem crossing and fluorescence study [12,19–22]. Ionic properties of aniline have also been investigated by two-color photoelectron spectroscopy [23], photoionization spectroscopy [24–26], zero kinetic energy (ZEKE) spectroscopy [27–30] and *ab initio* calculations [31–33]. Their results definitely indicate that aniline in the cationic ground state $(^2B_1)$ is planar and belongs to the point group of C_{2v}. Motivated by the solving the controversy of geometry in $1^1\pi\pi^*$ excited state, it needs to re-examine resonance-enhanced multiphoton ionization (REMPI) spectra of $1^1\pi\pi^*$ excited state in combination of high-level *ab initio* calculation to rationalize vibrational frequency assignment. And it is also indispensable to recheck vibrational modes in S_1 state and D_0 state excited in the photoionization process via REMPI photoelectron spectroscopy technique.

In recent years, pump-probe laser photoelectron spectroscopy has become a powerful tool for probing the dynamics of the excited state prepared by the pump, and locating ion internal structure. Velocity-map imaging (VMI) of photoelectrons has gained enormous impetus since its first demonstration by Eppink and Parker [34]. VMI becomes popular because of the excellent collection efficiency and the information on the photoelectron angular distribution. Many studies using this method can be found in the literatures [35–37]. In VMI experiments the pump and probe wavelengths are varied so that in slow electron velocity-map imaging (SEVI) experiments we employ the different wavelengths of pump and probe laser beam to be utilized to generate slow electrons associated with ion internal energy of interest. Compared

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with ZEKE and VMI photoelectron spectroscopy, SEVI technique provides the images of photoelectrons filled in the position sensitive detector by the choice of appropriate voltages with relatively high resolution and retains good collection efficiency and angular distribution information.

In this paper, we report the SEVI spectra of aniline cation using the two-color resonant two-photon ionization (2C-R2PI) SEVI technique. The precise adiabatic ionization potential (IP) of aniline has been determined. To obtain more information about the active vibrational modes in D_0 state, SEVI spectra are obtained by ionizing through the intermediate vibrational level in the S_1 state. We also performed *ab initio* and density functional theory (DFT) calculations to predict the electronic transition energies and vibrational frequencies, to provide a clear-cut assignment of the vibrational spectra of aniline and its cation.

2. Experiment and theory

The experimental apparatus used for this study has been previously described [38], and only a brief description is given here. The aniline (98%) purchased from J&K Scientific was used without any purification. A proportion of 1% aniline is seeded in He carrier gas (99.999%) and the stagnation pressure of the gas mixture is about 4 atm. The sample mixture is supersonically expanded into vacuum chamber through a pulsed valve of orifice diameter 0.5 mm (Parker, General Valve series 9) running at 10 Hz. After collimation by the skimmer with a 0.5 mm diameter, the aniline beam enters the interaction region between the repeller and extractor plates.

The excitation laser pulse (ω_1) is generated by frequency doubling of the dye laser output (Sirah) pumped by the second harmonic output of Nd:YAG laser (Spectra-Physics). The ionization laser pulse (ω_2) is generated by frequency-doubling of the output of another dye laser (ND6000, Continuum) pumped by another Nd:YAG laser (Powerlite Precision II, Continuum). Pyrromethene 597 and LDS 698 are used to acquire the required dye laser wavelengths. The laser bandwidth is approximate 0.1 cm^{-1}, and the duration of the laser pulse was about 6–8 ns.

One-color two-photon ($2\omega_1$) was performed near the $S_1 \leftarrow S_0$ transition of aniline by using a tunable frequency-doubling dye laser (Sirah) pumped by Nd:YAG laser (Spectra-Physics). Energy of ~40 μJ/pulse was held without focusing. The produced ions were perpendicularly accelerated by time-of-flight lenses. Ion signals were measured and analyzed by a multichannel scaler (MCS, SRS, SR245). The time-gated mass spectra were accumulated for 100 laser shots for each wavelength. And wavelength was scanned at 0.3 cm^{-1} spacing.

In the two-color two-photon ($\omega_1 + \omega_2$) ionization experiment, the pulse energy of the excitation laser (ω_1) is held below 10 μJ to prevent the one-color two-photon ionization process. The photoelectron signal is practically absent when only one of two laser pulses is applied to the system. Both laser pulses are linearly polarized with their E vectors perpendicular to the time-of-flight axis. The delay time between the excitation laser, the ionization laser and the pulse valve is controlled using two digital delay/pulse generators (DG535, SRS). Photoelectrons are accelerated along the time-of-flight axis in the velocity mapping condition and projected onto a home-made position-sensitive detector (50 mm diameter) coupled with a personal computer-interfaced CCD camera (Basler Scott, 782 × 582 pixels) system in conjunction with the photo-counting mode software interface embedded in LabVIEW code. The SEVI images are taken at low electric field condition (38 V/cm), and reconstructed through the BASEX program [39].

Geometry optimization and harmonic vibrational frequency calculations of aniline in the S_0, S_1, and D_0 states are all performed via the Gaussian 09 program package [40]. CAM-B3LYP methods are adopted for the calculations of the S_0 and D_0 states [41], while both TD-CAM-B3LYP and CASSCF(6, 6) methods are applied to the S_1 state. The basis set 6-311++G(d, p) is utilized in all the optimized calculations. The stationary points are characterized as the energy minimum by verifying

that all the corresponding frequencies are real. The calculated vibrational frequencies are scaled by a certain factor to approximately correct the combined errors stemming from the basis-set incompleteness and vibrational anharmonicity. The IP is obtained as the difference between the energy of aniline in the D_0 state and that in the S_0 state at the CCSD(T)/CBS level of theory, including the zero point energy correction [42].

3. Results

Aniline includes 36 normal modes, in which thirty are analogous to the normal modes of benzene and expressed in the Wilson notation based on benzene modes [29,32]. For other six normal modes involved in the vibrational motion of the NH_2 group are labeled with the letter I (inversion motion) and letters from A to E in order of increasing frequency [29]. In Table 1, we list 36 normal modes of aniline along with their symmetries, theoretical frequencies in the S_0, S_1 states of neutral and the D_0 state of cation in comparison to the experimental frequencies. Scaling factor of computed vibrational frequencies are utilized for well characterizing the experimental frequencies in the S_0, S_1 and D_0 states. As summarized in Table S1, most vibrational frequencies measured using REMPI-SEVI method are excellently consistent with previous experimental results. In current condition, experimental error in the S_1 state is under 3 cm^{-1} and total measured experimental error of vibrational frequencies in the D_0 state should be lower than 6 cm^{-1}.

3.1. Two-photon REMPI spectrum

Fig. 1 shows the one-color resonant two-photon ionization (1C-R2PI) spectrum of aniline in the energy range near its $S_1 \leftarrow S_0$ electronic transition. The band origin of this vibronic spectrum appears at 34,031 cm^{-1} in accordance with previous experimental investigations [9,23,24,29]. In term of reported assignment, transitions associated with totally symmetric modes, $6a_0^1$, 1_0^1 and 12_0^1 transitions are readily identified at 493, 798 and 954 cm^{-1} respectively for aniline, which agree well with the prior experimental and theoretical results [9,15]. The peaks at 348, 703, and 760 cm^{-1} are tentatively assigned to the transitions corresponding to 15_0^1, 15_0^2 and I_0^2 [9]. Some weakly spectral bands are assigned to the out-of-plane ring vibrational modes, which include $16a_0^1$, 4_0^1, $16a_0^2$, and $6b_0^1$ transitions [9]. To re-examine above assignment, two theoretical calculations are carried out. The vibrational frequencies calculated at the TD-CAM-B3LYP/6-311++G(d, p) level as listed in Table S2, supplementary material and associated geometry in the S_1 state of aniline are displayed in Fig. S1, supplementary material [43]. However, it gets worse when TD-CAM-B3LYP method is used for the prediction of vibrational modes in the S_1 state. Compared to the pyramidal feature around the N-atom in the S_0 state (Fig. 2a), geometry in the S_1 state demonstrates a planar feature, which is in agreement with the prior theoretical prediction using CIS method [14,15]. However, the calculations using CIS and TD-CAM-B3LYP methods yield large discrepancy in vibrational frequency between theory and experiment [9]. Thus, to get more reliable assignment of experimental vibrational frequencies, CASSCF method is utilized in this work to hope to narrow the gap between the experiment and theory. As depicted in Table 1, most vibrational frequencies predicted at the CASSCF(6, 6)/6-311++G(d, p) level agree well with experiment within the range of ± 30 cm^{-1}. For S_1 state, most vibrational frequencies calculated at the CASSCF method are better agreement with the experimental results than that using CIS method [15], especially for low-frequency transitions 4_0^1, $16a_0^1$, and $16b_0^1$. In addition, the corresponding geometric structure for the S_1 state is revealed to be non-planar nature as shown in Fig. 2c. Indeed, non-planar property also is verified by early theoretical investigations using multi-configuration methods (such as CASSCF and XMCQDPT2) [12,18]. Cartesian coordinates of aniline at neutral ground and ionic ground states from CAM-B3LYP/6-311++G(d, p) calculations and cartesian coordinates of aniline at neutral first excited state from