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

Zehua Qu, Zhengbo Qin*, Xianfeng Zheng*, Hui Wang, Guanxin Yao, Xianyi Zhang, and Zhifeng Cui

Institute of Atomic and Molecular Physics, Anhui Normal University, Wuhu, Anhui 241000, China

*To whom correspondence should be addressed. Email: asiake04@mail.ahnu.edu.cn (Z.B. Qin); Email: xfzheng@mail.ahnu.edu.cn (X.F. Zheng)

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 $62271 \pm 6 \text{ cm}^{-1}$. *Ab initio* calculations excellently reproduce the experimental IP value (Theo. 62242 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 at the TDDFT and CIS methods.

Key words: Velocity-map imaging, Time-of-flight, Resonance-enhanced multiphoton ionization (REMPI), Aniline

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 $\pi\text{-}\pi^*$ 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]. However, 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], 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

1 point group of C_{2v} . Motivated by the solving the controversy of geometry in $1^1\pi\pi^*$
2 excited state, it needs to re-examine REMPI spectra of $1^1\pi\pi^*$ excited state in
3 combination of high-level *ab initio* calculation to rationalize vibrational frequency
4 assignment. And it is also indispensable to recheck vibrational modes in S_1 state and
5 D_0 state excited in the photoionization process via resonance-enhanced multiphoton
6 ionization (REMPI) photoelectron spectroscopy technique.

7 In recent years, pump-probe laser photoelectron spectroscopy has been a powerful
8 tool for probing the dynamics of the excited state prepared by the pump, and locating
9 ion internal structure. Velocity-map imaging (VMI) of photoelectrons has gained
10 enormous impetus since its first demonstration by Eppink and Parker [34]. VMI
11 becomes popular because of the excellent collection efficiency and the information on
12 the photoelectron angular distribution. Many studies using this method can be found
13 in the literatures [35-37]. In VMI experiments the pump and probe wavelengths are
14 varied so that in slow electron velocity-map imaging (SEVI) experiments we employ
15 the different wavelengths of pump and probe laser beam to be utilized to generate
16 slow electrons associated with ion internal energy of interest. Compared with ZEKE
17 and VMI photoelectron spectroscopy, SEVI technique provides the images of
18 photoelectrons filled in the position sensitive detector by the choice of appropriate
19 voltages with relatively high resolution and retains good collection efficiency and
20 angular distribution information.

21 In this paper, we report the SEVI spectra of aniline cation using the two-color
22 resonant two-photon ionization (2C-R2PI) SEVI technique. The precise adiabatic
23 ionization energy of aniline has been determined. To obtain more information about
24 the active vibrational modes in D_0 state, SEVI spectra are obtained by ionizing
25 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 (ND6000, Continuum, Pyrromethene 597) pumped by Nd:YAG laser (Powerlite Precision II, Continuum). Energy of $\sim 40 \mu\text{J/pulse}$ 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

1 accumulated for 100 laser shots for each wavelength. And wavelength was scanned at
2 0.3 cm^{-1} spacing.

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

16 Geometry optimization and harmonic vibrational frequency calculations of
17 aniline in the S_0 , S_1 , and D_0 states are all performed via the Gaussian 09 program
18 package [40]. CAM-B3LYP methods are adopted for the calculations of the S_0 and D_0
19 states [41], while both TD-CAM-B3LYP and CASSCF(6, 6) methods are applied to
20 the S_1 state. The basis set 6-311++G(d, p) is utilized in all the optimized calculations.
21 The stationary points are characterized as the energy minimum by verifying that all
22 the corresponding frequencies are real. The calculated vibrational frequencies are
23 scaled by a certain factor to approximately correct the combined errors stemming
24 from the basis-set incompleteness and vibrational anharmonicity. The ionization
25 potential (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 letter 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 34031 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

1 weakly spectral bands are assigned to the out-of-plane ring vibrational modes, which
 2 include $16a_0^1$, 4_0^1 , $16a_0^2$, and $6b_0^1$ transitions [9]. To re-examine above assignment, two
 3 theoretical calculations are carried out. The vibrational frequencies calculated at the
 4 TD-CAM-B3LYP/6-311++G(d, p) level as listed in Table S2, supplementary material
 5 and associated geometry in the S_1 state of aniline is displayed in Fig. S1,
 6 supplementary material [43]. However, it gets worse when TD-CAM-B3LYP method
 7 is used for the prediction of vibrational modes in the S_1 state. Compared to the
 8 pyramidal feature around the N-atom in the S_0 state (Fig. 2a), geometry in the S_1 state
 9 demonstrates a planar feature, which is in agreement with the prior theoretical
 10 prediction using CIS method [14, 15]. However, the calculations using CIS and
 11 TD-CAM-B3LYP methods yield large discrepancy in vibrational frequency between
 12 theory and experiment [9]. Thus, to get more reliable assignment of experimental
 13 vibrational frequencies, CASSCF method is utilized in this work to hope to narrow
 14 the gap between the experiment and theory. As depicted in Table 1, most vibrational
 15 frequencies predicted at the CASSCF(6, 6)/6-311++G(d, p) level agree well with
 16 experiment within the range of $\pm 30 \text{ cm}^{-1}$. For S_1 state, most vibrational frequencies
 17 calculated at the CASSCF method are better agreement with the experimental results
 18 than that using CIS method [15], especially for low-frequency transitions 4_0^1 , $16a_0^1$,
 19 and $16b_0^1$. In addition, the corresponding geometric structure for the S_1 state is
 20 revealed to be non-planar nature as shown in Fig. 2c. Indeed, non-planar property also
 21 is verified by early theoretical investigations using multi-configuration methods (such
 22 as CASSCF and XMCQDPT2) [12, 18]. Cartesian coordinates of aniline at neutral
 23 ground and ionic ground states from CAM-B3LYP/6-311++G(d, p) calculations and
 24 cartesian coordinates of aniline at neutral first excited state from
 25 CASSCF/6-311++G(d, p) calculations and TDCAM-B3LYP/6-311++G(d, p)

calculations are listed in Table S3, supplementary material [43]. In addition, theoretical harmonic frequencies (cm^{-1}) and normal vibrational modes are tabulated in Table S4, supplementary material [43].

3.2. SEVI spectra via the S_1 – S_0 origin

As seen in Figs. 3a–3e, SEVI spectra of aniline are recorded by ionizing in five different wavelengths via S_1 0_0^0 intermediate state. The SEVI bands resulting from the active vibrations of the aniline cation are listed in Table 1, along with the calculated frequencies and possible assignments. The pronounced features at 816, 986, 1188, 1325 and 1594 cm^{-1} higher than the ionization threshold are assigned to be due to 1_0^1 , 12_0^1 , $9a_0^1$, $6a_0^1 1_0^1$ and $8a_0^1$ vibrations, respectively. The weak band shifted from the 0_0^0 band by 357 and 714 cm^{-1} corresponds to the $10b_0^2$ and $16a_0^2$ vibrations. The results are in excellent agreement with experimentally reported vibrational frequencies in the literature [29, 32]. Modes 6a, 1, 12, 9a and 8a mainly involve in-plane motions of the ring carbon atoms, whereas vibrational modes of 10b and 16a result from the out-of-plane NH_2 wagging and ring deformation vibration. To aid in the accurately spectral assignment, we performed theoretical calculation for the D_0 state of aniline. As shown in Fig. 2b, it is revealed that ground cationic aniline is changed to planar geometry compared to the geometry of S_0 state upon photoionization. All calculated vibrational frequencies of D_0 state are listed in Table 1 for comparison. Clearly, most vibrational frequencies agree well with the experimental results except for 8a mode with a slight deviation from experimental result.

3.3. SEVI spectra via the 6a, 1, 12 and I intermediate states

As seen in Figs. 4a–4d, when the $6a_0^1$, 1_0^1 , 12_0^1 , and I_0^2 vibronic level in the S_1 state are used as the intermediate levels, the same vibrational frequencies of the aniline cation display the strong SEVI bands. This observed propensity of $\Delta v = 0$

1 indicates that the geometries of S_1 and D_0 states have basically similar shapes except
 2 for amino moiety. As shown in Fig. 2, it suggests that no evident structural changes in
 3 benzene ring except for C-N bond and amino moiety. The strongest peak is observed
 4 at the ionic vibrational energy of 522 cm^{-1} in the SEVI spectrum via the $6a$ vibrational
 5 level in Fig. 4a is obviously recognized as the $6a^1$ vibrational level of the cation. The
 6 peaks at 1338 , 1509 and 1711 cm^{-1} are ascribed to combination vibrations of the $6a^1$
 7 with 1^1 , 12^1 , and $9a^1$, respectively. The combination vibration of $6a^110b^2$ is quite weak
 8 located at 877 cm^{-1} , and the small peak at 1849 cm^{-1} is assigned to the $6a^21^1$ vibration.
 9 The SEVI spectrum taken via the 1 vibrational level of the S_1 state (798 cm^{-1}) clearly
 10 shows that the vibrational level of 1^1 is located at 814 cm^{-1} , in Fig. 4b. Its first
 11 overtone vibration band of 1^2 is found at 1621 cm^{-1} . The 12^1 vibration is very weak
 12 located at 981 cm^{-1} , while the combination vibration of the 1^112^1 is quite strong
 13 observed at 1796 cm^{-1} . The peak at 1166 cm^{-1} correspond to 1^110b^2 combination
 14 vibration is weak, while the 1^16a^1 and 1^19a^1 combination vibrations can be easily
 15 identified at 1336 and 2002 cm^{-1} , respectively. The last observed peak at 2138 cm^{-1}
 16 could be assigned to 1^26a^1 or the other 1^11^2 vibration, because both combination
 17 vibrations are too close to be distinguished completely in our experimental condition.
 18 The 12^1 vibration is found to have the vibrational energy of 986 cm^{-1} as shown in the
 19 SEVI spectrum via the S_1 12 vibrational level (954 cm^{-1}) in Fig. 4c. Its first overtone
 20 12^2 vibration is found at 1969 cm^{-1} . The combination vibration of 12^11^1 is weak at
 21 1803 cm^{-1} , while the peak at 2314 cm^{-1} result from the $12^16a^11^1$ vibration is weaker
 22 than the former. The weakest band at 1358 cm^{-1} corresponds to the 12^110b^2 vibration.
 23 Other combination vibrations of 12^11^1 and 12^19a^1 are also observed at 1633 and 2314
 24 cm^{-1} , respectively. When the I_0^2 vibronic transition in the S_1 state is used as the
 25 intermediate level in Fig. 4d, the band at 1319 cm^{-1} is assigned to the I^2 vibration. The

other band result from the combination vibration of I^21^1 is observed at 2136 cm^{-1} . All vibrational bands observed in SEVI spectra are assigned and given in Table 2.

4. Discussion

4.1. Ionization energy

To measure the ionization potential of aniline, photoelectron images are taken at a number of different ionization wavelengths whereas the excitation wavelength is fixed for the S_1-S_0 origin at 34031 cm^{-1} . The peak position of the outmost ring associated with the D_0-S_1 origin transition is plotted versus the two photons energy, giving a linear relationship with respect to each other, in Fig. 5. Extrapolation of the linear fit to the center of the image corresponding to the zero-kinetic energy gives rise to the adiabatic ionization potential, which is determined to be $62271 \pm 6\text{ cm}^{-1}$ ($7.7204 \pm 0.0008\text{ eV}$). Our ionization potential data is in excellent agreement with the $62271 \pm 5\text{ cm}^{-1}$ value derived in the MATI study reported by Lin et al. [26] and the $62271 \pm 2\text{ cm}^{-1}$ value from the ZEKE spectra of aniline reported by Song et al.[29].

The hierarchy of Dunning's correlation-consistent polarization basis sets has been designed for recovering electron correlations in a systematic manner. When a series of these basis sets is used, the total correlation energy is found to exhibit a convergence behavior toward the limit of one-electron atomic basis functions, that is, the CBS limit. At the CBS limit, the basis set error is supposed to be zero and is isolated from the intrinsic error due to approximations of the wavefunction model. Based on the asymptotic convergence of the electronic correlation energy obtained with these basis sets, the CBS energies (E_{CBS}) have been estimated by the most commonly used three-point extrapolation scheme as shown in eq. (1) [42].

$$E_n = E_{\text{CBS}} + B \exp[-(n-1)] + C \exp[-(n-1)^2] \quad (1)$$

where $n=2, 3, 4$ are for the cc-pVDZ, cc-pVTZ, cc-pVQZ basis sets, respectively. In

1 order to achieve higher accuracy of IP prediction, we have included the zero-point
2 vibration energy (ZPVE) calculations. Thus, as displayed in Table 3, the
3 CCSD(T)/CBS IP(aniline) is calculated to be 7.7169 eV, which is involved in the
4 ZPVE correction. This value is excellent agreement with the experiment IP(aniline) =
5 7.7204 eV.

6 *4.2. Normal mode assignments*

7 Frequencies of vibrations $6a^1$, 1^1 and 12^1 are measured to be 522, 814, and 986
8 cm^{-1} for aniline cation in the D_0 state. The corresponding frequencies of these normal
9 modes in S_1 state are measured to be 493, 798, 954 cm^{-1} . Clearly, frequencies of these
10 vibrations of this molecule in the D_0 state are slightly higher than those in the S_1 state.
11 An interpretation is that the molecular geometry of aniline is slightly more rigid in the
12 cationic D_0 state than that in the neutral S_1 state as supported by theoretical prediction.
13 Nevertheless, the vibrational frequency of inversion mode I is measured to be 760
14 cm^{-1} in the S_1 state and 1319 cm^{-1} in the D_0 state. The CN bond of aniline molecule is
15 bent in the S_0 state, so the potential energy as a function of the inversion normal
16 coordinate has a double minimum. However, in the ion states, the molecule is
17 apparently planar, with a roughly harmonic potential. The shortening of the CN bond
18 upon ionization should give the deeper potential wells along the normal coordinates
19 associated with the out-of-plane amino motions, resulting in the higher vibrational
20 frequencies for cation. It is noted that discrepancy exists for I vibrational mode in the
21 S_0 state. The experimental value of 665 cm^{-1} reported by Song et al. [29] in 1993 is
22 larger than the reported result by Wojciechowski in 2003 (541 cm^{-1}) [32]. Theoretical
23 calculations show I vibrational frequency in the range of 650-700 cm^{-1} using HF
24 method [29]. It seems that the former experimental result is rational. Nevertheless, we
25 have repeated calculations at the CAM-B3LYP level and yield 554 cm^{-1} which agrees

well with the experimental result of 541 cm⁻¹ and previous theoretical prediction using B3LYP method [32]. So, the measurement of I vibrational mode in the current work is reasonable. For D₀ state, both of us and Wojciechowski et al. [32] well reproduce the experimental result for I vibrational frequency except for Song et al. [29] But the results calculated using current method (595 cm⁻¹) as well as CIS method (by Tzeng et al.) (589 cm⁻¹) fails to accurately evaluate I vibrational frequency in S₁ state [15].

4.3. PAD

The PAD is obtained by integrating the intensity of the Abel-inverted image. The PADs in the two-photon ionization with linearly polarized light are generally described by the function: [44, 45]

$$I(\theta) = k[I + \beta_2 P_2(\theta) + \beta_4 P_4(\theta)] \quad (2)$$

where θ is the angle between the electron velocity vector and the laser polarization direction in the laboratory frame, k is a normalization constant proportional to the total photoionization cross-section, and P_2 and P_4 are the second- and fourth-order Legendre polynomials. The angular dependence is completely defined by β , the anisotropy parameter, which can be determined by fitting eq. (2) to the experimental PAD.

The photoelectron angular distribution is determined by a photoelectron scattering wave that varies with the photoelectron kinetic energy and the vibronic state of the cation produced by ionization. In Fig. 6, the dependence of anisotropy parameter following excitation of 0₀⁰ on photoelectron kinetic energy is distinguished according to final ion vibrational level. Inspection of our data shows that β_2 and β_4 for various ion vibronic states at the same PKE are different. The β_2 parameter decreases with the increase of PKE, and fell rapidly through a distinct negative value within 0.8 eV above the ionization threshold. Dramatic PAD variation as a function of ionization

1 energy possibly indicates autoionization, a Cooper minimum, or a shape resonance. A
2 sharp structure of certain peaks in threshold usually should be discernible in the
3 energy range over which we investigated in autoionization processes [46]. Cooper
4 minima have been inspected in iodobenzene, bromobenzene, and chlorobenzene
5 usually associated with a lone pair electron ejection beyond threshold [47-49]. For
6 p-difluorobenzene, a shape resonance has been observed near threshold in R2PI
7 spectra [50]. It has been revealed that this shape resonance is directly correlated to the
8 virtual π^* antibonding orbital (benzene ring) and the rule holds true in related
9 substituted benzenes [51, 52]. In the case of aniline, π^* antibonding nature (S_1
10 intermediate state) is similar to these substituted benzenes [12]. So, there is every
11 reason to believe that this behavior of PAD trend near threshold in aniline is a
12 consequence of the shape resonance. All values of β_2 and β_4 for the following
13 excitation of various vibrational intermediate states are available in Table S5,
14 supplementary material and 1C-R2PI photoelectron velocity image and photoelectron
15 spectrum following the ionization of aniline in the 0_0^0 in the S_1 state are displayed in
16 Fig. S2, supplementary material [43].

17

5. Conclusion

We have performed high-level theoretical predictions for the spectroscopic and energetic properties of aniline. The geometric structures and vibrational frequencies of aniline in the first excited state of neutral and ground state of cation are studied in detail by combining the REMPI-VMI spectroscopy and theoretical calculations. For S_1 state, non-planar feature is unraveled to be the same as that of S_0 state at the CASSCF level. The 1C-R2PI spectrum of aniline gives the S_1 - S_0 electronic transition energy, $34031 \pm 3 \text{ cm}^{-1}$. In addition to the typical ring deformation modes, vibrations related to the NH_2 groups also appear in the low-frequency region of the REMPI spectrum. The non-planar geometric structure of S_1 state at the CASSCF/6-311++G(d, p) level is better consistent with vibrational assignment than that revealed for the planar structure in S_1 state at the TD-CAM-B3LYP/6-311++G(d, p) level. In the 2C-R2PI SEVI spectra, the accurate IP is obtained to be $62271 \pm 6 \text{ cm}^{-1}$ for aniline through the linear fit to the change of PKE versus ionization wavelength. The SEVI spectra taken via various S_1 vibrational intermediate states provide accurate vibrational frequencies of the aniline cationic ground state. Like many other substitute aromatic molecules, the 8a mode with in-plane ring distortion is significantly activated in the D_0 - S_1 ionization. It reveals that the drastically geometric change as aniline is being ionized. The vibrational frequencies of the D_0 state calculated at the CAM-B3LYP/6-311++G(d, p) level are in excellent agreement with the experimental results and give the unambiguous assignment. The coupled cluster base CCSD(T)/CBS including ZPVE correction renders the IP of aniline extraordinary accurate, 7.7169 eV, which is found only to be $\sim 4 \text{ meV}$ below the highly precise experimental IP value of $7.7204 \pm 0.0008 \text{ eV}$ determined in the SEVI spectra.

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References

- [1] B. B. Brady, L. A. Peteanu and D. H. Levy, Chem. Phys. Lett. 147 (1988) 538.
- [2] S. Ullrich, T. Schultz, M. Z. Zgierski and A. Stolow, Phys. Chem. Chem. Phys. 6 (2004) 2796.
- [3] B. N. Rajasekhar, A. Veeraiah, K. Sunanda and B. N. Jagatap, J. Chem. Phys. 139 (2013) 064303.
- [4] N. E. Agbor, J. P. Cresswell, M. C. Petty and A. P. Monkman, Sens. Actuators, B 41 (1997) 137.
- [5] A. Pron and P. Rannou, Prog. Polym. Sci. 27 (2002) 135.
- [6] O. Bludský, J. Šponer, J. Leszczynski, V. Špirko and P. Hobza, J. Chem. Phys. 105 (1996) 11042.
- [7] W. E. Sinclair and D. W. Pratt, J. Chem. Phys. 105 (1996) 7942.
- [8] P. Hobza and J. Šponer, Chem. Rev. 99 (1999) 3247.
- [9] W. B. Tzeng, K. Narayanan and G. C. Chang, Appl. Spectrosc. 52 (1998) 890.
- [10] X.-J. Hou, P. Quan, T. Höltzl, T. Veszprémi and M. T. Nguyen, J. Phys. Chem. A 109 (2005) 10396.

- [11] G. A. King, T. A. A. Oliver and M. N. R. Ashfold, *J. Chem. Phys.* 132 (2010) 214307.
- [12] G. M. Roberts, C. A. Williams, J. D. Young, S. Ullrich, M. J. Paterson and V. G. Stavros, *J. Am. Chem. Soc.* 134 (2012) 12578.
- [13] R. Spesyvtsev, O. M. Kirkby and H. H. Fielding, *Faraday Discuss.* 157 (2012) 165.
- [14] J. C. Jiang and C. E. Lin, *J. Mol. Struct. (Theochem)* 392 (1997) 181.
- [15] W. B. Tzeng, K. Narayanan, K. C. Shieh and C. C. Tung, *J. Mol. Struct. (Theochem)* 428 (1998) 231.
- [16] J. M. Hollas, M. R. Howson, T. Ridley and L. Halonen, *Chem. Phys. Lett.* 98 (1983) 611.
- [17] F. Wang, S. P. Neville, R. Wang and G. A. Worth, *J. Phys. Chem. A* 117 (2013) 7298.
- [18] M. Sala, O. M. Kirkby, S. Guérin and H. H. Fielding, *Phys. Chem. Chem. Phys.* 16 (2014) 3122.
- [19] H. Von Weyssenhoff and F. Kraus, *J. Chem. Phys.* 54 (1971) 2387.
- [20] R. Scheps, D. Florida and S. A. Rice, *J. Chem. Phys.* 61 (1974) 1730.
- [21] J. L. Knee and P. M. Johnson, *J. Chem. Phys.* 80 (1984) 13.
- [22] B. Kim, C. P. Schick and P. M. Weber, *J. Chem. Phys.* 103 (1995) 6903.
- [23] J. T. Meek, E. Sekreta, W. Wilson, K. S. Viswanathan and J. P. Reilly, *J. Chem. Phys.* 82 (1985) 1741.
- [24] M. A. Smith, J. W. Hager and S. C. Wallace, *J. Chem. Phys.* 80 (1984) 3097.
- [25] J. Hager, M. A. Smith and S. C. Wallace, *J. Chem. Phys.* 84 (1986) 6771.
- [26] J. L. Lin and W. B. Tzeng, *J. Chem. Phys.* 115 (2001) 743.
- [27] M. Takahashi, H. Ozeki and K. Kimura, *J. Chem. Phys.* 96 (1992) 6399.

- [28] X. Zhang, J. M. Smith and J. L. Knee, J. Chem. Phys. 97 (1992) 2843.
- [29] X. Song, M. Yang, E. R. Davidson and J. P. Reilly, J. Chem. Phys. 99 (1993) 3224.
- [30] B. Kim and P. M. Weber, J. Phys. Chem. 99 (1995) 2583.
- [31] Y. Honda, M. Hada, M. Ehara and H. Nakatsuji, J. Chem. Phys. 117 (2002) 2045.
- [32] P. M. Wojciechowski, W. Zierkiewicz, D. Michalska and P. Hobza, J. Chem. Phys. 118 (2003) 10900.
- [33] J. C. Choe, N. R. Cheong and S. M. Park, Int. J. Mass Spectrom. 279 (2009) 25.
- [34] A. T. J. B. Eppink and D. H. Parker, Rev. Sci. Instrum. 68 (1997) 3477.
- [35] A. Osterwalder, M. J. Nee, J. Zhou and D. M. Neumark, J. Chem. Phys. 121 (2004) 6317.
- [36] D. M. Neumark, J. Phys. Chem. A 112 (2008) 13287.
- [37] C. J. Hammond and K. L. Reid, Phys. Chem. Chem. Phys. 10 (2008) 6762.
- [38] Z. Qu, C. Li, Z. Qin, X. Zheng, G. Yao, X. Zhang and Z. Cui, Rev. Sci. Instrum. 86 (2015) 063106.
- [39] V. Dribinski, A. Ossadtchi, V. A. Mandelshtam and H. Reisler, Rev. Sci. Instrum. 73 (2002) 2634.
- [40] M. J. Frisch, G. W. Trucks, H. B. Schlegel and e. al., *Gaussian 09, revision D.01*. (2009).
- [41] T. Yanai, D. P. Tew and N. C. Handy, Chem. Phys. Lett. 393 (2004) 51.
- [42] K.-C. Lau and C.-Y. Ng, Acc. Chem. Res. 39 (2006) 823.
- [43] Supplementary data associated with this article can be found, in the online version, at [URL will be inserted](#).
- [44] C. N. Yang, Phys. Rev. 74 (1948) 764.
- [45] Y. Ogi, H. Kohguchi, D. Niu, K. Ohshimo and T. Suzuki, J. Phys. Chem. A 113

(2009) 14536.

- [46] P. Baltzer, L. Karlsson, B. Wannberg, G. Öhrwall, D. M. P. Holland, M. A. MacDonald, M. A. Hayes and W. von Niessen, Chem. Phys. 224 (1997) 95.
- [47] D. M. P. Holland, D. Edvardsson, L. Karlsson, R. Maripuu, K. Siegbahn, A. W. Potts and W. v. Niessen, Chem. Phys. 253 (2000) 133.
- [48] D. M. P. Holland, D. Edvardsson, L. Karlsson, R. Maripuu, K. Siegbahn, A. W. Potts and W. von Niessen, Chem. Phys. 252 (2000) 257.
- [49] A. W. Potts, D. Edvardsson, L. Karlsson, D. M. P. Holland, M. A. MacDonald, M. A. Hayes, R. Maripuu, K. Siegbahn and W. von Niessen, Chem. Phys. 254 (2000) 385.
- [50] S. M. Bellm and K. L. Reid, Phys. Rev. Lett. 91 (2003) 263002.
- [51] S. M. Bellm, J. A. Davies, P. T. Whiteside, J. Guo, I. Powis and K. L. Reid, J. Chem. Phys. 122 (2005) 224306.
- [52] M. Staniforth, S. Daly, K. L. Reid and I. Powis, J. Chem. Phys. 139 (2013) 064304.

Figure captions:

Figure 1:

Two-photon REMPI spectrum of aniline. The 0_0^0 transition of aniline is located at 34031 cm^{-1} . * denotes bands probably stem from other contaminations.

Figure 2:

Geometries of aniline at (a) ground state S_0 , (b) ionic ground state D_0 using the optimized CAM-B3LYP/6-311++G(d, p) structure, and (c) first excited state S_1 at the CASSCF/6-311++G(d, p) level. Bond distances are given in Å and angles in °. θ is the dihedral angle between the NH_2 and $\text{C}_6\text{H}_5\text{N}$ planes in °. H-N-H angle: 112.6° for S_0 , 111.7° for S_1 and 116.9° for D_0 .

Figure 3:

Two-color photoelectron velocity images (left columns) and photoelectron spectra (right columns) following the ionization of aniline in the 0_0^0 level in S_1 , recorded with the probe wavelength set to (a) 353.20 nm, (b) 346.48 nm, (c) 344.39 nm, (d) 338.82 nm, (e) 332.05 nm. The photoelectron images are reconstructed images after inverse Abel transformation. The double arrow indicates the directions of the laser polarization.

Figure 4:

Two-color photoelectron velocity images (left columns) and photoelectron spectra (right columns) following the ionization of aniline via $6a_0^1$, 1_0^1 , 12_0^1 , and I_0^2 in the S_0 intermediate states, recorded with the ionization wavelength set to (i) 346.48 nm, (ii) 341.11 nm, (iii) 336.08 nm. The photoelectron images are reconstructed images after inverse Abel transformation. The double arrow indicates the directions of the laser polarization.

Figure 5:

The total photon energy is plotted against the squares of the radial positions corresponding to the 0_0^0 transition of the aniline cation. Data points are marked with empty circles. Several photoelectron images are shown together. A linear regression enables the extrapolation of this peak position to zero radius from which the ionization potential denoted by an arrow is deduced.

Figure 6:

The photoelectron angular anisotropy parameters (β_2 and β_4) taken from the images pumping by S_1 0_0^0 level shown in Fig. 2 as a function of photoelectron kinetic energy. The solid and hollow

symbols indicate β_2 and β_4 values, respectively. Different symbols represent the values obtained for different vibronic states in the D_0 state.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table captions:

Table 1. Vibrational frequencies of aniline in the S_0 , S_1 and D_0 states (cm^{-1}). The scaling factor for frequencies was 0.98, except for modes Q_{30} - Q_{36} scaled by 0.96 in S_0 and D_0 states calculated by the CAM-B3LYP/6-311++G(d, p) method. And scaling factor for frequencies was 0.95 in S_1 state calculated by the CASSCF/6-311++G(d, p) method.

No.	Mode	$S_0 (^1A_1)$			S_1		$D_0 (^2B_1)$			Mode description
		Sym.	Calc. freq.	Obs. freq. ^a	Calc. freq.	Obs. freq.	Sym.	Calc. freq.	Obs. freq.	
Q ₁	10b	A'	220	217	166		B ₁	181	179	oop; NH ₂ wag; ring def.
Q ₂	A	A''	282	277	262		A ₂	569		oop; NH ₂ tors.
Q ₃	15	A''	379	390	375	348	B ₂	386		ip; CN rock
Q ₄	16a	A''	416	415	243	261	A ₂	365	357	oop; ring def.
Q ₅	16b	A'	497	501	368	374	B ₁	448		oop; CN def, ring tors.
Q ₆	6a	A'	532	526	473	493	A ₁	527	522	ip; ring def.
Q ₇	I	A'	554	541	631		B ₁	648	658	oop; NH ₂ inversion
Q ₈	6b	A''	631	619	551	568	B ₂	588		ip; ring def.; CH rock
Q ₉	4	A'	701	688	462	453	B ₁	627		oop; ring def.
Q ₁₀	11	A'	765	755	504		B ₁	788		oop; CH bend.
Q ₁₁	1	A'	829	822 ^c	778	798	A ₁	820	816	ip; ring breathing
Q ₁₂	10a	A''	830	812	471		A ₂	811		oop; CH wag
Q ₁₃	17b	A'	892	875	584		B ₁	934		oop; CH bend
Q ₁₄	17a	A''	976	957 ^c	567		A ₁	1007		oop; CH bend
Q ₁₅	5	A'	994	968	689		B ₁	1012		oop; CH bend
Q ₁₆	12	A'	1005	996	980	954	A ₁	985	986	ip; ring stretch; CH bend
Q ₁₇	18a	A'	1045	1028	926		A ₁	1004		ip; ring stretch; CH bend
Q ₁₈	B	A''	1056	1054	1134		B ₂	1019		ip; NH ₂ rock
Q ₁₉	18b	A''	1120	1115	946		B ₂	1121		ip; ring stretch; CH bend

Q ₂₀	9b	A''	1162	1152	1190	B ₂	1170		ip; ring stretch; CH bend
Q ₂₁	9a	A'	1186	1176	1169	A ₁	1195	1188	ip; CH scissor; ring stretch
Q ₂₂	20a	A'	1294	1282	1288	A ₁	1393		ip; ring stretch; CN stretch
Q ₂₃	14	A''	1319	1324	1735	B ₂	1368		ip; ring stretch
Q ₂₄	3	A''	1352	1340	1371	A ₁	1355		ip; CH bend
Q ₂₅	19b	A''	1492	1470	1440	B ₂	1468		ip; ring stretch; CH bend
Q ₂₆	19a	A'	1525	1503	1473	A ₁	1512		ip; CH bend; ring stretch
Q ₂₇	8b	A''	1636	1594	1578	B ₂	1547		ip; ring stretch; CH bend
Q ₂₈	C	A'	1634	1618	1709	A ₁	1664		ip; NH ₂ scissor; ring stretch
Q ₂₉	8a	A'	1660	1608	1606	A ₁	1628	1594	ip; ring stretch; NH ₂ scissor
Q ₃₀	7b	A''	3043	3025	3169	B ₂	3092		ip; CH stretch
Q ₃₁	13	A'	3042	3037	3164	A ₁	3072		ip; CH stretch
Q ₃₂	7a	A'	3058	3053 ^b	3174	A ₁	3082		ip; CH stretch
Q ₃₃	2	A'	3080	3072	3197	A ₁	3097		ip; CH stretch
Q ₃₄	20b	A''	3064	3088 ^b	3187	B ₂	3092		ip; CH stretch
Q ₃₅	D	A'	3454	3418 ^b	3591	A ₁	3407		ip; NH stretch
Q ₃₆	E	A''	3547	3500 ^b	3687	B ₂	3512		ip; NH stretch

^aReference 32.

^bReference 29.

Table 2. Observed peak locations (in cm^{-1}) in the D_0 state of aniline.

Assignments	Aniline transition excited				
	0_0^0	$6a_0^1$	I_0^2	1_0^1	12_0^1
0^0	0				
$10b^2$	357				
$16a^2$	714				
1^1	816			814	
12^1	986			981	986
$9a^1$	1188				
$6a^11^1$	1325	1338		1336	
$8a^1$	1594				
$6a^1$		522			
$6a^116a^1$		877			
$6a^112^1$		1509			
$6a^19a^1$		1711			
$6a^21^1$		1849			
I^2			1319		
I^21^1			2136		
1^116a^1				1166	
I^2				1621	
1^112^1				1796	1803
1^19a^1				2002	
1^26a^1 or 1^1I^2				2138	
12^116a^1					1358
12^1I^1					1633
12^2					1969
12^19a^1					2166
$12^16a^11^1$					2314

Table 3. Individual energy contributions to the CCSD(T)/CBS calculations for the IP(aniline). All quantities and energy differences are in eV.

Method	IP (eV)
CCSD(T)/ cc-pVDZ	7.2461
CCSD(T)/cc-pVTZ	7.5458
CCSD(T)/ cc-pVQZ	7.6464
ΔE_{ZPVE}	0.0128
CCSD(T)/CBS	7.7169
Experimental value	7.7204 ± 0.0008

*Graphical abstract