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Infrared Spectra of Isomers of Protonated Aniline in Solid $para$-Hydrogen

Masashi Tsuge, *,†,‡ Yu-Hsuan Chen, † and Yuan-Pern Lee*,†,§,⊥

†Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan
‡Institute of Low Temperature Sciences, Hokkaido University, Sapporo 060-0819, Japan
§Center for Emergent Functional Matter Science, National Chiao Tung University, Hsinchu 30010, Taiwan
⊥Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan
**ABSTRACT:** The protonation sites of aniline molecule play important roles in its chemical reactions, but the preferred protonation site of gaseous aniline has yet to be determined. In this work, we recorded infrared (IR) absorption spectra of three isomers of protonated aniline, H⁺C₆H₅NH₂, produced on electron bombardment during matrix deposition at 3.2 K of a mixture of aniline and *para*-H₂. The intensities of IR lines of H⁺C₆H₅NH₂ decreased during maintenance of the electron-bombarded matrix in darkness because of neutralization with electrons that were slowly released from their trapping sites. The observed lines were classified into three groups according to their behavior upon secondary photolysis with light at 375 and 254 nm and assigned to *para*-, *amino*-, and *ortho*-H⁺C₆H₅NH₂, the three most stable isomers of protonated aniline, according to comparison of experimental spectra with quantum-chemically predicted spectra of five possible isomers of H⁺C₆H₅NH₂. The spectra of *para*- and *ortho*-H⁺C₆H₅NH₂ are newly distinguished. The approximate relative abundance of these isomers in solid *p*-H₂ was *para* : *amino* : *ortho* ≈ (1.0 ± 0.1) : (1.0 ± 0.6) : (0.6 ± 0.1). The possible mechanisms of formation are discussed.
1. INTRODUCTION

The protonation of chemical species is important in many branches of physical science because a proton facilitates acid-base chemistry.\textsuperscript{1} Protonated aromatic molecules play critical roles in many chemical and biological phenomena.\textsuperscript{2-4} For example, the electrophilic aromatic substitution reaction of benzene (C\textsubscript{6}H\textsubscript{6}) proceeds via C\textsubscript{6}H\textsubscript{6} + E\textsuperscript{+} \rightleftharpoons [C\textsubscript{6}H\textsubscript{6}E]\textsuperscript{+} \rightarrow C\textsubscript{6}H\textsubscript{5}E + H\textsuperscript{+}, in which E\textsuperscript{+} is an electrophile; [C\textsubscript{6}H\textsubscript{6}E]\textsuperscript{+} can be regarded as a protonated substituted benzene.\textsuperscript{5-6} The preferred site of protonation in the substituted benzenes and the energetics of protonation are thus important in determining the rate of such chemical reactions. The physical conditions (e.g., temperature and pressure), the substitution by functional groups, and solvation might affect the preferential site of protonation. Spectral studies of isolated protonated aromatic species consequently provide insights to the intrinsic preference of the protonation sites.

Aniline (C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}) is the simplest aromatic amine, in which one hydrogen is substituted with an amino group (NH\textsubscript{2}). As shown in Figure 1, aniline has five distinct protonation sites, namely \textit{para}-, \textit{meta}-, \textit{ortho}-, \textit{ipso}-, and \textit{amino}-positions; hereafter we designate the protonated aniline as H\textsuperscript{+}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}. The proton prefers to attach to the \textit{amino}-position in aqueous solutions because of the stabilization by solvation,\textsuperscript{7-8} but the preferred sites of protonation in the gaseous phase are still uncertain according to numerous theoretical and experimental studies.\textsuperscript{9-23} The most stable H\textsuperscript{+}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} was predicted to be either \textit{para}- or \textit{amino}-H\textsuperscript{+}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} depending on the method of quantum-chemical calculation.\textsuperscript{10-11, 16-20} From systematic high-level computations, Russo et al. reported that \textit{para}-H\textsuperscript{+}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} has the least energy, but the energy difference between \textit{para}- and \textit{amino}-H\textsuperscript{+}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} is within 3 kJ mol\textsuperscript{-1} so that these isomers probably coexist.\textsuperscript{18} The G2MP2 and B3LYP methods with the triple-zeta basis sets give proton affinities similar to the experimental values, 874–877 kJ mol\textsuperscript{-1}.\textsuperscript{24-25}

Mass-spectrometric experiments indicated that both \textit{para}- and \textit{amino}-H\textsuperscript{+}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} are present in the gaseous phase but that their relative abundance depends strongly on the method.
of production (ionization) and possibly the method of detection. According to Nold et al., the fast-atom bombardment (FAB) produces predominantly amino-\(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\), whereas the chemical ionization induces mixed protonation with the ring-protonated species predominating.\(^{15}\) In chemical ionization by \(\text{H}^+, \text{CH}_3^+, \) or \(\text{C}_2\text{H}_5^+\) ions, Wood et al. suggested that para-\(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\) is the predominant species according to their MS/MS measurements with collision-induced dissociation (CID).\(^{26}\) In experiments with charge stripping followed by CID, Pachuta et al. identified that protonation occurs on the carbon ring,\(^ {12}\) consistent with the conclusion by Wood et al. In contrast, Smith et al. reported the predominant formation of amino-\(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\) from chemical ionization with \(\text{CH}_5^+/\text{CD}_5^+\).\(^ {14}\)

The electrospray ionization (ESI) has also been utilized to study protonation of aniline.\(^ {13,22-23}\) These experiments indicated that both the solvent used in ESI and the post-ESI source conditions greatly affect the ratio between para- and amino-\(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\). For example, Walker et al. demonstrated that \(\sim 96\%\) of amino-\(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\) and a minor proportion of para-\(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\) were produced in their ESI experiments; the proportion of para-\(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\) was significantly decreased when a protic solvent (methanol or water) was employed, compared to the use of an aprotic solvent (acetonitrile).\(^ {23}\) When clustered with solvent molecules, para-\(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\) can be converted to amino-\(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\) but not vice versa, indicating that, in ESI experiments, ion structures might be altered before mass-spectrometric characterization. Although challenging, non-perturbative formation and definitive spectral detection of these protonated isomers is hence desirable to provide more accurate relative populations among varied sites of protonation.

Dopfer and co-workers conducted infrared photodissociation (IRPD) spectroscopy on \(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\) tagged with Ar or N\(_2\); the \(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\) isomers were accumulated in an ion trap and IRPD spectra in the NH-stretching region were recorded. These authors reported the observation of lines in two groups that are assignable to amino-\(\text{H}^+\text{C}_6\text{H}_3\text{NH}_2\) and ortho- and/or
para-H⁺C₆H₅NH₂ according to the variation of the spectra depending on the ligands, dissociation pattern, and a comparison with theoretical predictions; the infrared (IR) spectra of ortho- and para-H⁺C₆H₅NH₂ were predicted to be similar in the NH-stretching region. Obtaining spectra with improved spectral resolution and in fingerprint regions is hence critical to distinguish these isomers unambiguously.

Our method to produce protonated species in solid para-hydrogen (p-H₂) by electron bombardment has several advantages to solve the problems discussed above. The IR spectra of protonated species obtained in this method exhibit narrow lines, true relative IR intensities, and a wide spectral coverage, suitable to distinguish the spectra of ortho- and para-H⁺C₆H₅NH₂. Although this method lacks mass selection, the electron bombardment of a p-H₂ matrix containing aromatic species has been proven to produce protonated and hydrogenated species with negligible fragmentations; methods to distinguish protonated and hydrogenated products have been established. Because the spectral shift from the gaseous phase is expected to be small in solid p-H₂, a comparison with quantum-chemically predicted IR spectra of potential carriers provides definitive assignments of these species. In this work, we applied this method to identify unambiguously the IR spectra of para-, ortho-, and amino-H⁺C₆H₅NH₂.

2. METHODS

The experimental setup for p-H₂ matrix-isolation IR spectroscopy, combined with electron bombardment during matrix deposition, is described elsewhere. A gaseous mixture was deposited onto a gold-plated copper substrate that also reflects the incident IR beam to the detector for reflective absorption measurements in spectral range 5000–450 cm⁻¹. Infrared absorption spectra were recorded with a Fourier-transform infrared (FTIR) spectrometer equipped with a KBr beam splitter and a HgCdTe detector cooled to 77 K with liquid nitrogen. Two hundred scans at resolution 0.25 cm⁻¹ were recorded at each stage of the experiment.
A gaseous mixture of C₆H₅NH₂/p-H₂ (prepared in a glass bulb with an estimated mixing ratio ~70 ppm) was bombarded with electrons during deposition at 3.2 K at a flow rate of 13 mmol h⁻¹ over a period of 8–10 h. An electron beam of kinetic energy 200 eV and current 30 μA was provided from an electron gun. The deposited matrix was maintained in darkness for a prolonged period to distinguish cationic and neutral species. Secondary photolysis was subsequently performed using light at 375 ± 10 nm from a light-emitting diode and light at 254 nm from a low-pressure Hg lamp to further differentiate various species.

Pure p-H₂ was prepared on catalytic conversion of normal-H₂ (n-H₂) at low temperatures; n-H₂ was introduced into a copper cell filled with a catalyst (iron(III)-oxide hydrated, 30–50 mesh, Aldrich) and maintained at 12–13 K with a closed-cycle helium refrigerator. The resultant p-H₂ typically contained ortho-H₂ at less than 100 ppm. The aniline was obtained commercially (≥99.5 %, Aldrich) and degassed with several freeze-pump-thaw cycles.

The mixing ratios of products in solid p-H₂ were estimated using the method developed by Tam and Fajardo.⁵⁷-⁵⁸ According to their method, the mixing ratio \( x \) (in ppm) in solid p-H₂ is estimated as

\[
x = \frac{2.303 \int \log_{10} (I/I_0) d\nu}{\varepsilon l} \times V_m \times 10^6,
\]

in which \( \varepsilon \) is the absorption coefficient in cm mol⁻¹ cm⁻¹, \( \int \log_{10} (I/I_0) d\nu \) is the observed integrated absorbance, \( l \) (in cm) is the length of the IR absorption path through solid p-H₂, and \( V_m \) (= 23.16 cm³ mol⁻¹) is the molar volume of solid p-H₂. Infrared intensities calculated with the B3LYP/ cc-pVTZ method were used for \( \varepsilon \). Length \( l \) of the IR path was estimated from the integrated band area of transition \( S_1(0) + S_0(0) \) of the p-H₂ matrix.³⁹-⁴⁰

Quantum-chemical calculations were performed with programs Gaussian 09 (Rev. E.01)⁴¹ and Gaussian 16 (Rev. B.01).⁴² The density-functional theory with B3LYP functionals⁴³-⁴⁴ and Dunning’s correlation-consistent basis set, cc-pVTZ,⁴⁵ were employed to perform geometry optimization and harmonic vibrational analysis. Scaling factors for harmonic vibrational
wavenumbers were obtained on comparing wavenumbers observed for C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} in solid \( p \)-H\textsubscript{2} with those predicted; see Sec. 4A for details. In addition, anharmonic vibrational wavenumbers were calculated with a second-order vibrational perturbation theory (VPT2),\textsuperscript{46} implemented in Gaussian 09. For the comparison of single point energies, the zero-point vibrational energy (ZPVE) was corrected using harmonic wavenumbers without scaling.

3. COMPUTATIONAL RESULTS

Figure 2 shows the geometries of aniline and five possible isomers of protonated aniline, \textit{para}-, \textit{meta}-, \textit{ortho}-, \textit{ipso}-, and \textit{amino}-H\textsuperscript{\textit{+}}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}, optimized with the B3LYP/cc-pVTZ method; representative bond lengths and angles are presented. Protonation at the benzene ring distorts the ring slightly as indicated by bond angles less than 120°, but the carbon atoms remain in one plane except for the \textit{ipso}-H\textsuperscript{\textit{+}}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} isomer. The C1–N bonds in \textit{para}-, \textit{ortho}-, and \textit{meta}-isomers are shortened from that of aniline (1.395 Å according to the B3LYP/cc-pVTZ method) and those in \textit{amino}- and \textit{ipso}-isomers are lengthened, indicating that protonation affects the resonance pattern of \( \pi \)-electrons; i.e., the double-bond character of the C1–N bond of aniline is enhanced in \textit{para}-, \textit{ortho}-, and \textit{meta}-isomers and diminished in other isomers.

Among these possible protonated-isomers, \textit{para}-H\textsuperscript{\textit{+}}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} has the least energy. The \textit{amino}- and \textit{ortho}-H\textsuperscript{\textit{+}}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} isomers have energies greater by 7.8 and 18.4 kJ mol\textsuperscript{-1}, respectively, than that of \textit{para}-H\textsuperscript{\textit{+}}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}; all energies are corrected for ZPVE. The energies of \textit{meta}- and \textit{ipso}-H\textsuperscript{\textit{+}}C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} are much greater (+96.0 and +168.3 kJ mol\textsuperscript{-1}, respectively). A potential-energy diagram for the protonation of aniline and the isomerization of protonated aniline is presented in Figure 3 and summarized in Table 1. As compared in Table 1, the order of the two most stable isomers differs between our work and that calculated with the B3LYP/6-311G(2df,2pd) method by Pasker et al.\textsuperscript{20} We also calculated the energies of these isomers with the B3LYP/6-311G(2df,2pd) method and found discrepancies between our results and those of
Pasker et al., as compared in Table 1; the literature values might be in error. The proton-transfer reactions from H$_3^+$ to aniline, C$_6$H$_5$NH$_2$ + H$_3^+$ → H$^+$C$_6$H$_5$NH$_2$ + H$_2$, have no barrier, with exothermicity ranging from 305.9 kJ mol$^{-1}$ for the formation of ipso-H$^+$C$_6$H$_5$NH$_2$ to 474.3 kJ mol$^{-1}$ for the formation of para-H$^+$C$_6$H$_5$NH$_2$. Although the barriers for isomerization from one site to a neighboring site via TS1–TS4 are smaller than the exothermicity of the protonation reactions, once a product is stabilized, thermal isomerization to other isomers is unlikely at low temperatures except for ipso-H$^+$C$_6$H$_5$NH$_2$, which might spontaneously isomerize to ortho-H$^+$C$_6$H$_5$NH$_2$.

Vibrational wavenumbers and IR intensities of the representative vibrational modes of para-, ortho-, and amino-H$^+$C$_6$H$_5$NH$_2$, predicted with the B3LYP/cc-pVTZ method, are listed in Tables 2, 3, and 4, respectively; the full lists are available in Tables S-1–S-3. Those predicted for meta- and ipso-H$^+$C$_6$H$_5$NH$_2$ are listed in Tables S-4 and S-5, respectively. For protonated aniline, the vibrational lines associated with the NH$_2$ (or NH$_3$) group are intense and characteristic. For para-H$^+$C$_6$H$_5$NH$_2$, the NH$_2$-stretching modes are predicted at 3510 ($\nu_{28}$) and 3407 ($\nu_{1}$) cm$^{-1}$, and the NH$_2$-scissoring mode at 1661 ($\nu_{5}$) cm$^{-1}$; similar wavenumbers are predicted for ortho-H$^+$C$_6$H$_5$NH$_2$. For amino-H$^+$C$_6$H$_5$NH$_2$, the NH-stretching modes are predicted at 3336 ($\nu_{1}$), 3311 ($\nu_{27}$), and 3255 ($\nu_{2}$) cm$^{-1}$, and the NH$_3$ umbrella mode at 1470 ($\nu_{13}$) cm$^{-1}$. Another group of relatively intense vibrational lines is associated with the CH$_2$ group; these include the CH$_2$-scissoring mode of para-H$^+$C$_6$H$_5$NH$_2$ at 1338 ($\nu_{32}$) cm$^{-1}$, the CH$_2$-scissoring and wagging modes of ortho-H$^+$C$_6$H$_5$NH$_2$ at 1347 ($\nu_{15}$) and 1189 ($\nu_{17}$) cm$^{-1}$, respectively. Some in-plane and out-of-plane CH-bending modes are predicted to be also intense. For para-H$^+$C$_6$H$_5$NH$_2$, the in-plane CH-bending modes are predicted at 1513 ($\nu_{7}$) and 1202 ($\nu_{10}$) cm$^{-1}$, and out-of-plane CH-bending modes at 891 ($\nu_{22}$), 823 ($\nu_{23}$), and 563 ($\nu_{25}$) cm$^{-1}$; for ortho-H$^+$C$_6$H$_5$NH$_2$, the in-plane CH-bending modes are predicted at 1506 ($\nu_{11}$), 1440 ($\nu_{12}$), and 1415 ($\nu_{13}$) cm$^{-1}$, and out-of-plane CH-bending modes at 833 ($\nu_{33}$) and 743 ($\nu_{34}$) cm$^{-1}$; for
amino-\textit{H}^+\text{C}_6\text{H}_5\text{NH}_2, the out-of-plane CH-bending modes are predicted at 744 (\nu_{34}) and 690 (\nu_{35}) cm\(^{-1}\). The corresponding vibrational modes of \textit{meta}- and \textit{ipso-H}^+\text{C}_6\text{H}_5\text{NH}_2 are also predicted to be intense; see Tables S-4 and S-5.

4. EXPERIMENTAL RESULTS

4A. IR Spectrum of \textit{C}_6\text{H}_5\text{NH}_2 in Solid \textit{p-H}_2. Figure 4(a) shows IR spectrum of a \textit{C}_6\text{H}_5\text{NH}_2/\textit{p-H}_2 matrix in the spectral range 1700–400 cm\(^{-1}\). Observed line positions and relative intensities are compared with those reported for aniline in solid Ar\(^{47}\) in Table S-6; they are in satisfactory agreement. Intense IR lines of \textit{C}_6\text{H}_5\text{NH}_2 in solid \textit{p-H}_2 were observed at 3416.2, 3503.6, 3048.4, 1621.4, 1503.4, 1282.8, 754.9, and 690.1 cm\(^{-1}\), with the most intense line at 1621.4 cm\(^{-1}\). Including weaker ones, 24 lines were identified, compared with 15 lines reported for aniline in solid Ar.

The observed vibrational wavenumbers are plotted against the harmonic vibrational wavenumbers predicted with the B3LYP/cc-pVTZ method in Figure S-1. Linear regression analyses yielded satisfactorily linear relations with scaling equations \(y = (0.9212 \pm 0.031) \times + (138 \pm 101)\) for wavenumbers above 2000 cm\(^{-1}\) and \(y = (0.9716 \pm 0.004) \times + (8.5 \pm 4.6)\) for wavenumbers less than 2000 cm\(^{-1}\); in these equations, \(y\) is the scaled vibrational wavenumber and \(x\) is the calculated harmonic vibrational wavenumber. We applied these equations to scale the harmonic vibrational wavenumbers predicted for \textit{C}_6\text{H}_5\text{NH}_2 and isomers of \textit{H}^+\text{C}_6\text{H}_5\text{NH}_2 to compare with experiment.

The predicted spectrum of \textit{C}_6\text{H}_5\text{NH}_2 simulated according to the scaled harmonic vibrational wavenumbers and IR intensities is shown in Figure 4(b) to compare with experiment [Figure 4(a)]. A satisfactory agreement is observed between experimental and predicted spectra in terms of line positions and relative intensities (Table S-6). The line marked with * at 589 cm\(^{-1}\) is predicted for the NH\(_2\)-wagging (inversion) mode. As the inversion barrier for the NH\(_2\) group
is small,\textsuperscript{48-49} this vibrational mode is significantly anharmonic, so that harmonic vibrational analysis predicts poorly its wavenumber and intensity. The fundamental and overtone transitions of this mode were observed at 40.8, 423.8, and 700.1 cm\textsuperscript{−1} in the gaseous phase,\textsuperscript{50-52} and the overtone transitions were observed at 421, 701 (700), and 1090 (1084.6/1090) cm\textsuperscript{−1} in an Ar matrix,\textsuperscript{49} in which the wavenumbers in parentheses are from Ref. 47. The absence of the inversion mode in solid \textit{p}-H\textsubscript{2} might indicates that this large-amplitude motion is restricted, similar to that in solid N\textsubscript{2}.\textsuperscript{49}

\textbf{4B. IR Spectrum of an Electron-Bombarded C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}/p-H\textsubscript{2} Matrix.} Figure 5 shows representative IR difference spectra obtained for an electron bombarded C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}/p-H\textsubscript{2} matrix in spectral ranges 3550–3200 and 1560–1150 cm\textsuperscript{−1}; other regions including 1150–500 cm\textsuperscript{−1} are presented in Figure S-2. Traces in Figure 5(a) present the spectra of aniline C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} deposited without electron bombardment and those in Figure 5(b) present the spectra recorded after deposition of electron-bombarded matrix for 10 h, with the lines of C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} stripped using Figure 5(a). The positive lines in this spectrum are hence induced by electron bombardment; some parent absorption lines shifted slightly so that they showed a band shape of first-derivative type. Figure 5(c) shows the difference spectrum after maintaining the matrix under darkness for 19 h; lines pointing upward indicate generation and those pointing downward indicate destruction. After this process, the matrix was irradiated at 375 nm for 10 min, followed by irradiation at 254 nm for 30 min. The difference spectra showing the results of these two steps are shown in Figures 5(d) and 5(e), respectively.

The electron bombardment of a \textit{p}-H\textsubscript{2} matrix during deposition is known to produce proton (H\textsubscript{3}\textsuperscript{+}) and hydrogen atom; proton-transfer and hydrogenation reactions produce protonated and hydrogenated products, respectively.\textsuperscript{27-28, 53} After maintaining the matrix in darkness for a prolonged period, the protonated products become slowly neutralized by originally solvated
electrons to produce their neutral counterparts; the trapped hydrogen atoms might react further with parent molecules to produce hydrogenated products. As a result, we expect that the intensities of lines of protonated species decrease while those for hydrogenated species increase after maintenance of the matrix in darkness for a prolonged period. We identified several groups of lines that decreased during this period and marked them with red circles (group A⁺), green squares (group B⁺), and blue diamonds (group C⁺) in trace (b). The classification of observed lines into three groups was made according to their behavior upon secondary photolysis at 375 and 254 nm. The intensities of lines in group A⁺ decreased upon irradiation at 254 nm (Figure 5(e)) to an extent similar to that observed after maintaining the matrix sample in darkness for 19 h (Figure 5(c)), but ~30 % that observed after deposition (Figure 5(b)). Slightly decreased intensities of lines in group A⁺ were also observed upon irradiation at 375 nm (Figure 5(c)). The intensities of lines in group B⁺ decreased upon irradiation at 375 nm with a proportion similar to that observed after maintaining the matrix sample in darkness for 19 h, but ~20 % that observed after deposition; no further decreased intensity was observed upon irradiation at 254 nm. In contrast, the intensities of lines in group C⁺ remained nearly unchanged upon secondary photolysis at 375 and 254 nm.

Lines in group A⁺ include the intense ones observed at 3482.7, 3395.5, 1669.2, and 1523.5 cm⁻¹ and weaker ones at 3289.0(?), 1440.7(?), 1337.2, 1197.5, 884.2, 874.1(?), 816.7, and 561.3 cm⁻¹; the two most intense lines are indicated in bold font and the ? mark indicates that the intensity correlation of the line was less consistent, likely because of interference from other lines. The integrated relative intensities are listed in Table 2. Lines in group B⁺ include intense ones at 3479.3, 3392.1, 3372.2, 1667.0, and 1515.7 cm⁻¹ and weaker ones at 1541.9, 1452.0, 1419.3, 1341.6, 1188.1, 966.2, 786.1, and 736.1 cm⁻¹ (Table 3). A smaller number of lines at 3303.3, 3278.8, 3234.2, 1470.0, and 737.7 cm⁻¹ are identified to belong to group C⁺ (Table 4).
To be discussed in Sec 5A, lines in groups A⁺, B⁺, and C⁺ are assigned to para-, ortho-, and amino-H⁺C₆H₅NH₂, respectively.

In addition to the lines of which intensities decreased after maintaining the sample in darkness for a prolonged period, we identified several groups of lines of which intensities increased with time; these lines presumably originated from mono-hydrogenated aniline isomers, H₅C₆H₃NH₂. We shall present the assignments of these species in a separate paper.

5. DISCUSSION

As discussed in Sec. 4B, lines that decreased in intensity after maintenance of the matrix sample in darkness likely correspond to isomers of protonated aniline, H⁺C₆H₅NH₂. We demonstrated that these lines are classified into three groups (A⁺, B⁺, and C⁺) according to their behavior upon secondary photolysis at 375 and 254 nm. In Figure 6, the lines in groups A⁺, B⁺, and C⁺ are compared with spectra predicted for five isomers of H⁺C₆H₅NH₂. The difference spectrum after the secondary photolysis at 254 nm, Figure 5(e), is inverted and presented in Figure 6(a) so that lines in group A⁺ are pointing upward and indicated with red circles. The difference spectrum after the secondary photolysis at 375 nm, Figure 5(c), is inverted and presented in Figure 6(c) so that the lines in group B⁺ are pointing upward and indicated with green squares. The difference spectrum after maintaining the electron-bombarded matrix in darkness for 19 h, Figure 5(b), is inverted and presented in Figure 6(e); lines in group C⁺ are indicated with blue diamonds. Figures 6(b), (d), (f), (g), and (h) present stick IR spectra of para-, ortho-, amino-, meta-, and ipso-H⁺C₆H₅NH₂, respectively, simulated according to the scaled harmonic vibrational wavenumbers and IR intensities calculated with the B3LYP/cc-pVTZ method.
5A. Assignment of Lines in Groups $A^+$ and $B^+$ to para- and ortho-$H^+C_6H_5NH_2$. The predicted spectra of para- and ortho-$H^+C_6H_5NH_2$ in the NH-stretching region above 3200 cm$^{-1}$ are similar; lines of para-$H^+C_6H_5NH_2$ are predicted at 3510 and 3407 cm$^{-1}$, slightly blue-shifted from those predicted for ortho-$H^+C_6H_5NH_2$ at 3508 and 3406 cm$^{-1}$. Those of meta-$H^+C_6H_5NH_2$ are further blue-shifted to 3563 and 3459 cm$^{-1}$, whereas those in ipso-$H^+C_6H_5NH_2$ are predicted at 3459 and 3380 cm$^{-1}$. In the experiments, partially overlapped lines were observed to belong to groups $A^+$ (3482.7 and 3395.5 cm$^{-1}$) and $B^+$ (3479.3 and 3392.1 cm$^{-1}$). The observed spectral patterns (wavenumber and intensity) indicate that these lines in groups $A^+$ and $B^+$ are most likely due to para-$H^+C_6H_5NH_2$ or ortho-$H^+C_6H_5NH_2$; the assignment to meta-$H^+C_6H_5NH_2$ is less likely, but cannot be positively excluded. Because the CH-stretching modes in $H^+C_6H_5NH_2$ are predicted to be weak (with IR intensities less than 5 km mol$^{-1}$) and because of severe interference from absorption of C$6H_5NH_2$, we could not positively identify lines of the CH-stretching modes of $H^+C_6H_5NH_2$.

The observed and predicted spectra are further compared in the spectral region below 1700 cm$^{-1}$, in which the predicted spectra of various isomers of $H^+C_6H_5NH_2$ are distinct. In this spectral region, lines in group $A^+$ were observed at 1669.2, 1523.5, 1440.7 (?), 1337.2, 1197.5, 884.2, 874.1 (?), 816.7, and 561.3 cm$^{-1}$ (Figure 6(a)), in satisfactory agreement with intense lines of para-$H^+C_6H_5NH_2$ predicted at 1661, 1513, 1463, 1338, 1202, 891, 882, 823, and 563 cm$^{-1}$ (Figure 6(b)); the NH$_2$-inversion mode was predicted at 616 cm$^{-1}$ but, similarly to the case of aniline, was unobserved. An additional weak line observed at 3289.0 cm$^{-1}$ is most likely due to the first overtone of the NH$_2$-scissoring mode ($2\nu_5$), which is predicted at 3307 cm$^{-1}$ according to the anharmonic vibrational calculation with the B3LYP/cc-pVTZ method. The spectral pattern of these observed 12 lines agrees poorly with those predicted for other isomers of $H^+C_6H_5NH_2$; these lines in group $A^+$ are thus assigned to para-$H^+C_6H_5NH_2$. The observed and predicted wavenumbers and relative intensities for para-$H^+C_6H_5NH_2$ are summarized in
Table 2. The average absolute deviation between experiments and scaled harmonic wavenumbers is $10.0 \pm 8.1 \text{ cm}^{-1}$.

In the spectral region below 1700 cm$^{-1}$, we observed intense lines in group B$^+$ at 1667.0, 1515.7, and 736.1 cm$^{-1}$, and weaker ones at 1541.9, 1452.0, 1419.3, 1341.6, 1188.1, 966.2, and 786.1 cm$^{-1}$ (Figure 6(c)). This observed spectral pattern agrees satisfactorily with those predicted for *ortho*-H$^+$C$_6$H$_5$NH$_2$ with intense lines at 1659, 1506, and 743 cm$^{-1}$ and weaker ones at 1536, 1440, 1415, 1347, 1189, 964, and 774 cm$^{-1}$ (Figure 6(d)); the NH$_2$-inversion mode was predicted at 595 cm$^{-1}$ but, similarly to the case of aniline, was unobserved. Although we could not distinguish absorption lines of the NH-stretching modes of *para* - and *ortho*-H$^+$C$_6$H$_5$NH$_2$ by simple comparison with calculations, we could clearly distinguish these two isomers from the spectral pattern in region 500–1700 cm$^{-1}$ and associate them with lines in the NH-stretching region. Our observation of wavenumbers of lines in group B$^+$ at 3479.3 and 3392.1 cm$^{-1}$ in the NH-stretching region, slightly red-shifted from those in group A$^+$, is consistent with quantum-chemical calculations that predict the wavenumbers of NH-stretching modes of *ortho*-H$^+$C$_6$H$_5$NH$_2$ to be slightly smaller than those of *para*-H$^+$C$_6$H$_5$NH$_2$. A weak line observed at 3372.2 cm$^{-1}$ appears to be correlated with other lines in group B$^+$, but no corresponding line was predicted in anharmonic vibrational calculations. We hence tentatively assign this line to originate from an anharmonic resonance (e.g., Fermi resonance). Based on these comparisons, we assign 13 lines in group B$^+$ to *ortho*-H$^+$C$_6$H$_5$NH$_2$. The observed and predicted wavenumbers and relative intensities for *ortho*-H$^+$C$_6$H$_5$NH$_2$ are summarized in Table 3. The average absolute deviation of $9.0 \pm 7.0 \text{ cm}^{-1}$ for *ortho*-H$^+$C$_6$H$_5$NH$_2$ indicates a satisfactory agreement between experimental and scaled harmonic wavenumbers.

5B. Assignment of Lines in Group C$^+$ to *amino*-H$^+$C$_6$H$_5$NH$_2$. For lines in group C$^+$, three intense lines in the NH-stretching region at 3303.3, 3278.8, and 3234.2 cm$^{-1}$ correlate well
with those predicted for *amino*-H\(^+\)C\(_6\)H\(_5\)NH\(_2\) at 3326, 3311, and 3255 cm\(^{-1}\). In addition to these lines, we identified two lines at 1470.0 and 737.7 cm\(^{-1}\) to belong to group C\(^+\). These lines agree, in terms of positions and relative intensities, with two intense lines at 1470 and 744 cm\(^{-1}\) predicted for *amino*-H\(^+\)C\(_6\)H\(_5\)NH\(_2\). Although additional intense lines were predicted at 1638 (\(\nu_8\)) and 1603 (\(\nu_9\)) cm\(^{-1}\) for the NH\(_2\)-scissoring modes, respectively, the corresponding lines were not identified because of severe interference from the parent. We assign these five lines in group C\(^+\) to *amino*-H\(^+\)C\(_6\)H\(_5\)NH\(_2\). The observed and predicted wavenumbers and relative intensities for *ortho*-H\(^+\)C\(_6\)H\(_5\)NH\(_2\) are summarized in Table 4. The average absolute deviation is 18.0 ± 13.0 cm\(^{-1}\) for the scaled harmonic wavenumbers. This deviation is slightly greater than those of the other two isomers, presumably because the appropriate scaling factors for the NH-stretching modes might differ slightly for the NH\(_3\) group of *amino*-H\(^+\)C\(_6\)H\(_5\)NH\(_2\) from those for the NH\(_2\) groups of *para-* and *ortho*-H\(^+\)C\(_6\)H\(_5\)NH\(_2\). The ultraviolet and visible spectra of various isomers of H\(^+\)C\(_6\)H\(_3\)NH\(_2\) predicted with time-dependent density functional theory (TD-DFT) support our assignment: see SI text, Figure S-3 and Table S-7.

5C. Comparison with IRPD Spectrum. The IRPD spectra of H\(^+\)C\(_6\)H\(_5\)NH\(_2\) tagged with Ar or N\(_2\) were reported by Pasker et al.;\(^{20}\) they measured IRPD spectra in the NH-stretching region for several tagged species and provided spectral assignments with the aid of theoretical calculations. The reported IRPD spectrum of Ar-tagged H\(^+\)C\(_6\)H\(_5\)NH\(_2\) is compared with our IR absorption spectrum of H\(^+\)C\(_6\)H\(_5\)NH\(_2\) isolated in solid \(p\)-H\(_2\) and the predicted IR spectrum in Figure 8. The IRPD bands of Ar-H\(^+\)C\(_6\)H\(_5\)NH\(_2\) (trace a) were reported at 3491, 3402, 3324, 3294, 3242, and 3175 cm\(^{-1}\). The first two bands were assigned to NH-stretching modes of *para-* and/or *ortho*-H\(^+\)C\(_6\)H\(_5\)NH\(_2\). Because of the expected similar absorption wavenumbers of *para-* and *ortho*-H\(^+\)C\(_6\)H\(_5\)NH\(_2\) for their NH-stretching modes and the broad bandwidth of IRPD spectra, those authors were unable to distinguish absorption bands of *para-* and *ortho*-H\(^+\)C\(_6\)H\(_5\)NH\(_2\). In
this work, we successfully resolved the NH-stretching absorption lines at 3482.7 (3479.3) and 3395.5 (3392.1) cm\(^{-1}\) of \textit{para-} (\textit{ortho-})\(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2\), as shown in Figure 7(b); numbers in parentheses pertain to the \textit{ortho}-isomer. Our observations agree satisfactorily with quantum-chemical predictions, as discussed in Sec. 5A and shown in Figure 7(c).

The three IRPD bands at 3324, 3294, and 3242 cm\(^{-1}\) were assigned to \textit{amino-}\(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2\); the most intense band at 3294 cm\(^{-1}\) band was assigned to be contributed from \textit{para-}, \textit{ortho-}, and \textit{amino-}\(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2\) isomers, as indicated in Figure 7(a). We observed lines at 3303.3, 3278.8, and 3234.2 cm\(^{-1}\) attributable to \textit{amino-}\(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2\), consistent with the IRPD bands at 3324, 3294, and 3242 cm\(^{-1}\) and quantum-chemical predictions at 3336, 3311, and 3255 cm\(^{-1}\). A weak line at 3175 cm\(^{-1}\) in the IRPD spectrum was assigned to the first overtone of NH\(_2\)-scissoring mode \(2\nu_8\) of \textit{amino-}\(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2\), but the corresponding line was unobserved in solid \(p\)-H\(_2\), likely because of its small intensity. The most intense band at 3294 cm\(^{-1}\) in the IRPD spectrum is resolved to two lines in our spectrum; according to the behavior on secondary photolysis, the line at 3278.8 cm\(^{-1}\) is associated with \textit{amino-}\(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2\), but that at 3289.0 cm\(^{-1}\) is associated with \textit{para-}\(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2\). As discussed above, the latter line might be due to the first overtone of the NH\(_2\)-scissoring mode \(2\nu_5\), which is predicted at 3307 cm\(^{-1}\) according to the anharmonic vibrational calculations. We observed an additional line at 3372.2 cm\(^{-1}\) to be associated with \textit{ortho-}\(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2\). This line was not reported in the IRPD spectrum and might originate from anharmonic resonance, which is affected significantly by the environment (i.e., solid \(p\)-H\(_2\) vs Ar-tagging).

The wavenumbers of lines in the NH-stretching region observed in solid \(p\)-H\(_2\) are slightly red-shifted from those observed in the IRPD spectrum. This trend is thought to be due to partial proton sharing between \(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2\) and ligands (or matrix). The proton affinities of aniline, Ar and H\(_2\) are 877, 371, and 422 kJ mol\(^{-1}\), respectively\(^{54}\), so the proton-sharing is slightly more enhanced for \(p\)-H\(_2\) than for Ar as a single ligand. The red shift was slightly larger for \textit{amino-}
H+\textsubscript{C}_6\textsubscript{H}_3\textsubscript{NH}_2 (~20 \text{ cm}^{-1}) compared with that for \textit{para}-H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2 (<10 \text{ cm}^{-1}). To consider the difference, we calculated the stabilization energy of forming a 1:1 complex between ligand (H\textsubscript{2} or Ar) and H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2 with the B3LYP/cc-pVTZ method. For \textit{para}-H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2, complexation of ligand at either the \textit{para}-position or the NH\textsubscript{2} group decrease little the total energy. In contrast, for \textit{amino}-H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2, complexation of H\textsubscript{2} with the NH\textsubscript{3} group decreases the total energy by 8.4 kJ mol\textsuperscript{-1}, and that of Ar decreases the total energy by 6.4 kJ mol\textsuperscript{-1}, where the energies are uncorrected for the ZPVE and basis set superposition error. These results indicate that a partial proton sharing between H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2 and ligand is more effective in \textit{amino}-H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2 and that the complexation with \textit{p}-H\textsubscript{2} induces a larger red shift, consistent with experimental observations.

5D. Mechanism of Formation. In this section, we discuss the mechanism of formation of H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2 isomers, including proton transfer from H\textsubscript{3}\textsuperscript{+} to \textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2 and possible subsequent rearrangements through tunneling. The mechanism to form H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2 is expected to be similar to those for the formation of protonated pyridine isomers\textsuperscript{32, 36} and polycyclic aromatic hydrocarbons.\textsuperscript{29-31, 34-35, 55} During \textit{p}-H\textsubscript{2} matrix deposition, H\textsubscript{2} molecules are ionized with electrons to produce H\textsubscript{2}\textsuperscript{+}; a subsequent rapid and exothermic proton transfer to a nearby H\textsubscript{2} molecule produces H and H\textsubscript{3}\textsuperscript{+}. Because the proton affinity of aniline is much greater than that of H\textsubscript{2}, a proton transfer from H\textsubscript{3}\textsuperscript{+} to aniline occurs readily to produce H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2: H\textsubscript{3}\textsuperscript{+} + \textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2 \rightarrow H_2 + H^+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2. Although spectral evidence for the formation of H\textsubscript{3}\textsuperscript{+} has yet to be established, the observation of protonated species supports its formation in electron-bombarded \textit{p}-H\textsubscript{2} matrices.

Because the exothermicity of proton transfer reactions (>300 kJ mol\textsuperscript{-1}) is significantly greater than the energy barriers separating H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2 isomers (Figure 3), any isomers can be produced with the proton-transfer reaction except \textit{ipso}-H+\textsubscript{C}_6\textsubscript{H}_5\textsubscript{NH}_2 that might spontaneously
isomerize to ortho-\(\text{CH}_3\text{H}_3\text{NH}_2\). An absence of meta-\(\text{CH}_3\text{H}_3\text{NH}_2\) in solid \(p\text{-H}_2\) might be due to tunneling isomerization to para-\(\text{CH}_3\text{H}_3\text{NH}_2\), of which the barrier height is 23 kJ mol\(^{-1}\). The other isomers, para-, ortho-, and amino-\(\text{CH}_3\text{H}_3\text{NH}_2\), are separated from others by sufficiently large (> 100 kJ mol\(^{-1}\)) barriers; these isomers are hence stable at low temperatures once stabilized in a solid \(p\text{-H}_2\) environment.

In contrast with the IRPD method, with which determining the relative abundance of protonated isomers is difficult because several parameters affect the signal intensity, IR absorption spectra in solid \(p\text{-H}_2\) allow us to estimate the mixing ratios of various isomers according to the method developed by Tam and Fajardo\(^{37}\) (introduced in Sec. 2). Using the integrated intensities of four intense lines in each group and the IR intensities predicted with the B3LYP/cc-pVTZ method, we determined the mixing ratios after matrix deposition to be 1.0 ± 0.1, 0.6 ± 0.1, and 1.0 ± 0.6 ppm for para-, ortho-, and amino-\(\text{CH}_3\text{H}_3\text{NH}_2\), respectively; the errors correspond to the standard deviations among mixing ratios estimated from each line. Assuming that the errors in IR intensities of all isomers of \(\text{CH}_3\text{H}_3\text{NH}_2\) predicted with the B3LYP/cc-pVTZ method are similar, we conclude that the two most stable isomers, para- and amino-\(\text{CH}_3\text{H}_3\text{NH}_2\), were produced in a similar proportion and greater than that of ortho-\(\text{CH}_3\text{H}_3\text{NH}_2\), consistent with the expected density of states at the energy of formation. However, more theoretical and experimental investigations are necessary to confirm the model of branching.

6. CONCLUSION

Three isomers of protonated aniline, para-, ortho-, and amino-\(\text{CH}_3\text{H}_3\text{NH}_2\), were produced in an electron-bombarded aniline/\(p\text{-H}_2\) matrix and characterized with IR spectroscopy. The IR lines of which the intensity decreased during maintenance of the electron-bombarded matrix in darkness were classified into three groups (\(A^+\), \(B^+\), and \(C^+\)) according to their behaviors upon
secondary irradiation at 375 and 254 nm. The spectral assignments were made on comparison with the scaled harmonic vibrational wavenumbers and IR intensities predicted with the B3LYP/cc-pVTZ method. Twelve lines in group A⁺, of which the intensity decreased slightly upon irradiation at 375 nm and significantly at 254 nm, were assigned to the most stable para-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \). Thirteen lines in group B⁺, of which the intensity decreased significantly upon irradiation at 375 nm but not at 254 nm, were assigned to ortho-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \), which is predicted to have greater energy than para-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \) by ~18 kJ mol\(^{-1} \). Five lines in group C⁺, which remained unchanged upon secondary photolysis at 375 and 254 nm, were assigned to the second stable amino-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \), lying ~8 kJ mol\(^{-1} \) above para-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \). The distinct UV-Vis spectra of various isomers of \( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \), calculated with the TD-CAM-B3LYP/cc-pVTZ method, can explain the behavior of these three isomers upon secondary photolysis. These IR spectra are consistent with the IRPD spectra in the NH-stretching region,\(^{20} \) but lines of para- and ortho-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \) in this region were clearly resolved in this work. The spectra in region 500–1700 cm\(^{-1} \) are new; they provide definitive identification of para- and ortho-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \). This identification was enabled through the sufficient spectral resolution and wide spectral coverage available in our method. Through the grouping with lines in the fingerprint region, lines of para- and ortho-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \) in the NH-stretching region are unambiguously assigned.

The mixing ratios of para-, ortho-, and amino-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \) after matrix deposition were determined to be 1.0 ± 0.1, 0.6 ± 0.1, and 1.0 ± 0.6 ppm, respectively. The observed branching ratios are consistent with the expectation that the more stable isomer has a greater density of states at the energy upon proton transfer.

ASSOCIATED CONTENT

Supporting Information. Full lists of vibrational wavenumbers and IR intensities of para-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \) (Table S-1), ortho-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \) (Table S-2), amino-\( \text{H}^+\text{C}_6\text{H}_5\text{NH}_2 \) (Table S-3),
meta-\text{H}^\text{+} \text{C}_6\text{H}_5\text{NH}_2 \text{ (Table S-4), } \text{ipso-} \text{H}^\text{+} \text{C}_6\text{H}_5\text{NH}_2 \text{ (Table S-5), and } \text{C}_6\text{H}_5\text{NH}_2 \text{ (Table S-6). List of vertical excitation energies and oscillator strengths predicted for isomers of H}^\text{+} \text{C}_6\text{H}_5\text{NH}_2 \text{ (Table S-7). Calibration curves for observed and calculated harmonic vibrational wavenumbers of C}_6\text{H}_5\text{NH}_2. \text{ (Figure S-1). Infrared spectra of an electron-bombarded C}_6\text{H}_5\text{NH}_2/p-\text{H}_2 \text{ matrix. (Figure S-2).}

AUTHOR INFORMATION

Corresponding Authors

* E-mail (MT): tsuge@lowtem.hokudai.ac.jp.

* E-mail (YPL): yplee@nctu.edu.tw.

Notes

The authors declare no competing financial interest.

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REFERENCES


Table 1. Relative Energies (in kJ mol\(^{-1}\)) of Isomers of Protonated Aniline and Transition States (TSs) for Isomerization Calculated with the B3LYP Method.

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<th>literature(^b)</th>
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<td>6-311G(2df,2pd)(^d)</td>
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\(^a\)See Figure 1 for protonation sites. \(^b\)The values in parentheses are from Ref. 20: calculated with the B3LYP/6-311G(2df,2pd) method and corrected for ZPVE. \(^c\)Energy changes in reactions C\(_6\)H\(_5\)NH\(_2\) + H\(^+\) → H\(^+\)C\(_6\)H\(_5\)NH\(_2\) + H\(_2\) calculated with the B3LYP/cc-pVTZ method. \(^d\)Basis set.
**Table 2.** Comparison of Experimental Vibrational Wavenumbers (cm$^{-1}$) and Relative IR Intensities of $para$-$H^+C_6H_5NH_2$ (Lines in group A$^+$) with Corresponding Values Predicted with the B3LYP/cc-pVTZ Method.$^a$

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<th>IRPD$^c$</th>
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</tr>
<tr>
<td>$v_{25}$ ($b_1$)</td>
<td>823 (6)</td>
<td>816.7 (12)</td>
<td></td>
</tr>
<tr>
<td>$v_{25}$ ($b_1$)</td>
<td>563 (20)</td>
<td>561.3 (12)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Table S-1 presents a list of all vibrational modes. $^b$Scaled harmonic vibrational wavenumbers; see text. $^c$Ar-tagged $para$- (and/or $ortho$-) $H^+C_6H_5NH_2$, from Ref. 20. $^d$The predicted IR intensities shown in parentheses are normalized to the intensity of the most intense line ($v_5$), 432 km mol$^{-1}$. $^e$Integrated IR intensities as a percentage of the most intense line at 1669.2 cm$^{-1}$ ($v_5$) are shown in parentheses. $^f$Wavenumber and IR intensity calculated with the anharmonic VPT2 calculation. $^g$Assignments are tentative.
Table 3. Comparison of Experimental Vibrational Wavenumbers (cm\(^{-1}\)) and Relative IR Intensities of ortho-H\(^{+}\)C\(_6\)H\(_5\)NH\(_2\) (lines in group B\(^{+}\)) with Corresponding Values Predicted with the B3LYP/cc-pVTZ Method.\(^a\)

<table>
<thead>
<tr>
<th>mode (sym.)</th>
<th>calculated(^b)</th>
<th>p-H(_2)</th>
<th>IRPD(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1) ((a'))</td>
<td>3508 (28)(^d)</td>
<td>3479.3 (120)(^e)</td>
<td>3491</td>
</tr>
<tr>
<td>(v_2) ((a'))</td>
<td>3406 (77)</td>
<td>3392.1 (81)</td>
<td>3402</td>
</tr>
<tr>
<td>(v_8) ((a'))</td>
<td>1660 (89)</td>
<td>1667.0 (72)</td>
<td></td>
</tr>
<tr>
<td>(v_{10}) ((a'))</td>
<td>1536 (13)</td>
<td>1541.9 (19)</td>
<td></td>
</tr>
<tr>
<td>(v_{11}) ((a'))</td>
<td>1506 (100)</td>
<td>1515.7 (100)</td>
<td></td>
</tr>
<tr>
<td>(v_{12}) ((a'))</td>
<td>1440 (9)</td>
<td>1452.0 (24)</td>
<td></td>
</tr>
<tr>
<td>(v_{13}) ((a'))</td>
<td>1415 (16)</td>
<td>1419.3 (15)</td>
<td></td>
</tr>
<tr>
<td>(v_{15}) ((a'))</td>
<td>1347 (12)</td>
<td>1341.6 (25)</td>
<td></td>
</tr>
<tr>
<td>(v_{17}) ((a'))</td>
<td>1189 (12)</td>
<td>1188.1 (19)</td>
<td></td>
</tr>
<tr>
<td>(v_{21}) ((a'))</td>
<td>964 (12)</td>
<td>966.2 (9)</td>
<td></td>
</tr>
<tr>
<td>(v_{23}) ((a'))</td>
<td>774 (2)</td>
<td>786.1 (11)</td>
<td></td>
</tr>
<tr>
<td>(v_{34}) ((a''))</td>
<td>743 (16)</td>
<td>736.1 (65)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Table S-2 presents a list of all vibrational modes. \(^b\)Scaled harmonic vibrational wavenumbers; see text. \(^c\)Ar-tagged para- (and/or ortho-)H\(^{+}\)C\(_6\)H\(_5\)NH\(_2\), from Ref. 20. \(^d\)The predicted IR intensities shown in parentheses are normalized to the most intense line (\(v_{11}\)), 260 km mol\(^{-1}\). \(^e\)Integrated IR intensities as a percentage of the intense line at 1515.7 cm\(^{-1}\) (\(v_{11}\)) are shown in parentheses. \(^f\)This observed line might be due to anharmonic resonance, because the anharmonic VPT2 calculation predicts no line nearby.
Table 4. Comparison of Experimental Vibrational Wavenumbers (cm$^{-1}$) and Relative IR Intensities of amino-H'C$_6$H$_5$NH$_2$ (lines in group C+) with Corresponding Values Predicted with the B3LYP/cc-pVTZ Method.$^a$

<table>
<thead>
<tr>
<th>mode (sym.)</th>
<th>calculated$^b$</th>
<th>$p$-H$_2$</th>
<th>IRPD$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1 (a')$</td>
<td>3336 (71)$^d$</td>
<td>3303.3 (75)$^e$</td>
<td>3324</td>
</tr>
<tr>
<td>$v_{27} (a'')$</td>
<td>3311 (91)</td>
<td>3278.8 (90)</td>
<td>3294</td>
</tr>
<tr>
<td>$v_2 (a')$</td>
<td>3255 (48)</td>
<td>3234.2 (40)</td>
<td>3242</td>
</tr>
<tr>
<td>$v_{13} (a')$</td>
<td>1470 (100)</td>
<td>1470.0 (100)</td>
<td></td>
</tr>
<tr>
<td>$v_{34} (a'')$</td>
<td>744 (49)</td>
<td>737.7 (50)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Table S-3 presents a list of all vibrational modes. $^b$Scaled harmonic vibrational wavenumbers; see text. $^c$Ar-tagged amino-H'C$_6$H$_5$NH$_2$, from Ref. 20. $^d$The predicted IR intensities shown in parentheses are normalized to the intensity of the most intense line ($v_{13}$), 116 km mol$^{-1}$. $^e$Integrated IR intensities as a percentage of the most intense line at 1470.0 cm$^{-1}$ ($v_{13}$) are shown in parentheses.
Figure 1. Five distinct protonation sites in aniline (C₆H₅NH₂).

(single column)
Figure 2. Geometries of (a) C₆H₅NH₂, (b) para-H⁺C₆H₅NH₂, (c) amino-H⁺C₆H₅NH₂, (d) ortho-H⁺C₆H₅NH₂, (e) meta-H⁺C₆H₅NH₂, and (f) ipso-H⁺C₆H₅NH₂ optimized with the B3LYP/cc-pVTZ method. The bottom figure in (f) is tilted so that the ipso-position is visible. For H⁺C₆H₅NH₂ isomers, the ZPVE-corrected relative energies are shown in parentheses. Bond lengths are in Å.

(single column)
Figure 3. Calculated relative energies of isomers of protonated aniline (para-, meta-, ortho-, ipso-, and amino-\(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2\)) and transition states (TS) connecting them. Calculations were performed with the B3LYP/cc-pVTZ method; zero-point vibrational energies were corrected with unscaled harmonic vibrational energies. The energy level of \(\text{H}^+\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\) are relative to the most stable "para-H\(^+\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\)" pair.
Figure 4. Comparison of experimental and predicted IR spectra of C₆H₅NH₂. (a) Experimental absorption spectrum in solid p-H₂; red dots indicate the lines assigned to C₆H₅NH₂. (b) Simulated stick spectrum of C₆H₅NH₂ according to scaled harmonic vibrational wavenumbers and IR intensities predicted with the B3LYP/cc-pVTZ method. The line marked with * is due to the NH₂ wagging (inversion) mode, which cannot be predicted properly with the harmonic vibrational analysis; see text. The observed and predicted wavenumbers and IR intensities are listed in Table S-6.
Figure 5. Representative infrared spectra of an electron-bombarded C₆H₅NH₂/p-H₂ matrix in spectral regions 3550–3200 and 1560–1150 cm⁻¹. (a) IR spectrum of C₆H₅NH₂. (b) IR spectrum of an electron-bombarded C₆H₅NH₂/p-H₂ matrix recorded after matrix deposition for 10 h; the lines of C₆H₅NH₂ are stripped according to (a). (c) Difference spectrum of the matrix after maintenance in darkness for 19 h. (d) Difference spectrum after secondary photolysis at 375 nm for 10 min. (e) Difference spectrum after further secondary photolysis at 254 nm for 30 min. In the difference spectra, lines pointing upward indicate generation and those pointing downward indicate destruction. The lines in groups A⁺, B⁺, and C⁺ are indicated with red circles, green squares, and blue diamonds, respectively. The regions suffering from interference are indicated with gray rectangles.
Figure 6. Comparison of experimental and predicted IR spectra of various isomers of H⁺C₆H₅NH₂. (a) Difference spectrum after secondary photolysis at 254 nm for 30 min; inverted Figure 5(e). The lines in group A⁺ are indicated with red circles. (b) Predicted IR spectrum of para-H⁺C₆H₅NH₂. (c) Difference spectrum after secondary photolysis at 375 nm for 10 min; inverted Figure 5(d). The lines in group B⁺ are indicated with green squares. (d) Predicted IR spectrum of ortho-H⁺C₆H₅NH₂. (e) Difference spectrum after maintaining the matrix in darkness for 19 h; inverted Figure 5(b). The lines in group C⁺ are indicated with blue diamonds. (f) Predicted infrared spectrum of amino-H⁺C₆H₅NH₂. (g) Predicted IR spectrum of meta-H⁺C₆H₅NH₂. (g) Predicted IR spectrum of ipso-H⁺C₆H₅NH₂. Predicted spectra were simulated according to scaled harmonic vibrational wavenumbers and IR intensities calculated with the B3LYP/cc-pVTZ method. Predicted lines marked with * are due to the NH₂-wagging (inversion) modes, which cannot be predicted properly with the harmonic vibrational analysis. (double column)
Figure 7. Comparison of IR spectra in the NH-stretching region. (a) IR photodissociation (IRPD) spectrum of Ar-tagged H’C₆H₃NH₂; taken from Ref. 20. (b) IR absorption spectrum of an electron-bombarded C₆H₃NH₂/p-H₂ matrix; taken from Figure 5(b). (c) Stick spectrum according to scaled harmonic vibrational calculations with the B3LYP/cc-pVTZ method. The lines assigned to para-, ortho-, and amino-H’C₆H₃NH₂ are indicated with p, o, and a, respectively.
Protonated Aniline in Solid para-H₂