Infrared spectra and structures of aniline$^+$–furan and aniline$^+$–phenol: Preference between π-type and σ-type hydrogen-bonded structures

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Abstract

Infrared photodissociation spectra of aniline$^+$–M (M = thiophene, furan and phenol) are measured in the 2700–3700 cm^{-1} region and analyzed by density functional theory calculations. Only a structure with a π-type hydrogen bond is found for aniline$^+$–thiophene. Two structural isomers are identified for aniline$^+$–furan and aniline$^+$–phenol, which have either a π-type or a σ-type hydrogen bond, where an amino proton of aniline$^+$ interacts with the π-electrons or the oxygen atom of the neutral molecules, respectively. The isomer with a σ-type hydrogen bond is more stable for aniline$^+$–phenol, while less stable for aniline$^+$–furan.

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1. Introduction

Ion–molecule interactions play an important role in a diverse range of chemical and biochemical systems [1]. In particular, the interaction between a charged aromatic amine and a neutral molecule is relevant for biophysical processes where ionic amines interact with a hydrophobic environment [2]. For investigating ion–molecule interactions from a microscopic point of view, gas-phase complex ions have served as model systems. Complexes of the aniline ion with neutral molecules have been studied by infrared (IR) spectroscopy and theoretical calculations. These studies have revealed the formation of a σ-type hydrogen bond between aniline$^+$ and neutral molecules such as water [3–6], alcohols [5,7] and amines [7,8]. On the other hand, a π-type hydrogen bond is formed between aniline$^+$ and neutral molecules with π-electron systems [9–14].

Aromatic molecules containing an oxygen atom, such as furan and phenol, provide several proton-accepting sites. Nakanaga and Ito reported the results of IR spectroscopy and ab initio calculations of aniline$^+$–furan [11]. From calculations at the UHF/6-31G** level, they obtained two structures in which an NH bond of aniline$^+$ interacts with either the π-electrons (NH–π-type) or the oxygen atom (NH–O-type) of furan. They assigned a broad band observed at 3315 cm^{-1} in the IR spectrum to the hydrogen-bonded NH oscillator of the NH–π-type structure. However, the assignment needs to be re-examined as in the case of aniline$^+$–benzene. Nakanaga and co-workers assigned the 3280 cm^{-1} band of aniline$^+$–benzene to the hydrogen-bonded NH oscillator [9], but we have revised the assignment to an overtone transition [12]. Such a revision may be necessary for the assignment of the 3315 cm^{-1} band of aniline$^+$–furan, because a similar overtone band appears around 3300 cm^{-1} in the spectra of other complex ions containing aniline$^+$ [12,14–17]. In addition, the previous measurement was not undertaken at frequencies below 3250 cm^{-1} [11], where we expect the transition of the NH oscillator interacting with the oxygen atom. Thus, the presence of the NH–O-type isomer of aniline$^+$–furan has yet to be ascertained experimentally.

In this work, we investigate hydrogen-bonding interactions in aniline$^+$–thiophene, aniline$^+$–furan and aniline$^+$–phenol by measuring the IR photodissociation spectra. For aniline$^+$–furan, we extend the measurement to the frequency region below the lower limit of the previous work [11]. The spectra of aniline$^+$–thiophene and aniline$^+$–phenol are reported for the first time. The oxygen atom in furan is replaced by a sulfur atom in thiophene. Since sulfur atoms are not involved in hydrogen bonds, only an NH–π-type hydrogen bond is possibly formed between aniline$^+$ and thiophene. Thus, the spectrum of aniline$^+$–thiophene serves as a reference for assigning the spectrum of aniline$^+$–furan. Theoretical calculations are also performed to obtain minimum-energy structures and corresponding IR spectra of aniline$^+$–furan and aniline$^+$–phenol. The comparison of the experimental and theoretical results provides information about the preferential formation of a π-type or a σ-type hydrogen bond in these complex ions.

2. Experimental and Computational

IR spectra of aniline$^+$–thiophene, aniline$^+$–furan and aniline$^+$–phenol are measured by using a photodissociation spectrometer with two quadrupole mass filters and a quadrupole ion guide [18]. The complex ions are produced in an ion source of electron-impact type. The parent ions are isolated by the first quadrupole mass filter. After deflection by an ion bender, the ions are introduced into the ion guide and irradiated by an IR laser (Continuum, Mirage 3000). The IR photoexcitation induces vibrational predissociation of the parent ions. After leaving the ion guide, the resulting fragment ions are analyzed by the second quadrupole mass filter and detected by a secondary electron multiplier. The photodissociation spectra are obtained from the yields of the fragment ions as a function of wavenumber of the IR laser.

Density functional theory (DFT) calculations are carried out with GAUSSIAN 98 program package [19]. The geometries of the ions are optimized and the vibrational frequencies along with the IR absorption intensities are evaluated at the B3LYP/cc-pVDZ level of theory. The calculations at this level have been successful in predicting the IR spectra of aniline complex ions [5–7,13].

3. Results and discussion

3.1. Charge distribution

In complex ions composed of aniline and aromatic molecules, charge resonance (CR) interaction may be possible between the π-electron systems [20]. However, we have shown that the CR interaction is absent in aniline$^+$–benzene and that the positive charge is localized on the aniline molecule with lower ionization energy (IE) [12]. Similarly, the charge is expected to be carried by the aniline moiety in the complex ions studied here, because the IE values of aniline, thiophene, furan and phenol are 7.7206 [21], 8.85 [22], 8.9 [23] and 8.5088 [24] eV, respectively. As a result, the vibrational predissociation processes of these complex ions predominantly yield aniline$^+$ as the fragment ion.

3.2. Vibrational spectra

Fig. 1 exhibits the IR photodissociation spectra of (a) aniline$^+$–benzene, (b) aniline$^+$–thiophene, (c) aniline$^+$–furan, (d) aniline$^+$–phenol and (e) (aniline)$_2^+$. All the spectra are obtained from the yields of aniline$^+$. The spectra of aniline$^+$–benzene and (aniline)$_2^+$ have been already published [12]. A brief review of the previous studies is helpful in assigning the spectra obtained in this work. The structure of aniline$^+$–benzene involves an NH–π-type hydrogen bond between an amino proton of aniline$^+$ and the π-electrons of benzene. The 3200 and 3440 cm^{-1} bands of the spectrum (Fig. 1a) are attributed to the stretching vibrations of the hydrogen-bonded and free NH oscillators (abbreviated as ν_b and ν_f hereafter), respectively. The 3280 cm^{-1} band is assigned to the first overtone of the NH$_2$-bending vibration [16,17]. Two isomers are suggested for (aniline)$_2^+$, which have either an NH–π-type or an NH–N-type hydrogen bond, where an amino proton of one molecule interacts with the π-electrons or the nitrogen atom of the other, respectively. The broad feature in the 2800–3500 cm^{-1} region (shaded area in Fig. 1e) is due to the ν_b band of the NH–N-type isomer. The ν_f mode of this isomer mainly contributes to the intensity of the 3415 cm^{-1} band. A small portion of the 3415 cm^{-1} band and the transitions at 3180 and 3270 cm^{-1} are ascribed to the NH–π-type isomer.

Three distinct bands are observed at 3195, 3290 and 3445 cm^{-1} in the spectrum of aniline$^+$–thiophene (Fig. 1b). The spectrum of aniline$^+$–furan shows three maxima at 3205, 3310 and 3445 cm^{-1} and a shoulder around 3120 cm^{-1} (Fig. 1c). The spectral features in the 3000–3400 cm^{-1} region can be decomposed into three components (dotted curves). The positions of the 3310 and 3445 cm^{-1} bands are in agreement with those reported by Nakanaga and Ito [11], while the 3120 and 3205 cm^{-1} components were not observed previously. There are four prominent bands at 3200, 3295, 3440 and 3635 cm^{-1} with a reproducible feature peaked at 3345 cm^{-1} in the spectrum of aniline$^+$–phenol (Fig. 1d). In addition, a broad feature extends from 2900 to 3400 cm^{-1} (shaded area).

3.3. Aniline$^+$–thiophene

The spectrum of aniline$^+$–thiophene (Fig. 1b) bears a resemblance to that of aniline$^+$–benzene (Fig. 1a), suggesting a similarity of the structure and intermolecular interaction between the two complexes; aniline$^+$–thiophene probably has an NH–π-type structure with a hydrogen bond between an amino proton of aniline$^+$ and the π-electrons of thiophene. The 3195 and 3445 cm^{-1} bands are assigned to the ν_b and ν_f modes of aniline$^+$, respectively. The 3290 cm^{-1} band is attributed to the overtone transition of the NH_2-bending vibration, like the 3280 cm^{-1} band of aniline$^+$–benzene. Weak absorption around 3100 cm^{-1} is assignable to CH stretching vibrations. The spectrum gives no indication of absorption due to structural isomers. Preliminary calculations confirm that there are no stable structures involving an NH–S-type hydrogen bond. Thus, the spectrum of the NH–π-type structure of aniline$^+$–thiophene serves as a reference for identifying structural isomers of aniline$^+$–furan.

3.4. Aniline$^+$–furan

Nakanaga and Ito investigated aniline$^+$–furan by the IR spectroscopy and ab initio calculations [11]. Two absorption bands were observed at 3315 and 3446 cm^{-1} in the IR spectrum and assigned to the NH-stretching vibrations of aniline$^+$. The frequency shifts of these bands from the corresponding transitions of the bare aniline$^+$ are 81 and 42 cm^{-1}, respectively. They obtained two isomeric structures from calculations at the UHF/6-31G** level. One structure involves an NH–π-type hydrogen bond and the other an NH–O-type hydrogen bond. The shifts of the NH-stretching transitions were estimated to be 75.8 and 33.7 cm^{-1} for the NH–π-type structure, while 157.9 and 44.3 cm^{-1} for the NH–O-type structure. Since the estimated values for the NH–π-type structure were close to the observed ones, they suggested the NH–π-type structure for aniline$^+$–furan.

Figs. 1a–c clearly demonstrate that the 3205, 3310 and 3445 cm^{-1} bands of aniline$^+$–furan correspond to the 3195 (3200), 3290 (3280) and 3445 (3440) cm^{-1} bands of aniline$^+$–thiophene (aniline$^+$–benzene), which are ascribed to the NH–π-type hydrogen-bonded structure. Then, we assign the 3205 cm^{-1} component, instead of the 3310 cm^{-1} band as proposed by Nakanaga and Ito [11], to the ν_b band of the NH–π-type structure. The 3310 cm^{-1} band probably originates from the overtone transition of the NH$_2$-bending vibration. On the other hand, the 3120 cm^{-1} component has no corresponding features in the spectra of aniline$^+$–benzene and aniline$^+$–thiophene, although weak absorption assignable to CH stretching vibrations is seen around 3100 cm^{-1} in the spectra of these two complexes.

Figs. 2b and c represent the minimum-energy structures and the corresponding IR spectra of aniline$^+$–furan calculated at the B3LYP/cc-pVDZ level. We obtain an NH–π-type structure (Fig. 2b) and an NH–O-type (Fig. 2c) structure, as in the case of the previous calculations at the UHF/6-31G** level [11]. For the NH–π-type structure, the ν_b and ν_f transitions are located at 3220 and 3448 cm^{-1}, respectively. The shift of the ν_b transition upon complex formation (176 cm^{-1}) is at variance with the previous result (75.8 cm^{-1}) [11]. This transition is responsible for the 3205 cm^{-1} component in the experimental spectrum (Fig. 2a), as anticipated from the analogy with aniline$^+$–thiophene. On the other hand, the ν_b transition of the NH–O-type structure is predicted at 3103 cm^{-1} (Fig. 2c). The existence of the NH–O-type isomer needs to be invoked, because the 3120 cm^{-1} component is too strong to be attributed to CH stretching vibrations. The ν_f transitions of both NH–π-type and NH–O-type structures contribute to the intensity of the 3445 cm^{-1} band.

The intensity ratio of the 3205 and 3120 cm^{-1} components is approximately 1 : 0.6 in the experimental spectrum. On the other hand, the IR intensity of the ν_b mode is calculated to be 228 and 588 km mol^{-1} for the NH–π-type and NH–O-type isomer, respectively. From these quantities, we can roughly estimate the relative abundance of the NH–π-type and NH–O-type isomers as 1 : 0.2. The NH–π-type isomer is more abundant under our experimental conditions. In the electron-impact ion source of our apparatus, the complex ions are produced predominantly in their lowest-energy form [16,17]. Therefore, we conclude that the NH–π-type isomer is the most stable structure of aniline$^+$–furan.

3.5. Aniline$^+$–phenol

The minimum-energy structures and the corresponding IR spectra predicted from the DFT calculations for aniline$^+$–phenol are exhibited in Figs. 3b–d. In addition to an NH–π-type structure (Fig. 3b), two isomers with an NH–O-type hydrogen bond are obtained. The theoretical calculations estimate that the intensity of the ν_b mode of the NH–π-type isomer (747 km mol^{-1}) is nearly equal to that of the NH–O(I)-type isomer (826 km mol^{-1}) but much stronger than that of the NH–O(II)-type isomer (67 km mol^{-1}).

Figs. 1a and d show that the 3200 and 3295 cm^{-1} bands of aniline$^+$–phenol correspond to the 3200 and 3280 cm^{-1} bands of aniline$^+$–benzene. The theoretical spectrum (Fig. 3b) is consistent with the assignment of the 3200 cm^{-1} band to the ν_b mode of the NH–π-type structure. The broad feature extending from 2900 to 3400 cm^{-1} (shaded area in Fig. 3a) has a resemblance to that of (aniline)$_2^+$, which is ascribed to the NH oscillator involved in the NH–N-type hydrogen-bond [12]. Similarly, we assign the broad feature to the ν_b mode of the NH–O-type isomer(s). The integrated intensity of the broad feature is quite large, suggesting the NH–O(I)-type isomer, since the ν_b transition of this isomer is more intense than that of the NH–O(II)-type isomer. However, the coexistence of the NH–O(II)-type isomer cannot be ruled out, because both NH–O-type isomers give similar IR spectra as far as the band positions are concerned. The 3635 cm^{-1} band is assignable to the OH oscillator of the neutral phenol, as the frequency is close to that of the phenol monomer (3657 cm^{-1}) [25]. We tentatively attribute the 3345 cm^{-1} band to a combination band or a sequence transition, because it has no corresponding bands in the theoretical spectra.

In the experimental spectrum, the integrated intensity of the ν_b transition assigned to the NH–O-type isomer(s) (2900–3400 cm^{-1}) is approximately one order of magnitude larger than that of the NH–π-type isomer (3200 cm^{-1}). In a similar manner as that of aniline$^+$–furan, the relative abundance of the NH–O-type and NH–π-type isomers can roughly be estimated as ≈10 : 1 when the NH–O(I)-type structure is assumed and ≈100 : 1 when the NH–O(II)-type structure is assumed. The predominance of the NH–O-type isomer(s) is also supported by the relative intensity of the ν_b and ν_f transitions. The theoretical spectrum for the NH–π-type isomer (Fig. 3b), as well as the spectrum of aniline$^+$–benzene (Fig. 1a), shows that the ν_f band is almost one order of magnitude weaker than the ν_b band. In the experimental spectrum of aniline$^+$–phenol, however, the 3440 cm^{-1} band is as intense as the 3200 cm^{-1} band. The result can be accounted for by considering that the contribution to the intensity of the 3440 cm^{-1} band is mainly from the NH–O-type isomer(s) rather than the NH–π-type isomer. From the predominance of the NH–O-type isomer(s) under our experimental conditions, where the complex ions are produced in the electron-impact ion source, we conclude that the most stable form of aniline$^+$–phenol is the NH–O-type hydrogen-bonded structure(s).

3.6. Strength of π-type and σ-type hydrogen bonds

For aniline$^+$–phenol, the isomer with an NH–π-type hydrogen bond is less stable than the isomer(s) with an NH–O-type hydrogen bond. The result is in line with the view that π-type hydrogen bonds are generally weaker than σ-type hydrogen bonds. For aniline$^+$–furan, on the other hand, the isomer with an NH–π-type hydrogen bond turns out to be more stable than the one with an NH–O-type hydrogen bond. The stability of the former may be assisted by an interaction between a CH bond at the ortho position of aniline$^+$ and the oxygen atom of furan (see Fig. 2b). However, the CH–O interaction is considered to be negligibly weak, because the DFT calculations indicate that the CH bond scarcely lengthens upon complex formation. It seems, therefore, that the π-type hydrogen bond is apparently stronger than the σ-type hydrogen bond in aniline$^+$–furan.

The strength of hydrogen bonds is mirrored by the frequency shift of hydride-stretching modes [26]. It is not likely that the π-type hydrogen bond in aniline$^+$–furan is particularly strong compared to the one in other systems, because the ν_b frequency is similar to each other among the NH–π-type structures of aniline$^+$–benzene, aniline$^+$–furan, aniline$^+$–phenol and (aniline)$_2^+$. Therefore, we speculate that the predominance of the NH–π-type isomer results from the weakness of the NH–O-type hydrogen bond in aniline$^+$–furan. The strength of the NH–O-type hydrogen bond can be estimated from the negativity of the oxygen atom. According to Mulliken population analysis based on the DFT calculations, the charge carried by the proton-accepting oxygen atom is –0.16, –0.26, –0.28 and –0.27 for furan, water, methanol and ethanol, respectively. The value of furan is not appreciable compared to the other proton acceptors. The result suggests that the NH–O-type hydrogen bond in aniline$^+$–furan is not so strong as the one in the other complex ions. The weakness of the NH–O interaction is probably responsible for the smaller stability of the isomer with the NH–O-type hydrogen bond. However, it is not safe to state that the σ-type hydrogen bond in aniline$^+$–furan is weaker than the π-type hydrogen bond, because other types of non-local interactions also contribute to the total stability of the complex ions.

4. Conclusions

We have investigated the IR spectra and structures of aniline$^+$–furan and aniline$^+$–phenol by the photodissociation spectroscopy and DFT calculations. Two isomers are found for both complex ions, in which an amino proton of aniline$^+$ forms a hydrogen bond with different sites of the solvent molecules: one with the π-electrons of the aromatic ring and the other with the lone pair of the oxygen atom. The comparison of the experimental and theoretical IR spectra indicates that, for aniline$^+$–phenol, the isomer with a σ-type hydrogen bond is produced more abundantly in our electron-impact ion source and is hence the most stable structure. For aniline$^+$–furan, on the other hand, the isomer with a π-type hydrogen bond turns out to be the most stable form. The difference in the preference between π-type and σ-type hydrogen-bonded isomers can be explained by the anomalously weak NH–O interaction in aniline$^+$–furan. The weak NH–O interaction results in smaller stability of the isomer with the σ-type hydrogen bond. As a result, the most stable structure of aniline$^+$–furan is formed through the π-type hydrogen bond, although π-type hydrogen bonds are usually weaker than σ-type hydrogen bonds.

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Figure Captions

Fig. 1. IR photodissociation spectra of (a) aniline$^+$–benzene [12], (b) aniline$^+$–thiophene, (c) aniline$^+$–furan, (d) aniline$^+$–phenol and (e) (aniline)$_2^+$ [12]. Absorption features in the 3000–3400 cm^{-1} region of the aniline$^+$–furan spectrum are decomposed into three components represented by Lorentzian functions (dotted curves). Partially deuterated phenol (C_6D_5OH) is used to measure the aniline$^+$–phenol spectrum, because the mass-selected aniline$^+$–C_6H_5OH ions are easily contaminated by neighboring $(C_6H_5OH)_2^+$ and (aniline)$_2^+$.

Fig. 2. (a) Experimental IR spectrum of aniline$^+$–furan reproduced from Fig. 1c. Theoretical spectra obtained from DFT calculations at the B3LYP/cc-pVDZ level for (b) NH–π-type and (c) NH–O-type structures of aniline$^+$–furan. A factor of 0.960 is used to scale the theoretical spectra.

Fig. 3. (a) Experimental IR spectrum of aniline$^+$–phenol reproduced from Fig. 1d. Theoretical spectra obtained from DFT calculations at the B3LYP/cc-pVDZ level for (b) NH–π-type and (c, d) NH–O-type structures of aniline$^+$–phenol. The aromatic ring of phenol is located close to an ortho hydrogen atom of aniline$^+$ in NH–O(I)-type isomer (c), while away from it in NH–O(II)-type isomer (d). A factor of 0.967 is used to scale the theoretical spectra.

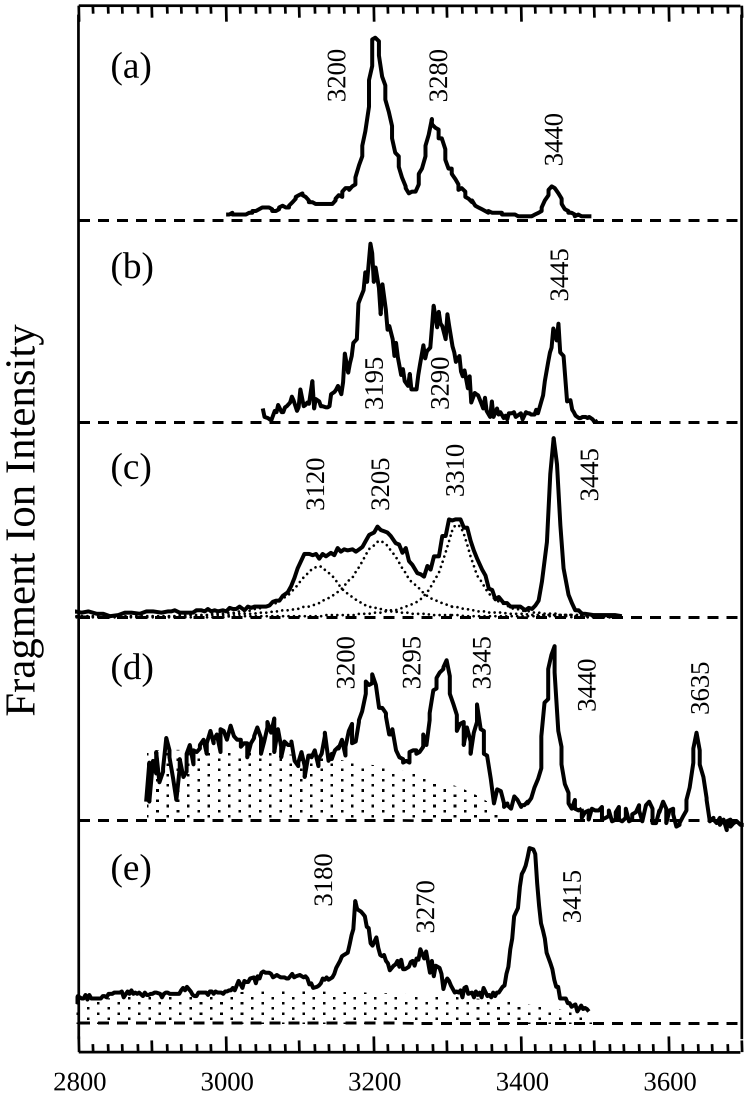

Fig. 1. Honkawa et al.

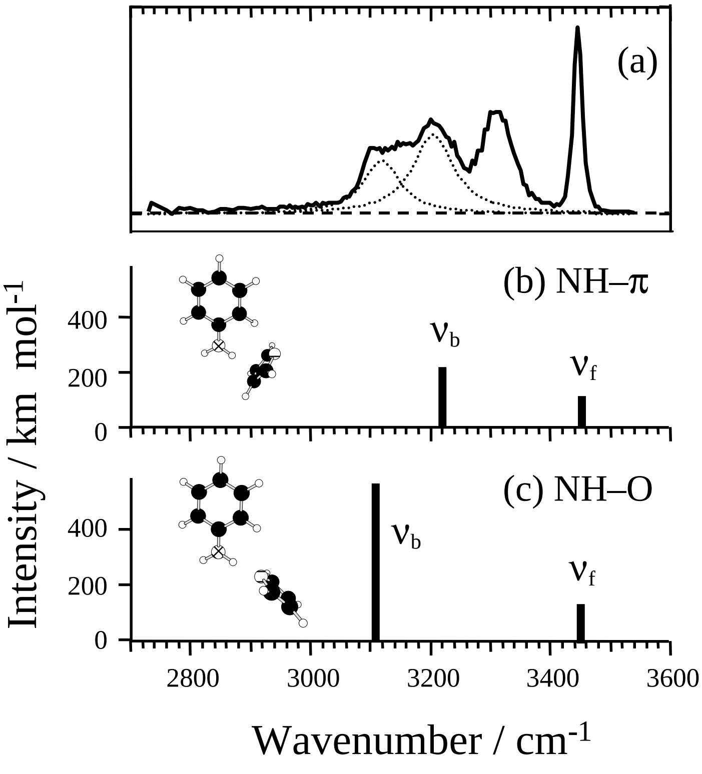

Fig. 2. Honkawa et al.

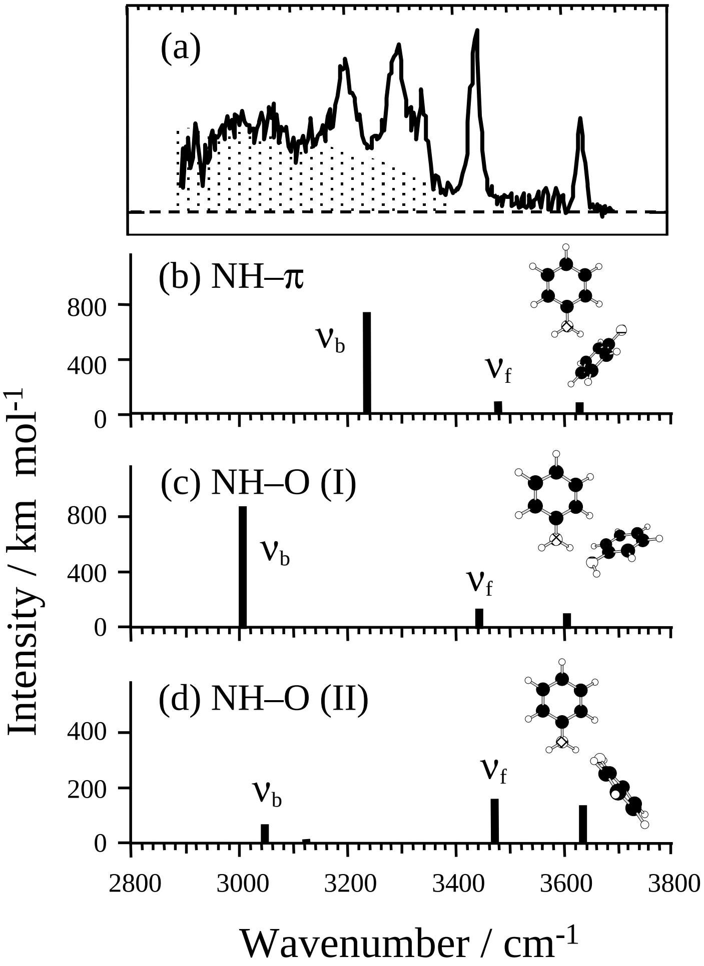

Fig. 3. Honkawa et al.