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A New Electronic State of Aniline Observed in the Transient IR Absorption Spectrum from S_1 in a Supersonic Jet

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Newly developed ultraviolet(UV)−infrared(IR) double resonance spectroscopy with relaxed fluorescence detection has been applied to the observation of the IR spectrum of aniline in the first electronically excited (S_1) state. In the 2900−3900 cm^{-1} region above the origin of the S_1 state, two types of IR transitions have been observed. One is the vibrational transition involving the NH_2 and CH stretching vibrations in the S_1 state. By examining the IR spectra for several deuterium substituted species, we found that the NH_2 stretching vibrations of the S_1 state are located at 3000 cm^{-1}, representing extremely large frequency decrease (500 cm^{-1}) upon electronic excitation. The other type is the anomalously broad transition appearing above 3300 cm^{-1}. This transition cannot be assigned to any particular vibrational transition of the S_1 state since it occurs in all the isotopomers examined, and we conclude that it is a vibronic transition to a new electronic excited state, which may be called the new "S_2" state. We examined the same energy region by measuring the one-photon laser-induced fluorescence (LIF) and two-photon absorption spectra from the ground electronic (S_0) state, and we found an intense band origin of the new "S_2" state at 37104 cm^{-1} in the two-photon spectrum. From the consideration of the symmetry, the new "S_2" state is thought to have B_1 symmetric species, which is in good agreement with the recent SAC-CI calculation reported by the Nakatsuji group, and the new "S_2" state is assigned to the 3s-Rydberg($^1B_1$) state.

Introduction

Aniline is the simplest aromatic molecule having an amino (NH_2) group. The pyramid-like nonplanar structure of the NH_2 group in the electronic ground state (S_0) changes to the planar one in the first electronic excited state (S_1). In this respect, many experimental[1−5] and theoretical[6−11] studies on the potential energy curve of the inversion motion of the NH_2 group have been reported in both S_0 and S_1 states. Aniline is also a very interesting molecule as a chromophore of *p*-dimethylaminobenzonitrile (p-DMABN), which exhibits an intramolecular charge transfer (ICT) reaction after photoexcitation to the S_1 state. Although there have been many discussions about ICT of p-DMABAN, the reaction is thought to occur through the potential curve crossing between the $S_1(^1L_b)$ and the ^1L_a states in polar solvents.[12] Very recently, however, Sobolewski and Domcke[13−16] proposed that in several aromatic molecules, a $\pi\sigma^*$ state exists in the vicinity of the S_1 state and its potential surface intersects with that of the S_1 state. If this is the case, this state may also play an important role in the ICT reaction. In this respect, the observation of this state and the investigation of the coupling of this state with the S_1 or the L_a state will be very important. However, to the best of our knowledge, there has been no report of the direct observation of the $\pi\sigma^*$ state, which we call the new "S_2" state since it is located between the S_1 and the ^1L_a states.

In the present work, we observed transient IR spectra of jet-cooled aniline in the S_1 state. The aim of this work is the following. The first is the direct observation of the new "S_2" state and its assignment. The second is the investigation how the new "S_2" and the S_1 states interact with each other. A new detection scheme of UV-IR double resonant spectroscopy has been developed to observe the transient IR spectrum. This spectroscopy, which we refer as "relaxed fluorescence-detected IR spectroscopy (RFDIRS)", has provided us with background-free IR spectra in the 2900−3900 cm^{-1} region. The observed spectrum was rich in the spectral features and we found that the bands involve vibrational transitions in the S_1 state as well the electronic transition to the new "S_2" state. We discuss the assignment of the new "S_2" state on the basis of similar study for deuterium-substituted species, the two-photon spectroscopic study, and by comparison with a recent theoretical calculation by the Nakatsuji group.[17]

Experimental Section

In UV-IR double resonance spectroscopy, jet-cooled molecules are first prepared to the zero-point level of the S_1 state by a tunable UV laser. After a delay of several nanoseconds, tunable IR laser light is introduced to pump the S_1 molecules further to vibrationally or electronically excited state(s). Up to now, two types of detection schemes have been reported for observation of the IR spectra in our group.[18−20] One scheme utilizes the difference of the fluorescence quantum yield (Q_f) between the zero-point level and higher vibronic levels of the S_1 state.[18,20] In general, Q_f of the vibronic level of aromatic molecules is much smaller than that of the zero-point level. Thus, when the IR laser pumps the molecules from the zero-point level to the upper levels, the total fluorescence signal decreases. By scanning the IR frequency while monitoring the total fluorescence intensity, we obtain the IR spectrum of the S_1 state as a fluorescence-dip spectrum.

The other scheme utilizes the predissociation of van der Waals or hydrogen-bonded clusters after the IR excitation. Since the

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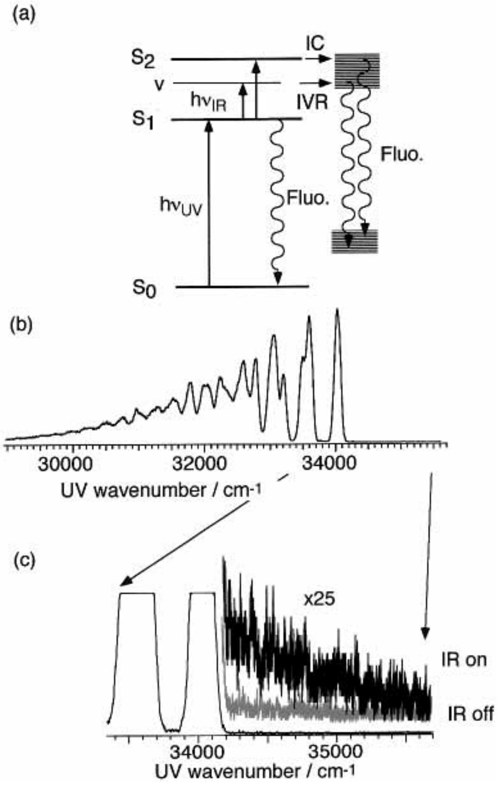


Figure 1. (a) Energy level diagram and excitation schemes of relaxed fluorescence-detected IR spectroscopy (RFDIRS). (b) Dispersed fluorescence (DF) spectrum of aniline after the excitation to the S_1 band origin. (c) Expanded region of the DF spectrum with IR laser frequency tuned to the CH stretching vibration and with IR laser off.

energy of the X−H (X = C, N, or O) stretching vibration is usually larger than the hydrogen-bond energy, the cluster excited to the X−H stretch vibration dissociates into photofragments. By monitoring only the emission of the photofragment while scanning the IR frequency, we obtain the background free IR spectrum for the cluster. We called this spectroscopy "photofragment-detected IR spectroscopy (PFDIRS)", which was first demonstrated for the hydrogen-bonded clusters of 2-naphthol.[19]

In the present work, we developed another detection scheme of the IR spectroscopy of the S_1 molecules, which is shown in Figure 1a. Jet-cooled aniline, pumped to the zero-point level of the S_1 state by a UV laser pulse, is further excited to the NH or CH vibration of the S_1 state or to a higher electronic state by a tunable IR laser pulse. The vibrationally or electronically excited aniline relaxes immediately to the isoenergetic vibrational levels of the S_1 state through IVR or internal conversion (IC). If the vibrational levels generated by IVR are fluorescent, we will observe an broad emission as a result of the relaxed fluorescence which appears in the wide wavelength region. By monitoring the broad emission selectively with a use of a monochromator while scanning the IR laser frequency, we obtain the background-free IR spectrum of the molecule in the S_1 state. We call this as "relaxed fluorescence-detected IR spectroscopy (RFDIRS)". We also measured the IR spectrum in the S_0 state by IR−UV double resonance spectroscopy with fluorescence detection.[21] In this case, the IR laser light was introduced prior to the UV laser light, and the depletion of the population induced by the vibrational excitation with the IR light was recorded as a dip in the fluorescence intensity monitored with the UV light. In addition to the vibrational spectroscopy, we measured the two-photon resonant four-photon ionization (2+2 REMPI) spectrum from the S_0 state to the corresponding energy region.

Jet-cooled aniline was generated by a pulsed supersonic expansion of aniline/He gaseous mixture into vacuum through a nozzle having a 800 μm orifice. Aniline was heated to 100 °C to obtain a sufficient vapor pressure. A tunable UV light source was a frequency-doubled output of a Nd^{3+}:YAG laser (Continuum Surelite III) pumped dye laser (Lumonics HD-500). Tunable IR light was generated by difference frequency mixing between the second harmonic of a Nd^{3+}:YAG laser (Quanta-ray GCR-250) and the YAG laser-pumped dye laser (Continuum ND 6000) in a $LiNbO_3$ crystal. The two laser beams were coaxially introduced into the vacuum chamber in a counter-propagating manner. Emission was focused on the slit of a monochromator (Nikon G250) by a series of lenses and was detected by a photomultiplier tube (Hamamatsu Photonics 1P28). For the measurement of 2+2 REMPI spectrum, we replaced the optics by a 25 cm time-of-flight tube. The ions generated by 2+2 REMPI were mass-resolved and detected by a channel electron multiplier (Murata Ceratron). The photocurrent or ion-current was integrated by a boxcar integrator connected to a personal computer. Aniline and aniline-d_5($C_6D_5NH_2$) were purchased from Aldrich Chem. Co., where aniline was purified by vacuum distillation before use. Aniline-d_2($C_6H_5ND_2$) was synthesized by adding a few drops of deuterated water to aniline.

Results and Discussion

Figure 1b shows the dispersed fluorescence (DF) spectrum of aniline obtained by exciting the zero-point level (34030 cm^{-1}) of the S_1 state. Figure 1c shows the expanded region between 33400 and 35700 cm^{-1}, in which two spectra are shown. One, indicated as "IR on", is the DF spectrum obtained when the IR laser is introduced 4 ns after the UV laser and the IR frequency is tuned to the CH stretching band at 3082 cm^{-1} of the S_1 state. The other, indicated as "IR off", is the DF spectrum without the IR laser light. The broad emission is seen beneath the sharp (0,0) band when the IR laser is introduced. This broad emission is attributed to the fluorescence from the relaxed vibronic levels generated by IVR from the CH stretch level pumped by IR light. We then fixed the monochromator at 34800 cm^{-1} to monitor only the broad emission and scanned the IR laser frequency. The resulting spectrum (RFDIRS) is shown in Figure 2a, which represents the IR spectrum of aniline in the S_1 state.

Before discussing the IR spectrum of aniline in the S_1 state, we first describe the IR spectrum in the S_0 state obtained with IR−UV double resonance spectroscopy, which is shown in Figure 2b. As seen in the figure, the spectrum is very simple, where the bands appearing in the 3000−3100 cm^{-1} region are the CH stretching vibrations and the two sharp bands at 3423 and 3509 cm^{-1} are the symmetric and asymmetric stretching vibrations of NH_2, respectively. The IR spectrum of the NH_2 stretching vibration in the S_0 state is essentially the same as that reported by Nakanaga et al.[21]

Different from the simple vibrational structure of the S_0 state, many bands appeared in the IR spectrum of the S_1 state (Figure 2a), resulting in a complicated spectrum. Among the many bands that appeared, however, the bands in the 2900−3100 cm^{-1} region can be safely assigned to the CH stretching vibrations. On the other hand, the assignment of the bands appearing in the 3300−3400 cm^{-1} region is not so straightforward, because it is not obvious that they are due to the NH_2 stretching vibrations. We will discuss this issue later. A striking feature in the spectrum of the S_1 state is the appearance of relatively broad bands in the region above 3500 cm^{-1}. It should be noted that aniline does not have such high-frequency fundamentals and that the intensities of overtone or combination bands are

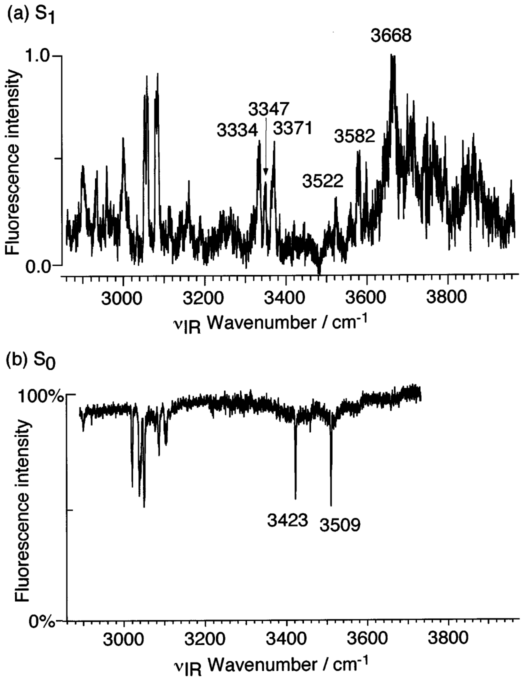


Figure 2. The IR spectrum of aniline in (upper) the S_1 state, and in (lower) the S_0 state. For the IR spectroscopic measurement in the S_1 state, the IR laser pulse was introduced 4 ns after the UV pulse, while in the S_0 state, the UV pulse was delayed at 50 ns from the IR pulse. The UV frequency is fixed to the (0,0) band at 34030 cm^{-1}.

known to be very weak. Thus, the intense bands above 3500 cm^{-1} cannot be assigned to the vibrational transitions of the S_1 state, but are strongly suggestive of the vibronic transitions to "an electronic state lying above the S_1 state". As will be discussed later, this "new electronic state" is much lower in energy than the $^1L_a(^1A_1)$ state which has been generally thought as the S_2 state, and hence we refer to the observed electronic state as the new "S_2" state.

To confirm the discovery of the new "S_2" state and to search for the NH_2 stretching vibration in the S_1 state, we carried out similar measurements for deuterated anilines; aniline-d_5 (C_6D_5-NH_2) and aniline-d_2 ($C_6H_5ND_2$). The electronic spectra of aniline isotopomers were reported by Sinclair et al.[3] and by Lin et al.[23] In the present work, we obtained the (0,0) band frequencies of aniline-d_5 and aniline-d_2 to be 34194 and 34039 cm^{-1}, respectively, which are in good agreement with their results. Upper spectra of Figure 3a−c show the RFDIR spectra of aniline, aniline-d_5, and aniline-d_2 in the S_1 state and the lower ones the IR spectra in the S_0 state, where the UV frequencies were fixed to the (0,0) band in each spectrum.

We first discuss the NH_2 stretching bands in the IR spectrum of the S_1 state by comparing them to that of the S_0 state for these isotopomers. In the IR spectrum of aniline-d_5 in the S_0 state (lower spectrum of Figure 3b), two sharp bands are observed at 3423 and 3510 cm^{-1}, which are the sym. and asym. NH_2 stretch vibrations, respectively. These frequencies are almost the same as those of aniline, indicating that the deuteration of the CH group gives a very small effect on the NH_2 stretching frequency. In addition, no band is seen in the 2900−3100 cm^{-1} region because aniline-d_5 does not have the CH group. On the other hand, in the IR spectrum of aniline-d_5 in the S_1 state (upper spectrum of Figure 3b), a few sharp peaks are seen in the 2900−3000 cm^{-1} region. Since aniline-d_5 has no CH group, these sharp bands cannot be due to the CH stretch vibrations and should be assigned to the NH_2 stretching vibration. As a consequence, the relatively broad band appearing in the 3300−3400 cm^{-1} region cannot be due to the NH_2 stretching vibrations in the S_1 state, and this must also be true for the bands appearing in the 3300−3400 cm^{-1} region of aniline. Actually, the spectral features in this energy region are quite different between aniline-d_5 and aniline. That is, in the spectrum of aniline-d_5 a relatively broad band is seen at 3340 cm^{-1}, while three sharp peaks appear at 3334, 3347, and 3371 cm^{-1} in aniline. This disagreement contradicts the close resemblance of the NH_2 stretching vibration in the S_0 state between the two species, leading to the conclusion that they are not due to the NH_2 stretching vibrations. Thus, we conclude that the NH_2 stretching vibrations of aniline in the S_1 state occur in the 2900−3000 cm^{-1} region, which overlaps with the CH stretching bands. Since the NH_2 stretching frequencies in the S_0 state occur at 3423 and 3509 cm^{-1}, it is concluded that an extremely large frequency reduction, as large as 500 cm^{-1}, takes place upon the electronic excitation to the S_1 state.

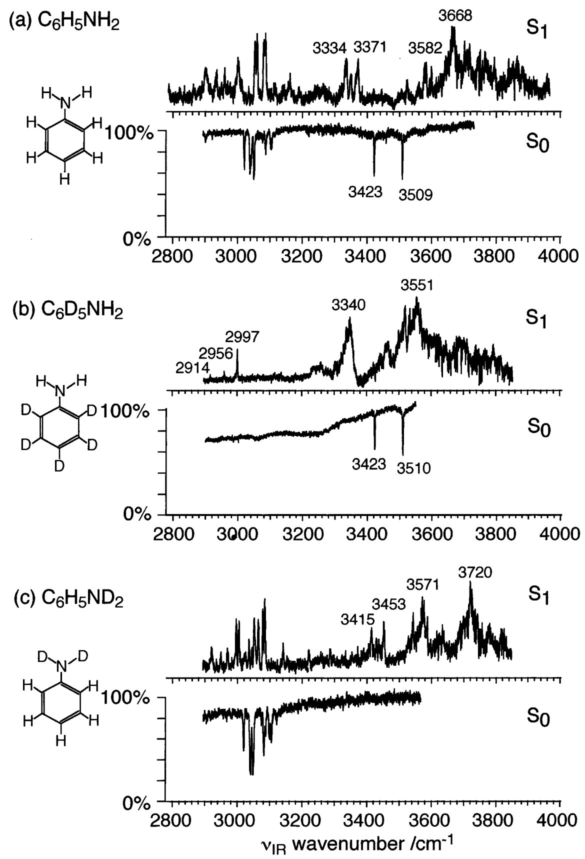
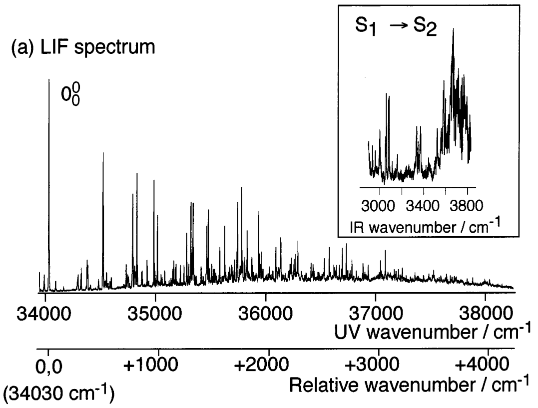


Figure 3. The IR spectra of the S_1 (upper) and S_0 (lower) states of (a) aniline, (b) aniline-d_5, and (c) aniline-d_2.

Now we discuss the new "S_2" state. As was described in the RFDIR spectrum of aniline, we have proposed that the relatively broad bands appearing above 3500 cm^{-1} are due to vibronic transitions to the new "S_2" state. This is because aniline does not have any high-frequency fundamentals in that region and any combination bands should have much weaker intensities than those observed. The best way to confirm this is to compare the IR spectra in the S_1 state for its isotopomers. Indeed, in Figure 3 we see similar broad bands above 3500 cm^{-1} in all the isotopomers examined, though the band structures are different from each other. Thus, the bands above 3500 cm^{-1} commonly occur irrespective of isotope substitution, and therefore we conclude that they are the transitions to the electronic state lying close to the S_1 state, that is the new "S_2" state. At this moment, we should mention the bands appearing

(a) LIF spectrum



(b) 2+2 REMPI spectrum

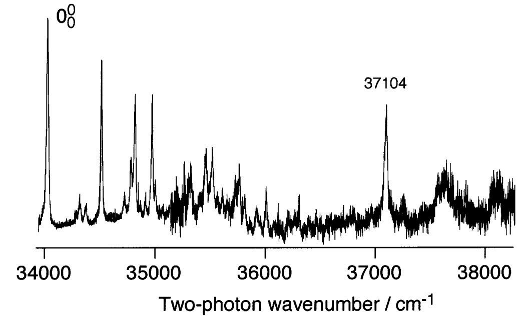


Figure 4. (a) The LIF spectrum of jet-cooled aniline in the region from the S_1 to the S_2 state. (b) (2+2) REMPI spectrum in the same energy region. The IR spectrum of the S_2−S_1 transition is shown in the inset.

in the 3300−3400 cm^{-1} region in aniline and aniline-d_5. As discussed above, they are not due to the NH_2 stretching vibration and they can also be assigned to the vibronic bands of the new "S_2" state. In aniline-d_2, the corresponding bands seem to be shifted to the 3400−3500 cm^{-1} region. Another noticeable characteristics of the bands appearing above 3300 cm^{-1} is that they are commonly broad in all the isotopomers, indicating a strong coupling with the S_1 state. Then, we have questions about the location of the band origin of the new "S_2" state and the symmetry species to which this state belongs.

To answer the above questions, we measured one-photon and two-photon absorption spectra in the corresponding energy region from S_0. Figure 4a,b shows the one-photon LIF and (2+2) REMPI spectra of aniline. In the (2+2) REMPI spectroscopic study, we found that the ion intensities exhibit a quadratic dependence on the input laser intensity, so that the spectrum was normalized with respect to the square of the laser intensity. As seen in the LIF spectrum (Figure 4a), the vibronic bands of the S_1 state extend up to the energy region of the new "S_2" state, so the transition to "S_2" can hardly be identified. This indicates that the one-photon "S_2" ← S_0 transition cross section must be much weaker than that of the S_1 ← S_0 transition. In the (2 + 2) REMPI spectrum, on the other hand, a sharp band appears at 37104 cm^{-1}, and relatively broad bands occur on the higher frequency side. We note that the position of the broad band at 37700 cm^{-1} matches well with the IR spectrum of the S_1 state. Thus, the sharp band at 37104 cm^{-1} is thought to be the (0,0) band of the new "S_2" state, which is not observed in the IR spectrum of the S_1 origin. This result indicates that the "S_2" ← S_1 ($^1B_2$) transition is symmetry forbidden, leading to the conclusion that the "S_2" state belongs to the B_1 symmetry species.

Two important results have been obtained in the present work. First, the NH_2 stretching frequency decreases by almost 500 cm^{-1} upon the electronic excitation from the S_0 to the S_1 state. Second, the new "S_2" state occurs at 37104 cm^{-1} (4.600 eV) from the S_0 state, which is only 3074 cm^{-1} above the S_1 ($^1B_2$) state. The anomalously large frequency decrease of the NH_2 stretch vibration cannot be simply explained by the planarity of aniline in S_1, because the frequencies of the planar aniline cation are known to be 3393 and 3486 cm^{-1} for sym. and asym. NH_2 stretches,[23] respectively. Thus the frequency shift from the nonplanar S_0 to the planar cation is only 20−30 cm^{-1}, which is very small compared with that of the S_1 state. Theoretical calculation of aniline by Tzeng et al. at the CIS/6-31+G* level[24] predicted the frequencies of the sym. and asym. modes of the NH_2 stretch in the S_1 state to be 3206 and 3317 cm^{-1}, respectively. Though the predicted values exhibit rather large frequency decrease in the S_1 state, they are not large enough to explain the observed results. One of the possibilities for the large frequency reduction of the NH_2 stretch mode is the vibronic coupling between the S_1 and new "S_2" state through the NH_2 stretch mode. However, this possibility is unlikely since neither the "sym (A_1)" nor the "asym (B_2)" mode can couple S_1($^1B_2$) with "S_2($^1B_1$)" due to the symmetry restriction. At this moment, it is not clear whether the large frequency reduction of NH_2 stretch is intrinsic to the S_1 state or due to the coupling with the new "S_2" state.

Now we will discuss the candidates for the new "S_2" state. One of them is the ^1L_a ($^1A_1$) state. However, the ^1L_a state is known to be located at 41000 cm^{-1} from the S_0 state,[25] which is much higher than the present energy region. Furthermore, the ^1L_a state has a large oscillator strength from S_0 so that it does not agree with the observed result. Thus, the new "S_2" state cannot be the ^1L_a state. Other electronic states, such as other $\pi\pi^*$ state or the $n\pi^*$ state, are located higher than the ^1L_a state,[17,25] so they are not the possible candidates, either. The other possibility is the low-lying $\pi\sigma^*$ or Rydberg state. Very recently, Honda et al. calculated the electronic excited states of aniline by SAC-CI (Symmetry Adapted Cluster with Configuration Interaction) method.[17] They predicted that the 3s-Rydberg state is located at 4.53 eV (36500 cm^{-1}), which lies between the $S_1(\pi\pi^*)$ and the $^1L_a(\pi\pi^*)$ states. In addition, the 3s-Rydberg state belongs to the $^1B_1$ symmetry in the planar form and the calculated oscillator strength from the S_0 state to this state is 4 times weaker than that to the S_1 state.[17] Thus, the results obtained in this work agree very well with their prediction with respect to energy, symmetry, and transition cross section, and we conclude that the observed new "S_2" state is assigned to the 3s-Rydberg state.

The assignment of the new "S_2" state to the 3s-Rydberg state is further supported by obtaining a quantum defect of the state with the following equation:

$$E_{S_2} = \mathrm{IP}_0 - \frac{R}{(n-\delta)^2}$$

Here, R is the Rydberg constant and δ is the quantum defect. By substituting the reported ionization potential of aniline (IP_0 = 62268 cm^{-1})[26] and setting the principal quantum number n = 3, we obtain the quantum defect $\delta = 0.912$ for the "S_2" state. Since the s-Rydberg state normally has the quantum defect between 0.9 and 1.2,[27] the value of $\delta = 0.912$ obtained in the present work also supports the new state to be the 3s-Rydberg state. The presence of the 3s-Rydberg state was also reported in aniline derivatives, such as dimethyl aniline in a similar energy region,[28−30] from the difference of the gas-phase absorption spectra from that in solution.

Finally, we would like to make a short comment on the role of the newly found 3s-Rydberg state of aniline in its photochemical process. As was described in the Introduction, recently Sobolewski and Domcke proposed[13−16] that the $\pi\sigma^*$ state is located above the S_1 state, and its potential energy surface (PES) intersects with that of the S_1 state at a relatively short X−H distance. The PES of the $\pi\sigma^*$ state further intersects with that of the S_0 state at a longer X−H distance, leading to the internal conversion to the S_0 state. They also pointed out that this $\pi\sigma^*$ state is the 3s-Rydberg state.[16] Therefore, we conclude the "S_2" 3s-Rydberg state observed in the present experiment is the $\pi\sigma^*$ state. As shown above, a strong interaction between the S_1 and the "S_2" states is seen as the broadening of the "S_2" vibronic bands. In addition, the dramatic decrease in the NH_2 stretching frequency of the S_1 state may be also related to the $S_1 \leftrightarrow$ "S_2" interaction, since the PES of the "S_2" state is essentially repulsive along the X−H coordinate.[13−16] From the symmetry consideration, we point out an interesting factor which can promote the $S_1 \leftrightarrow$ "S_2" coupling. That is, since the S_1 and the "S_2" states have $^1B_1$ and $^1B_2$ symmetric species, respectively, the two states can couple via the vibration corresponding to the A_2 symmetric species. The torsional motion of the NH_2 group along the C_2 axis is one such the vibration. For further understanding of the role of the "S_2" state in the photochemistry of the S_1 and the ^1L_a states, it is necessary to extend this work to other aniline derivatives, which is in progress in our laboratory.

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References and Notes

(1) Song, X.; Yang. M.; Davidson, E. R.; Reilly, J. P. *J. Chem. Phys.* **1993**, *99*, 3224.

(2) Mikami, N.; Hiraya, A.; Fujiwara, I.; Ito, M. *Chem. Phys. Lett.* **1980**, 74, *531*.

(3) Sinclair, W. E.; Pratt, D. W. *J. Chem. Phys.* **1996**, *105*, 7942.

(4) Kerstel, E. R. Th.; Becucci, M.; Pietraperzia, G.; Consalvo, D.; Castelucci, E. *J. Mol. Spectrosc.* **1996**, *177*, 74.

(5) Hollas, J. M.; Howson, M. R.; Ridley, T.; Halonen, L. *Chem. Phys. Lett.* **1983**, *98*, 611.

(6) Lombardi, J. R. D. *J. Chem. Phys.* **1969**, *50*, 3780.

(7) Castella-Ventura, M.; Kassab, E. R. *Spectrochim. Acta* **1994**, *50A*, 69

(8) Wang, Y.; Saebo, S.; Pittman C. C., Jr. *J. Mol. Struct. (THEOCHEM)* **1993**, *281*, 91.

(9) Niu, Z.; Dunn, K. M.; Boggs, J. E. *Mol. Phys.* **1985**, *55*, 421.

(10) Spoerel, O.; Stahl, W. *J. Mol. Spectrosc.* **1998**, *190*, 278.

(11) Haeckel, M.; Stahl, W. *J. Mol. Spectrosc.* **1999**, *198*, 263.

(12) Lippert, E.; Luder, W.; Boos, H. In *Advances in Molecular Spectroscopy*; Mangini, A., Ed.; Pergamon Press, Oxford, 1962; p 443.

(13) Sobolewski, A. L.; Domcke, W. *Chem. Phys. Lett.* **1999**, *315*, 291.

(14) Sobolewski, A. L.; Domcke, W. *Chem. Phys. Lett.* **2000**, *329*, 130.

(15) Sobolewski, A. L.; Domcke, W. *J. Phys. Chem. A* **2001**, *105*, 9275.

(16) Sobolewski, A. L.; Domcke, W.; Dedonder-Lardeux, C.; Jouvet, C. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1093.

(17) Honda, Y.; Hada, M.; Ehara, M.; Nakatsuji, H. *J. Chem. Phys.* **2002**, *117*, 2045.

(18) Ebata, T.; Mizuochi, N.; Watanabe, T.; Mikami, N. *J. Phys. Chem.* **1996**, *100*, 546.

(19) Matsumoto, Y.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2001**, *105*, 5727.

(20) Minejima, C.; Ebata, T.; Mikami, N. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1537.

(21) Nakanaga, T.; Ito, F.; Miyawaki, J.; Sugawara, K.; Takeo, H. *Chem. Phys. Lett.* **1996**, *261*, 414.

(22) Lin, J. L.; Tzeng, W. B. *J. Phys. Chem.* **2001**, *115*, 743.

(23) Fujii, A.; Honda, M.; Ebata T.; Mikami, N. To be published.

(24) Tzeng, W. B.; Narayanan, K.; Shieh, K. C.; Tung, C. C. *J. Mol. Struct. (THEOCHEM)* **1998**, *426*, 231.

(25) Kimura, K.; Tsubomura, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1336.

(26) Takahashi, M.; Ozeki, H.; Kimura, K. *J. Phys. Chem.* **1992**, *96*, 6399.

(27) Herzberg, G. *Molecular Spectra and Molecular Structure III*; Van Nostrand Reinhold Company: New York, Cincinnati, Toronto, London, Melbourne, 1966; p 341.

(28) Tsubomura, H.; Sakata, T. *Chem. Phys. Lett.* **1973**, *21*, 511.

(29) Davidsson, Å.; Norden, B. *Chem. Phys. Lett.* **1974**, *28*, 39.

(30) Fuke, K.; Nagakura, S. *J. Mol. Spectrosc.* **1977**, *64*, 139.