The Lowest Triplet States of 2-Amino- and 2-Amino-d_2-pyrimidines

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Synopsis. The vibrational analyses of the sublevel phosphorescence spectra of 2-amino- and 2-amino-d_2-pyrimidines were made. The result shows that the lowest triplet $^3A_1(\pi,\pi^*)$ state is strongly perturbed by closely lying $^3B_1(n,\pi^*)$ and $^3A_2(n,\pi^*)$ states and the polarization of the very weak 0–0 bands in the dark sublevel spectra suggests that the symmetry of the molecular structure in the lowest triplet state is slightly lowered from the point group C_{2v} to the C_2.

Kleinwacher et al.[1] studied the absorption and emission spectra of 2-aminopyrimidine and assigned the lowest triplet state to a $^3A_1(\pi,\pi^*)$ state based on the polarization behavior of the phosphorescence. Since $^3B_1(n,\pi^*)$ and $^3A_2(n,\pi^*)$ states were considered to lie closely above the phosphorescent state,[2,3] it was expected that the lowest triplet state would be strongly perturbed by these two $^3(n,\pi^*)$ states. Nishi and Kinoshita[4] studied the individual sublevels of the lowest triplet state of 2-aminopyrimidine by the microwave induced delayed phosphorescence method and showed that the short-, medium-, and long-lifetime phosphorescences originate from the *y*, *z*, and *x* sublevels, respectively. They analyzed the phosphorescence spectrum based on the normal vibrations determined by Lafaix and Lebas[5] and concluded that the most effective phosphorescence mechanism for the *y* sublevel of the phosphorescent state is the first-order spin-orbit coupling between the $^1B_1(n,\pi^*)$ and $^3A_1(\pi,\pi^*)$ states, and that of the *z* sublevel is the second-order spin-orbit-vibronic coupling between the $^1A_1(\pi,\pi^*)$ and $^3A_1(\pi,\pi^*)$ states via the $^3A_2(n,\pi^*)$ state.

Very recently we reexamined the assignments of the normal vibrations of 2-amino- and 2-amino-d_2-pyrimidines and gave new assignments.[6] In this paper the vibrational analyses of the sublevel phosphorescence spectra of 2-amino- and 2-amino-d_2-pyrimidines are discussed based on the polarization behavior of the phosphorescence bands and normal vibrations newly determined and the phosphorescence processes of these molecules are restudied.

Experimental

Materials. 2-Amino-d_2-pyrimidine was obtained by the exchange reaction of 2-aminopyrimidine (Tokyo Kasei) with D_2O. The samples were purified by repeated distillation under reduced pressure. The solvent, benzene (Dotite Spectrosol Grade), was completely desiccated with an alloy of sodium and potassium because 2-amino-d_2-pyrimidine turned into 2-amino-d_1- and/or 2-aminopyrimidines quite easily by the exchange reaction with water containing in the solvent.

Optical Measurements. The phosphorescence lifetimes and the time-resolved phosphorescence spectra of 2-amino- and 2-amino-d_2-pyrimidines were measured in benzene matrices at 1.4 K. Using the relative values of the populations and radiative rate constants and the lifetimes for the lowest triplet sublevels of 2-aminopyrimidine determined by Nishi and Kinoshita,[4] the intensity ratio of the 0–0 bands of the phosphorescence spectra originating from the *y*, *z*, and *x* sublevels was calculated changing the sampling time after interrupting the excitation. The calculated intensity ratios indicate that the three sublevel phosphorescence could be mechanically separated if the adequate sampling time was chosen.

The short-lifetime phosphorescence was observed by sampling the emission from 3 ms to 40 ms after the cessation of the excitation. For the observation of the medium- and long-lifetime phosphorescences, the sampling times were set at 300—400 ms and 4000—5000 ms, respectively, after cutting off the exciting light.

The polarized phosphorescence spectrum was observed in a benzene host crystal at 1.4 K in the same way as described previously.[7] Since we have no knowledge about the orientation of the 2-aminopyrimidine molecule in the benzene single crystal, the polarized phosphorescence spectrum was observed with a rotatable polarizer whose orientation was set in such a way that the intensity of the 0–0 band in the short-lifetime spectrum became strongest and the rotation of the polarizer by 90° made the intensity weakest. The spectra observed at the former and latter orientations of the polarizer are drawn with solid and dotted lines and are referred to as solid and dotted spectra hereafter, respectively. The optical and electric apparatus used for the measurements of the time-resolved phosphorescence spectra, the polarized phosphorescence spectra and the phosphorescence lifetimes are exactly the same as those described previously.[7–9]

Results and Discussion

The phosphorescence lifetimes of 2-amino- and 2-amino-d_2-pyrimidines in benzene at 1.4 K were determined through the analysis of the phosphorescence decays. The short-, medium-, and long-lifetimes obtained for 2-amino-d_2-pyrimidine were 35, 395, and 1500 ms, respectively, and the lifetimes obtained for 2-aminopyrimidine were approximately equal to the sublevel lifetimes determined by Nishi and Kinoshita in *p*-xylene.[4] The mechanically resolved sublevel phosphorescence spectra of 2-amino- and 2-amino-d_2-pyrimidines in benzene at 1.4 K are shown in Figs. 1 and 2, respectively, where the intensity of the strongest band in each spectrum is normalized to unity.

The vibrational analysis of the short-lifetime phosphorescence spectrum of 2-aminopyrimidine will be discussed first. The shortest wavelength band at 27646 cm^{-1}, whose intensity is the strongest in the spectrum, was taken as the 0–0 band. The strong bands

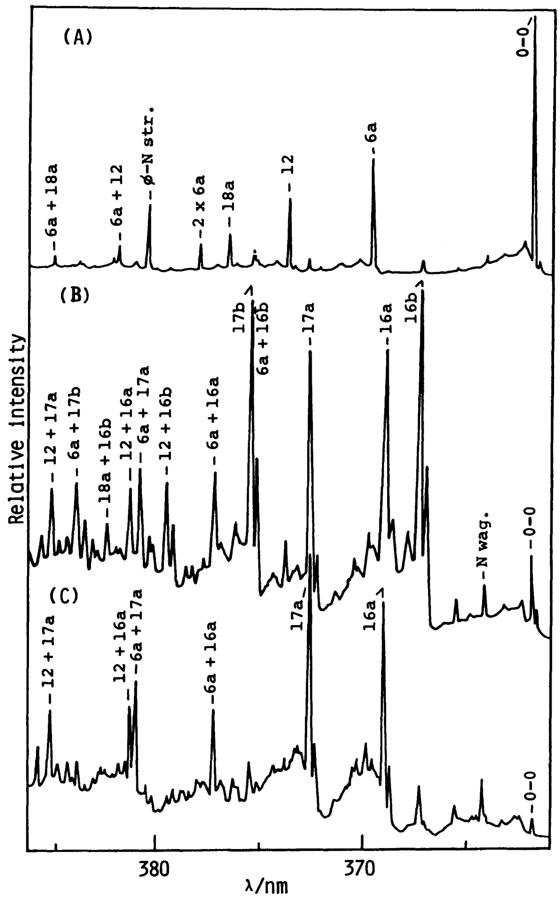

Fig. 1. The (A) short-, (B) medium-, and (C) long-lifetime phosphorescence spectra of 2-aminopyrimidine in benzene at 1.4 K.

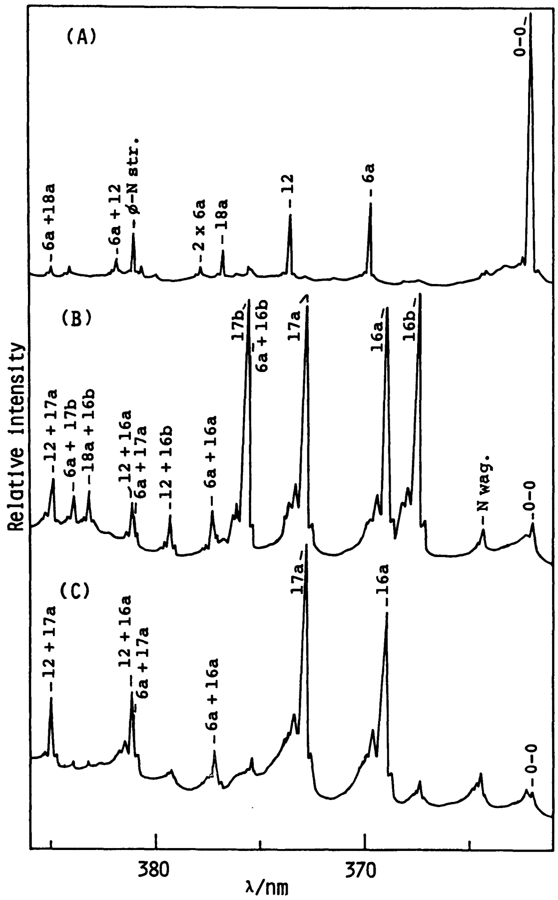

Fig. 2. The (A) short-, (B) medium-, and (C) long-lifetime phosphorescence spectra of 2-amino-d_2-pyrimidine in benzene at 1.4 K.

separated by 586, 876, 1090, and 1357 cm^{-1} from the 0–0 band were assigned to the totally symmetric ν_{6a}, ν_{12}, ν_{18a}, and ϕ–N stretching vibrations, respectively. The overtone and combination bands of these vibrations were also observed with medium or weak intensity.

The polarized time-resolved phosphorescence spectra of a benzene single crystal doped with 2-aminopyrimidine are shown in Fig. 3. For the 0–0 and totally symmetric ν_{6a} and ν_{12} bands observed in the polarized short-lifetime spectrum, the intensity of the solid spectrum is stronger than that of the dotted one. Since the symmetry representation of the y sublevel is B_1, the 0–0, ν_{6a}, and ν_{12} bands are to be polarized along the x direction. The x-polarized bands were also observed at 532 and 807 cm^{-1} from the 0–0 bands in the polarized long-lifetime spectrum. Since the symmetry representation of the x sublevel is B_2, these bands should be assigned to the a_2 vibration. We assigned these bands to the ν_{16a} and ν_{17a} vibrations. The ν_{16a} and ν_{17a} vibronic bands were also observed in the medium-lifetime spectrum where the band intensity of the dotted spectrum is stronger than that of the solid one. The z sublevel belongs to the symmetry representation A_2 and thus these bands are to be polarized along the z direction. The z-polarized bands were also observed at 190, 409, and 1000 cm^{-1} from the 0–0 band in the short-lifetime spectrum. These bands should be ascribed to the b_1 vibration and thus the bands were assigned to the N wagging, ν_{16b}, and ν_{17b} vibrations, respectively. The ν_{16b} and ν_{17b} vibronic bands were strongly observed in the medium-lifetime spectra with nearly equal intensity of the solid and dotted spectra. These bands are to be polarized along the y direction. The observed characteristic polarization behavior of these vibronic bands in the time-resolved phosphorescence spectra clearly shows that the main bands observed in the short-, medium-, and long-lifetime spectra are the bands originating from the y, z, and x sublevels, respectively.

The spectral structure of the sublevel phosphorescence spectra of 2-amino-d_2-pyrimidine is essentially the same as that of 2-aminopyrimidine. The strong bands separated by 570, 848, 1076, and 1366 cm^{-1} from the 0–0 band located at 27619 cm^{-1} in the short-lifetime spectrum were assigned to the ν_{6a}, ν_{12}, ν_{18a}, and ϕ–N stretching vibrations, respectively. The prominent bands separated by 522 and 785 cm^{-1} from the 0–0 band in the long-lifetime spectrum were assigned to the ν_{16a} and ν_{17a}, vibrations, respectively. In addition to the ν_{16a} and ν_{17a} bands, relative strong bands were observed at 407 and 990 cm^{-1} from the 0–0 band in the medium-lifetime spectrum and these bands were assigned to the ν_{16b} and ν_{17b} vibrations, respectively.

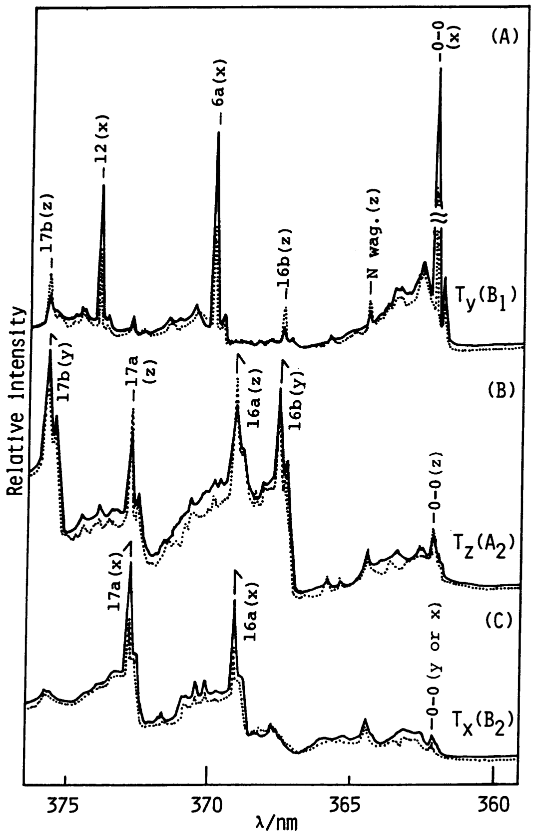

Fig. 3. The polarized (A) short-, (B) medium-, and (C) long-lifetime phosphorescence spectra of 2-aminopyrimidine in a benzene single crystal at 1.4 K. (x), (y), and (z) indicate the polarization directions of the bands.

The detailed vibrational analyses are given in Figs. 1 and 2.

The vibrational analyses made on two molecules distinctly indicate that (1) the emission from the y sublevel borrows the intensity from the $^1B_1(n,\pi^*)$–$^1A_1$ transition through the first-order spin-orbit coupling, (2) the emission from the z sublevel borrows the intensity almost equally from the $^1A_1(\pi,\pi^*)$–$^1A_1$ and $^1B_2(\pi,\pi^*)$–$^1A_1$ transitions via the $^3A_2(n,\pi^*)$ and $^3B_1(n,\pi^*)$ states, respectively, through the second-order spin-orbit-vibronic coupling, although Nishi and Kinoshita considered only the second-order process via the $^3A_2(n,\pi^*)$ state as the main perturbing process, and (3) the emission from the x sublevel borrows the intensity from the $^1B_1(\sigma,\pi^*)$–$^1A_1$transition via the $^3A_2(n,\pi^*)$ state. The dominant vibronic coupling is expected to take place among the triplet states because of the small energy separation between the $^3A_1(\pi,\pi^*)$ and $^3A_2(n,\pi^*)$ or $^3B_1(n,\pi^*)$ states.

A question that may be asked is: why do the dark $z(A_2)$ and $x(B_2)$ sublevels give the 0–0 bands polarized along the z and y(or x) directions, respectively? If the symmetry of the molecular structure reduces to the point group C_s due to the amino-substitution, the symmetry representations of the y, z, and x sublevels turn into the symmetry species A′, A″, and A″, respectively. This molecular geometry gives the 0–0 bands polarized along the y direction in both the z and x sublevel spectra contrary to the observaton. If the molecular structure reduces to the point group C_2, the symmetry representations of the y, z, and x sublevels turn into the species B, A, and B, and the z and x sublevel spectra could show the 0–0 bands polarized along the z direction and in the xy plane, respectively, in accord with the observation. However, the distortion of the molecular geometry, which may be caused by the vibronic coupling or the crystal force, should be small because the intensity of the 0–0 bands is much weaker than that of the a_2 and b_1 vibronic bands in the dark sublevel spectra, and the overtone bands of the ν_{16a} and ν_{17a} vibrations belonging to the a_2 symmetry species could not be observed. In the parent molecule, pyrimidine, whose lowest triplet state is the $^1B_1(n,\pi^*)$ state, the molecular distortion and the second-order spin-orbit-vibronic coupling give almost equal contributions to the phosphorescence processes for the dark sublevel.[7]

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