Electronic Spectrum of Jet-Cooled 9-Hydroxyphenalenone-d. Vibrational Mode Specific Proton Tunneling in the S_0 State

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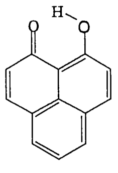
The fluorescence excitation and dispersed fluorescence spectra of jet-cooled 9-hydroxyphenalenone-d have been measured to investigate vibrational mode specific proton tunneling in the S_0 state. Tunneling splittings of a few vibrationally excited states have been determined.

9-Hydroxyphenalenone (9HPO-h, **1**) is one of the most extensively studied molecules which undergo proton tunneling. Haddon and Stillinger[1] proposed a switching memory utilizing hydrogen bonding and investigated proton transfer in 9HPO. Mochida *et al.*[2] investigated the dielectric relaxation in a 9HPO crystal. The S_1-S_0 fluorescence and dispersed fluorescence spectra of 9HPO-h and 9-hydroxyphenalenone-d (9HPO-d, **2**) were measured in rare gas matrices.[3,4] The tunneling splittings



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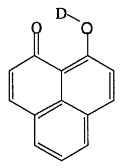

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of the zero-point level in the S_0 and S_1 states, Δ_0'' and Δ_0', of 9HPO-h have been determined to be 69 and 311 $\mathrm{cm^{-1}}$, respectively[4]. These tunneling splittings decrease to Δ_0'' =12 $\mathrm{cm^{-1}}$ and Δ_0'=179 $\mathrm{cm^{-1}}$ in 9HPO-d.[4] Recently, the tunneling splitting in the zero-point level of the ground-state 9HPO-d cation has been estimated to be 1 $\mathrm{cm^{-1}}$ through measuring the zero kinetic energy (ZEKE) photoelectron spectrum in a molecular beam.[5] The measurement of the tunneling splittings in the vibrationally excited states provides valuable information on the potential energy surface of proton transfer.[6,7] However, the tunneling splittings in the vibrationally excited levels of 9HPO-h and 9HPO-d have not been determined both for the S_0 and S_1 states. In this work, we have measured the S_1-S_0 electronic spectra of jet-cooled 9HPO-d. The 0- level in S_0 of 9HPO-h was thermally inaccessible in a supersonic free jet expansion due to a very large tunneling splitting (69 $\mathrm{cm^{-1}}$).[4]

The experimental apparatus was essentially the same as that described previously[8,9] except for the use of a commercial pulsed valve and a pulsed driver (General Valve Iota 1) to heat the nozzle housing up to 220 °C. 9-hydroxyphenalenone-h was synthesized following a procedure in a literature,[10] and purified by sublimation. 9-hydroxyphenalenone-d was prepared by introducing D_2O into the nozzle housing.

Figure 1 shows the fluorescence excitation spectra of 9HPO-d near the region of the electronic origin. The lower spectrum was measured under higher backing pressure and longer downstream distance to obtain colder spectrum. The electronic

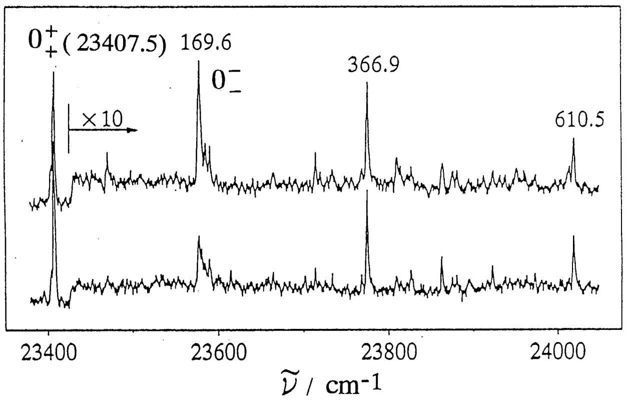

Figure 1. Fluorescence excitation spectra of 9HPO-d. The backing pressure and the dowstream distance were 2.5 x 10^5 Pa and 1.0 cm for the upper spectrum, and 3.5x10^5 Pa and 3.0 cm for the lower spectrum, respectively.

origin band (0_+^+) is observed at 23407.5 $\mathrm{cm^{-1}}$. It should be noted that the intensity of the band at 0_+^++169.6 $\mathrm{cm^{-1}}$ is much smaller in the lower spectrum than that in the upper one, suggesting that the band at 0_+^++169.6 $\mathrm{cm^{-1}}$ is originating from a thermally populated state in S_0. Thus, we have assigned the band at 169.6 $\mathrm{cm^{-1}}$ to the 0_-^- transition. Ozeki *et al.*[5] measured the resonance enhanced multiphoton ionization (REMPI) spectrum of 9HPO-d, and assigned the band at 0_+^+ + 167 $\mathrm{cm^{-1}}$ to the 0_-^- transition. This frequency is in good agreement with our value.

Figures 2a and 2b display the dispersed fluorescence spectra of 9HPO-d measured by exciting the 0^+ and 0^- levels, respectively. The observation of various vibrational modes in Figure 2b is consistent with the assignment of the 0_-^- transition in the fluorescence excitation spectrum. The intensity distribution and the frequencies in the vibronic structure in Figure 2b are somewhat different from those in Figure 2a. In addition, several extra bands such as X- and 2X- are observed in Figure 2b. These spectra could be compared to the dispersed fluorescence spectra of tropolone (TRN) measured by exciting the 0^+ and 0^- levels.[8] The vibronic pattern as well as the frequencies of vibronic bands is very similar in the two spectra of TRN-h. In the case of TRN-h, the Franck-Condon overlapping between the 0^- and ν_- levels must be similar to that between the 0^+ and ν_+ levels, where ν_+ and ν_- indicate the (+) and (-) tunneling doublet components of a vibrational level ν in the S_0 state, respectively. In contrast with the transitions in 9HPO-d, the Franck-Condon overlapping between the 0^- and ν_- levels may be different from the corresponding overlapping between the 0^+ and ν_+

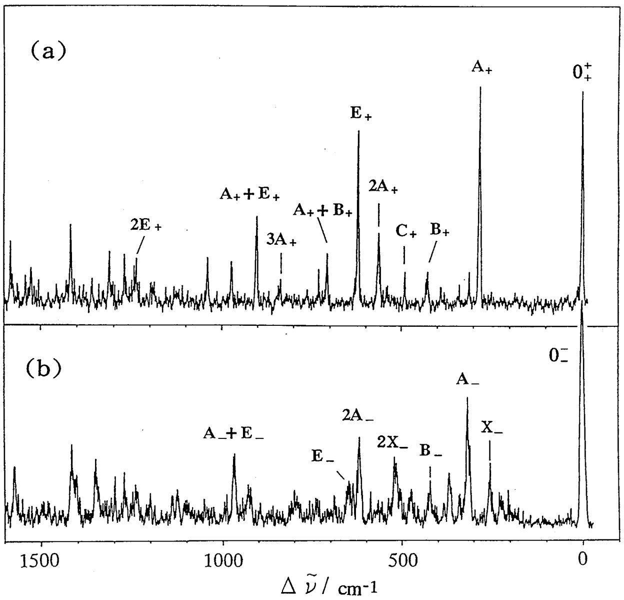

Figure 2. Dispersed fluorescence spectra measured by exciting the 0^+ level (a) and the 0^- level (b).

levels for many transitions of 9HPO-d. It is worth noting that the Δ'_0 value of 9HPO-d (179 cm^{-1})[4] is much larger than that of TRN-h (19.9 cm^{-1}).[9] The different vibronic pattern in the two dispersed fluorescence spectra of 9HPO-d may be explained by assuming a strongly perturbed 0^- wavefunction in the S_1 state. Possible candidates for the perturbation is a Fermi resonance between the 0^- state and an unidentified vibronic state. We noticed that the vibronic pattern in the ZEKE spectrum of 9HPO-d ionized via the 0^- intermediate state is fairly different from that ionized via the 0^+ state, although the tunneling splitting in the zero-point level of the ground state cation is very small (1 cm^{-1}).[5] The difference in the two ZEKE spectra could also be explained by considering a perturbed 0^- wavefunction in the S_1 state.

Although the dispersed fluorescence spectrum measured by exciting the 0^-_- transition is somewhat different from that measured by exciting the 0^+_+ transition, similarities in the intensity distribution and frequencies still exist between the two spectra, which allowed us to correlate a few vibronic bands in Figure 2b to those in Figure 2a. The normal coordinate analysis for both 9HPO-h and 9HPO-d has not been made. Since the dispersed fluorescence in Figure 2a is very similar to that measured in neon matrix by Bondybey *et al*,[4] we used their assignment. A few vibronic bands in Figure 2b were correlated to those in Figure 2a by noting that the difference in the frequency between $\nu(v_+) - \nu(v_-)$ for a given v level should not exceed $\Delta''_0 \approx 12$ cm^{-1}. The frequency of level A_+ is 281 cm^{-1}. The corresponding A^+ level in S_1 is observed at 366.9 cm^{-1}. The excitation of the band at 366.9 cm^{-1} has provided strong transitions which terminate into the A_+ and $2A_+$ levels. Ozeki *et al.*[5] observed a low frequency transition at 0^+_++167 cm^{-1} in the REMPI spectrum of 9HPO-h. The corresponding frequency in the S_0 state has been measured to be 259 cm^{-1} from the dispersed fluorescence obtained by exciting the 0^+_+ +167 cm^{-1} level. The bands at 254 and 515 cm^{-1} in Figure 2b may correspond to a fundamental X and its overtone 2X, respectively. Thus, several vibrational bands have been assigned, which are indicated in Figure 2.

The 0^0_0 tunneling splitting of 9HPO-d measured in the isolated state is very similar to that in a neon matrix, suggesting that the perturbation from the solvent neon atoms is small. Therefore, it is reasonable to approximate Δ''_0=12 cm^{-1} for the isolated 9HPO-d. The tunneling splittings of levels A, B, 2A, E, and A+E have been estimated to be 46, 6, 67, 42, and 79 cm^{-1}, respectively. It is worth noting that the vibrational excitation of level A or E considerably increases the tunneling splitting as compared to Δ''_0. The excitation of a combination state A+E also enhances tunneling. These results indicate that proton motion effectively couples with the normal coordinates of A and E. The excitation of $\nu_{13}(a_1)$ or ν_{14} (a_1) in the S_1 state of TRN considerably increases the tunneling splitting.[9] Both $\nu_{13}(a_1)$ and ν_{14} (a_1) have been suggested to involve the modulation of the O...O distance.[9] By analogy with TRN, we expect that A and E are low frequency modes involving the modulations of the O...O distance. Our preliminary *ab initio* calculations at RHF 3-21G level suggested that close similarities exist in the normal coordinates between A and ν_{14}, and in E and ν_{13}.[11] In contrast with the excitation of level A or E, the excitation of level B supresses tunneling significantly. These results may provide insights into multi-dimensional character of proton tunneling in large molecules.

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