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Laser Fluorescence Excitation Spectrum of Jet-cooled 3-Isopropyltropolone. Proton Tunneling in the S_1 State

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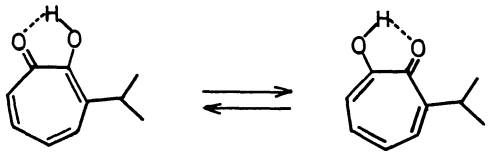
Laser excited fluorescence spectra and dispersed fluorescence spectra of 3-isopropyltropolone have been measured in ultracold gas phase by a supersonic expansion. The tunneling splittings in the zero-point level of the S_1 state have been determined to be 58 and 14 cm^{-1} for normal and deuterated species, respectively.

Intramolecular hydrogen bonds of tropolone have been of considerable interests in respect of proton tunneling.[1-7] In contrast with numerous information on the proton tunneling of tropolone, very little is known about tropolone derivatives. The IR and Raman studies by Ikegami[8] suggested that 3-isopropyltropolone (α-thujaplicin) has two tautomeric forms:



(1)

However, to our knowledge, no direct evidence for the occurrence of the proton tunneling in 3-isopropyltropolone has been reported. In this work, we have measured laser fluorescence excitation spectra of normal 3-isopropyltropolone (3-IPT-h) and its OD derivative (3-IPT-d) in order to study the effect of asymmetric substitution of the isopropyl group on the tunneling dynamics.

Laser fluorescence excitation spectra were measured for molecular jet samples of 3-IPT-h and 3-IPT-d using He as a carrier gas. Dispersed fluorescence spectra

were also measured for 3-IPT-h. 3-IPT-h was synthesized by using a procedure described in literature.[9] 3-IPT-d was prepared by deuteration of D_2O vapor in the nozzle housing. The sample was placed in the housing of a pulsed nozzle with an orifice of 0.4 mm diameter and heated to 50 °C to increase the vapor pressure. The stagnation pressure was between 0.2 and 0.4 atm. The S_1-S_0 (π, π^*) transitions of 3-IPT-h and 3-IPT-d were excited by a nitrogen-laser-pumped dye laser source (Molectron UV22-DL14P) and total fluorescence was detected with a Hamamatsu R955 photomultiplier and averaged with a boxcar integrator (NF BX-531). Dispersed fluorescence spectra were measured by using a 0.5 m monochromator (Baush & Lomb).

The tunneling leads to splitting of the zero-point-level and other zeroth-order levels between the barrier into symmetric and asymmetric components, which are usually designated with 0^+ and 0^-. In a symmetric double-minimum potential, only the $0^+ \leftrightarrow 0^+(0_+^+)$ and $0^- \leftrightarrow 0^-(0_-^-)$ transitions are allowed. On the other hand, in the case of an asymmetric substitution, vibronic transitions involving double-minimum potential energy curve will be the 0_+^+ and 0_+^- transitions as depicted in Fig. 1. When the 0^- level of S_0 is thermally accessible, the 0_-^- and 0_-^+ transitions are also possible.

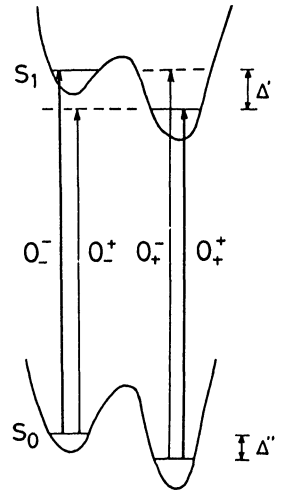


Fig. 1. Schematic diagram of vibronic transitions involving asymmetric double-minimum potential energy curve.

Typical exciation spectra of 3-IPT-h and 3-IPT-d are shown in Figs. 2a and 2b. The electronic origins for 3-IPT-h and 3-IPT-d have been measured to be 26920 and 26979 cm^{-1}, respectively. A number of weak bands are detected in Fig. 2a. Among them a prominent band appears at 58 cm^{-1} from the origin band. This band disappeared upon the deuteration, and a new prominent band has been detected at 14 cm^{-1} from the origin band as indicated in Fig. 2b. The intensities of the 58 and 14 cm^{-1} bands relative to the origin band were independent of the stagnation pressure and the downstream distance, suggesting that these bands originate from the vibrational ground state. On the basis of these findings, the 58 and 14 cm^{-1} bands could be assigned to the 0_+^- transitions in 3-IPT-h and 3-IPT-d, respectively. The frequency difference between the 0_+^+ and 0_+^- transitions immediately corresponds to the tunneling splitting Δ' in S_1. A significant decrease in the Δ' value upon the deuteration is consistent with the results of tropolone,[4,5] 9-hydroxyphenalenone, and 9-hydroxyphenalenone derivatives.[10-13]

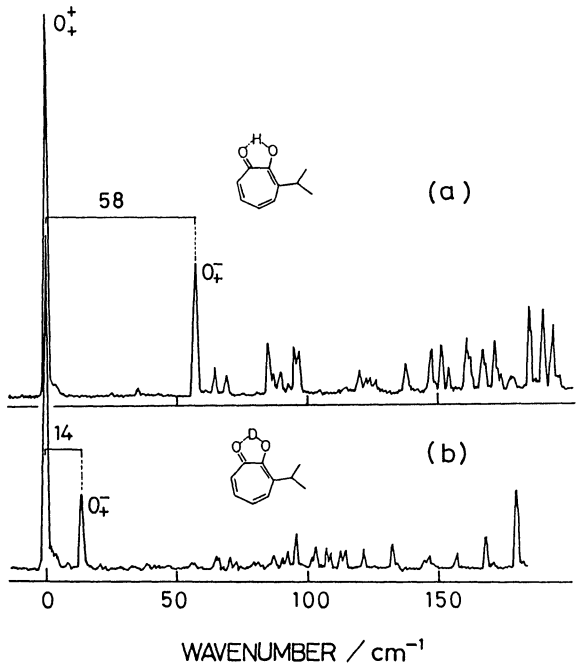


Fig. 2. Laser excitation spectra of jet-cooled (a) 3-IPT-h and (b) 3-IPT-d in the S_1-S_0 region.

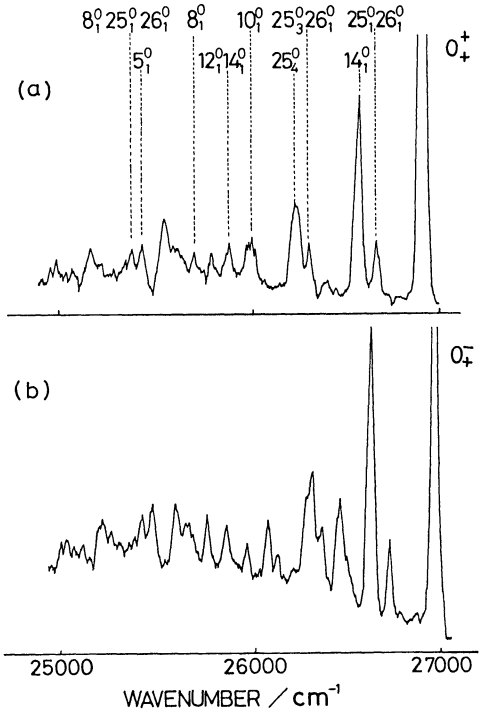


Fig. 3. Dispersed fluorescence spectrum obtained by the excitation of (a) the 0_+^+ band and (b) the 0_+^- band.

Dispersed fluorescence spectra have been measured for 3-IPT-h, in order to confirm the above assignment. In Fig. 3 are shown the dispersed fluorescence spectra obtained by the excitation of the 0_+^+ and 0_+^- transitions. Some of the observed vibronic bands have been assigned on the basis of the IR and Raman data of 3-IPT-h[8] and the assignment of the vibrational modes in single vibronic level fluorescence spectra of tropolone in the vapor phase.[3] It should be noted that the fluorescence spectrum originating from the 0^- level is very similar to that from the 0^+ level, although the positions of the vibronic bands originating from the 0^- level shift from those of the 0^+ level by 58 cm^{-1}. This result supports the validity of the assignment of the 0_+^- transition in the excitation spectrum of 3-IPT-h. In order to determine the Δ'' value, we attempted to observe the $0^+ \rightarrow 0^+$ and $0^+ \rightarrow 0^-$ transitions by measuring more high-resolution fluorescence spectra than those in Fig. 3. However, these transitions could not be separately detected. We have estimated an upper limit to be 10 cm^{-1} for the Δ'' value from the spectral resolution. The Δ' value is much larger than the Δ'' value, suggesting that the barrier to tunneling is substantially lower in the excited state.

The tunneling splittings of 3-IPT-h (Δ'(h)=58 cm^{-1}) and 3-IPT-d (Δ'(d)=14 cm^{-1} are significantly larger than those of tropolone (Δ'(h)=19.6, Δ'(d)$\approx$2 cm^{-1}

).[5,7] The increase of the Δ' values in 3-IPT-h and 3-IPT-d suggests that the substitution of the isopropyl group induces an asymmetry in the potential minima of S_1. Asymmetry tends to localize the 0^+ and 0^- wave functions. According to Rossetti et al.[10] wave function localization becomes significant when the asymmetry introduced by a structual modification is comparable to the tunneling splitting in the absence of asymmetry. The intensity of the 0_+^- transition relative to the 0_+^- transition will depend on the degree of the localization in S_1 and S_0. The observation of relatively strong 0_+^- transition in the excitation spectrum of 3-IPT-h suggests that either the excited or ground state wave function is partially localized. It is expected that the wave function is partially localized in S_0 since the potential energy barrier in S_0 will be higher than that in S_1.

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