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Electronic Spectrum of Jet-Cooled Tropolone-3-d

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The $\tilde{A}^1B_1$-$\tilde{X}^1A_1$ laser fluorescence excitation spectrum of jet-cooled tropolone-3-d has been measured to investigate the effect of an unsymmetrical substitution of a deuterium on proton tunneling and the equilibrium geometry.

Electronic spectrum of tropolone (TRP) has been of considerable interests in respect to proton tunneling.[1-5] However, little is known about proton tunneling in TRP derivatives. Previously, we reported the electronic spectra of jet-cooled 3-, 4-, and 5-isopropyltropolones.[6] It has been found that the substitution of an isopropyl group on TRP affected the intramolecular hydrogen bond and the vibrational structure in the S_1 state significantly. In the fluorescence excitation spectra of isopropyltropolones, the vibrational structure was too complicated to provide assignment for individual vibrational levels. In this study, we have investigated the electronic spectrum of jet-cooled tropolone-3-d (3DTRP) to examine the effect of a very weak perturbation on proton tunneling and the equilibrium geometry in the vibrationally excited state through introducing a deuterium on the skeletal seven-membered ring of TRP.

Experimental apparatus used was essentially the same as that described previously.[4-6] 3DTRP was obtained by catalytic hydrogenation of 3-bromotropolone with deuterium.[7] 3DTRP was mounted in a nozzle housing, and heated to 50-60 °C by using a coiled heater to increase the vapor pressure. The $\tilde{A}^1B_1$-$\tilde{X}^1A_1$ transition of 3DTRP was excited by using a nitrogen-laser pumped dye laser source (Molectron UV22-DL14P). The fluorescence was detected with a photomultiplier (Hamamatsu R955) and averaged by utilizing a boxcar integrator (NF BX-531). Dispersed fluorescence spectrum was measured with a 0.75 m monochromator (Spex 1702).

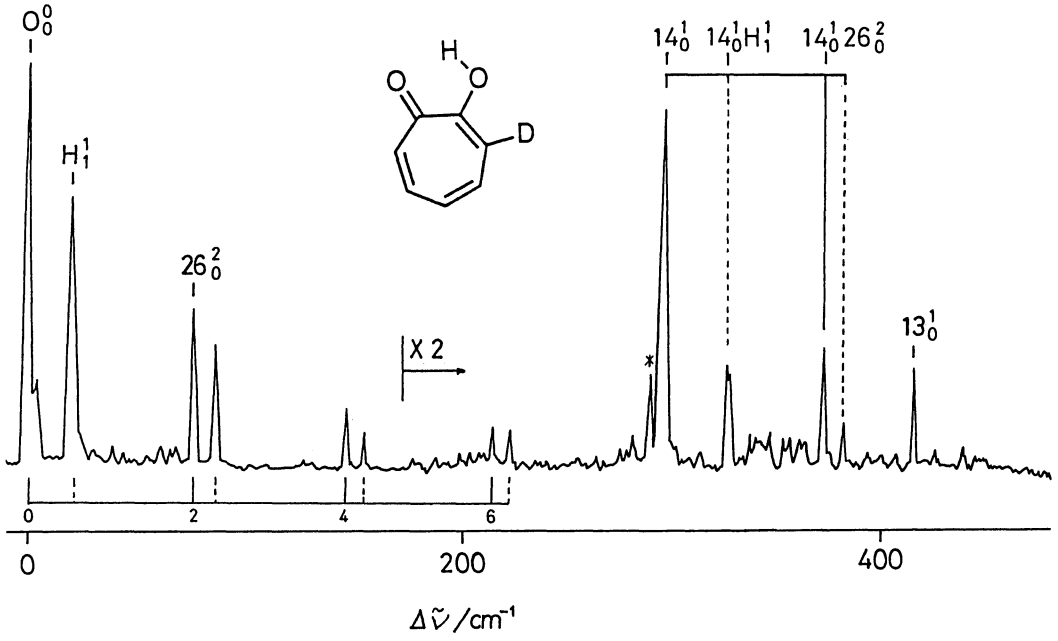

Fig. 1. Fluorescence excitation spectrum of jet-cooled 3DTRP. $\Delta\tilde{\nu} = \tilde{\nu} - \tilde{\nu}_0^0$. The stagnation pressure of He was 0.4 atm. The high-wavenumber tunneling doublet components are indicated by broken lines. The asterisk indicates band due to the hydrogen-bonded complex between 3DTRP and water involved in the sample and the nozzle housing as an impurity.

In Fig. 1 is shown a typical fluorescence excitation spectrum of 3DTRP. The vibrational assignment has been made by analogy with the fluorescence excitation spectrum of TRP and the measurement of the dispersed fluorescence spectrum.[4,5] The most prominent feature in Fig. 1 is that the intensities of the $25_0^1 26_0^n$ (n=1,3) and 25_0^2 bands are diminished remarkably, which have appeared more strongly in the excitation spectra of TRP[4,5] and tropolone-5-d (5DTRP). The $25_0^1 26_0^3$ band has disappeared almost completely in the fluorescence excitation spectrum of tropolone-4-d (4DTRP), although the $25_0^1 26_0^1$ and 25_0^2 bands have been identified. The results of 5DTRP and 4DTRP will be described in detail elsewhere.[8] It was suggested that a strong Duschinsky effect[9] exists between the $\nu_{25}(b_1)$ and $\nu_{26}(b_1)$ out-of-plane bending modes in the electronic spectrum of TRP.[1] The normal coordinates of ν'_{25} has been considered to be very similar to ν''_{26}. A significant decrease of the intensities of the bands involving ν'_{25} in Fig. 1 will be due to lowering of the symmetry of ν'_{25} and/or ν'_{26} from b_1 in the C_{2v} point group to a" in the C_s point group. This implies that the Duschinsky effect is very sensitive to the symmetry of the vibrational mode. To our knowledge, such an unsymmetrical effect due to a weak perturbation on the Duschinsky effect has not been reported.

The wavenumbers and the tunneling doublet separation $|\Delta'_v - \Delta''_0|$ for

several vibrational levels of 3DTRP are summarized in Table 1, where Δ'_v and Δ''_0 are the tunneling doublet splitting for the v level in the $\tilde{A}^1B_1$ state and that for the $\tilde{X}^1A_1$ state, respectively. We suggested that the $\nu'_{13}(a_1)$ and $\nu'_{14}(a_1)$ modes are very important to understand the proton tunneling dynamics.[4,5] The vibrational fundamental for ν'_{13} (ω'_{13}=412 cm^{-1}) in 3DTRP deviates considerably from that of TRP (ω'_{13}=421 cm^{-1}), whereas ω'_{14}=298 cm^{-1} for 3DTRP is very similar to a value of ω'_{14}=301 cm^{-1} for TRP. As defined previously,[10] $\omega' = \omega'_L + (\Delta'_v - \Delta'_0)/2$, where ω'_L is the frequency of the low-wavenumber tunneling doublet component, and Δ'_0 is the tunneling doublet splitting for the zero-point level in the $\tilde{A}^1B_1$ state. A very small change in ω'_{14} between 3DTRP and TRP is inconsistent with the previous assignment of ν'_{14} as the ring deformation mode.[3] The $^{18}O/^{16}O$ isotope effect on the vibrational fundamental and the tunneling splitting has been found to be relatively large for ν'_{14}. Combining with these results, we reassigned ν'_{14} as the CCO bending mode. On the other hand, ν'_{13} must include the motion of the atoms in the seven-membered ring.

The tunneling doublet separation for 3DTRP is slightly larger than that for TRP. The potential energy function along the proton transfer coordinate has been described by using a symmetrical double-minimum potential energy well.[1-5] The increase of the tunneling doublet separation in 3DTRP suggests that the potential function of 3DTRP is slightly unsymmetrical in the $\tilde{A}^1B_1$ and/or $\tilde{X}^1A_1$ states. In the excitation spectrum of TRP, the 13^1_0 and 14^1_0 bands show very larger tunneling doublet separations than that for the zero-point level.[4] It is worth noting that the high-wavenumber tunneling doublet component (H^1_1) for 13^1_0 has not been detected in Fig. 1, probably due to remarkable decrease of the tunneling doublet splitting in $\tilde{A}^1B_1$ of 3DTRP. In contrast with ν'_{13}, Δ'_0 and Δ'_{14} changed very slightly upon the deuteration,[11] where we approximated $|\Delta'_v - \Delta''_0| \approx \Delta'_v$ since Δ''_0 is expected to be very small ($\leq$1 cm^{-1}) by analogy with TRP.[3] A significant decrease of Δ'_{13} will be

Table 1. Vibrational assignment in the fluorescence excitation spectrum of 3DTRP [a]

Wavenumber	Assignment	$\Delta'_v - \Delta''_0$ [b]
27033	0^0_0	21 (19)
27054	H^1_1	21 (19)
27108	26^2_0	10 (7)
27118	$26^2_0H^1_1$	10 (7)
27177	26^4_0	9 (5)
27186	$26^4_0H^1_1$	9 (5)
27245	26^6_0	8 (4)
27254	$26^6_0H^1_1$	8 (4)
27321	complex	
27327	14^1_0	29 (30)
27356	$14^1_0H^1_1$	29 (30)
27403	$14^1_026^2_0$	9 (4)
27412	$14^1_026^2_0H^1_1$	9 (4)
27445	13^1_0	$\leq$1 (32)

a) Units are in cm^{-1}. b) The value for TRP is shown in parentheses.[4]

ascribed to lowering of the symmetry from a_1 to a'. When ν'_{13} is excited, the positions of the two oxygen atoms in the O-H-O chelate ring are expected to be not equivalent before and after the proton transfer, which will increase the effective barrier height to tunneling.

In contrast with the 13_0^1 band, the tunneling doublet separations for the 26_0^n(n=2,4,6) bands are larger in 3DTRP than the corresponding values for TRP, 4DTRP, and 5DTRP.[8] The tunneling doublet separations for the 26_0^n progression decrease with increasing the vibrational quantum number. Redington et al.[3] discussed about the tunneling doublet separations for the 26_0^n progression detected in TRP spectrum in terms of the geometry of the vibrationally excited molecule. They suggested that the barrier height to tunneling for ν'_{26} increases due to the deviation of the molecular geometry from almost completely planar structure in the zero-point level. The increase of the tunneling doublet separations for the 26_0^n progression in 3DTRP implies that the geometry of the 3DTRP molecule is different from that of TRP, when ν'_{26} is excited.

Thus, we have demonstrated that the unsymmetrical substitution of a deuterium on the seven-membered ring of TRP influences the proton tunneling process and the equilibrium geometry of TRP significantly.

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