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The Electronic Spectra of Jet-Cooled Tropolone. Vibrational Assignment for the $\tilde{A}^1B_2$-$\tilde{X}^1A_1$ Transition

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The laser fluorescence excitation spectrum and the single vibronic level fluorescence spectra from the $\tilde{A}^1B_2$ state of tropolone have been measured in a supersonic free jet. Some vibronic bands observed in the region of 270—450 cm^{-1} from the 0^0_0 band have been assigned. A tunneling doublet separation for the ν'_{14} in-plane ring deformation mode has been measured to be 30 cm^{-1}, which is significantly larger than 19 cm^{-1} for that for the zero-point level, suggesting that the average geometry of the ν'_{14} mode deviates significantly from that of the zero-point level.

A tropolone molecule possesses an intramolecular hydrogen bond, and the hydroxyl proton tunnels from one oxygen atom to the other. Spectroscopic studies indicate that tropolone exhibits a double-minimum potential energy function along the proton tunneling coordinate.[1—7] Tunneling doublings have been detected in many vibronic bands in the absorption spectra[1,2,6] and the laser fluorescence excitation spectra.[4,5,7] The separation of tunneling doublings involves information on the interaction between the normal mode and the proton tunneling coordinate. On the other hand, these tunneling doublings make it difficult to assign vibronic bands.

The assignment for the vibronic transitions between the $\tilde{A}^1B_2$ and $\tilde{X}^1A_1$ states has long been a problem. Recently, Alves et al.[6] indicated that some of the complexity in vibrational bands around the 0^0_0 band is due to strong Duschinsky effect[8] involving the two lowest b_1 modes ν_{26} and ν_{25}. Very recently, Redington et al.[7] observed the laser fluorescence excitation spectrum of jet-cooled tropolone, and newly assigned about thirty vibronic bands in the region of 270—450 cm^{-1} from the 0^0_0 band. We have measured single vibronic level fluorescence (SVLF) spectra from about twenty vibronic bands in the $\tilde{A}^1B_2$ state of tropolone in order to confirm the previous assignment, since Redington et al.[7] observed no SVLF spectra. It has been found that previous assignments for vibronic bands involving the ν'_{39} and ν'_{14} modes and $25^n_0 26^{2n+1}_0$ (n=1—4) and 26^n_0 (n=9—14) progressions are invalid. New assignments have been proposed for some vibronic bands.

Experimental

Experimental apparatus used is essentially the same as that used for the observation of the electronic spectra of 3-isopropyltropolone.[9] Briefly, laser fluorescence excitation spectrum was measured for jet-cooled sample of tropolone in He as a carrier gas. Tropolone was commercially available and used without further purication. The sample was excited by a nitrogen laser pumped dye laser source (Molectron UV22 and DL14P), and total fluorescence was detected with a Hamamatsu R955 photomultiplier and averaged with a boxcar integrator (NF BX-531). SVLF spectra were measured with a 0.75 m monochromator (Spex 1702). The sample was placed in the housing of a pulsed nozzle with an orifice of 0.4 mm diameter and heated to about 70 °C to increase the vapor pressure.

Results and Discussion

In Fig. 1 is shown a typical laser excitation spectrum of tropolone, which is essentially the same as that reported previously.[5,7] The band origin was identified at 27018 cm^{-1}.

Figure 2 shows the SVLF spectrum obtained by the excitation of band ***b*** with $\Delta\nu(\nu-0^0_0)$=293 cm^{-1}, which had been assigned as 39^2_0 by Redington et al.[7] They concluded that the $\Delta\nu$=230.8 cm^{-1} band observed in the absorption spectrum of Alves et al.[6] was $14^1_0 39^1_1$. On the basis of this assignment, $\nu''_{39}(b_1)$ was estimated to be 147 cm^{-1}. However, as is clear from Fig. 2, no $2\nu''_{39}$ band is detected in the SVLF spectrum and dominant bands are combinations of ν''_{25} and ν''_{26}. This suggests that the corresponding upper state involves ν'_{25} and/or ν'_{26}. We have assigned band ***b*** as $25^1_0 26^3_0$ for the reason that $\nu'_{25}+3\nu'_{26}\simeq$289 cm^{-1} is close to 293 cm^{-1}.

Redington et al.[7] had assigned the 295.82 and 326.41 cm^{-1} bands as $39^2_0H^1_1$ and 26^{10}_0 respectively. These assignments contradict to the result of SVLF spectra, which are shown in Figs. 3a and 3b. Figure 3a has been obtained by the excitation of band ***c*** at 296 cm^{-1}, which shows a long progression in $\nu''_{14}(a_1)$. This clearly indicates that the corresponding upper state is 14^1. A similar spectrum has been obtained by the excitation of band ***d*** at 326 cm^{-1} as is shown in Fig. 3b, and this band has been assigned to $14^1_0H^1_1$, where H^1_1 designates the high wavenumber tunneling doublet component.[1]

It is worth noting that the separation between 14^1_0 and $14^1_0H^1_1$ (30 cm^{-1}) is much larger than 19 cm^{-1} for the separation between 0^0_0 and H^1_1. Since the tunneling splitting in the zero-point level of the ground state has been estimated to be very small ($\simeq$0.3 cm^{-1})[7] these separations nearly equal to the tunneling doublet splitting in the upper state. The increase in the tunneling splitting for the ν'_{14} mode from that for the

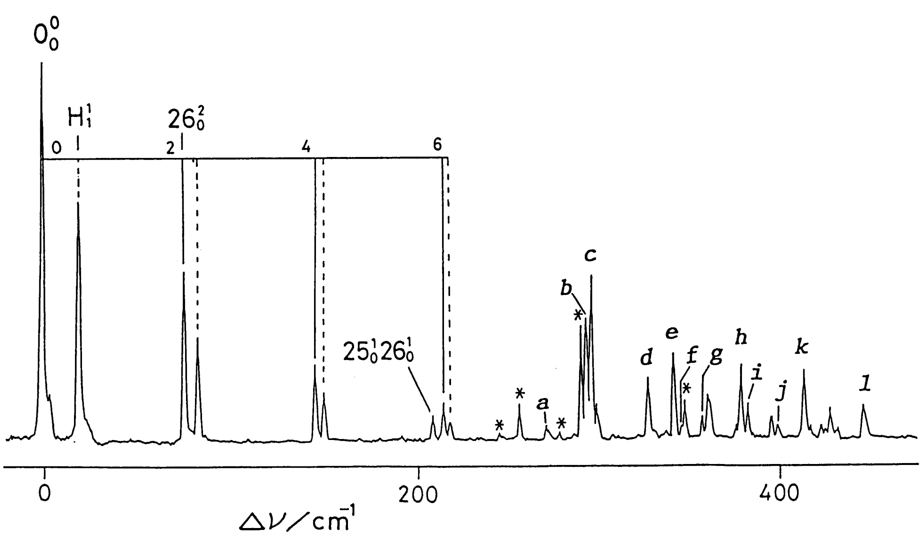

Fig. 1. Laser fluorescence excitation spectrum of tropolone. The stagnation pressure was 0.4 atm. SVLF spectra were measured for bands ***a***—***l***. The broken lines indicate high wavenumber tunneling doublet component. The asterisks indicate bands due to the hydrogen-bonded complex between tropolone and water.

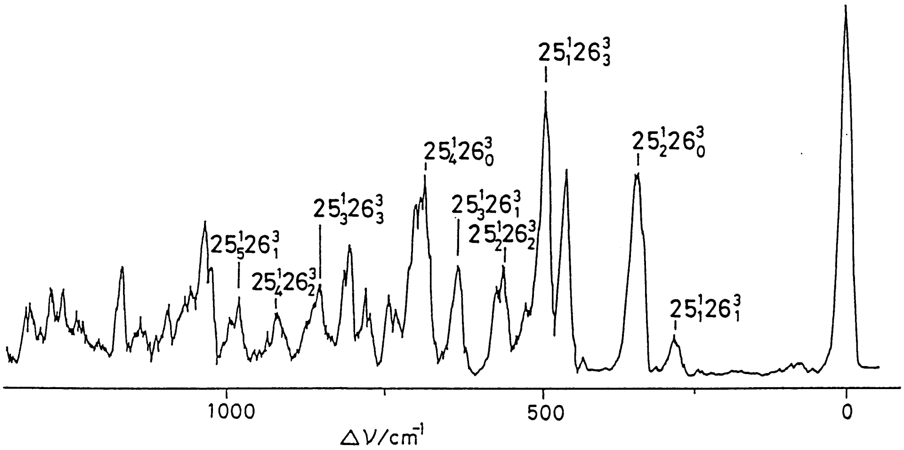

Fig. 2. Part of the SVLF spectrum obtained by the excitation of band ***b***.

zero-point level implies that the average geometry of ν'_{14} deviates significantly from that of the zero-point level. From the above result ν'_{14} is considered to be a C-C-O bending in the chelate moiety such that the O···O distance is modulated as suggested by Rossetti et al.[4] rather than a C-C-C bending in the seven-membered ring proposed by Redington and Redington.[3]

The SVLF spectra obtained by the excitation of bands ***h*** and ***i*** at 378 and 382 cm^{-1} show one and two quanta of ν''_{14} and various combinations of one and two quanta of ν''_{25} and ν''_{26}, which suggests that the upper state involves both the ν'_{14} and ν'_{26} modes or ν'_{14} and ν'_{25} modes. We have assigned band ***h*** as $14^1_0 26^2_0$, since the frequency $\nu'_{14}+2\nu'_{26}(\simeq 381\ \mathrm{cm}^{-1})$ nearly equals to 378 cm^{-1}. Similarly, band ***i*** has been assigned as $14^1_0 26^2_0 H^1_1$. These bands had been assigned as 14^1_0 and 26^{12}_0, respectively.[7] A long progression in ν''_{14} was observed in the SVLF spectrum obtained by the excita-

Table 1. Vibrational Assignment of the Fluorescence Excitation Spectrum of Tropolone

Band	$\Delta\nu/\mathrm{cm}^{-1}$	Assignment	
		This work	Redington et al.[a]
a	272	26^8_0	26^8_0
b	293	$25^1_0 26^3_0$	39^2_0
c	296	14^1_0	$39^2_0 H^1_1$
d	326	$14^1_0 H^1_1$	26^{10}_0
e	341	25^2_0	25^2_0
f	345	$25^2_0 H^1_1$	$25^2_0 H^1_1$
h	378	$14^1_0 26^2_0$	14^1_0
i	382	$14^1_0 26^2_0 H^1_1$	26^{12}_0
k	414	13^1_0	13^1_0
l	446	$13^1_0 H^1_1$	$13^1_0 H^1_1$

a) From Ref. 7.

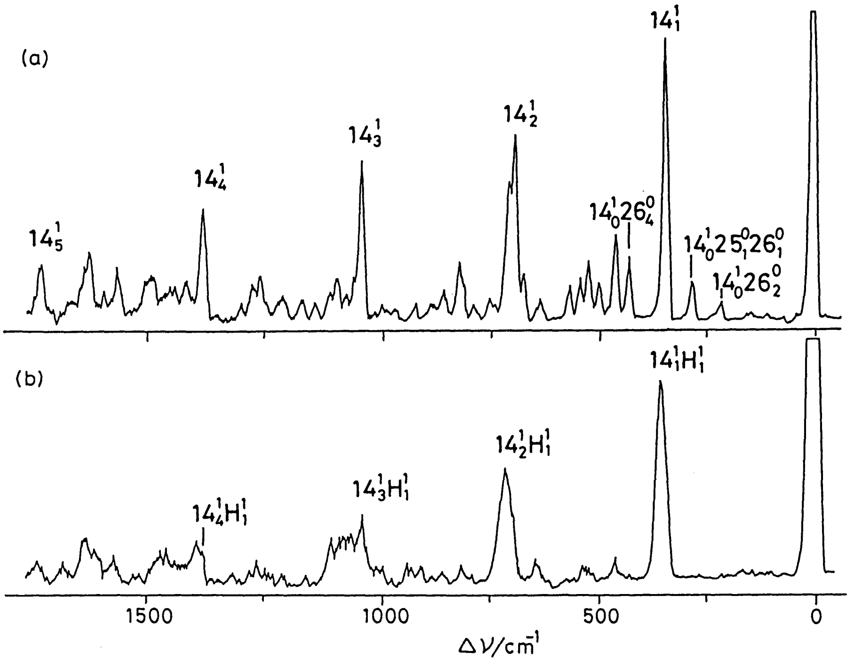

Fig. 3. Part of the SVLF spectra obtained by the excitation of bands *c* (a) and ***d*** (b).

tion of the $\Delta\nu=230.8\ \mathrm{cm}^{-1}$ band in the absorption spectrum.[6)] Since this band is not detected in Fig. 1, the 230.8 cm^{-1} band must be a hot band.

The ν''_{13} fundamental (438 cm^{-1}) has been observed in the SVLF spectra obtained by exciting into bands ***k*** and ***l*** at 415 and 447 cm^{-1}, which suggests that the transitions are from 13^1 and 13^1H^1. Therefore, bands ***k*** and ***l*** should be 13_0^1 and $13_0^1H_1^1$, respectively, which agree with previous assignments.[7)]

The 25_0^2 and $25_0^2H_1^1$ bands were identified by Redington et al.[7)] at 340.74 and 344.92 cm^{-1}, respectively. The SVLF spectra obtained by the excitation of bands ***e*** and ***f*** at 341 and 345 cm^{-1} show various combinations of one, two, three, and four quanta of ν''_{25} and ν''_{26}. This result is consistent with the previous assignments.[7)]

The SVLF spectra obtained by the excitation of bands ***g*** and ***j*** at 355 and 400 cm^{-1} show very low-frequency (65 cm^{-1}) unidentified vibration. Such a low-frequency band was observed in temperature dependent microwave spectrum of tropone.[10)] The 65 cm^{-1} vibration would be very low-frequency skeletal wag. The observation of the low-frequency vibration in the ground state suggests that corresponding low-frequency vibration is involved in vibronic bands in the upper state, although bands ***g*** and ***j*** were assigned as 26_0^{11} and $14_0^1H_1^1$, respectively.

In Table 1 are listed the vibronic bands assigned this work together with those assigned by Redington et al.[7)] Since the previous assignments of 26_0^{10}, and 26_0^{12}, $25_0^1 26_0^3$ are invalid, the assignments of 26_0^n(n=9,11,13,14) and $25_0^n 26_0^{n+2}$(n=5,7) are also dubious. Further study is needed to assign these bands.

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