TABLE II. Observed tunneling-rotation transitions of tropolone by FTMW.[a]

$0^- \leftarrow 0^+$	Obs.	O–C[b]	$\Delta\nu$[c]
$2_{1,1} \leftarrow 3_{2,2}$	17 861.439	0.018	0.582
$2_{1,2} \leftarrow 3_{2,1}$	15 080.416	0.014	0.704
$2_{2,0} \leftarrow 3_{3,1}$	14 221.663	0.003	0.611
$2_{2,1} \leftarrow 3_{3,0}$	13 974.973	0.001	0.623
$3_{1,2} \leftarrow 4_{2,3}$	16 112.189	0.019	0.995
$3_{2,1} \leftarrow 4_{3,2}$	11 923.651	0.003	2.536
$3_{2,2} \leftarrow 4_{3,1}$	10 733.132	0.004	2.668
$4_{1,4} \leftarrow 5_{0,5}$	17 892.035	0.000	0.749
$4_{0,4} \leftarrow 5_{1,5}$	17 726.264	0.005	0.632
$4_{2,3} \leftarrow 5_{1,4}$	17 033.723	−0.012	1.589
$4_{1,3} \leftarrow 5_{2,4}$	14 566.054	0.016	1.382
$4_{2,2} \leftarrow 5_{3,3}$	10 065.601	0.008	4.408
$5_{1,5} \leftarrow 6_{0,6}$	15 771.448	−0.004	1.683
$5_{0,5} \leftarrow 6_{1,6}$	15 713.895	0.002	1.218
$5_{2,4} \leftarrow 6_{1,5}$	14 272.929	−0.011	1.794
$5_{1,4} \leftarrow 6_{2,5}$	13 015.714	0.006	2.211
$6_{1,6} \leftarrow 7_{0,7}$	13 682.960	−0.009	0.624
$6_{0,6} \leftarrow 7_{1,7}$	13 666.187	−0.005	2.322
$6_{2,5} \leftarrow 7_{1,6}$	11 847.244	−0.011	2.499
$6_{1,5} \leftarrow 7_{2,6}$	11 299.012	0.002	4.102
$7_{1,7} \leftarrow 8_{0,8}$	11 610.548	−0.014	3.436
$7_{0,7} \leftarrow 8_{1,8}$	11 606.485	−0.012	5.099
$8_{3,6} \leftarrow 8_{4,5}$	17 748.931	−0.022	33.234

[a]In MHz unit. Tunneling-rotation transitions were analyzed together with pure rotational transitions listed in Tables I and III and so on.
[b]Observed minus calculated frequencies in MHz.
[c]Shift by the tunneling-rotation interaction, that is, the transition frequency calculated using the constants in Table IV minus that calculated with F set to zero and the other constants kept the same.

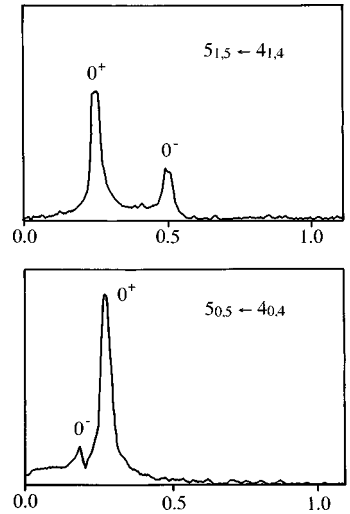

FIG. 6. The $5_{1,5}-4_{1,4}$ and $5_{0,5}-4_{0,4}$ rotational transitions in the ground state observed by FTMW spectroscopy, which are split into doublets, 0^+ and 0^-, due to proton tunneling. The abscissa represents the offset in MHz units from 11 343.785 (upper trace) and 11 423.385 (lower trace) MHz. The temperature describing the population ratio of the 0^+ and 0^- levels was calculated to be 0.99 and 1.23 K from the line intensities of the $5_{1,5}-4_{1,4}$, and $5_{0,5}-4_{0,4}$ transitions. The signals were recorded with 20 times integration.

$5_{1,5}-4_{1,4}$ and one-tenth for $5_{0,5}-4_{0,4}$, from which the temperature describing the population distribution between the 0^+ and 0^- levels was estimated to be 1.23 and 0.99 K for the $K_a=0$ and 1 stacks, respectively. It is noted that the 0^+ and 0^- components are associated with the nuclear spin weights of 6:10 in the case of $5_{1,5}-4_{1,4}$, whereas the weights are 10:6 in the case of $5_{0,5}-4_{0,4}$.

The line intensity of the tunneling-rotation transitions is much weaker than that of the pure rotational transitions. To record the tunneling-rotation spectrum shown in Fig. 5, a maximum microwave power of about 50 mW was used, which was roughly ten times larger than that used for the observation of the pure rotational spectra in Fig. 6. The integration of signal was 200 times for Fig. 5, but only 20 times for Fig. 6.

TABLE III. Observed pure rotational transitions of tropolone by FTMW.[a]

State	Transition	Obs.	O–C[b]	$\Delta\nu$[c]
0^+	$3_{2,1} \leftarrow 2_{2,0}$	8784.056	0.006	−0.449
0^-	$3_{2,1} \leftarrow 2_{2,0}$	8784.960	−0.002	0.537
0^+	$3_{2,2} \leftarrow 2_{2,1}$	8082.421	0.000	−0.394
0^-	$3_{2,2} \leftarrow 2_{2,1}$	8083.169	0.004	0.604
0^+	$5_{1,5} \leftarrow 4_{1,4}$	11 344.035	0.002	−0.062
0^-	$5_{1,5} \leftarrow 4_{1,4}$	11 344.280	−0.007	0.821
0^+	$5_{0,5} \leftarrow 4_{0,4}$	11 423.658	−0.001	−0.105
0^-	$5_{0,5} \leftarrow 4_{0,4}$	11 423.560	−0.023	0.513
0^+	$6_{1,5} \leftarrow 6_{1,6}$	10 736.576	−0.003	−0.155
0^-	$6_{1,5} \leftarrow 6_{1,6}$	10 738.897	−0.004	2.454
0^+	$9_{2,7} \leftarrow 9_{2,8}$	14 409.046	−0.028	15.343
0^-	$9_{2,7} \leftarrow 9_{2,8}$	14 411.987	−0.021	18.473

[a]In MHz unit.
[b]Observed minus calculated frequencies in MHz.
[c]Shift by the tunneling-rotation interaction, that is, the transition frequency calculated using the constants in Table IV minus that calculated with F set to zero and the other constants kept the same.

IV. ANALYSIS

The effective Hamiltonian used for the analysis consists of four terms,

$$H=H_{\rm tun}+H_{\rm rot}+H_{\rm cd}+H_{\rm int}. \tag{1}$$

The first term represents the energy of the tunneling motion; the difference between the 0^- and 0^+ states being equal to the tunneling splitting Δ_0. The second and third terms represent the rotational and centrifugal distortion energies,

$$H_{\rm rot}=AJ_a^2+BJ_b^2+CJ_c^2, \tag{2}$$

$$\begin{aligned}H_{\rm cd}=&-\Delta_J J^4-\Delta_{JK}J^2J_a^2-\Delta_K J_a^4-(\delta_J J^2+\delta_K J_a^2)\\&\times(J_b^2-J_c^2)-(J_b^2-J_c^2)(\delta_J J^2+\delta_K J_a^2).\end{aligned} \tag{3}$$

The last term in Eq. (1) represents the tunneling-rotation interaction, which connects the 0^+ and 0^- states,

$$\langle 0^+|H_{\rm int}|0^-\rangle=\langle 0^-|H_{\rm int}|0^+\rangle=F(J_aJ_b+J_bJ_a), \tag{4}$$

where F is a real constant representing the magnitude of the interaction, and the a and b axes are located in the molecular plane (Fig. 1). The particular form of the interaction term is a consequence of the choice of the molecule-fixed axes; they are not chosen to be coincident with the instantaneous principal axes, but they are chosen so that the angular momentum caused by the tunneling motion vanishes when viewed from this frame. The Hamiltonian with the interaction term in Eq. (4) has often been used in the analysis of microwave spectra of molecules with tunneling motion, e.g.,