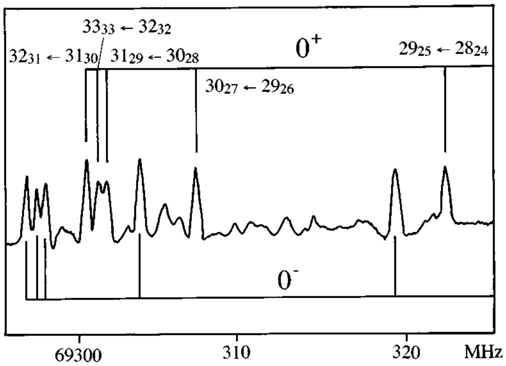


FIG. 3. Rotational transitions observed at around 69.3 GHz both for the $0^+$ and $0^-$ states. Asymmetry doubling is not resolved for these lines. The $J_{K_c} = 33_{33} - 32_{32}$ line, e.g., consists of the two unresolved asymmetry doublet components, $33_{0,33} - 32_{0,32}$ and $33_{1,33} - 32_{1,32}$.

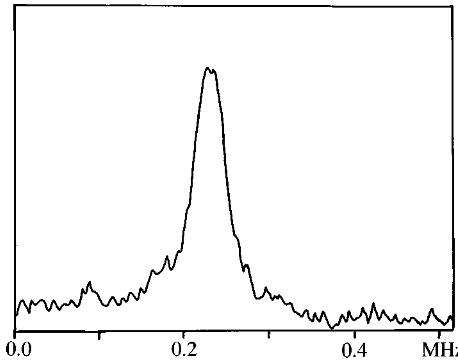


FIG. 5. The tunneling-rotation transition from the $0^+$, $3_{2,1}$ level to the $0^-$, $2_{1,2}$ level observed by FTMW spectroscopy. The abscissa represents the offset from 15 080.185 MHz. The signal was recorded with 200 times integration.

the asymmetry doubling was not resolved in this frequency region. Therefore, the $J_{K_c} = 33_{33} - 32_{32}$ line, e.g., consists of the two overlapping asymmetry doublet components, $33_{0,33} - 32_{0,32}$ and $33_{1,33} - 32_{1,32}$.

Figure 4 shows the group of lines with $2J - K_c = 18 \leftarrow 17$ at around 38.3 GHz, where the $16_{14} - 15_{13}$ transitions are split into asymmetry doublets. It is noted that the line intensity patterns of the asymmetry doublets are different for the $0^+$ and $0^-$ tunneling states. The higher-frequency component ($16_{3,14} - 15_{3,13}$) is stronger than the lower one ($16_{2,14} - 15_{2,13}$) in the $0^+$ state. On the contrary, in the $0^-$ state, the lower component is stronger than the higher one. The separation between the relevant lines in the $0^+$ and $0^-$ states is as narrow as 2 MHz in this frequency region.

Tropolone has two pairs of equivalent protons, because it has an effective $C_{2v}$ symmetry. According to the Fermi–Dirac statistics for protons, the spin weights are calculated to be 6 and 10 for rotational levels with even and odd $K_a$ values, for the $0^+$ state with a symmetric tunneling wave function. In contrast, the weight ratio is reversed to 10:6 for the $0^-$ state with an antisymmetric tunneling wave function. The observed line intensities agree well with the calculation, giving confirming evidence for their assignment to the $0^+$ and $0^-$ tunneling states.

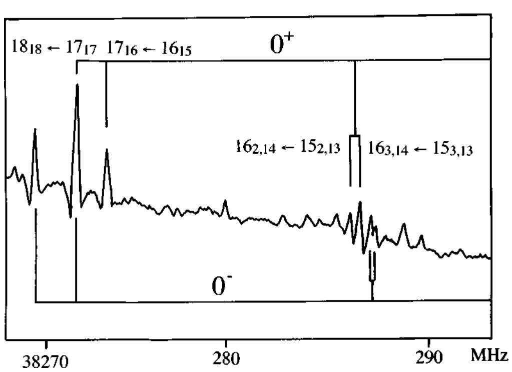


FIG. 4. Observed rotational lines at around 38.3 GHz for the $0^+$ and $0^-$ states. The line intensity patterns for the asymmetry doublets $16_{2,14} - 15_{2,13}$ and $16_{3,14} - 15_{3,13}$ are inverted for the $0^+$ and $0^-$ states, confirming the present assignment of the tunneling states.

## B. Tunneling-rotation spectrum

A preliminary analysis of the above data yielded the tunneling splitting $\Delta_0 = 29\,288 \pm 88$ MHz (or $0.976\,93 \pm 0.002\,94$ cm$^{-1}$). Frequencies of the tunneling-rotation transitions were then predictable with an accuracy of $\pm 100$ MHz using the molecular constants. However, careful searches for tunneling-rotation lines in the frequency regions around 30, 50, and 70 GHz with a conventional free-space type microwave spectrometer were unsuccessful.

The dipole moment of tropolone was estimated by transferring the dipole moment vector of the carbonyl moiety from tropone ($\mu = 4.3$ D)[21] and that of the hydroxyl moiety from phenol ($\mu_a = 0.13$ and $\mu_b = 1.26$ D).[22] By a simple vector addition method, the *a* component responsible for the pure rotational transitions was calculated to be 3.2 D, whereas the *b* component responsible for the tunneling-rotation transitions was calculated to be 0.7 D. Therefore, the tunneling-rotation transitions are expected to be much weaker than the rotational lines.

Further, such transitions might be obscured by strong and dense pure rotational lines belonging to the excited states of low frequency skeletal vibrations.[11] In such a case, the supersonic jet expansion technique will be effective to identify the weaker *b*-type lines buried among the congested rotational lines thanks to the spectral simplification caused by rotational as well as vibrational cooling.

Within the frequency region of 10.0–17.8 GHz, 22 tunneling-rotation signals were thus observed with the FTMW spectrometer and assigned to the *P*–branch lines in the *J*-range of 3–8. A *Q*-branch line, $8_{3,6} - 8_{4,5}$, was also observed, but other *Q*-branch lines and all *R*–branch lines are out of the accessible frequency region. The $2_{1,2} - 3_{2,1}$ spectrum observed at 15 080. 416 MHz is shown in Fig. 5, where the linewidth is about 350 kHz FWHM. The observed tunneling-rotation transitions are summarized in Table II with their assignments.

Pure rotational signals newly observed in the FTMW experiment, six each for the $0^+$ and $0^-$ states, are listed in Table III. The $5_{0,5} - 4_{0,4}$ and $5_{1,5} - 4_{1,4}$ rotational lines shown in Fig. 6 are split by 0.078 and $-0.245$ MHz, respectively, due to the proton tunneling. The intensity ratio of the $0^-$ components to the $0^+$ component is about one-third for