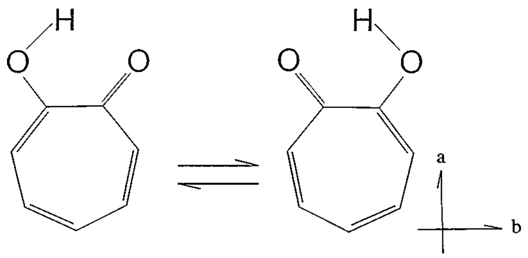


FIG. 1. Conformations of tropolone corresponding to two equivalent potential minima and approximate orientations of the molecule-fixed $a$ and $b$ axes.

conventional free-space absorption cell. More than 150 pure rotational lines were observed for each of the $0^+$ and $0^-$ states. Some transitions were observed to be heavily perturbed, the shift often amounting to several tens of MHz. The anomaly was well interpreted as caused by the tunneling-rotation interaction between the $0^+$ and $0^-$ states. A detailed analysis resulted in values of the proton tunneling splitting $\Delta_0$ in the ground state and the constant $F$, which is the coefficient in the tunneling-rotation interaction term, $F(J_aJ_b+J_bJ_b)$.

Observation of the tunneling-rotation transitions which directly connect the $0^+$ state with the $0^-$ state will not only confirm definitively the above interpretation of the rotational spectra, but also provide much more precise values of the tunneling splitting $\Delta_0$ and the interaction constant $F$. Thus, we also report the tunneling-rotation transitions between the $0^+$ and $0^-$ doublet components observed in a supersonic jet expansion by Fourier transform microwave (FTMW) spectroscopy. In total, 23 $b$-type $P$- and $Q$-branch lines were identified in the frequency region of 10–18 GHz, resulting in an improved set of molecular constants.

## II. EXPERIMENT

### A. Microwave spectrometer

A source modulation spectrometer equipped with a free-space absorption cell[16,17] at Kyushu University was used for the measurement of the pure rotational spectrum. The cell was a 1 m long Pyrex tube with an outer diameter of 10 cm, whose ends were sealed by Teflon convex lenses with a focal length of 35 cm. Millimeter-wave radiation in the range of 28–84 GHz was generated by Oki klystrons and detected by a silicon diode detector at room temperature. The source frequency was modulated by a 83 kHz bipolar square wave to a full width of about 300 kHz. The output of the silicon detector was demodulated in the $2f$ mode by a phase-sensitive detector (PSD) to give a second derivativelike line shape. A 5–10 MHz wide frequency region was swept at a repetition rate of 5 Hz, and the output of the PSD with a time constant of 1 ms was accumulated in a microcomputer for several hundred sweeps.

A sample of tropolone purchased from Aldrich was purified by sublimation before use. The sample was filled at about 25 mTorr in the cell, when the sample reservoir was slightly warmed up by a heater. The cell was heated up and pumped out carefully for days before the measurement. Otherwise, the signal deteriorated presumably because of water adsorbed on the surface of the glass tube.

### B. FTMW spectrometer

A Balle-Flygare-type FTMW spectrometer at the University of Tokyo, with the frequency coverage from 4 to 18 GHz, was used. Details of the apparatus have been reported previously.[18,19] The crystalline tropolone sample contained in a small vessel placed just upstream of the nozzle was heated to 30 °C, and the vapor was injected in a cavity with Ar at a stagnation pressure of 0.2 atm. The repetition rate of the pulsed valve was 15 Hz. The signal was accumulated for 100–200 shots at each frequency point. For the Stark effect measurement, a region downstream of the pulsed nozzle was flanked by a pair of $20\times 20\ \text{cm}^2$ wire-mesh electrodes separated by about 24 cm.[19]

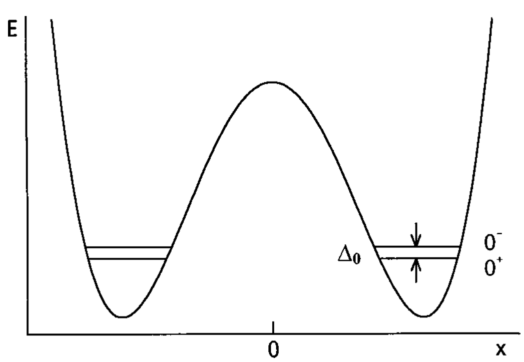


FIG. 2. Schematic diagram of the double minimum potential for the proton tunneling motion of tropolone (one-dimensional model). The lower and upper components of the tunneling doublet in the ground vibrational state are denoted by $0^+$ and $0^-$, respectively, and their energy separation by $\Delta_0$.

## III. OBSERVED SPECTRA

### A. Rotational spectrum

Microwave spectra of tropolone in the ground vibrational state consist of three groups of transitions. Transitions connecting rotational levels within the $0^+$ state constitute the first group, and the corresponding transitions within the $0^-$ state the second group. The third group is composed of transitions connecting rotational levels in the $0^+$ state with those in the $0^-$ state. We refer to the transitions belonging to the first and second groups as (pure) rotational transitions, and those in the third group as tunneling-rotation transitions.

Tropolone has components of the electric dipole moment along the $a$ and $b$ molecule-fixed axes (Fig. 1). The $a$ component $\mu_a$ is a symmetric function of $x$, which is the coordinate describing the tunneling motion (Fig. 2), whereas the $b$ component $\mu_b$ is an antisymmetric function. Since the eigenfunctions of the $0^+$ and $0^-$ states are symmetric and antisymmetric, respectively, with respect to $x$, the only nonvanishing matrix elements for $\mu_a$ are $\langle 0^+|\mu_a|0^+\rangle$ and $\langle 0^-|\mu_a|0^-\rangle$, whereas those for $\mu_b$ are $\langle 0^+|\mu_b|0^-\rangle$ and $\langle 0^-|\mu_b|0^+\rangle$. The elements $\langle 0^+|\mu_a|0^+\rangle$ and $\langle 0^-|\mu_a|0^-\rangle$ give rise to pure rotational transitions within the $0^+$ and $0^-$ states, respectively; therefore, these transitions obey $a$-type dipole selection rules ($\Delta J=0$ or $\pm 1$, $\Delta K_a=\text{even}$, and $\Delta K_c=\text{odd}$). In contrast, tunneling-rotation transitions are caused