Determination of the proton tunneling splitting of tropolone in the ground state by microwave spectroscopy

Keiichi Tanaka,[a),b)] Hiroaki Honjo, and Takehiko Tanaka
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812-8581, Japan

Hiroshi Kohguchi,[b)] Yasuhiro Ohshima,[c)] and Yasuki Endo
Department of Pure and Applied Sciences, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguroku, Tokyo 153-8902, Japan

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Rotational spectra of tropolone in the ground vibronic state were measured by microwave spectroscopy. Due to the proton tunneling motion, the ground state is split into a doublet, of which the lower and upper components are denoted by 0^+ and 0^-, respectively. In the frequency region 28–84 GHz, more than 150 pure rotational transitions obeying *a*-type selection rules were observed for each of the 0^+ and 0^- states. Additionally, tunneling-rotation transitions connecting the lower (0^+) and upper (0^-) components of the tunneling doublet were observed by pulsed Fourier transform microwave spectroscopy. Twenty-three *P*- and *Q*-branch lines were observed in the frequency region of 10–18 GHz, and analyzed combined with the pure rotational transitions for each of the 0^+ and 0^- states. The proton tunneling splitting in the ground state, $\Delta_0 = 29\,193.788 \pm 0.026$ MHz, and the tunneling-rotation interaction constant $F = 16.456 \pm 0.015$ MHz, were determined, as well as the rotational and centrifugal distortion constants. The dipole moment along the *a* axis, responsible for the rotational transitions, was determined to be 3.428 ± 0.050 and 3.438 ± 0.050 D for the 0^+ and 0^- states, respectively.
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I. INTRODUCTION

Tropolone, a seven-membered-ring molecule, is of great interest with respect to the intramolecular proton transfer between the two oxygen atoms (Fig. 1). The proton transfer is governed by a double minimum potential whose barrier is low enough to allow the proton to tunnel (Fig. 2). The tunneling effect produces a splitting of each vibrational state into a doublet. Hereafter, the lower and upper components of the doublet in the ground vibrational state are denoted by 0^+ and 0^-, respectively. The energy separation between the 0^+ and 0^- levels is designated by Δ_0 and the corresponding value for the first excited state of the OH stretching vibration by Δ_1.

Proton tunneling in tropolone has been extensively studied by a variety of experimental[1–11] as well as theoretical[12–15] means. Redington and Redington[3] reported matrix-isolation infrared spectra, derived the tunneling splitting Δ_0 in the ground state as 2.2 cm^{-1} for the normal species and 3.0 cm^{-1} for the deuterated species, and estimated the barrier of the double minimum potential to be less than 5600 cm^{-1} from the splitting observed in the OD stretch band of the deuterated species. An NMR experiment by Jackman *et al.*[4] suggested that the tunneling splitting Δ_0 in tropolone-*d* is less than 0.17 cm^{-1}. Redington *et al.*[6] observed jet-cooled fluorescence excitation spectra for the $S_1 \leftarrow S_0$ electronic band of the normal species and concluded that the tunneling splitting Δ_0 in the ground state was at most about 0.3 cm^{-1}, from the fact that the tunneling doublet separations observed in the 26_0^v progression decrease to become unresolvable and that no tunneling doublets are resolved in the $25_0^1 26_0^v$ progression.

Frost *et al.*[7] measured fluorescence-dip infrared (FDIR) spectra of jet-cooled tropolone. Two sharp FDIR peaks observed at 3134.9 and 3133.9 cm^{-1} were assigned to the transitions from the 0^+ and 0^- levels to one of the doublet components in the excited state of the ν_1 (OH stretch) vibration, the difference, 1.0 ± 0.4 cm^{-1}, corresponding to the tunneling splitting Δ_0 in the ground state. However, the FDIR peaks corresponding to transitions to the other component were not definitely identified. Very broad bands located about 12 cm^{-1} below the sharp peaks were tentatively attributed to those transitions, suggesting that the tunneling splitting Δ_1 in the ν_1 excited state is 12 cm^{-1}. This Δ_1 value is far smaller than the value of 220 cm^{-1} previously derived from infrared absorption spectra.[3,8] For tropolone-*d*, the neon matrix study[3] gave $\Delta_1 + \Delta_0 = 18.9$ cm^{-1}. The tunneling splitting in the ground state, together with that in the OH (OD) stretch state, is essential to determine the potential surface for the proton tunneling. Unfortunately, the reported values are rather inconsistent.

In the present study, we investigated tropolone in the ground vibronic state by microwave spectroscopy with a

[a]Author to whom correspondence should be addressed; electronic mail: tanakscc@mbox.nc.kyushu-u.ac.jp
[b]Present address: Institute for Molecular Science Myodaiji, Okazaki 444-8585, Japan.
[c]Present address: Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606-01, Japan.

