

understood that the evaluated $F(x_{\min})$ value is very sensitive to the change in the equilibrium geometry. A third calculation based on a considerably different equilibrium structure gave $F(x_{\min}) = -48.3$ MHz. We may conclude from these results that the experimentally obtained value $F = 16.456$ MHz lies in an acceptable range of magnitude. It seems probable that the proton transfer occurs along a curved path. However, calculations based on models with nonlinear trajectories would not change the conclusion about the F value.

Finally, the accurate and reliable value of Δ_0 derived from the present study is certainly a very important piece of information for the experimental determination of the potential barrier separating the two equivalent minima. Of course, the Δ_0 value alone is not sufficient for this purpose. Supposing that we can use the one-dimensional model, consider the Schrödinger equation in Eq. (13). Energy eigenvalues depend on the constant K as well as on the potential function. Even if we assume a potential function of the simplest type, for example, $U(x) = c_1x^4 - c_2x^2$, we need at least two parameters to express it. Therefore, estimation of a crude potential function requires three or more experimentally determined energy intervals, one of which can be Δ_0 . In this context, it is very important to measure the transition to the first excited state of the OH stretching vibration and the tunneling splitting Δ_1 in this state. Frost *et al.*⁷ claimed that they observed the transition to one of the doublet components in the OH stretch state, but their Δ_1 value seems rather unreliable.

The present experiment yielded precise values of the rotational constants, their differences between the 0^+ and 0^- states, and the F constant. However, they would be of little use for the determination of the potential, because they are more strongly dependent on the geometrical model rather than the potential model.

Considerable evidence has been accumulated for the multidimensionality of the potential governing the tunneling motion in the S_1 electronic excited state.^{6,9,13-15} It is probable that this is also the case for the ground electronic state. Thus, the determination of the potential function will require measurement of dependences of the tunneling splitting on the various vibrationally excited states.

VI. CONCLUSIONS

Pure-rotational spectra of tropolone in the ground vibronic state were measured by microwave spectroscopy. Tunneling-rotation transitions connecting the lower (0^+) and upper (0^-) components of the proton tunneling doublet in the ground state were observed by pulsed Fourier transform microwave spectroscopy. 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 tunneling-rotation interaction constant was found to be reasonable in magnitude by a simple one-dimensional model for the proton tunneling motion. The molecule was confirmed to be planar in the ground state although it has a negative inertial defect. 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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- ¹A. C. P. Alves and J. M. Hollas, *Mol. Phys.* **23**, 927 (1972).
- ²A. C. P. Alves and J. M. Hollas, *Mol. Phys.* **25**, 1305 (1973).
- ³R. L. Redington and T. E. Redington, *J. Mol. Spectrosc.* **78**, 229 (1979).
- ⁴L. M. Jackman, J. C. Trewella, and R. C. Haddon, *J. Am. Chem. Soc.* **102**, 2519 (1980).
- ⁵Y. Tomioka, M. Ito, and N. Mikami, *J. Phys. Chem.* **87**, 4401 (1983).
- ⁶R. L. Redington, Y. Chen, G. J. Scherer, and R. W. Field, *J. Chem. Phys.* **88**, 627 (1988).
- ⁷R. K. Frost, F. C. Hagemester, C. A. Arrington, and T. S. Zwier, *J. Chem. Phys.* **105**, 2595 (1996).
- ⁸Y. Ikegami, *Bull. Chem. Soc. Jpn.* **34**, 91 (1961).
- ⁹H. Sekiya, Y. Nagashima, and Y. Nishimura, *J. Chem. Phys.* **92**, 5761 (1990).
- ¹⁰H. Sekiya, Y. Nagashima, T. Tsuji, Y. Nishimura, A. Mori, and H. Takeshita, *J. Phys. Chem.* **95**, 10,311 (1991).
- ¹¹A. C. P. Alves, J. M. Hollas, H. Musa, and T. Ridley, *J. Mol. Spectrosc.* **109**, 99 (1985).
- ¹²R. L. Redington and C. W. Bock, *J. Phys. Chem.* **95**, 10,284 (1991).
- ¹³M. V. Vener, S. Scheiner, and N. D. Sokolov, *J. Chem. Phys.* **101**, 9755 (1994).
- ¹⁴S. Takada and H. Nakamura, *J. Chem. Phys.* **102**, 3977 (1995).
- ¹⁵J. J. Paz, M. Moreno, and J. M. Lluch, *J. Chem. Phys.* **103**, 353 (1995).
- ¹⁶K. Tanaka, T. Okabayashi, and T. Tanaka, *J. Mol. Spectrosc.* **132**, 467 (1988).
- ¹⁷T. Tanaka, K. Kato, T. Okabayashi, and K. Tanaka, *Rev. Sci. Instrum.* **60**, 104 (1988).
- ¹⁸Y. Hirahara, Y. Ohshima, and Y. Endo, *J. Chem. Phys.* **101**, 7342 (1994).
- ¹⁹M. Iida, Y. Ohshima, and Y. Endo, *J. Phys. Chem.* **97**, 357 (1992).
- ²⁰See AIP Document No. PAPS JCPSA6-110-011904 for 8 pages of a table with the assigned microwave transition frequencies of tropolone in the ground vibrational state. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 500 Sunnyside Boulevard, Woodbury, NY 11797-2999. Fax: 516-576-2223, e-mail: paps@aip.org. The price is \$1.50 for each microfiche (98 pages) or \$5.00 for photocopies of up to 30 pages, and \$0.15 for each additional page over 30 pages. Air mail additional. Make checks payable to the American Institute of Physics.
- ²¹A. D. Giacomo and C. P. Smith, *J. Am. Chem. Soc.* **74**, 4411 (1952).
- ²²T. Pedersen, N. W. Larsen, and L. Nygaard, *J. Mol. Struct.* **4**, 59 (1969).
- ²³W. F. Rowe, R. W. Duerst, and E. B. Wilson, *J. Am. Chem. Soc.* **98**, 4021 (1976).
- ²⁴S. L. Baughcum, R. W. Duerst, W. F. Rowe, Z. Smith, and E. B. Wilson, *J. Am. Chem. Soc.* **103**, 6296 (1981).
- ²⁵S. L. Baughcum, Z. Smith, E. B. Wilson, and R. W. Duerst, *J. Am. Chem. Soc.* **106**, 2260 (1984).
- ²⁶P. Turner, S. L. Baughcum, S. L. Coy, and Z. Smith, *J. Am. Chem. Soc.* **106**, 2265 (1984).
- ²⁷D. W. Firth, K. Beyer, M. A. Dvorak, S. W. Reeve, A. Grushow, and K. R. Leopold, *J. Chem. Phys.* **94**, 1812 (1991).
- ²⁸D. R. Johnson, F. J. Lovas, and W. H. Kirchhoff, *J. Phys. Chem. Ref. Data* **3**, 221 (1974).
- ²⁹K. Tanaka, H. Honjou, T. Tanaka, H. Kohguchi, Y. Ohshima, and Y. Endo, *The Ohio State University International Symposium on Molecular Spectroscopy*, 1992 Abstract FD09.