

TABLE V. Dipole moment of tropolone.<sup>a</sup>

Transition	0 <sup>+</sup>	0 <sup>-</sup>	Unit
3 <sub>2,1</sub> ←2 <sub>2,0</sub>	3.380(30)	3.460(51)	D
3 <sub>2,2</sub> ←2 <sub>2,1</sub>	3.476(21)	3.416(78)	D
ave.	3.428(50)	3.438(50)	D

<sup>a</sup>Dipole moment along the *a* axis. The figures in the parentheses are uncertainties ( $3\sigma$ ) to be attached to the last digit.

that the tunneling splitting  $\Delta_0$  in the ground state was precisely and unambiguously determined. The determined tunneling splitting  $\Delta_0 = 29\,193.788 \pm 0.026$  MHz ( $0.973\,799\,95 \pm 0.000\,000\,87$  cm<sup>-1</sup>) in the ground state is smaller by 94 MHz, but much more precise than the microwave value  $29\,288 \pm 88$  MHz ( $0.9769 \pm 0.0029$  cm<sup>-1</sup>) derived from the pure rotational spectrum. The present value is smaller than the previous value  $2.2$  cm<sup>-1</sup> determined by matrix infrared spectroscopy.<sup>3</sup> However, the discrepancy could simply be attributed to large experimental uncertainty in the previous result. A recent jet-cooled laser induced fluorescence (LIF) study<sup>6</sup> concluded that the ground state splitting was at most  $0.3$  cm<sup>-1</sup> from vibrational changes in the tunneling splitting. The conclusion, however, seems imprudent in view of the wide linewidth of  $2$  cm<sup>-1</sup>. The most recent FDIR experiment of Frost *et al.*<sup>7</sup> gave the  $\Delta_0$  value of  $1.0 \pm 0.4$  cm<sup>-1</sup> in good agreement with the present value; note that they made assignment by referring to our preliminary report.<sup>29</sup> Recent theoretical studies by multidimensional treatments with *ab initio* potential energy surfaces have provided  $\Delta_0$  values of  $0.9$ ,<sup>13</sup>  $1.05$ ,<sup>14</sup> and  $1.50$  cm<sup>-1</sup>,<sup>15</sup> which are reasonably close to the present experimental result.

The interaction causes positive shifts in the tunneling-rotation lines as shown in the last column of Table II, meaning that the repulsion between the 0<sup>+</sup> and 0<sup>-</sup> states increases the energy separation. The shift amounts to only a few MHz when the *J* and *K<sub>a</sub>* quantum numbers are small, but is as large as 33.3 MHz for the 8<sub>3,6</sub>–8<sub>4,5</sub> transition, for instance.

The interaction constant determined is  $F = 16.456 \pm 0.015$  MHz, which is also consistent with the value,  $F = 16.391 \pm 0.078$  MHz, given by the analysis of the pure rotational spectrum. The interaction constant is of the same order of magnitude but smaller than that of malonaldehyde,  $F = 46.01 \pm 0.02$  MHz.<sup>27</sup> The present interaction constant is shown to be within an acceptable range of magnitude by using a simple one-dimensional model for the proton transfer motion, as will be described in the next section.

The rotational and centrifugal distortion constants in the 0<sup>+</sup> and 0<sup>-</sup> states are compared in Table IV. The *B* rotational constants are almost identical for the two tunneling states. However, the *A* rotational constant for the 0<sup>+</sup> state is slightly but significantly larger (by  $0.375 \pm 0.012$  MHz) than that of the 0<sup>-</sup> state. The observed rotational constant corresponds to the average of the instantaneous rotational constant over the proton tunneling motion. In the case of sufficiently high barrier, the probability distribution is almost identical for the 0<sup>+</sup> and 0<sup>-</sup> states. However, the most conspicuous difference occurs in the vicinity of the *C*<sub>2*v*</sub> configuration corresponding to the top of the barrier. That is, the symmetric wave func-

tion  $|0^+\rangle$  has a finite amplitude but the antisymmetric function  $|0^-\rangle$  a negligible one. In the *C*<sub>2*v*</sub> configuration, when the tunneling proton lies on the *a* axis, the moment of inertia *I<sub>a</sub>* takes the minimum value, and therefore, the instantaneous *A* rotational constant the maximum value. This explains the slightly larger *A* rotational constant in the 0<sup>+</sup> state than in the 0<sup>-</sup> state. On the other hand, no significant change is expected for the rotational constant *B* around the *C*<sub>2*v*</sub> configuration, explaining the almost identical *B* values for both the tunneling states.

The inertial defects of tropolone for the 0<sup>+</sup> and 0<sup>-</sup> states calculated from the present rotational constants have negative values,  $-0.122\,56$  (53) and  $-0.124\,65$  (98) amu Å<sup>2</sup>, respectively, which are anomalous for a planar molecule. The molecular planarity is often discussed by using the inertial defect, and a planar molecule usually has a small positive value of the inertial defect in the ground vibrational state, e.g., fluorobenzene (0.033),<sup>30</sup> benzonitrile (0.083),<sup>31</sup> sulfur dioxide (0.1359),<sup>32</sup> and vinyl fluoride (0.0885 amu Å<sup>2</sup>).<sup>33</sup> Malonaldehyde has also positive inertial defects of 0.1028 (33) and 0.0839 (33) amu Å<sup>2</sup>, respectively, for the 0<sup>+</sup> and 0<sup>-</sup> states,<sup>27</sup> confirming the planarity of this molecule.

However, the inertial defect has small negative values of  $-0.4811$  and  $-0.1909$  amu Å<sup>2</sup> in nitrobenzene<sup>34</sup> and formic anhydride,<sup>35</sup> respectively. These molecules have out-of-plane vibrations with extremely low frequencies ( $\omega_i = 50$  and  $85$  cm<sup>-1</sup>) to which the anomalous negative inertial defects are attributed. Each low-frequency out-of-plane vibration contributes to the ground state inertial defect approximately by<sup>36,37</sup>

$$(1/2)\Delta_i = -(h/4\pi^2c)(1/\omega_i), \quad (7)$$

where  $\omega_i$  denotes the out-of-plane vibrational frequency. Positive inertial defects of 0.193 and 0.206 amu Å<sup>2</sup> are obtained for nitrobenzene and formic anhydride, respectively, if these contributions are subtracted. This is also the case for tropolone, which has low-frequency out-of-plane vibrations such as the  $\nu_{25}$  (176 cm<sup>-1</sup>) and  $\nu_{26}$  (110 cm<sup>-1</sup>) modes.<sup>11</sup> The contributions of the  $\nu_{25}$  and  $\nu_{26}$  modes are calculated to be  $-0.191$  and  $-0.307$  amu Å<sup>2</sup>, respectively, and correction for them results in small positive inertial defects around 0.374 amu Å<sup>2</sup>. In conclusion, the tropolone molecule is planar, although its inertial defect in the ground vibrational state has a negative value.

## B. Dipole moment

The Stark effect was measured employing the FTMW spectrometer for the two rotational lines 3<sub>2,1</sub>–2<sub>2,0</sub> and 3<sub>2,2</sub>–2<sub>2,1</sub> to derive the dipole moments along the *a* axis given in Table V. The average values are 3.428 (50) and 3.438 (50) D for the 0<sup>+</sup> and 0<sup>-</sup> states, respectively, which are almost identical. The *b* component of the dipole moment was safely neglected in the analysis, because no levels connected by the *b* dipole moment accidentally come close to the relevant rotational levels to cause an appreciable Stark effect.

The observed *a* component of the dipole moment responsible for the pure rotational transitions agrees fairly well with the estimated value, 3.2 D. Although the measurement of the *b* component responsible for the tunneling-rotation