THE ROTATIONAL SPECTRUM OF DEUTERATED ISOPROPANOL \((\text{CH}_3)_2\text{CHOH}\)

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Isopropanol has already been investigated by microwave spectroscopy and has been confirmed to exist in both trans and gauche; the two equivalent gauche forms were found split by tunneling by 46 798.5 MHz.\(^a\) The observation was extended to the deuterated species that has a deuterium in the hydroxyl group, and the trans spectra were detected. However, the gauche spectra have eluded assignment, presumably because the tunneling splitting was comparable with the rotational energy, making the rotational spectrum complicated.

In the present study we have employed a Fourier transform microwave spectrometer and have succeeded in unambiguously assigning the gauche spectra, because the low temperature simplified the spectrum and because the deuterium nuclear quadrupole coupling effect resulted in hyperfine structure only for the spectra of the deuterated species. In an initial stage, we observed two lines for each of the four transitions: \(\Delta I \equiv 0_{00}, \Delta I \equiv 0_{11}, 2_{02} \equiv 1_{11},\) and \(2_{12} \equiv 1_{01}\) with the splitting ranging from 8.5 MHz to 36.0 MHz. By carefully examining all the possible assignments of the two lines to the symmetric and antisymmetric states, we finally arrived at the tunneling splitting of about 4400 MHz, which was much larger than that previously estimated (about 2000 MHz). We then extended the assignment to other transitions of \(J\) up to 5, including some between the symmetric and antisymmetric rotational levels. As in the case of the parent species, these inter-state transitions were stronger than those within the symmetric or antisymmetric state. The main molecular parameters we obtained from the analysis are symmetric state: \(A = 8198.9104 \pm 0.019\), \(B = 7998.3213 \pm 0.014\), \(C = 4611.6717 \pm 0.015\). \(\chi_{zz} = -0.1051 \pm 0.057\), \(\chi_{zz} - \chi_{xy} = -0.0437 \pm 0.027\); antisymmetric state: \(A = 8199.4366 \pm 0.017\), \(B = 7998.0368 \pm 0.020\), \(C = 4611.6876 \pm 0.020\), \(\chi_{zz} = -0.0987 \pm 0.054\), \(\chi_{zz} - \chi_{xy} = -0.0444 \pm 0.027\); symmetric/antisymmetric cross terms: \(R_{zz} = 180.330 \pm 0.013\), \(R_{xy} = 271.2791 \pm 0.060\), \(\chi_{zz} = -0.030 \pm 0.030\), \(\chi_{xy} = -0.143 \pm 0.039\), \(\Delta E = 4431.4581 \pm 0.027\) in MHz with the standard deviations in parentheses.

\(^a\)E. Hirota, J. Phys. Chem. 83, 1457 (1979)