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Proton Tunneling and Nuclear Spin Conversion of Molecules

Fourier-transform microwave spectroscopy in the frequency region of 8~29 GHz has been applied for the ^{13}C -substituted tropolone [3]. There are seven ^{13}C -substitutes (C-1~C-7) for tropolone and the potential energy curve for the proton tunneling becomes to be asymmetric for the C-1 -2, C-3 -7, and C-4 -6 pairs due to the difference in the zero point vibrational energy (DZPE) which affects substantially to the tunneling effect.

The tunneling-rotation transitions were observed for C-46, C-37 and C-5, but only weak b-type rotational transitions for C-12. The tunneling splitting $\Delta E_{i,j}$ as well as DZPE were determined for the C-5, C-46, C-37 and C-12 pairs to give the tunneling mixing ratios to be 50, 43, 25 and 8 %, respectively, indicating that proton tunneling is occurring efficiently for C-5, C-46, but hindered moderately for C-37 and obstructed seriously for C-12 due to the larger DZPE. Present spectroscopic method will be applied for the study of parity violation of chiral molecules with ultrahigh resolution.

For the vinyl radical, the proton tunneling-rotation transitions, as well as the pure rotational transitions, have been observed for the H_2CCH [2], H_2CCD [3] and D_2CCD isotopic species. Although H_2CCH , H_2CCD and D_2CCD have very different tunneling splitting ΔE_0 of 16.185, 1.164 and 0.770 GHz, respectively, due to the mass effect of D/H, they have almost the same barrier heights h of 1680, 1580, and 1640 cm^{-1} .

We also observed the larger off-diagonal ($\Delta I = \pm 1$) Fermi contact interaction, $\Delta F(I)S \cdot I$, for H_2CCD and D_2CCD which causes the extremely rapid nuclear spin conversion between the ortho ($I = 1$) and para ($I = 0$) H_2CCD vinyl radical [3], for example, due to the large magnetic interaction of electron spin (S) and H/D nuclear spin (I).

1) J. Chem. Phys. 110, 1969 (1999), 2) *ibid*, 120, 3604 (2004), 3) *ibid*, 131, 111101 (2009).