MILLIMETER-WAVE SPECTROSCOPY OF THE D$_2$CCD RADICAL

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The tunneling-rotation transitions of the vinyl-d$_3$(D$_2$CCD) radical produced by the 193 nm excimer laser photolysis of vinyl-d$_3$ chloride(D$_3$CCDCl) have been observed by millimeter-wave spectroscopy combined with a pulsed supersonic jet technique. The $b$-type transitions, $N_{K,K'}=1_{11}-0_{00}$, $1_{10}-1_{01}$, $2_{12}-1_{01}$, for both the $0^--0^+$ and $0^+-0^+$ tunneling subbands were observed in the frequency region of 101-183 GHz, split into fine and hyperfine components due to the spin-rotation interaction and the spin-spin interaction of the (CD)- and the (CD$\delta$)-deuterons. The molecular constants such as rotational constants, spin-rotation interaction constants, and hyperfine interaction constants were determined by a simultaneous analysis of the observed spectrum and previously reported $J=1-0$ pure rotational transition$^a$ together with the tunneling splitting $\Delta E_0 = 771.843(23)$ MHz between the $0^+$ and $0^-$ states.

The tunneling splitting for D$_2$CCD is less than 1/20 of that for H$_2$CCH (16 271.842 9(59) MHz)$^b$ due to the mass effect of the $\alpha$-$H$ and D, and it is about 2/3 of H$_2$CCD (1 186.820(26) MHz) indicating the mixing of the vibrational modes for $\alpha$-H/D and $\beta$-H$_2$/D$_2$. From the observed tunneling splitting, the barrier height $h$ of the double minimum potential for D$_2$CCD was estimated to be 1549 cm$^{-1}$ using one dimensional model. The barrier height $h$ for D$_2$CCD is almost the same as those for H$_2$CCH and H$_2$CCD, 1580 and 1520 cm$^{-1}$, respectively, as expected by B.O. approximation and the isotopic effect due to zero point energies. The off-diagonal Fermi interaction constant, $\delta F_{EF}$, which is responsible to the mixing of the wavefunctions of $ortho(I_{\beta}=0, 2)$ and $para(I_{\beta}=1)$ states, has been determined to be 19.8(30) MHz. The off-diagonal Fermi interaction may cause the nuclear spin conversion between the $ortho$- and $para$-states for D$_2$CCD.
