

ビノキシラジカルのフーリエ変換マイクロ波分光

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Fourier-Transform Microwave Spectroscopy of the Vinyloxy Radical

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ABSTRACT Pure rotational transitions for the vinyloxy radical have been observed by Fourier-transform microwave (FTMW) spectroscopy in the cm-wave region and double resonance spectroscopy in the mm-wave region. The hyperfine coupling constants for the third proton in the -CHO moiety of the vinyloxy radical were determined for the first time. One *b*-type transition, that escaped to be detected in a previous study, was detected, yielding a more accurate set of molecular constants for the ground vibronic state.

The vinyloxy radical, CH_2CHO , is an important reaction intermediate observed in many oxidation reactions of hydrocarbons. Its pure rotational spectrum was observed in 1985 in the mm-wave region, where all the observed transitions were of *a*-type.^a Although most of the molecular constants in the ground vibronic state have been determined precisely, hyperfine splittings due to the third proton were partially resolved for transitions perturbed by ϵ_{ab} , so that only T_{ab} was marginally determined. Observation of rotational transitions in the cm-wave region by FTMW spectroscopy was reported in 2001, where however no hyperfine splitting due to the third proton was observed.^b Quite recently, we have observed pure rotational transitions of related species, CH_2CFO^c and CH_2CHS^d by FTMW spectroscopy, where hyperfine splittings due to three coupling nuclei were well resolved and accurate coupling constants have been determined for all the nuclei. It is thus interesting to compare the hyperfine coupling constants among these species.

Since the FTMW spectrometer and the double resonance system have been reported previously, no explanations are given here. We used 0.6% of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_3$ diluted in Ar as a sample gas, which was discharged in a pulsed discharge nozzle to produce the vinyloxy radical in a supersonic jet. Prior to starting the observation, we performed an *ab initio* calculation to predict the hyperfine coupling constants for the three protons at QCISD/cc-pVTZ. The dipole moment was also calculated, where μ_a was about three times larger than μ_b . Although observation of only one *b*-type rotational transition, $1_{11}-2_{02}$ at 13 GHz was reported in the previous FTMW study, which is expected to be much weaker than *a*-type transitions, because of the frequency coverage of the FTMW spectrometer they used, there is a much stronger

a-type transition $1_{01}-0_{00}$ at 21 GHz. Since we were unable to observe the reported transitions at 13 GHz in a preliminary experiment, transitions at 21 GHz were searched for based on the molecular constants previously determined^a and the predicted hyperfine coupling constants for the third proton. A number of lines were observed with good S/N ratios at frequencies very closed to the predicted, where hyperfine splittings due to the third proton were clearly resolved. The double resonance method was then applied to observe other possible transitions in the mm-wave region, $2_{02}-1_{01}$ at 42 GHz and $1_{11}-0_{00}$ at 76 GHz. Signals were so strong that we had to reduce the power of the mm-wave sources for both of the transitions to avoid saturation, even though the latter is a *b*-type transition. After a preliminary analysis of the observed transition frequencies for the three rotational transitions, transitions for the 13 GHz transition were observed at exactly the predicted frequencies, which were different from those reported previously.^b Intensities were more than 10 times weaker than those of the 21 GHz transition, partly due to smaller μ_b and the unfavorable Boltzmann factor for the 13 GHz transition at the rotational temperature 3 K, for which the term energy of the lower level is 2 cm^{-1} higher than the lowest level.

Frequencies of 76 lines were precisely measured, which were subjected to a least squares analysis together with the 24 previously observed mm-wave transitions with resolved splittings due to the third proton. We had to readjust many of the molecular constants to fit the newly observed transitions with the standard deviation of the fit 13 kHz. The determined hyperfine coupling constants are in reasonable agreement with those predicted by the *ab initio* calculation. The hyperfine coupling constants for the third proton were compared with those predicted and those of CH_2CHS in the Table. Global fit including all the observed mm-wave transitions together with the present data is also performed to determine all the molecular parameters in the ground vibronic state.

Table Hyperfine coupling constants for the third proton (in MHz)

	CH_2CHO		CH_2CHS	
	obs.	calc.	obs	calc.
$a_F(\text{H}_3)$	-0.557(6)	-1.04	4.60	6.19
$T_{aa}(\text{H}_3)$	2.24(2)	3.94	4.31	-1.41
$T_{bb}(\text{H}_3)$	2.78(2)	1.40	-0.18	0.87
$T_{ab}(\text{H}_3)$	5.3(2)	5.3	-0.02	3.79

References

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