LIST of SUPPORTING INFORMATION

The rotational spectrum and structure of HOOOH

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1. Observed and simulated Microwave spectra of DOOOD

The observed and simulated FTMW spectra of DOOOD for transitions, $1_{10}-1_{01}$ (a), $3_{03}-2_{12}$ (b), and $2_{11}-2_{02}$ (c). These spectra were obtained by averaging 17000, 12000, and 15000 signals in the parallel jet configuration with Ne buffer gas to increase the Doppler doublings to distinguish the hyperfine splittings from the Doppler doublings. The arrows point the *extra* lines mentioned in the text.

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Simulated spectra were calculated by using the electric quadrupole constants of DOOOD obtained by B3LYP/cc-pVQZ as below (in MHz).

χ_{aa}	0.2587
χ_{bb}	-0.1285
χ_{cc}	-0.1302
χ_{ab}	-0.1009
χ_{bc}	0.0340
χ_{ac}	-0.0242

2. Triple resonance spectroscopy

The rotational transition, $1_{10} - 1_{01}$, of H_2O_3 was observed by FTMW-mmw-mmw triple resonance spectroscopy. A detailed technical description of this spectroscopic method will be published elsewhere, and is explained only briefly. The principle of this technique is quite simple and similar to that of the double resonance technique as reported previously [Sumiyoshi, Y.; Katsunuma, H.; Suma, K.; Endo, Y. *J. Chem. Phys.* **2005**, 123, 054324]. The signal intensity of the transition at 20838.6 MHz (H_2O_3 , $3_{03} - 2_{12}$) is monitored while pumping the population of 2_{12} from 1_{01} by irradiating the millimeter-wave 1, (79213.1 MHz, $2_{12} - 1_{01}$). This situation is essentially the same as the double resonance method. Under this configuration, another millimeter wave 2, whose frequency corresponds to $1_{10} - 1_{01}$, is irradiated into the cavity in the direction perpendicular to the gas beam, the microwave, and the millimeter-wave 1. The frequency of the millimeter-wave 2 is scanned. When it resonates to the transition, $1_{10} - 1_{01}$, the population pumped by the millimeter-wave 1 decreases and a triple resonance signal is observed as a dip in intensity of the monitored microwave transition. The observed triple resonance spectrum is shown below.

Triple resonance spectrum of H_2O_3 ($1_{10} - 1_{01}$).

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3. Observed microwave transition frequencies of HOOOH and DOOOD (in MHz)

J'	$K_a' K_c'$	J''	$K_a'' K_c''$	HOOOH	DOOOD
3	0 3	2	1 2	20838.5626	22887.2514
1	1 0	1	0 1	41792.989**	34296.9122
3	1 2	3	0 3	45266.650*	36795.655*
2	1 2	1	0 1	79213.128*	-
3	2 1	2	1 2	185654.359*	-
2	1 1	2	0 2	-	35281.0305
2	1 2	1	0 1	-	69277.298*

* Transition observed by double resonance spectroscopy

** Transition observed by triple resonance spectroscopy

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4. Molecular constants of HOOOH and DOOOD

Molecular constants of HOOOH and DOOOD (in MHz).

	HOOOH	DOOOD
A	51149.308	43042.667
B	10688.077	9708.654
C	9355.062	8745.256
Δ_J	0.0157	0.0150
Δ_{JK}	-0.0343*	-0.00698*
Δ_K	1.277	0.554*
δ_J	0.00246*	-0.000782
δ_K	0.0198*	-0.0191*

* Fixed to the *ab initio* values by B3LYP/VQZ.

Since only the $K_a = 0$ and 1 lines were observed for DOOOD, Δ_J and δ_J were determined. On the other hand, since a *b*-type transition of the $K_a = 2$ manifold was observed for HOOOH, the centrifugal distortion constants, Δ_J and Δ_K , were determined.

If the molecular constants are determined by fixing the centrifugal distortion constants to the *ab initio* values, the standard deviations become much larger than the experimental accuracy: 1.013 MHz and 0.1074 MHz for HOOOH and DOOOD, respectively. These fits give the rotational constants listed below. Numbers in the parentheses represent 1σ .

	HOOOH	DOOOD
A	51148.21(31)	43042.683(55)
B	10687.89(17)	9708.648(19)
C	9354.93(20)	8745.159(21)

5. Rotational energy level diagram and observed transitions

The rotational energy levels and the observed transitions of HOOOH. The arrows with dashed, solid, and dashed and single-dotted lines indicate the transitions observed by the FTMW, double resonance, and triple resonance methods, respectively. The FTMW spectrum for the $3_{03}-2_{12}$ transition is also shown. This spectrum was obtained by averaging 100 free induction decay signals.

Supporting Information

The rotational energy levels and the observed transitions of DOOOD, along with the total nuclear spins. The arrows with dashed and solid lines indicate the transitions observed by the FTMW and double resonance techniques, respectively.

6. Complete lists of authors for references 11 and 12

Reference 11

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