Accidental resonance between torsional tunneling pairs detected in HOOD

(Univ. Kassel[a], AIST[b])

Doris Herberth[a], Koichi MT Yamada[b], Thomas F Giesen[a]

A few years ago we measured the gas phase spectra of HOOD in the region from 15 to 700 cm^{-1} at the SOLEIL Synchrotron facility in France using the AILES beam-line, equipped with a Bruker IFS 125 Fourier Transform Infrared Spectrometer [1]: the resolution of 0.0011 cm^{-1} was achieved. Because local perturbations were observed in the energy levels of K_a = 0 and 1 as shown in Fig. 1, only the unperturbed and less-perturbed transitions were analyzed at that time using the analysis tool PGOPHER [2]. More than 1000 transitions of the molecule were assigned to the vibrational ground state in the frequency range up to J = 30 and K_a = 8. We reported in 2012 [1] the effective constants determined solely from the unperturbed and less-perturbed transitions. Although the fit of the unperturbed and less-perturbed transitions was extremely good, the standard deviation of the fit 0.0004 cm^{-1}, the predictions of the low-K_a transitions were so poor that we could not identify the perturbed transitions at that time.

In order to assign the perturbed transitions, which are mainly in the low frequency region, we have measured additionally in the present study the spectra in the sub-millimeter wave region of 180 – 800 GHz (6.1 – 25.9 cm^{-1}), employing the THz spectrometer in Kassel University, the radiation source of which is a MW-synthesizer (8 – 20 GHz) equipped with amplifier-multiplier chains. With careful comparison of the simulated and observed spectra in Far Infrared (previous measurements) and THz (new measurements) region using PGOPHER [2], we have finally succeeded to assign a number of perturbed transitions. Altogether, more than 1300 transitions have been assigned now.

We found that the perturbations are caused by centrifugal-correction terms:

$$H' = W_{ac}(J_aJ_c + J_cJ_a)/2 + W_{bc}(J_bJ_c + J_cJ_b)/2 , \quad (1)$$

where the interaction constants W_{ac} and W_{bc} contain the displacement coordinate of the internal rotation. The interaction selection rues are, in the symmetric-top approximation,

$$\Delta v_{\mathrm{LAM}} = \pm 1, \ \Delta K_a = \pm 1, \pm 2 \quad (2)$$

$$\text{parity} \pm \leftarrow\!\!\rightarrow \pm . \quad (3)$$

In addition to a set of Watsonian parameters for each tunneling component, the

interaction constants between the tunneling pairs are determined very accurately by the least-squares procedure provided in PGOPHER as

$$|W_{ac}| = 0.007\,017(27)\ \text{cm}^{-1} \quad \text{and} \quad |W_{bc}| = 0.005\,720\,674(61)\ \text{cm}^{-1}\,.$$

Baum *et al.* [3] observed a similar kind of interaction in the spectra of HSOH earlier. The present analysis of the HOOD spectra, however, strongly suggests that the interaction analysis reported in Ref. [3] for HSOH might be inadequate. Thus, we are planning to reanalyze the spectra of HSOH.

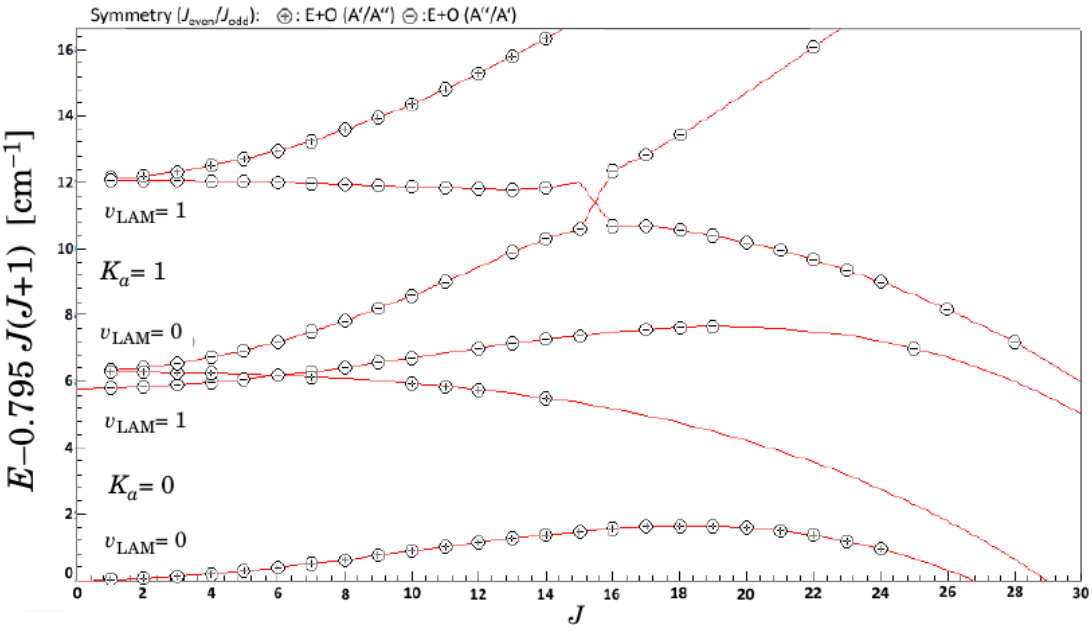

Fig. 1: Observed lowest energy levels of HOOD.

[1] Doris Herberth, Oliver Baum, Oliver Pirali, Pascale Roy, Sven Thorwirth, Koichi M. T. Yamada, Stephan Schlemmer and Thomas F. Giesen, *J. Quant. Spectrosc. Radiat. Transfer*, **113**, 1117-1133 (2012).

[2] C. M. Western, "PGOPHER: A program for simulating rotational, vibrational and electronic spectra," *J. Quant. Spectrosc. Radiat. Transfer,* **186**, 221 (2017).

[3] Oliver Baum, Monika Koerber, Oliver Ricken, Gisbert Winnewisser, Sergei N. Yurchenko, Stephan Schlemmer, Koichi M. T. Yamada, and Thomas F. Giesen, *J. Chem. Phys.* **129**, 224312:1-6 (2008).