ASSIGNMENT OF THE LOWEST EXCITED VIBRATIONAL STATES IN $tt-$DIETHYL ETHER

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We report the assignment and detailed analysis of the rotational spectrum in the two lowest-lying vibrational states of $trans - trans$ diethyl ether. The pertinent states are first excited states of the two lowest frequency vibrational modes, which are both near 100 cm^{-1} in energy. The states are coupled by strong c-axis Coriolis interaction, which gives rise to many rather spectacular spectroscopic manifestations. These include considerable perturbations in the prominent Q-type bands, several instances of strong short range interaction of the avoided crossing type, and the appearance of interstate transitions. The assignment was not easy and was finally reached by various graphical methods based on the availability of the very broad-band FASSST spectrum of diethyl ether. The final fit is based on nearly 2500 measured frequencies, including some for interstate transitions. All frequencies are fitted to within their nominal measurement accuracy, and the resulting interstate separation is $\Delta E = 10.400211(7)$ cm^{-1}. The derived value for the relevant Coriolis interaction constant is found to be consistent with the value calculated from the $ab\ inito$ force field.

This work completes a comprehensive reinvestigation of the rotational spectrum of diethyl ether, based on an almost continuous 108-366 GHz spectrum recorded in Ohio with the FASSST technique. In combination with the data obtained for the ground state of the tt conformer[a], and the ground state of the newly assigned tg conformer (reported at this conference) we are now able to account for all of the strongest spectroscopic features in the room-temperature rotational spectrum of diethyl ether.

[a] I. Medvedev, M. Winnewisser, F. C. De Lucia, E. Herbst, Y. Enyi, L. P. Leong, R. P. A. Bettens, E. Białkowska-Jaworska, O. Desyatnyk, L. Pszczółkowski, Z.Kisiel, Astrophys. J. Suppl. Ser. 148, 593 (2003).