PROGRESS IN THE ROTATIONAL ANALYSIS OF THE GROUND AND LOW-LYING VIBRATIONALLY EXCITED STATES OF MALONALDEHYDE

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Despite being an important prototype molecule for intramolecular proton tunnelling, the far-IR spectrum of the internally hydrogen-bonded species malonaldehyde ($C_3O_2H_4$) is not yet well understood. In the talk I gave at the ISMS meeting in 2015 I discussed the high-resolution spectra we obtained at the Canadian Light Source synchrotron in Saskatoon, Saskatchewan. These spectra include a number of fundamental vibrational bands in the 100-2000 cm^{-1} region. In our efforts to analyze these bands we have noticed that our ground state combination differences show a large drift (up to an order of magnitude larger than our experimental error) away from those calculated using constants established by Baba *et al*.,[a] particularly in regions of high J (above 30) and low K_a (below 5). An examination of the previous microwave and far-IR studies[bc] reveals that this region of J-K_a space was not represented in the lines that Baba *et al*. used to generate the values for their fitting parameters. By including our own measurements in the fitting, we were able to improve the characterization of the ground state so that it is now consistent with all of the existing data. This characterization now covers a much larger range of J-K_a space and has enabled us to make significant progress in analyzing our far-IR synchrotron spectra. These include an excited vibrational state at 241 cm^{-1} as well as several states split by the tunnelling effect at higher wavenumber.

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[a] T. Baba, T. Tanaka, I. Morino, K. M. T. Yamada, K. Tanaka. *Detection of the tunneling-rotation transitions of malonaldehyde in the submillimeter-wave region*. J. Chem. Phys., **110**. 4131-4133 (1999)

[b] P. Turner, S. L. Baughcum, S. L. Coy, Z. Smith. *Microwave Spectroscopic Study of Malonaldehyde. 4. Vibration-Rotation Interaction in Parent Species*. J. Am. Chem. Soc., **106**. 2265-2267 (1984)

[c] D. W. Firth, K. Beyer, M. A. Dvorak, S. W. Reeve, A. Grushow, K. R. Leopold. *Tunable far-infrared spectroscopy of malonaldehyde*. J. Chem. Phys., **94**. 1812-1819 (1991)