THE BENDING-ROTATION APPROACH APPLIED TO THE METHYLENE RADICAL CH_2

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Quasi-linear molecules display a large amplitude bending mode allowing them to sample their linear configuration. This leads to a strong coupling between the overall rotation and the bending mode and to a singularity in their Hamiltonian. Quasi-linearity has been extensively studied in many species including the closed shell water molecule and the open shell amidogen (NH_2) and methylene (CH_2) radicals. For these three species, the barrier to linearity ranges from 12 000 cm^{-1} for NH_2 to less than 2000 cm^{-1} for CH_2.[a] Their rovibrational energy levels can be computed with almost spectroscopic accuracy using variational approaches or, if a higher accuracy is required, with reduced dimensionality models such as the effective Bending-Rotation approach,[b] already applied to treat the anomalous centrifugal distortion of the water molecule[b] and of the amidogen radical.[c]

In this talk, the Bending-Rotation approach[b] is extended, adding the spin-rotation and spin-spin fine couplings, so as to be used in the case of the methylene radical. The new approach is applied to the fitting of high-resolution data pertaining to this species. In addition to the ground state data previously analyzed,[d] the data set includes FIR transitions belonging to the ν_2 band.[e] 336 transitions were reproduced with a standard deviation of 1.3 using 42 spectroscopic parameters.[f] In the talk, the results of this analysis will be reported and the dependence on the bending angle retrieved for the spin-rotation and spin-spin fine couplings will be discussed. We will also try to see if the analysis results[f] can be further improved.

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[a] Jungen, Hallin, and Merer, *Molec. Phys.* **40** (1980) 25; Bunker, Jensen, Kraemer, and Beardsworth, *J. Chem. Phys.* **85** (1986) 3724; Partridge and Schwenke, *J. Chem. Phys.* **106** (1997) 4618

[b] Coudert, Marin-Drumel, and Pirali, *J. Mol. Spectrosc.* **303** (2014) 36

[c] TD03, Martin-Drumel, Pirali, and Coudert, 72nd ISMS, Urbana-Champaign, June 19–23, 2017

[d] Brünken, Müller, Lewen, and Giesen, *J. Chem. Phys.* **123** (2005) 164315

[e] Sears, Bunker, and McKellar, J. Chem. Phys. **77** (1982) 5363; McKellar, Yamada, and Hirota, *J. Chem. Phys.* **79** (1983) 1220; and Marshall and McKellar, *J. Chem. Phys.* **85** (1986) 3716

[f] Coudert, *J. Chem. Phys.* **153** (2020) 144115