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EXPERIMENTAL AND THEORETICAL INVESTIGATIONS OF THE THRESHOLD PHOTOELECTRON SPECTRUM OF THE CH_2 RADICAL

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The methylene cation CH_2^+ is spectroscopically poorly characterized as it is difficult to produce in large amounts. It is subject to the Renner-Teller effect giving rise to ground $\widetilde{X}^+\,^2A_1$ and excited $\widetilde{A}^+\,^2B_1$ electronic states. Photoelectron spectroscopy of the methylene radical CH_2 allows us to gain information about both CH_2 and its cation. The former is also theoretically challenging as it is a very non-rigid species characterized by a barrier to linearity of less than 2000 cm^{-1} in its ground $\widetilde{X}\,^3B_1$ electronic state. The first photoelectron spectra of CH_2 were investigated using pulsed-field-ionization zero-kinetic-energy spectroscopy.[a] A rotationally resolved spectrum containing $\widetilde{X}^+\,^2A_1 \leftarrow \widetilde{X}\,^3B_1$ transitions was recorded from 83600 to 84070 cm^{-1} and analyzed in terms of CH_2^+ rotational constants.

The threshold photoelectron spectrum of CH_2 has been recorded from 9.8 to 12 eV (79040 to 96800 cm^{-1}) using a recently developed flow tube reactor[b] and VUV synchrotron radiation. This new spectrum spans a larger energy range than the previous ones,[a] but with less resolution. It displays narrow and broad features due respectively to the $\widetilde{X}^+\,^2A_1 \leftarrow \widetilde{X}\,^3B_1$ and $\widetilde{A}^+\,^2B_1 \leftarrow \widetilde{X}\,^3B_1$ ionizing transitions. Using new *ab initio* potential energy surfaces and available ones,[c] the photoelectron spectrum is currently being computed using two models. The first one accounts for the large amplitude bending mode and the rotation only; the second one, also accounts for the stretching modes. The experimental and theoretical spectra will be discussed in the paper.

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[a] Willitsch *et al., J. Chem. Phys.* **117** (2002) 1939; and Willitsch & Merkt, *ibid.* **118** (2003) 2235

[b] Garcia *et al., J. Chem. Phys.* **142** (2015) 164201

[c] Jensen & Bunker, *J. Chem. Phys.* **89** (1988) 1327; and Jensen, Brumm, Kraemer & Bunker, *J. Molec. Spectrsoc.* **172** (1995) 194