THE RENNER-TELLER AND JAHN-TELLER EFFECTS IN PROTOTYPICAL MOLECULAR CATIONS SUBJECT TO A VERY LARGE SPIN-ORBIT COUPLING

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PFI-ZEKE photoelectron spectra of the $\mathrm{X}^{+}\ {}^{2}\Pi \leftarrow \mathrm{X}\ {}^{1}\Sigma^{+}$ transition of HC_2I and of the $\tilde{\mathrm{X}}^{+}\ {}^{2}\mathrm{E}_{3/2} \leftarrow \tilde{\mathrm{X}}\ {}^{1}\mathrm{A}_{1}$ transition of CH_3I have been recorded at a resolution sufficiently high to observe, at least partially, their rotational structure. The spin-rovibronic energy-level structures of HC_2I^+ and CH_3I^+ could be determined at low energies and enabled us to study the Renner-Teller and Jahn-Teller effects in molecular cations subject to a very large spin-orbit coupling with unprecedented details.

In the case of HC_2I, the nominally forbidden 5^1_0 band has been observed in addition to the origin band and allowed us to determine a splitting of 2 cm^{-1} between the two Renner-Teller components of the 5^1 vibrational level of the cation. In the case of CH_3I, the rotational structure of the origin and of the 2^1_0 and 3^1_0 bands are dominated by satellite bands of spin-rovibronic origin[a]. The 5^1_0 and 6^1_0 bands reveal an additional splitting corresponding to the separation between the two Jahn-Teller components of $j = 1/2$ and $j = 3/2$ symmetry of the 5^1 and 6^1 levels of the cation[b].

[a] M. Grütter, J.M. Michaud and F. Merkt, *J. Chem. Phys.* **134**, 054308 (2011).

[b] T.A. Barckholtz and T.A. Miller, *Int. Rev. Phys. Chem.* **17** (4), 435 (1998).