Jahn-Teller effects on molecular electronic ring currents

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The generation and control of electronic currents in ring-shaped molecular systems is an active area of research [1-3], both experimentally and theoretically. The ring currents in molecules are supported by the doubly degenerate (E) electronic states, which feature opposite circulation directions of the electrons, and are present in systems with at least one 3-fold symmetry axis of rotation. Vibronic coupling effects have been so far perceived to be of minor relevance in the description of ring currents [1-3]. However, our recent investigations showed that vibronic coupling effects play crucial role in determing the generated ring currents [4,5]. By symmetry, the (E) electronic states inevitably undergo Jahn-Teller (JT) distortions through coupling to doubly degenerate (e) nuclear vibrations, the well-known ($E \times e$) JT effect. The dynamical ($E \times e$) JT effect results in strong mixing of the two pure ring-current circulation directions defined in the uncoupled limit, and strongly modifies the properties of the ring currents, e.g. their magnitude and stability, and thus their controllability [5]. The first-princples analysis of the eigenstate currents shows that circulation direction of the electrons in an eigenstate does not necessarily coincide with the polarization direction of the generating circularly polarized laser pulse, a direct consequence of strong vibronic coupling effects. In the first part of the talk, these fundamental and non-trivial properties of ring currents and their generation in molecules on the basis of the paradigmatic ($E \times e$) JT Hamiltonian will be presented.

[1] I. Barth; J. Manz; Y. Shigeta; K. Yagi; J. Am. Chem. Soc. **128** 7043 (2006).
[2] K.-J. Yuan; C.-C. Shu; D. Dong; A. D. Bandrauk; J. Phys. Chem. Lett. **8** 2229 (2017).
[3] C. Liu; J. Manz; K. Ohmori; C. Sommer; N. Takei; J. C. Tremblay; Y. Zhang, Phys. Rev. Lett. **121** 173201 (2018).
[4] K. R. Nandipati; O. Vendrell; J. Chem. Phys. **153** 224308 (2020).
[5] K. R. Nandipati; O. Vendrell, Phys. Rev. Research **3** L042003 (2021).