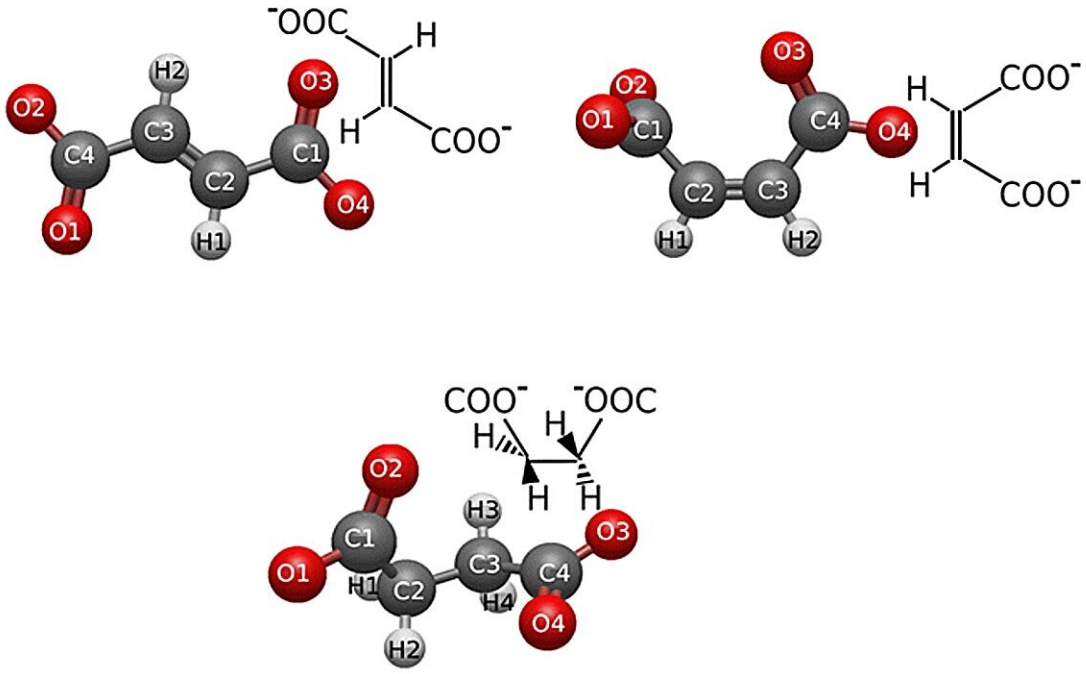
Examining how molecular orbitals determine stability

February 7 2024



Molecular geometry of the trans- and cis-isomers fumarate and maleate (above, left to right) together with their hydrogenated molecule, succinate−dianions (below) . Credit: HZB

Carboxylic acid dianions (fumarate, maleate, and succinate) play a role in coordination chemistry and, to some extent, also in the biochemistry

of body cells. An HZB team at BESSY II has now analyzed their electronic structures using RIXS in combination with DFT simulations. The results provide information not only on electronic structures but also on the relative stability of these molecules, which can influence an industry's choice of carboxylate dianions, optimizing both the stability and geometry of coordination polymers.

Carboxylic acid dianions of type $C_4H_2O_4$ or $C_4H_4O_4$ (fumarate, maleate, and succinate) can have different geometries (cis or trans) and different properties. Some variants are key in coordination chemistry, incorporating metallic elements into organic compounds; others play a role in biological processes.

Fumarate and succinate, for example, are formed as intermediate products in the mitochondria of cells. Maleate, on the other hand, which is usually not formed in natural processes, is used in industrial applications that require durable materials. For environmental reasons, however, the question arises as to whether these compounds last forever or are biodegradable.

The stability of fumarate, maleate, and succinate dianions is not only influenced by their molecular geometries but also by the electronic structure of the molecules, in particular, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). However, the influence of the molecular orbitals on the stability of these molecules has not been researched.

Now, a team at HZB led by Prof. Alexander Föhlisch has elucidated the influence of the electronic structure on the stability of fumarate, maleate, and succinate dianions.

"We analyzed these compounds at BESSY II with two different, very powerful methods," says Dr. Viktoriia Savchenko, first author of the

study. X-ray absorption spectroscopy (XAS) can be used to investigate the unoccupied electronic states of a system, while resonant inelastic X-ray scattering (RIXS) provides information about the occupied highest orbitals and about interactions between the HOMO-LUMO orbitals. The results can be related to macroscopic properties, especially stability.

The analysis of the spectral data shows that maleate is potentially less stable than fumarate and succinate. What's more: The analysis also explains why: The electronic density in the HOMO orbital at the C=C bond between carboxylate groups could lead to weaker binding of maleate with molecules or ions. Fumarate and succinate, on the other hand, could be more stable as their HOMO orbitals are equally delocalized.

"This means that there is a chance that maleate could be degraded by certain substances," says Savchenko.

The work is published in the journal *Physical Chemistry Chemical Physics*.

More information: Viktoriia Savchenko et al, Electronic structure, bonding and stability of fumarate, maleate, and succinate dianions from X-ray spectroscopy, *Physical Chemistry Chemical Physics* (2023). DOI: 10.1039/D3CP04348G

Provided by Helmholtz Association of German Research Centres