Supplementary material

A computational study of the chemical reactivity of the (2S,3R) and (2S,3S) isomers of dehydrated hydroxycitric acid.

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Evaluation of the Fukui Function

Fukui function (FF) is evaluated as the variation of electron density ρ (r) with a fixed geometry and external potential constant (*v* (r)) as the number of electrons changes (N). FF may be evaluated following three approximations which are: a) Frozen-Core (FC), b) Finite Difference (FD) [1] and c) atomic charges [2].

For the evaluation of FF in the case of FC approximation, the equations employed are (1S-2S):

$$f^{-}(r) = \varphi_H^{*}(r)\varphi_H(r) = \rho_H(r) \quad (1S)$$

$$f^{+}(r) = \varphi_L^{*}(r)\varphi_L(r) = \rho_L(r) \quad (2S)$$

In these equations, $\rho_H(r)$ is the electron density of the HOMO orbital, and $\rho_L(r)$ is the electron density of the LUMO orbital.

In the Finite Difference (FD) approximation the equations for the evaluation of FF is given by equation 3S-5S.

$$f^{-}(r) = \rho_N(r) - \rho_{(N-1)}(r) \quad (3S)$$

$$f^{+}(r) = \rho_{(N+1)}(r) - \rho_N(r) \quad (4S)$$

$$f^{0}(r) = \frac{1}{2}\left[\rho_{(N+1)}(r) - \rho_{(N-1)}(r)\right] \quad (5S)$$

In these equations, $\rho_{N+1}(r)$, $\rho_N(r)$, and $\rho_{N-1}(r)$ correspond to the electron densities of the anionic, neutral, and cationic species, respectively. Also, it is possible to condense the FF for an atomic position by employing the atomic charge approximation, as shown in equations (6S), (7S) and (8S).

$$f_j^-(r) = q_{j(N-1)} - q_{j(N)} \quad (6S)$$

$$f_j^+(r) = q_{j(N)} - q_{j(N+1)} \quad (7S)$$

$$f_j^0(r) = \frac{1}{2}\left[q_{j(N-1)} - q_{j(N+1)}\right] \quad (8S)$$

where q_j is the atomic charge at the j_{th} anionic (N+1), neutral (N), and cationic (N-1) active sites of the chemical species.

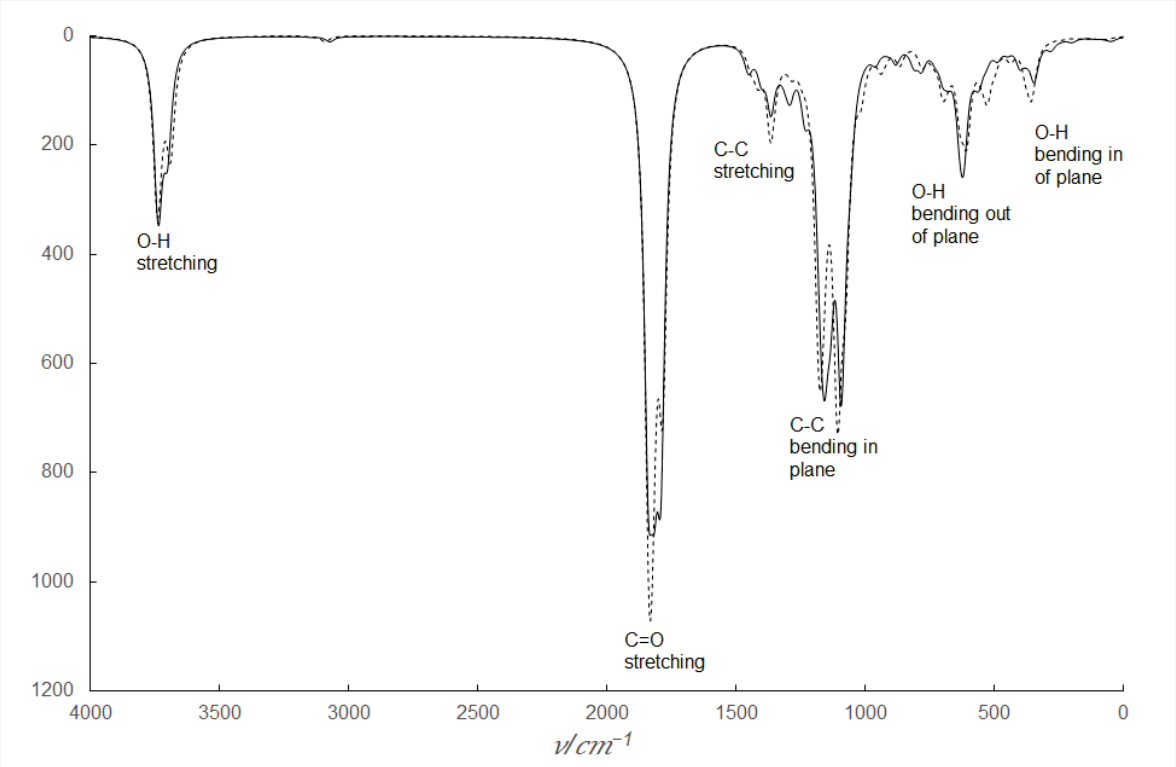

Fig. 1S. Theoretical IR spectra of HA (broken line) and GA (solid line) in the aqueous phase obtained at the B3LYP / 6-311G (d,p) level of theory

References

1 R.G. Parr and W. Yang, *J. Am. Chem. Soc.*, **106**, 4049 (1984).

2 W. Yang and W.J. Mortier, *J. Am. Chem. Soc.*, **108**, 5708 (1986).