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Reply to “Comment on the Paper ‘On the Limits of Highest-Occupied Molecular Orbital Driven Reactions: The Frontier Effective-for-Reaction Molecular Orbital Concept’”

Rodrigo R. da Silva,[†] Teodorico C. Ramalho,[‡]
Joana M. Santos,[§] and J. Daniel Figueroa-Villar[*,†]

Departamento de Química, Instituto Militar de Engenharia, Praça General Tibúrcio, 80, 22290-070, Rio de Janeiro-RJ, Brazil, Departamento de Química Geral e Inorgânica, Instituto de Química, Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier, 524, 20550-013 Rio de Janeiro-RJ, Brazil, and Departamento de Química, Universidade Federal de Lavras, Campus Universitário, CP 3037, 37200-000 Lavras-MG, Brazil

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Recently, we proposed the frontier effective-for-reaction molecular orbital (FERMO) concept terminology to identify the molecular orbital (MO) that drives a type of reaction.[1] The comment on our paper made by Maksić and Vianello[2] raises some discussion about our work that we want to clarify.

First of all, we do not make any statement saying that Fukui’s concept is obsolete and unsatisfactory. On the basis of Fukui’s own words,[3] we just showed cases where highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) arguments fail to explain the reactivity. However, we did not say that the frontier MO concept was obsolete. On the contrary, we used that concept to support our work.

Moreover, the comment by Maksić and Vianello[2] was written to show that the FERMO concept was not new. However, this seems completely unnecessary, since we do not claim that this is a new concept. As was written in the Introduction of our paper,[1] Fujimoto and co-workers have already given some insights[4] about the problem concerning the use of the HOMO to explain chemical reactivity. The idea of a MO localized on the reaction site was introduced by Fujimoto,[4] and we think this fact is quite clear in our paper. However, since our procedure is different from that developed by Fujimoto and co-workers, we found it necessary to name that reactive MO by FERMO because we think that frontier effective-for-reaction molecular orbital is a very clear and intuitive term for the reactive MO. Maksić and Vianello prefer to call it principal MO, and they stated that the FERMO and the principal MO are the same.[2] They are similar when one considers the idea of localized and reactive MOs introduced by Fujimoto and co-workers.[4] Although the FERMO and the principal MO share the same definition, the MOs selected by us, using our criterion,[1] are different from those selected by Maksić and Vianello.[5]

We also want to make clear that the aim of our work was to understand and to show why HOMO−LUMO arguments sometimes fail and how one can identify the MO that better describes the reactivity. The protonation reaction was adopted as a case of study, because of the large and accessible number of experimental data. Nevertheless, the FERMO idea can be applied to other systems[6] and can recall other MO concepts such as Hoffmann’s isolobal analogy.[7] Our main interest was not to explain why one compound is more acidic than others but to build a criterion (which still needs to be improved) to identify the MOs that describe the electron donation process and to explain why those MOs are favored among other MOs. Another important result from our work is that Hartree−Fock and Kohn−Sham MOs are equivalent and display the same energy behavior (although their energy values are different, as is well-known in the literature[8]).

The work of Maksić and his group has a different motivation than ours.[5,9] They are interested in the study of the acidity of many molecules and in exploring superacid properties, and the triadic analysis is successful for their purposes.

Another point raised by the comment of Maksić and Vianello[2] is that they have already done acidity studies for carboxylic acids.[5] That specific claim is fair, as we were not clear enough in our Introduction. It was written in our paper that “...there is a lack of studies concerning the most common and important organic acids, the carboxylic acids, and the relationship of their acid−base behavior with their MO energies.” In fact, the term acid−base behavior is quite general, and it is true that Maksić and Vianello have previously analyzed the acid−base behavior of carboxylic acids.[5] In fact, in the Introduction of our article, when we mentioned acid−base behavior, we meant pK_a and MO energy correlations only, but unfortunately, this sentence was not clear enough, thus leading to this unnecessary conflict with the work of Maksić and Vianello.[5] We deeply regret this error and the misunderstanding and hope that we have now given the due credit for the work of Maksić and Vianello.[5]

As a concluding remark, Maksić and Vianello pointed out that the FERMO concept has its predecessor. As mentioned above, it is clearly stated in our article that the idea of a MO localized on a reaction center was introduced by Fujimoto and co-workers,[4] and their work should be considered the predecessor of ours. In fact, this is true not only for Fujimoto’s work but also for the work of Fukui,[3] Woodward and Hoffmann,[10] Salem,[11] and others.[12]

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[*] Corresponding author. E-mail: figueroa@ime.eb.br.
[†] Instituto Militar de Engenharia.
[‡] Universidade Federal de Lavras.
[§] Universidade do Estado do Rio de Janeiro.

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