

Interactive comment on “A theoretical study on UV-spectroscopy, electronic structure and reactivity properties of sesquiterpenes” by S.-X. Hu et al.

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Comments to the Author * This manuscript focuses on the prediction and assignment of vertical electronic transitions in a number of sesquiterpenes by different electronic structure methods (DFT, TDDFT, CIS, ZINDO). The vertical transitions energies are calculated with Gaussian 03 and correlated to structures of the sesquiterpenes.

* It is well known that alkenes have strong π to π^* transitions in the UV range (around 200 nm). According to Woodward's rules, the transition wavelengths can be shifted to the red by conjugation or by certain substituent groups. However, even for the sesquiterpenes containing conjugated double bonds, the π to π^* bands are expected

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to be below 250 nm. Therefore, sesquiterpenes, which never reach the stratosphere due to their exceptionally high reactivity, cannot be electronically excited under realistic atmospheric conditions.

Response: Our objective was to investigate the effects of structural conjugation (type of double bonds or substituent groups) on UV-spectra and reactivity by comparing the transition wavelengths of different sesquiterpenes with their structures. Due to the exothermicity of the reaction, ozonolysis of sesquiterpenes can occur in the atmosphere, which has been previously reported.

* The authors hope that results of their calculations will be useful for distinguishing different sesquiterpenes. I doubt it will be the case as the absorptions below 250 nm are not very specific; a number of different organic and inorganic atmospheric molecules absorb in this region.

Response: The objective of the present study was to determine the relative reactivities of sesquiterpenes in terms of reaction with O₃, from which their contribution to the formation of SOAs was predicted. We were not intended to distinguish different sesquiterpenes.

* I think the paper should be published, however, given that UV absorptions by sesquiterpenes are not going to be of much interest to atmospheric scientists, Atmospheric Chemistry and Physics is clearly not the best choice for this publication. The authors should consider submitting the manuscript to a more specialized journal focusing on theoretical calculations of electronic properties.

Response: Theoretical calculation of the electronic properties of sesquiterpenes provides information for analyses of the reactivity of different sesquiterpenes, and for prediction of their contributions to the formation of SOAs. Thorough understanding of the properties and the compositions of SOAs and their corresponding sources is the basis for further investigations on the formation and evolution of SOAs. Although the results from the present study are incomplete, they should be useful for fulfilling the above-

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mentioned objective. Therefore, Atmospheric Chemistry and Physics is an appropriate choice for our manuscript.

* I also recommend that the authors re-write some of the sentences in their manuscript before the resubmission. In several instances they are using terminology that is not in wide use and likely to be misinterpreted by readers. Examples of phrases that are guaranteed to raise readers' eyebrows include: conceptual DFT; transit energies; sub-particles; formational mechanism; sub-volatile; isomeric changes; etc.

Response: "conceptual DFT" is a commonly used term in theoretical chemistry. "transit energies", subparticles, "formational mechanism", sub-volatile and "isomeric changes" have been revised to "transition energies", particles, "formation of SOAs", semivolatile, and "structural changes", respectively. (lines 24, 43, 38, 40 and 83, respectively, in the revised manuscript)

* Finally, I want to stress that the authors do not calculate "absorption spectra". They calculate vertical transition energies. There is an important distinction between the two.

Response: We agree with the reviewer's suggestion. Results of CIS are the band heads of UV-spectra which stand for vertical transition energies. So, "UV-absorption spectra" has been revised to "UV-spectra" (lines 17, 156, 162, 163, 171, 319 and 395 in the revised manuscript).

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 24325, 2010.

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