

## ***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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\* The authors failed to make a connection between the reactivity of sesquiterpenes with tropospheric oxidants and the nucleophilicity of sesquiterpenes, since reactivity is controlled not by nucleophilicity but also by other factors, such as spatial hindrance.

Response: Because spatial hindrance and other factors affect a molecule's reactivity through an impact on its electronic structure, a connection between the reactivity and electronic structure also accounts for spatial hindrance and other factors.

\* The title implies the reactivity properties of sesquiterpenes, but the work provides no kinetics of sesquiterpenes with OH, O<sub>3</sub>, or other atmospheric oxidants.

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Response: Reactivity is a vague concept used in chemistry in which both thermodynamic and kinetic factors are involved. For an single molecule, reactivity is regulated by its physiochemical properties, and eventually dictated by its electronic properties. The objective of the present study was to determine the relative thermodynamic reactivities of sesquiterpenes via theoretical calculation of their electronic properties.

\* It is pointed out in the abstract that “Sesquiterpenes, a class of biogenic volatile organic compounds, are important precursors to secondary organic aerosols (SOAs) in nature”, but the authors didn’t show how the results contribute to the understanding of SOA formation from sesquiterpenes.

Response: A sentence has been added in the conclusion, “A congener with an exo C=C bond or containing a large-size alkyl substituent attached to any of the C=C bonds (if more than one) and its degradation product in the atmosphere contribute more to the formation of SOAs than other isomers” (lines 319-322 in the revised manuscript).

\* The transition intensities and positions obtained by the authors are not very useful. Those results are not really exciting, since the first transition energy of conjugated double bonds is definitely lower than the transition energy of separated double bonds. Most of the results of this kind can be inferred easily from the chemical intuition without calculations.

Response: The transition energy and intensity were not the only subject matters of the present study. It is more important to investigate the relationship between the structures and spectral properties and reactivity. Prior to calculation, it was difficult to identify the dominant factor (i.e., the type of double bonds, conjugation, or substituents.) dictating the reaction of sesquiterpenes and O<sub>3</sub>.

\* Their theoretical approaches need to be put into the context of other previously established methods, which have validated for accuracy in investigation of atmospheric chemistry of biogenic hydrocarbons [e.g., Suh et al., J. Phys. Chem. 105, 6471, 2001; Zhang et al., J. Am. Chem. Soc. 124, 9600, 2002].

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Response: Although the two articles mentioned by the reviewer dealt with atmospheric degradation of isoprene and its related oxides, there is no significant relationship to our discussion of the electronic structure and reactivity properties of sesquiterpenes. Besides, two similar references have been cited, i.e. Shu, Y. H., J. Geophys. Res., 100, 7275, 1995; Lewin, A. G., Phys. Chem. Chem. Phys., 3, 1253, 2001.

\* Are there any higher level of theory calculations besides B3LYP/6-31G(d,p).

Response: For calculation of UV-spectra, CIS is the most appropriate method in Gaussian03 Programme. Although CASSPT2 can perform this job, the cost is too high for these systems. The B3LYP method is the most favorable one for conceptual DFT calculation. CCSD(T)/6-31G(d,p) was also used to perform single-point calculation; however, such results are irrelevant for conceptual DFT calculations. Although CCSD(T) is the best choice for calculation of potential energy surfaces, the present study was not intended to calculate potential surface surfaces

\* The electronic chemical potential would be more appropriate than the chemical potential ( $\mu$ ) to describe . Because is the chemical potential, in analogy the partial derivative of electronic energy E with respect to N is the electronic chemical potential.

Response: “chemical potential” has been revised as suggested to “Electronic chemical potential” (line 83 in the revised manuscript).

\* There are some inconsistencies in the formulas of conceptual DFT. This formula is inconsistent with formula (4), but it is consistent with formula (6) in the scope of Koopmanns theorem. In addition, the definition also gives the correct formulas (7) and (8).

Response: Revised as suggested. (line 100 in the revised manuscript)

\* “Chemical hardness measures the resistance to the change in electron density” is more appropriate if it is phrased like “Chemical hardness measures the resistance of Electronic Chemical Potential to the change in total number of electrons in the system”.

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Response: This sentence has been revised to “Chemical hardness ( $\eta$ ) measures the resistance of  $\mu$  to the change in the total number of electrons”. (lines 85 and 86 in the revised manuscript)

\* A table of CIS excitation values compared with experimental excitation values would be preferable.

Response: There is lack of experimental excitation values and available UV-spectrum of sesquiterpenes currently; therefore, such a table can not be prepared.

\* “According to the Franck-Condon principle, a rigid ring system with similar geometries for the ground and excited states has weak transition intensity”. This statement is wrong. According to Franck-Condon principle, a system with similar geometries for the ground and excited states has stronger transition intensity.

Response: The sentence has been revised to “According to the Franck-Condon principle, a loosen ring system with large structural changes for the ground and excited states has weak transition intensity” (lines 254-256 in the revised manuscript).

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

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