

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

Anonymous Referee #2

Received and published: 4 December 2010

This manuscript reports on a straightforward theoretical investigation of sesquiterpenes using density functional theory (DFT), conceptual DFT, time-dependent (TD) DFT, configuration interaction with single 5 excitation (CIS), and Zerner's intermediate neglect of differential overlap (ZINDO) methods. The transition intensities and positions of the sesquiterpenes were obtained and compared. In addition, the nucleophilicity of the sesquiterpenes was calculated by the conceptual DFT method and was invoked in understanding of the reactivity with tropospheric oxidants and the SOA formation. While the electronic structures, spectroscopy, and nucleophilicity of sesquiterpenes determined in this study were helpful, the work provide little insight into the chemistry of those compounds in the atmosphere. A major revision is required before this work can

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be published.

Major points:

(1) 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. The title implies the reactivity properties of sesquiterpenes, but the work provides no kinetics of sesquiterpenes with OH, O₃, or other atmospheric oxidants. 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. (2) 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. (3) 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].

Detailed comments

(1) Are there any higher level of theory calculations besides B3LYP/6-31G(d,p).
(2) The electronic chemical potential would be more appropriate than the chemical potential (μ) 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.
(3) There are some inconsistencies in the formulas of conceptual DFT. In formula (1) . Using finite difference methods for derivatives, , , , , So, 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). (4)

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“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”. (5) A table of CIS excitation values compared with experimental excitation values would be preferable. (6) “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. The reason why exo transition intensity is higher than endo transition intensity is that the structure change of exo excitation is small, while the structure change of endo excitation is large. This is probably because the tension force in the ring structure changes the excited structure a lot from the ground state structure.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C10721/2010/acpd-10-C10721-2010-supplement.pdf>

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

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