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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Iodine chemistry after dark” *by* Alfonso Saiz-Lopez et al.

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This paper presents a very interesting study on the iodine atmospheric chemistry using two modelling approaches: one at the molecular level, one at the global level. The potential energy surfaces for three different reactions were explored for the first time by theoretical calculations: HOI + NO2, HOI + HNO3, and HOI + NO3. I have several comments concerning this work. 1) Spin-orbit correction (SOC) is very important for iodine-containing species. The authors stated on page 6 line 12 that "spin-orbit splittings of -17 and -5 kJ mol-1 were applied to energies of I and IO". These values do not correspond to the well known value for I atom (-30.3 kJ mol-1 from C.E. Moore, Atomic Energy Levels, USGPO, Vols. II and III. NSRDS-NBS 35, Washington, DC, 1971). Over the last years, my group performed theoretical calculations to get the SOC values for numerous iodine-containing species using the CASPT2/RASSI methodology. The corresponding values for I, IO, and HOI are -30.0, -14.4, and -5.9 kJ/mol (Meciarova

et al., CPL, 2011, 517, 149; Khanniche et al., JPCA, 2016, 120, 1737; Sulkova et al., JPCA, 2013, 117, 771). These calculations were also validated by comparison to few available data. I recommend the authors to update their energetics according to the correct SOC values. 2) In Table 2, there are several low frequency modes for molecular complexes and transition state. Are they among them one or several which should be treated as hindered rotors? It is also interesting to compare calculated vibrational frequencies for HOI, NO3, IO, HNO3 with their available experimental counterparts. 3) Nitrogen oxides also exhibits often an instability of the wavefunction (internal or RHF -> UHF). Is-it the case here for all stationary points? This instability will affect the energetics. The Gaussian09 software includes an option to check it. 4) What is the level of theory used for the energetics? It is not clear.

Concerning the atmospheric modelling, the reaction of NO3 with iodocarbons is important as noticed on page 8 line 15, it could be also important to see if adding the reactivity of atmospheric VOC with iodine-containing species will affect the results because this reaction will produce iodocarbons.

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