Does the "reef structure" on the ozone transition state towards the dissociation exist ? New arguments for the shape of the PES from accurate calculations and spectra analyses

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An accurate description of the complicated shape of the potential energy surface (PES) and that of the highly excited vibration states is of crucial importance for various unsolved issues in the spectroscopy and dynamics of ozone and remains a challenge for the theory. Most of previous ab initio calculations predicted an activation barrier at the entrance of the dissociation channel followed by a shallow van der Waals (vdW) minimum along the dissociation reaction coordinate. Various calculations at high level of the electronic structure calculations have suggested that the minimum energy path (MEP) shape has a "reef"-like structure [1,2] with a submerged barrier below the dissociation limit. The important impact of the barrier height and the depth of the vdW minimum on the dynamics of the formation and fragmentation of the excited ozone molecule have been discussed in several studies (see Schinke et al [3], Dawes et al [4] and references therein). These studies suggested that rate coefficient of the O + O_2 exchange reaction should be very sensitive to the shape of the PES in the transition state (TS) region and one of the major obstacles in our understanding of the ozone kinetics is the lack of a quantitatively accurate PES. In this work we compare our vibrational predictions using two versions of the full dimensional ozone PES obtained from recent very accurate ab initio calculations [5] (one keeping the "reef structure" on the TS and another without the "reef barrier") and new experimental ozone band centers. The letter ones have been derived from analyses [6,7], not yet fully published, of new spectra recorded with extremely sensitive laser CRDS technique [8, 9] in the range approaching the dissociation energy. The impact of the shape of the PES near the TS (existence or not of the "reef structure") on vibration energy levels was studied here for the first time. We conclude that the ab initio PES without the reef structure provides vibrational prediction with an average error of 1 cm^{-1} which is much better than all available calculations that involve the activation barrier on the TS. Our result can be considered as the first spectroscopically supported argument that the "reef structure" would be an artefact of previous ab initio calculations.

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