

# Ozone high-energy states: state of the art in *ab initio* calculations, dynamics and isotopic effects near the dissociation threshold

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## **ABSTRACT**

Knowledge of highly excited rovibrational states of ozone isotopologues is of key importance for modelling the dynamics of exchange reactions, for understanding longstanding problems related to isotopic anomalies of the ozone formation, and for analyses of ultra-sensitive laser spectral experiments currently in progress. New theoretical studies of high-energy states for the main isotopologue  $^{48}\text{O}_3 = ^{16}\text{O}^{16}\text{O}^{16}\text{O}$  and for the family of  $^{18}\text{O}$ -enriched isotopomers  $^{50}\text{O}_3 = \{^{16}\text{O}^{16}\text{O}^{18}\text{O}, ^{16}\text{O}^{18}\text{O}^{16}\text{O}, ^{18}\text{O}^{16}\text{O}^{16}\text{O}\}$  of the ozone molecule considered in a full-symmetry approach accounting to the three “open” potential wells due to Jahn-Teller effect will be discussed. Energies and wave functions of bound and metastable states near the dissociation threshold were computed [1] in hyperspherical coordinates accounting for the permutation symmetry of three identical nuclei in  $^{48}\text{O}_3$  and of two identical nuclei in  $^{50}\text{O}_3$ , using our *ab initio* potential energy surface (PES) that permitted an accurate description of metastable states of  $\text{O}_3$  as well as of the  $^{16}\text{O}^{16}\text{O} + ^{18}\text{O} \rightarrow ^{16}\text{O}^{18}\text{O} + ^{16}\text{O}$  isotopic exchange reactions [2,3]. The time-dependent dynamics corresponding to this reaction will be discussed.

The three-wells effect results in a new type of perturbations [1] in observable vibration–rotation bands: the bands will be split in sub-bands corresponding to  $A_1$  and  $B_1$  symmetry types of upper vibrational states of  $^{50}\text{O}_3$  with shifted centers and different rotational constants. In the case of  $^{48}\text{O}_3$ , the tunneling splitting of sub-bands will correspond to  $A_1/E$  or to  $A_2/E$  irreps of upper state vibrations. Another consequence is that the delocalized states, corresponding to classical large amplitude “roaming” motion of an O atom around an  $\text{O}_2$  molecule, would be missing in the traditional one-well approximation. A part of theoretical conclusions have been recently confirmed by the analyses of ultra-sensitive laser experiments near 95 % of the dissociation threshold [4].

Mass-dependent diagonal Born-Oppenheimer corrections (DBOC) to the *ab initio* electronic ground state potential energy surface for the main  $^{16}\text{O}_3$  isotopologue and for homogeneous isotopic substitutions  $^{17}\text{O}_3$  and  $^{18}\text{O}_3$  of the ozone molecule will be also discussed. The comparison with experimental band centers shows a significant improvement [5] of the accuracy with respect to the best Born-Oppenheimer *ab initio* potential energy surface. In case of bending band centers directly observed under high spectral resolutions, the errors are reduced by more than order of magnitude down to  $0.02 \text{ cm}^{-1}$  from observed levels, approaching nearly experimental accuracy.

## **References**

- [1] Kokoouline V., Lapiere D., Alijah A., Tyuterev V., PCCP, 2020, 22(28), 15885 DOI: 10.1039/d0cp02177f
- [2] Guillon G., Honvault P., Kochanov R., Tyuterev V. JPC Lett, 2018, 9(8),1931 DOI: 10.1021/acs.jpcllett.8b00661
- [3] Yuen C., Lapiere D., Gatti F., Kokoouline V., Tyuterev V., JPCA, 2019, 123 (36),7733 DOI: 10.1021/acs.jpca.9b06139
- [4] Vasilchenko S., Barbe A., Starikova E., Kassi S., Mondelain D., Campargue A., Tyuterev V., PRA , 2020, 102 (5), art. no. 052804, . DOI: 10.1103/PhysRevA.102.052804
- [5] Tajti A., Szalay P., Kochanov R., Tyuterev V., PCCP, 2020, 22 (42), 24257 DOI: 10.1039/d0cp02457k