

VIBRATIONAL LEVELS AND RESONANCES ON A NEW POTENTIAL ENERGY SURFACE FOR THE GROUND ELECTRONIC STATE OF OZONE

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The isotopic ratios for ozone observed in laboratory and atmospheric measurements, known as the ozone isotopic anomaly,[1,2] have been an open question in physical and atmospheric chemistry for the past 30 years. The biggest limitation in achieving agreement between theory and experiment has been the availability of a satisfactory[3-5] ground state potential energy surface (PES). The presence of a spurious reef feature in the asymptotic region of most PESs has been associated with large discrepancies between calculated and observed rates of formation especially at low temperature. We recently proposed a new global potential energy surface for ozone[6,7] possessing 4 features that make it suitable for kinetics and dynamics studies: excellent equilibrium parameters, good agreement with experimental vibrational levels, accurate dissociation energy and a transition region with accurate topography (without the reef artifact). This PES has been used recently to simulate the temperature dependent exchange reaction ($^{16}\text{O}+^{16}\text{O}_2$) with a quantum statistical model[6,7], and, for the first time, a negative temperature dependence which agrees with experiments was obtained, indicating the good quality of this global surface. A quantum description of the ozone exchange and recombination reaction requires knowledge of the resonances but also the rovibrational levels just below the dissociation. We present results of global 3-well vibrational-state calculations up to the dissociation threshold and ($J = 0$) resonances up to 1000 cm^{-1} beyond. The calculations were done using a large DVR basis (24 million functions) with a symmetry-adapted Lanczos algorithm as well as MCTDH. Results indicate the presence of localized bound states at energies close to the dissociation threshold beyond which some long-lived resonances follow, contrasted with a few delocalized bound states with density at large values of the stretching coordinates. References: 1- K. Mauersberger et al., *Adv. At. Mol. Opt. Phys.* 50, 1 (2005) 2- R. Schinke et al., *Ann. Rev. Phys. Chem.* 57, 625 (2006) 3- R. Siebert et al., *J. Chem. Phys.* 116, 9749 (2002) 4- M. Ayouz and D. Babikov, *J. Chem. Phys.* 138, 164311 (2013) 5- V.G. Tyuterev et al., *J. Chem. Phys.* 139, 134307 (2013) 6- R. Dawes et al., *J. Chem. Phys.* 135, 081102 (2011) 7- R. Dawes et al., *J. Chem. Phys.* 139, 201103 (2013)