MOLECULAR OXYGEN TETRAMER (O_2)_4: INTERMOLECULAR INTERACTIONS AND IMPLICATIONS FOR THE ε SOLID PHASE

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The recently determined structure[1,2] of the high pressure dark-red ε phase of solid oxygen, which consists of layers of well defined (O_2)_4 aggregates, has risen the interest for the study of the interaction in molecular oxygen oligomers. A few theoretical studies[3-5] have attempted to interpret and rationalize the stability and the bonding of the (O_2)_4 species in the framework of the density functional theory, but with no definitive conclusions. Here we report a reliable theoretical characterization of (O_2)_4 by using high level ab initio supermolecular calculations. In particular restricted coupled cluster [RCCSD(T)] and complete active space perturbation (CASPT2) levels of theory have been employed and combined to obtain an accurate estimation of the singlet ground state of the complex whose nonmagnetic character is consistent with the observed magnetic collapse[6] and spectroscopy[7] of the ε phase. From the analysis of the interaction energy profiles and comparison with pairwise (O_2)_2 potential estimations it is found that, in contrast to previous suggestions[4], the oxygen tetramer is a van der Waals like cluster with the exchange interaction preferentially stabilizing the ground singlet state, as already observed in the case of the oxygen dimer[8,9]. However for short cluster sizes there is an extra stabilization due to many-body exchange interactions, i.e., an incipient chemical bonding that yields a significant softening of the repulsive wall[10]. We show that these findings can be used to model the intra- and intercluster distances of ε-O_2 observed as functions of pressure.

References