Ab initio study of a quasi van der Waals molecule: N_2O_4.

Y. ELYOUSSOUFI, J. LIEVIN and M. HERMAN, *Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CPI 160/09, B-1050 Bruxelles, BELGIUM.*

A critical review of the *ab initio* literature on the ground electronic state of N_2O_4 is presented. It is completed by new calculations including higher order electron correlation effects using the MP4 and internally-contracted MRCI methods and some open questions are revisited. They concern the harmonic and anharmonic force fields, the torsional energy barrier, the dissociation path into two NO_2 radicals and the assignment of the IR spectrum. Most properties affected by the quasi van der Waals nature of the NN bond are shown to require a high level of theory (MRCI/cc-pVTZ). Reliable harmonic vibrational frequencies (within 3%) are however obtained from the MP4/6-31G* method. This level has been adopted to calculate the IR spectrum from anharmonic variational calculations within a 4 dimensional effective model. An unambiguous assignment of the experimental spectrum[a] below 600 cm^{-1} is proposed.

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[a] J. Koput, J.W.G. Seibert and B.P. Winnewisser, Chem. Phys. Lett., **204**, 183 (1993).