INTRAMOLECULAR DYNAMICS IN X_4 RHOMBIC CLUSTERS

ROBERTO LINGUERRI, ISABELLE NAVIZET, and PAVEL ROSMUS, *Laboratoire de Chimie Théorique, Université de Marne la Vallée, F 77454 - Champs sur Marne, France*; STUART CARTER, *Department of Chemistry, University of Reading, Reading RG6 2AD, U.K.*; JOHN P. MAIER, *Department of Chemistry, University of Basel, Klingelbergstr. 80 CH-4056 Basel, Switzerland*.

Two independent approaches are applied to study the intra-molecular dynamics in B_4 electronic ground state. First, a double minimum six-dimensional potential energy surface (PES) is determined in symmetry coordinates for the most stable rhombic (D_{2h}) B_4 isomer in its ^1A_g electronic ground state by fitting to energies calculated by the CCSD(T) approach. The PES exhibits a barrier to the D_{4h} square structure of 255 cm^{-1}. The vibrational levels (J = 0) are calculated variationally using the MULTIMODE[a] code, which involves the Watson kinetic energy operator expressed in normal coordinates. The pattern of about 65 vibrational levels up to 1600 cm^{-1} for all stable isotopomers is analyzed. Analogous to the inversion in ammonia-like molecules, the rhombus rearrangements lead to splittings of the vibrational levels. In B_4 it is the b_{1g} (D_{4h}) mode which distorts the square molecule to its planar rhombic form. It is shown that the rhombic ground states of B_4^+ and B_4^- consist of two vibronically coupled electronic states. The PES for B_4 is used also in time-dependent molecular dynamics calculations using the multi-configurational time-dependent Hartree[b] (MCTDH) method. The 6-D wavepackets are analyzed and the results are compared with time-independent results.

[a] S. Carter, S. Culik and J. M. Bowman *J. Chem. Phys.* **107**, 10458 (1997).
[b] H.-D. Meyer, U. Manthe, and L. S. Cederbaum. *Chem. Phys. Lett.* **165**, 73 (1990).