ON THE NIR–VIS SPECTROSCOPY OF NO_2: POTENTIAL ENERGY CURVES OF THE X^2A_1, A^2B_2, B^2B_1, and C^2A_2 STATES AND THE $\widetilde{A}^2B_2$–$\widetilde{X}^2A_1$ CONICAL INTERSECTION

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Ab initio SCF MRD–CI electronic structure calculations are carried out in C_s symmetry for the three lowest $^2A'$ and $^2A''$ states of NO_2. The four lowest-lying species correspond, respectively, to $X^2A_1(1^2A')$, $A^2B_2(2^2A')$, $B^2B_1(1^2A'')$ and $C^2A_2(2^2A'')$ in C_{2v} symmetry. A cc–pVQZ basis set augmented with s, p, and d Rydberg functions is employed together with an extensive treatment of electron correlation. One–dimensional (1D) potential energy curves (PECs), associated to the equilibrium geometrical parameters of the X^2A_1 ground state (GS), were computed for the four aforementioned doublet states located in the near-IR and visible regions. These 1D cuts are related loosely to the bending, symmetric stretch and asymmetric stretch vibrational modes of the GS. The PECs are then employed to discuss the NIR-Vis absorption/emission spectroscopy of NO_2 and the strong conical intersection (CI) between the ground and first excited A^2B_2 states. In spite of being a small triatomic made up of 2nd-row atoms only, NO_2, a relatively "simple" molecule turns out to be an important testing ground for the study of a number of fundamental molecular processes such as the dynamics of intramolecular energy redistribution which involves the coupling of electronic and nuclear motions and entails the breakdown of the adiabatic BO approximation (e.g., the $\widetilde{A}$–$\widetilde{X}$ conical intersection, Renner-Teller interactions, electronic-to-vibrational (E-V) energy transfer, relaxation of vibrational energy), and for studies of the dynamics of photodissociation/predissociation and photoionization/autoionization. The NO_2 PECs reported in this work may be instrumental to visualize some of the above processes.

[a]While this manuscript was underway Dr. Osman Atabek passed away suddenly; in this posthumous contribution the authors would like to pay homage to the scientist, colleague and friend.