The ionic states of difluoromethane: A reappraisal of the low energy photoelectron spectrum including *ab initio* configuration interaction computations

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Streszczenie

A new synchrotron-based study of the photoelectron spectrum (PES) of difluoromethane is interpreted by an *ab initio* analysis of the ionic states, which includes Franck-Condon (FC) factors. Double differentiation of the spectrum leads to significant spectral sharpening; the vibrational structure observed is now measured with greater accuracy than in previous studies. Several electronic structure methods are used, including equation of motion coupled cluster calculations with single and double excitations (EOM-CCSD), its ionization potential variant EOM-IP-CCSD, 4th order Møller-Plesset perturbation theory (MP4SDQ) configuration interaction (CI), and complete active space self-consistent-field (CASSCF) methods. The adiabatic ionization energies (AIEs) confirm the assignments as band I, one state 1^2B_1 (12.671 eV); band II, three states, 1^2B_2 (14.259) < 1^2A_1 (15.030) < 1^2A_2 (15.478 eV); and band III, three states, 2^2B_2 (18.055) < 2^2A_1 (18.257) < 2^2B_1 (18.808 eV). The three ionizations in each of the bands II and III lead to selective line broadening of the PES structure, which is attributed to vibronic overlap. The apparent lack of a vibrational structure attributable to both the 1^2A_1 and 2^2A_1 states in the PES arises from line broadening with the preceding states 1^2B_2 and 2^2B_2, respectively. Although these $^2A_1$ states clearly overlap with their adjacent higher IE, some vibrational structure is observed on the higher IE. The effects of vibronic coupling are evident since the observed structure does not fit closely with the calculated Born-Oppenheimer FC profiles. Correlation of the lowest group of four AIEs in the PES of other members of the **CH_2X_2** group, where **X = F, Cl, Br,** and **I**, clearly indicate these effects are more general.