Interpretation of the vacuum ultraviolet photoabsorption spectrum of iodobenzene by *ab initio* computations

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Streszczenie

Identification of many Rydberg states in iodobenzene, especially from the first and fourth ionization energies (IE1 and IE4, X2B1 and C2B1), has become possible using a new ultraviolet (UV) and vacuum-ultraviolet (VUV) absorption spectrum, in the region 29 000-87 000 cm−1 (3.60-10.79 eV), measured at room temperature with synchrotron radiation. A few Rydberg states based on IE2 (A2A2) were found, but those based on IE3 (B2B2) are undetectable. The almost complete absence of observable Rydberg states relating to IE2 and IE3 (A2A2 and B2B2, respectively) is attributed to them being coupled to the near-continuum, high-energy region of Rydberg series converging on IE1. Theoretical studies of the UV and VUV spectra used both time-dependent density functional (TDDFT) and multi-reference multi-root doubles and singles-configuration interaction methods. The theoretical adiabatic excitation energies, and their corresponding vibrational profiles, gave a satisfactory interpretation of the experimental results. The calculations indicate that the UV onset contains both 11B1 and 11B2 states with very low oscillator strength, while the 21B1 state was found to lie under the lowest ππ∗ 11A1 state. All three of these 1B1 and 1B2 states are excitations into low-lying σ∗ orbitals. The strongest VUV band near 7 eV contains two very strong ππ∗ valence states, together with other weak contributors. The lowest Rydberg 4b16s state (31B1) is very evident as a sharp multiplet near 6 eV; its position and vibrational structure are well reproduced by the TDDFT results.

Słowa kluczowe

Density functional theory, Excitation energies, Rydberg states, Rydberg series, Vacuum ultraviolet radiation, Photoabsorption, Ions and properties, Absorption spectroscopy, Oscillator strengths, Resonance-enhanced multiphoton ionization