Interpretation of the photoelectron, ultraviolet, and vacuum ultraviolet photoabsorption spectra of bromobenzene by *ab initio* configuration interaction and DFT computations

Autorzy

Michael H. Palmer

Trevor Ridley

Søren Vrønning Hoffmann

Nykola C. Jones

Marcello Coreno

Monica de Simone

Cesare Grazioli

Teng Zhang

Małgorzata Biczysko

Alberto Baiardi

Kirk Peterson

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Streszczenie

New photoelectron, ultraviolet (UV), and vacuum UV (VUV) spectra have been obtained for bromobenzene by synchrotron study with higher sensitivity and resolution than previous work. This,together with use of ab initio calculations with both configuration interaction and time dependent density functional theoretical methods, has led to major advances in interpretation. The VUV spectrum has led to identification of a considerable number of Rydberg states for the first time. The Franck-Condon (FC) analyses including both hot and cold bands lead to identification of the vibrational structure of both ionic and electronically excited states including two Rydberg states. The UV onset has been interpreted in some detail, and an interpretation based on the superpo-sition of FC and Herzberg-Teller contributions has been performed. In a similar way, the 6 eV absorption band which is poorly resolved is analysed in terms of the presence of two ππ* states of 1A1 (higher oscillator strength) and 1B2 (lower oscillator strength) symmetries, respectively. The detailed analysis of the vibrational structure of the 22B1 ionic state is particularly challenging, and the best interpretation is based on equation-of-motion-coupled cluster with singles and doubles computations. A number of equilibrium structures of the ionic and singlet excited states show that the molecular structure is less subject to variation than corresponding studies for iodobenzene. The equilibrium structures of the 3b13s and 6b23s (valence shell numbering) Rydberg states have been obtained and compared with the corresponding ionic limit structures.

Język

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Typ publikacji

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Coupled-cluster methods, Ab initio configuration interaction, Rydberg states, Vacuum ultraviolet radiation, Photoabsorption, Leptons, Synchrotrons, Oscillator strengths, Heterocyclic compounds, Absorption band

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