A combined theoretical and experimental study of the ionic states of iodopentafluorobenzene

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Streszczenie

A new synchrotron radiation photoelectron spectral (PES) study of iodopentafluorobenzene, together with a theoretical analysis of the spectrum, where Franck-Condon factors are discussed, gives detailed insight into the ionization processes, and this exposes the need for a reinvestigation of the vacuum ultraviolet spectral (VUV) assignments. We have calculated adiabatic ionization energies (AIEs) for several ionic states, using the equation-of-motion coupled cluster method for ionic states combined with multi-configuration self-consistent field calculation study. The AIE sequence is: $X^2B1 < A^2A_2 < B^2B_2 < C2^2B_1 < D^2A_1 < E3^2B_1$. This symmetry sequence has a major impact on previous VUV spectral assignments, which now appear to be to optically forbidden states. Changes in the equilibrium structures for these ionic states are relatively small, but a significant decrease and increase in the C–I bond length relative to the X^1A_1 structure occurs for the X^2B_1 and C^2B_1 states, respectively. The PES shows major vibrational overlaps between pairs of ionic states, X with A, and A with B. The result of these overlaps is the loss of vibrational structure and considerable broadening of the higher energy PES state. Although the baseline is nearly re-established between the A and B states, where the two bands are nearly separate, the B state is also broadened by the A state. Only the C ionic state, which shows the most highly developed vibrational structure, can be regarded as free from vibrational coupling to a neighbor state. The Franck-Condon analysis of the PES bands X, A, B, and C is described in detail; the apparent simplicity of some of these bands is illusory, since almost all the observed peaks arise from super-position of several calculated vibrational states. The experimental AIE of the A state, which is submerged under the X state envelope, has been determined by the subtraction of the calculated X state envelope from the observed PES spectrum. The overlap of these PES bands and

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the apparent closeness of the potential energy curves describing them have been investigated, using the state-averaged, complete active space self-consistent field method. We have identified two structures, one where the potential energy curves for the X and A states cross and another for the A and B states. At these two conical intersections (ConInts), there is zero-energy difference within each pair of states. Although similar in energy, the ConInt for the crossing of the X with A states, and that for the A with B states, shows that the open-shell occupancies correspond to the 4 lowest AIE states, and all four states that are quite different from each other.

Słowa kluczowe

Multi-configurational self-consistent field, Coupled-cluster methods, Complete-active space self-consistent field, Potential energy surfaces, Vibrational states, Vacuum ultraviolet radiation, Franck Condon principle, Franck Condon factors, Ions and properties, Gas phase

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