HIGH RESOLUTION ANION PHOTOELECTRON SPECTRA OF CRYOGENICALLY COOLED SILICON CARBIDES

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High-resolution anion photoelectron spectra of cryogenically cooled Si_3C^-, $Si_2C_2^-$, and SiC_3^- obtained using slow photoelectron velocity-map imaging (cryo-SEVI) are presented, providing insight into the geometries, energetics, and vibronic structure of the anionic and the neutral clusters. These spectra yield accurate vibrational frequencies for the neutral clusters. They also yield refined adiabatic detachment energies (ADEs) for the ground states of Si_3C^- and $Si_2C_2^-$ of 1.5374(6) eV and 1.9019(4) eV, respectively, while the ADE of a low-lying isomer of SiC_3^- is found to be 1.9050(7) eV. The cryo-SEVI spectra show that the ground state of $Si_2C_2^-$ is a distorted trapezoid, and represent the first confirmation of the distorted trapezoid structure of $Si_2C_2^-$, the only low-lying isomer of this cluster with a permanent dipole moment. Additional transitions are observed from two low-lying anion isomers: a linear structure and a rhombus. The spectrum of SiC_3^-, in combination with electronic structure calculations, suggests that the true ground state of SiC_3 is a ring structure with a transannular C–C bond, addressing a longstanding controversy surrounding this cluster. All three spectra exhibit Franck-Condon forbidden transitions; these are attributed to Herzberg-Teller coupling in Si_3C and SiC_3 and autodetachment from an excited electronic state of $Si_2C_2^-$.