

OBSERVATION OF VIBRATIONALLY EXCITED STATES OF SiC₂ BY STIMULATED EMISSION PUMPING (SEP) SPECTROSCOPY

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Recent observations of the evolved carbon star IRC+10216 with unprecedented high angular resolution have revealed a plethora of unassigned (U) rovibrational lines associated with the dust formation zone. Because SiC₂ is a known, abundant molecular constituent of this region, it is a reasonable supposition that some fraction of the observed U lines arise from vibrationally excited levels of SiC₂ populated at elevated temperatures. At present, the laboratory rotational data that would permit testing of this hypothesis are largely absent: *ab initio* prediction of relevant spectroscopic constants has proved particularly challenging for SiC₂, and its excited vibrational levels are not efficiently populated in supersonic jet sources. However, the electronic transition responsible for the well-known blue-green Merrill-Sanford bands of SiC₂ admits Franck-Condon access to vibrational levels at least 4000 K above ground, inviting the application of SEP spectroscopy for the observation of vibrationally excited states. SiC₂ has been generated in our laboratory in a jet-cooled discharge of silane and acetylene, optically pumped via the M-S bands, and fluorescence depletion SEP spectra observed for dump transitions terminating in a variety of excited rovibrational levels for all three modes in the \tilde{X} -state. For known rotational levels of $1\nu_3$ and $2\nu_3$ (the pinwheel mode), the rotational energies derived from SEP spectra are in generally excellent agreement (a factor of at least 5 smaller than the dump laser linewidth) with previous observations, giving us good faith in our experimental procedure. The $1\nu_2$ level is notably perturbed, which likely accounts for its as-yet non-observation in the laboratory by rotational spectroscopy. A Fermi resonance with $6\nu_3$ depresses the $1\nu_2$ *B* and *C* constants significantly below the predictions of high-level theory. Vibrationally averaged rotational constants calculated using Fermi resonance mixing coefficients obtained from \tilde{A} -state zero-point dispersed fluorescence are broadly consistent with this interpretation.