THE EFFECTS OF TRIPLET PERTURBERS ON PHOTOPHYSICAL PROCESSES IN ACETYLENE

Stephen Drucker, Jonathan P. O'Brien, Paresh Patel, and Robert W. Field, *MIT, 77 Massachusetts Avenue, Cambridge, MA 02139.*

We have recorded excitation spectra of the acetylene $\tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma_g{}^+$ transition by measuring simultaneously the total emission in two spectral regions: UV (200-400 nm) and NIR (0.9-1.5 μm). UV emission is due to well-characterized[1] $\tilde{A} \rightarrow \tilde{X}$ transitions. The source of the NIR signal is suggested by the emission patterns within the subbands studied, $V_0^2K_0^1$ and $V_0^3K_0^1$. (V denotes the *trans*-bending mode.) The NIR:UV intensity ratio is approximately constant throughout the $V_0^2K_0^1$ subband. This is consistent with excited C_2H or C_2 as the carrier of the NIR signal, because these species, capable of emitting in the NIR[2,3], could be produced *via* multiphoton processes[2] resonantly enhanced by the $\tilde{A}$ state as intermediate. The $V_0^3K_0^1$ subband shows significantly more fluctuation in the NIR:UV intensity ratio than does the $V_0^2K_0^1$ subband. The one-quantum increase in *trans*-bending excitation enables accidental resonances with background states to modulate the NIR emission pattern. Triplet perturbers could participate in this process by modifying the resonance enhancement of C_2H or C_2 production. Mixed S_1–triplet states could additionally contribute to the NIR signal through $T_n \rightarrow T_1$ ($n > 1$) transitions.

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