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Near-IR photodissociation of peroxy acetyl nitrate

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Abstract. Measurements of the C-H overtone transition strengths combined with estimates of the photodissociation cross sections for these transitions suggest that near-IR photodissociation of peroxy acetyl nitrate (PAN) is less significant ($J_{\text{near-IR}} \approx 3 \times 10^{-8} \text{ s}^{-1}$ at noon) in the lower atmosphere than competing sinks resulting from unimolecular decomposition and ultraviolet photolysis. This is in contrast to the photochemical behavior of a related peroxy nitrate, pernitric acid (PNA), that undergoes rapid near-IR photolysis in the atmosphere with $J_{\text{near-IR}} \approx 10^{-5} \text{ s}^{-1}$ at noon (Roehl et al., 2002). This difference is attributed to the larger binding energy and larger number of vibrational degrees of freedom in PAN, which make $4\nu_{\text{CH}}$ the lowest overtone excitation with a high photodissociation yield (as opposed to $2\nu_{\text{OH}}$ in PNA).

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