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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Near-IR photodissociation of peroxy acetyl nitrate" *by* S. A. Nizkorodov et al.

Anonymous Referee #2

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This is an well written and interesting paper that investigates the potential role of infrared excitation in promoting atmospheric photochemistry of peroxy acetyl nitrate (PAN). The present work is in some sense an extension of an earlier study by the same group in which they demonstrated that a significant contribution to HOx formation in the lower stratosphere at high solar zenith angle arises from unimolecular dissociation of pernitric acid (HO2NO2) molecules vibrationaly excited in the region of its first OH stretching overtone by IR solar flux. Based on known thermochemistry, the dissociation threshold energy of PAN falls between the excitation energy associated with the second and third overtone of its C-H stretching vibration. Thus with the presence of initial thermal energy the molecule can, in principle, dissociate upon excitation in the region of its second C-H stretching overtone vibration. The authors estimate the efficiency of excitation to the second and third C-H stretching overtone states of PAN

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by directly measuring the absorption cross section for the CH stretching fundamental and its corresponding first and second overtones and then using this information in conjunction with known overtone cross section for C-H stretching excitation in several other reference molecules, to estimate the cross section of the third overtone band of PAN. The authors also estimate the quantum yield for dissociation as a function of altitude and pressure. The authors conclude from their study that due to the larger binding energy, increased density of vibrational states and the weaker oscillator strength of the C-H stretching overtone, that PAN is more resistant (by roughly a factor of 1000) to overtone induced photolysis by IR solar flux than pernitric acid. Thus, IR induced dissociation can occur only for small subset of atmospherically relavent molecules.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 1269, 2004.