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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 #1

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General comments

This is an interesting and timely paper. Photodissociation of atmospherically important molecules via solar overtone excitation has been demonstrated to be important in a few X-O-H type molecules, with a recent review (in Chem Rev., Dec 2003) suggesting other overtone excitations might also be important. If PAN were to suffer rapid photolysis in the visible-near IR region, it would change its ability to transport NOx significantly, and so would be a very important process to understand. The authors have done a good job of bringing together experimental measurements and calculations to estimate the importance of the near-IR photolysis of PAN, via C-H overtone excitation. This process turns out to be possible, even likely, but not very important to PAN's atmospheric fate.

Specific comments

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page 1271: HNO3 is known to dissociate following v(OH) = 5 excitation [Sinha et al, JCP 92, 401 (1990)].This is perhaps a more relevant example of themally-assisted barrier crossing.

page 1273: In experiments which measure absolute absorption cross sections, it is important to carry out a pressure dependence study, to ensure that absorption is in the Beer's law regime. The authors have probably done this; it should be stated. If they have not, the experiment should be done. One might suspect that some dimerization of PAN is possible, even at moderately low pressures.

page 1274: An RRKM calculation will give a dissociation rate which is relevant here, if one assumes "infinite" coupling among all modes - that PAN excited into CH overtone levels has this energy statistically distributed very rapidly on the timescale of the dissociation or energy loss through collisions. Since the CH stretch is rather far removed (in "bond space" from the bond which will break, I would guess that an RRKM estimate would yield an upper limit to the dissociation rate. The authors might want to comment on that possibility.

page 1275: Staikova et al. [JPC A 106, 3023 (2002)] also come up with a lower dissociation energy for PNA.

page 1278: Why did the authors not look for the NO2 product, using LIF. Surely that primary product is a very much better bet?? NO2 is also quite bright, so its detection is straightforward.

Technical comments:

The paper is well and clearly written. Figure 1 is very small and should be expanded.

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

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Interactive Comment