

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

S. A. Nizkorodov et al.

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Author's comments on "Near-IR photodissociation of peroxy acetyl nitrate" by S.A. Nizkorodov et al.

First of all, let me thank the reviewer for his/her comments on the manuscript. We have done the following changes to the manuscript to improve its quality and readability:

Reviewer #1: "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)...." Revision: The first draft of the paper was written in 2002, before the review came out. We have incorporated the above review in the list of references.

Reviewer #1: "page 1271: HNO₃ is known to dissociate following $\nu(\text{OH}) = 5$ excitation [Sinha et al, JCP 92, 401 (1990)]. This is perhaps a more relevant example of thermally-

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assisted barrier crossing." Revision: We have added this reference to the list.

Reviewer #1: 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." Response: The reviewer is correct in pointing out the importance of verifying the pressure dependence in absolute cross section measurements. However, I would like to stress that we measured relative absorption cross sections in this work. For very weak transitions like CH-overtone there is no reason to believe that their integrated absorbances will deviate from a linear dependence on PAN concentration. Therefore, the ratio of say 2vCH to 3vCH should be independent of pressure. For the stronger fundamental transitions, deviations from linearity are certainly possible, but we measured the ratio of the integrated absorbance of the CH fundamental to that of NO₂-stretches at multiple partial pressures of PAN and always obtained the same result. This is an indirect proof that Beer's law was obeyed for these transitions under our experimental conditions. Dimerization of PAN under the pressures of the experiment is very unlikely, but even if it occurs, it should not affect the relative band intensities of high frequency CH stretching modes in zero-order approximation. (CH hydrogen bonding is very weak). Revision: Section on cross section measurements has been modified slightly to address the reviewer's concerns.

Reviewer #1: 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. Response: This is correct. The quantum yield determina-

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tion presented here is based on the assumptions that: i) energy can exchange freely between different vibrational degrees of freedom (K-rotor states are also counted towards the total available energy); ii). The transition strengths for sequence bands from low-frequency vibrational states that build upon CH overtones (e.g., $2\nu_{\text{CH}} + \nu_8 - \nu_8$) are the same as for the corresponding overtones itself ($2\nu_{\text{CH}}$ in this example). The high frequency CH vibrations are known to couple quite weakly with the low-frequency vibrational modes. Therefore, the second assumption is likely to hold, whereas the first one may break down leading to non-statistically long lifetimes of the vibrationally excited molecules. Therefore, at finite pressures, the quantum yield for dissociation may be reduced by these non-statistical effects. The yield we are predicting will be an upper limit under these non-statistical conditions. Revision: A shortened version of the explanations above has been added to the manuscript.

Reviewer #1: "page 1275: Staikova et al. [JPC A 106, 3023 (2002)] also come up with a lower dissociation energy for PNA." Revision: We have added this reference to the list.

Reviewer #1: 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. Response: At the time of the measurement, we were not equipped to measure NO₂ fluorescence in Paul Wennberg's photodissociation apparatus (it is still the case). Prof. Sinha at UCSD would have been in a better position to try this experiment using the NO₂ photodissociation channel detection. In addition, the NO₂ background signal in the system is much higher (relative to the expected photodissociation signal) compared to that for OH.

Reviewer #1: "Figure 1 is very small and should be expanded." Revision: Figure 1 was made (falsely) assuming that the journal will publish it in a column format. Since this is not the case, we have made a landscape version of Figure 1. The publisher is free to choose any one of these two versions for the final publication.

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