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Interactive Comment

Interactive comment on "Near-UV photolysis cross sections of CH₃OOH and HOCH₂OOH determined via action spectroscopy" by C. M. Roehl et al.

Anonymous Referee #2

Received and published: 30 November 2006

This short paper deals with the determination of the near-UV photolysis absorption cross sections of CH_3OOH and HOCH_2OOH via action spectroscopy in the wavelength range 305-365 nm. In this study the yield of the photodissociation product yield OH is measured via laser induced fluorescence as a function of excited energy. Since the OH quantum yield is unity for both compounds, accurate cross sections can be obtained. For CH_3OOH the OH signals were referenced against the OH photolysis quantum yield of H_2O_2 + hv \rightarrow 2 OH, using established absolute absorption cross sections for H_2O_2 . In these studies the OH signals in the photolysis of H_2O_2 and CH_3OOH were determined back-to-back at each wavelength. In the case of HOCH $_2\text{OOH}$, the OH signals were referenced to the published cross section data of Bauerle and Moortgat (1999). This paper is well organized and the results of this paper are clearly presented and dis-

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cussed. It should be published after consideration of the comments, mentioned below, especially the integration of the results of the missing reference, listed below.

- 1) The authors mention in the text (p 11602, line 3) that for HOCH₂OOH, the cross sections were referenced to the published cross sections at 320 nm of Bauerle and Moortgat (1999), $\sigma = 1.3 \times 10^{-21} \text{ cm}^2$ molecule⁻¹. One expects that at wavelength the HMHP cross section listed in Table 2 should be identical. This is not the case, instead the value $\sigma = 1.22 \times 10^{-21} \text{ cm}^2$ molecule⁻¹ is mentioned. This should be corrected.
- 2) The authors compare their data with those of Vaghjiani and Ravishankara (1989) and Matthews et al. (2005). However they did not consider the recent work of Blitz et al. (2005). Ref: M.A. Blitz, D. E. Heard and M. J. Pilling, Wavelength dependent photodissociation of CH₃OOH. Quantum yields of CH₃O and OH, and measurements of the OH + CH₃OOH rate coefficient, J. Photochem. Photobiol. A: Chemistry 176, 107-113 (2005). The results of this paper should be integrated in text, table 1 and Figures.
- 3) The authors compare HMHP cross sections being 40 % lower at 350 nm than the published values by Bauerle and Moortgat (1999). As the authors note on page 11603 (line 29) HMHP decomposes rapidly on the walls. The decomposition occurs via the reaction $HOCH_2OOH \rightarrow HCOOH + H_2O$ (see Neeb et al., 1997). By monitoring by FTIR the production of HCOOH the degree of decomposition can be followed and thus the concentration of HMHP corrected. Have the authors considered this possibility?

Technical comments and corrections

Page 11604, line 17: write Neeb et al., 1997 (not Neeb, 1997).

Page 11607, line 9: give reference of JPL recommendation.

Page 11613, Table 1: correct name Vaghjiani (not Vaghijiani)

Page 11615, Figure 1: the boxes (top left of drawing) should be wider, so the text within \$4952

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the box (Lambda Physik Dye and SP Nd-YAG) can be read. Also, the meaning of OPO and SFM should be given in the figure caption.

Page 11616, Figure 2a: Figure caption: cite the current JPL recommendation. Also mention that the values of Matthews et al. (2005) are referenced at 355 nm to the values of Vaghjiani and Ravishankara (1989a).

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 11597, 2006.

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