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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Absolute absorption cross-section and photolysis rate of I_2" *by* A. Saiz-Lopez et al.

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We would like to thank the referees for their comments and suggestions, and Bauer *et al.* for bringing to our attention their unpublished measurements of the I_2 cross-section. The error made in the absolute calibration of the I_2 cross-section (see the on-line comment of 24^{th} May 2004), has now been corrected in the text and the relevant diagrams.

Response to the referees:

Referee #1
The corrections described above address the issues raised in paragraphs 1-4 of this referees comment. Our cross-section values in the continuum region ($\lambda < 500$ nm) are now in very good agreement with the values calculated from the referees own study of

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1973. A description of our additional measurements using a grating spectrometer has been added to the revised manuscript.
With regard to the concerns about the magnitudes of our quoted uncertainties for the absorption cross-section (σ) and photolysis rate (J) of I_2:

σ - the quoted uncertainty (12%) for the maximum measured value at 533 nm was derived by combining the standard deviation (9%) of the series of absorption spectra taken to determine the cross-section, and the uncertainty (9%) in the measured vapor pressure of I_2 at 295 K.

J - The uncertainty of 25% in the experimentally-determined value of *J* is the standard deviation of the data from separate runs performed under identical experimental conditions at each light irradiance level. The experimental error for each individual measurement was of course much smaller ($\sim$ 5%).

Additional points raised in paragraphs 5 and 6 of the referees comment have been addressed as follows:

1. The paragraph describing the photo-dissociation channels appropriate to I_2 has been re-structured and re-numbered in the light of the comments made. Description of the *direct* channels (including the C - X transition for which the work of Tellinghuisen, 1973 and Gray *et al.*, 2001 have been cited) now precedes the *indirect* dissociation channels. In turn, the excited I_2 state has been re-labelled as I_2*(B) in accordance with the suggestion of the referee. Also it is now noted in the paper that photolysis via the B - X transition will only occur for excitation above the B state dissociation limit.

2. Regarding the concerns raised with the absorption measurements at 546 nm, we have added a description of the experimental pressure in the absorption cell (1 atmosphere of air). This was used to provide a spectrum appropriate for tropospheric spectroscopy, with the added advantage that this helped to prevent line saturation, so that the absorption remained in the Beer-Lambert regime.

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Minor correction:
infra-read now reads *infra-red*

Referee #2

As the referee has pointed out, the main motivation of this work was to provide an absolute absorption cross-section at sufficiently high resolution for DOAS measurements of molecular iodine. Even though the spectroscopy of I_2 has been widely studied at very high resolution (mostly by laser induced fluorescence), an absorption spectrum suitable for DOAS measurements over a wavelength range of several 10s of nanometers does not appear to exist in the literature. Also, to the best of our knowledge the rate of photolysis of I_2 has not been published previously, *particularly* at 1 atmosphere pressure relevant to the lower atmosphere. The good agreement that we report between the measured rate and that calculated from the cross section is a useful check that the quantum yield is unity over the wide wavelength range where photolysis occurs in the troposphere. Note that in order to calculate the photolysis rate at reasonably high resolution (1 nm) it was neccesary to determine the cross-section at a resolution higher than the 10 nm resolution reported by Tellinguisen (1973).

With reference to the referees final questions, the abstract of the paper states that the cross-section was measured at room temperature (295 K), as was the vapor pressure measurement (see section 2.1). Our corrected cross-section at 500 nm (2.29 x 10^{-18} cm^2 $molecule^{-1}$) is in excellent agrement with that of Tellinghuisen (2.19 x 10^{-18} cm^2 $molecule^{-1}$). A brief description of the grating spectrometer and its application will be given in the revised manuscript.

References

Tellinghuisen, J.: Resolution of the visible-infrared absorption spectrum of I_2 into three contributing transitions, *J. Chem. Phys.*, **58**, 2821-2834, 1973.

Gray, R.I., Luckett, K.M., and Tellinghuisen, J.: Component analysis of the visible absorption spectra of I_2 and Br_2 in inert solutions: A critique of band decomposition by least-squares fitting, *J. Phys. Chem.*, **105**, 11183-11191, 2001.

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