

Interactive comment on “Absolute absorption cross-section and photolysis rate of I₂” by A. Saiz-Lopez et al.

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Several years ago, in our study of HOI photochemistry, we re-measured the absorption cross sections of I₂, as these were necessary for conversion of transient HOI optical densities to absolute cross sections (Bauer et al., 1998). These experiments were conducted with the aim of confirming the available data of Tellinghuisen (1973) and were certainly not as detailed as that study. We reported a value of the cross section of I₂, $\sigma(\text{I}_2) = (2.25 \pm 0.09) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 500 nm. The corresponding value of $2.19 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ (estimated errors of $\sim 3\%$) from Tellinghuisen (1973) is clearly in excellent agreement. We note that our cross section at 436 nm, $\sigma(\text{I}_2) = (1.41 \pm 0.05) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ is also consistent with interpolated values taken

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from the table of Tellinghuisen (1973).

Below, we present some details of these experiments, which were not reported in our manuscript on HOI (see Bauer et al. (1998), section 3.1.3, page 2861).

The experiments were conducted using a 130 cm absorption cell at room temperature (23–25 °C) equipped with a 10 Torr capacitance manometer to determine, in-situ, the pressure of pure I₂. According to the manufacturers specifications, the accuracy of the pressure measurements should be better than 1%. A filtered halogen lamp served as light source, the output of which was collimated, passed through the absorption cell and dispersed by a monochromator before detection by a diode array spectrometer. After measuring the transmitted light intensity in the empty cell (residual pressure of < 0.01 mTorr achieved by using a turbo molecular pump and measured using a Penning gauge), pure I₂ was admitted and the spectrum taken over a period of ~ 40 s. A cell leak rate of about 0.01 Torr per minute was observed and used to correct the true I₂ pressure which was varied between 0.01 and 0.15 Torr. I₂ vapour was introduced into the cell from a flask containing I₂ crystals that had been purified by thorough degassing.

The cross sections at 500 and 436 nm listed above were derived from the slopes of the linear plots of optical density (OD) versus I₂ pressure according to Beer's law, $OD = \sigma[I_2]$. The errors reported stem largely from the correction to I₂ pressure due to a slow leak (see above). The linear plot of optical density at 500 and 436 nm versus I₂ pressure may be viewed at <http://www.mpch-mainz.mpg.de/~crowley/I2.jpg>. In contrast to the continuum, and as described by Tellinghuisen (1973) and Saiz-Lopez (2004), a significant dependence of the cross sections on I₂ pressure was observed in the banded part of the spectrum, which was not further analysed.

The excellent agreement between our cross sections of I₂ in the continuum, obtained using in-situ measurements of I₂ pressures, and those of Tellinghuisen (1973), which relied on the known vapour pressure of I₂ and its temperature dependence, would appear to confirm the established cross sections of Tellinghuisen (1973) at wavelengths

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of 500 nm and below. Should the cross sections of Saiz-Lopez et al (2004) prove however to be correct, the absorption cross section of HOI will require rescaling.

References

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