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Absolute absorption cross-section and photolysis rate of I₂

A. Saiz-Lopez¹, R. W. Saunders¹, D. M. Joseph¹, S. H. Ashworth², and J. M. C. Plane¹

¹School of Environmental Sciences, University of East Anglia, Norwich, UK

²School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich, UK

Abstract. Following recent observations of molecular iodine (I₂) in the coastal marine boundary layer (MBL) (Saiz-Lopez and Plane, 2004), it has become important to determine the absolute absorption cross-section of I₂ at reasonably high resolution, and also to evaluate the rate of photolysis of the molecule in the lower atmosphere. The absolute absorption cross-section (σ) of gaseous I₂ at room temperature and pressure (295K, 760Torr) was therefore measured between 182 and 750nm using a Fourier Transform spectrometer at a resolution of 4cm⁻¹ (0.1nm at $\lambda=500$ nm). The maximum absorption cross-section in the visible region was observed at $\lambda=533.0$ nm to be $\sigma=(4.24\pm0.50)\times10^{-18}\text{cm}^2\text{molecule}^{-1}$. The spectrum is available as supplementary material accompanying this paper. The photodissociation rate constant (J) of gaseous I₂ was also measured directly in a solar simulator, yielding $J(\text{I}_2)=0.12\pm0.03\text{s}^{-1}$ for the lower troposphere. This is in excellent agreement with the value of $0.12\pm0.015\text{s}^{-1}$ calculated using the measured absorption cross-section, terrestrial solar flux for clear sky conditions and assuming a photo-dissociation yield of unity. A two-stream radiation transfer model was then used to determine the variation in photolysis rate with solar zenith angle (SZA), from which an analytic expression is derived for use in atmospheric models. Photolysis appears to be the dominant loss process for I₂ during daytime, and hence an important source of iodine atoms in the lower atmosphere.

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