

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

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Comments on "Absolute Absorption ... I₂," by Saiz-Lopez, et al.

GENERAL –PARA1–. The authors have noted an increased interest in iodine photochemistry in atmospheric processes and have used this to justify measuring and reporting a moderately high-resolution absorption spectrum for gaseous I₂. They have also measured a rate for I₂ photodissociation in a solar simulator and compared it with a rate calculated from their new absorption cross section. The case for presenting a high-resolution absorption cross section appears to be fundamentally sound, even though the relevant spectroscopy of I₂ in the visible region has been considered fairly well-known for several decades. As a reader whose acquaintance with this problem is almost entirely from the spectroscopic side, I have focused my attention primar-

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ily on that part of this work. The general consistency between predictions based on the absorption cross section and the photolysis measurements and their interpretation suggests that the latter aspect of the work is also sound, but I have not scrutinized it very closely. –PARA2–. My main concern is with the scale of the reported absorption cross section, which is 30-35% greater than I reported (Tellinghuisen, 1973; see also followup works published in 1982 and 1997). This problem is discussed in more detail below. It is also disappointing that the key measurements presented in this paper are accompanied by such large uncertainties (12% for the absorption cross section, 25% for the photodissociation yield directly measured). The absorption cross section, in particular, should be measureable with much greater precision than this: I estimated 3% in my 1973 paper, a value which is supported by comparisons with other work, as noted below.

SPECIFIC –PARA1–. In reviewing the literature on the visible absorption spectrum of I2, the authors have noted that in regions of absorption by sharp lines, a low- to moderately high-resolution spectrum may give an apparent absorption cross section that is systematically too small. The reason is that the spectrum in such regions does not obey Beer's law, because the absorption effectively saturates in the sharp lines while remaining small away from such lines. There are two experimental cures for this problem: (1) Measure the spectrum in the presence of a large pressure of an inert gas, which serves to pressure-broaden the lines into a pseudocontinuum. (2) Measure absorption in the limit of zero absorption, where Beer's law does apply. The authors of the present work chose the former course and then attributed their differences with my 1973 results to my failure to do this. However, I chose the equally valid second approach (which they failed to note), so this explanation cannot suffice. Note especially that the I2 absorption at wavelengths below 500 nm is purely continuous, so no such special efforts are needed to obtain correct absorption cross sections in this region. Yet the present spectrum is about 35% stronger than mine at 500 nm, and presumably at shorter wavelengths not included in the comparison of Fig. 3. –PARA2– Both the present measurements and mine relied on control of the I2 vapor pressure via cooling

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of a "cold finger" on the cell. In searching for an explanation of the discrepancy, I have checked the authors' vapor pressure measurement, stated to be 0.225(20) Torr at 295 K. This vapor pressure is actually quite accurately calculable from thermodynamics data, and its calculated value in this T region has remained stable to within better than 1% in the time since I computed it for my 1973 study. The computed value at 295 K is 0.236 Torr, which is only 5% greater than the authors' value; hence this cannot explain the discrepancy. –PARA3– The authors cite an early paper by Rabinowitch and Wood (1936) to support their results. There are detailed results for the region I .LE. 500 nm by Tamres and Bhat (1971, missed by me in my 1973 paper and also by the present authors). Although these were obtained at slightly elevated temperatures (60°- 120°C), their extrapolation to room T yields values in reasonable accord with my 1973 values. Also, Tamres and Bhat's method did not rely on vapor pressure data to determine [I2], rather used a weighing procedure. –PARA4– In summary, while my 1973 measurements were intentionally taken at medium resolution (2.6 nm) and hence cannot be quantitatively compared with present results in the banded region of the spectrum (I .GT. 500 nm), their average should be more in the mid-range of the highly structure spectrum presented in Figs. 2 and 3 of the present work. If consistent, the two spectra should also converge near 500 nm. I think it is highly unlikely that my 1973 estimates of the molar absorptivity are off by much more than my quoted 3% (or 1 L mol⁻¹ cm⁻¹ where this is larger). Yet the discrepancy cannot be attributed to a problem with either the calculated or measured (present work) vapor pressure of I2. This is a potentially very damaging flaw that will affect most other determinations in this paper and could be perpetuated in future works by others. It needs to be checked very carefully, preferably with instrumentation other than the FT spectrometer used so far. –PARA5– There are some other problems of a spectroscopic nature in the paper, though these are less important to the success of the work. Thus, I2 photodissociation is first introduced via the indirect predissociation processes in (R2a & b); then the direct processes (R5a & b) are delayed for almost a page. It would be better to present these together, with direct before indirect. Further, in addition to the B-X and A-X transitions now given in

(R5a & b), there is a third system (1Plu-X) that was a primary target of my 1973 paper. My colleagues and I have recently suggested that this transition be relabeled C-X, for consistency with usage in the other halogens (Gray, et al., 2001). Also, the direct photodissociation via the B state (R5a) occurs only for excitation above the B-state dissociation limit. Finally, for complete specification, the indirect processes now given in (R2) should show I2*(B) rather than just I2*. –PARA6– In Section 2.2, the authors say they monitored I2 by absorption of Hg 546-nm radiation. I am a bit concerned about this, because absorption in this region is via one or two strong absorption lines, meaning the absorption deviates strongly from Beer's Law. This is particularly problematic at low total gas pressures and would normally require a specific calibration. What were the total pressures in the cell during these measurements, and was such a calibration done? It would be much better to choose a wavelength below 500 nm, where the absorption obeys Beer's Law.

TECHNICAL: "infra-read" (p 2383, line 5)

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