

Comment on the uv resonance spectrum and ground-state dissociation energy of I₂

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In recent years, there has been some disagreement¹⁻³ about the correct identification and interpretation of one of the fluorescence series associated with the uv resonance spectrum of I₂ reported in Ref. 1. This has given rise to controversy regarding the value of the dissociation energy of ground-state I₂.¹⁻⁵ In order to resolve this question, one of us (R. V. D.) has now rephotographed this spectrum using the 35 ft vacuum spectrograph at the NRC Laboratories in Ottawa.

The new experiment has shown that the lines listed in Table V of Ref. 1 and assigned there as being part of the I₂ emission doublet series IVb are actually due to NO impurity (the 0-1 band of the γ system). This correction means that vibrational levels of ground-state I₂ have in fact only been observed up to $v=84$, and hence invalidates both the dissociation energy and the uppermost part of the RKR potential curve reported in Ref. 1. It also means that Ref. 2's reassignment of the lower state of this fluorescence series as a shallow O_g⁺(³Π) state of I₂ with a 13 cm⁻¹ high rotationless potential hump, is erroneous. However, it does affirm the validity of the

arguments² that indicated that some reassignment was necessary. The present conclusions also confirm the validity of Stwalley's objections to an assignment of these levels to *any* state correlating with ground state iodine atoms, and hence illustrates the power of the type of long range analysis he used.³ However, these corrigenda cast *no* aspersions on the rest of the I₂ resonance emission data of Ref. 1, on the molecular constants and RKR potential obtained from it in Ref. 6, or on the ground-state dissociation energy reported in Ref. 2. Indeed, within the stated uncertainties, this value of D_0^0 is in good agreement with the more precise value recently reported by Barrow and Yee.⁵

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