

Advanced Kinetic Package for COIL

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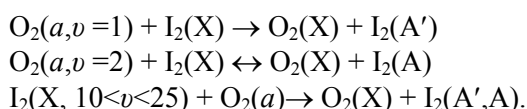
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An advanced kinetic package for COIL is proposed. The standard kinetic package was revised by adding processes describing the vibrational excitation and relaxation kinetics of I₂ and O₂. A multi-pathway I₂ dissociation mechanism and new kinetic data are key elements of the advanced kinetic package.

The standard chemical oxygen-iodine laser (COIL) kinetic package summarized by Perram [1] has been in use for over ten years. Kinetic measurements carried out over the past several years have established that improvement of COIL kinetic package was need. A particularly problematic part of the standard COIL kinetic package is the I₂ dissociation mechanism. The mechanism by which singlet oxygen dissociates I₂ in COIL remains as an important unsolved problem because of its complexity. It is well known that the I₂ dissociation process has initiation and chain stages, and that excited intermediate states of iodine (I₂[†]) are involved. Vibrationally excited iodine I₂(X, v>20) is an important reaction intermediate in the standard COIL dissociation model. It was assumed that this was produced in both the initiation and chain propagation stages of the reaction. Chain propagation was ascribed to



It has been shown [2] that the relaxation kinetics for I₂(X, v>20) are not in agreement with the deactivation kinetics of the excited intermediate in the standard COIL model [1]. The total excitation probability for I₂(X, v>23) in reaction (1) is $\gamma_{v>23} \leq 0.1$, as reported in Ref. [3]. The standard dissociation model with this branching fraction cannot reproduce the observed dissociation rates. Furthermore, in the analysis of recently recorded flow tube data, the number of singlet oxygen molecules O₂(a) required to dissociate one I₂ molecule was predicted to be ≥ 20 if the standard model is the predominant dissociation pathway with $\gamma_{v>23} \leq 0.1$. Overall, the dependence of the I₂[†] deactivation rate constant on the identity of the collision partner is more consistent with the quenching of an electronically excited intermediate². In the model proposed recently⁴ the intermediate during I₂ dissociation is the electronically excited states I₂(A') or I₂(A). The I₂ A' and A states are populated in the following reactions [3,4]:



In the present paper reports the details of the advanced kinetic package and we examine the ability of this model to predict the dissociation rates observed in recent experimental investigations.

[1] Perram G.P. Int. J. Chem. Kinet. **27**, 817 (1995)

[2] Lilenfeld H.V. Final report of McDonnell Douglas Research Laboratories AFWL-TR-83-1 (1983)

[3] Azyazov V.N., Heaven M.C. and Pichugin S.Yu. Proc. SPIE **6874**, 687404 (2008)

[4] Azyazov V.N. and Heaven M.C., AIAA Journal **44**, 1593 (2006)

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