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Mechanism and kinetics of iodine dissociation in COIL

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ABSTRACT

Dissociation of I_2 by $O_2(a^1\Delta)$, with subsequent excitation of I*, was first observed by Arnold et al.[1] in 1966. This key discovery led to the eventual development of the chemical oxygen iodine laser (COIL). The mechanism by which I_2 is dissociated was not determined by Arnold et al.[1] and has remained elusive, despite many experimental attempts to unravel this question. Although the details are not known, it is apparent that a complex interplay between vibrationally and electronically excited states of I_2 is involved. Vibrationally excited states of O_2 have also been implicated. Characterization of the dissociation process is an important issue for COIL as the efficiency is impacted by the energy cost of dissociating the iodine. In this paper we provide a historical summary of work on the dissociation mechanism, and summarize the current understanding of the problem.

Keywords: Chemical lasers, oxygen, iodine, reaction kinetics, energy transfer.

1. INTRODUCTION

In 1966 Arnold et al.[1] reported the key observations that led to the eventual development of the chemical oxygen iodine laser (COIL). They found that adding I_2 to a flow of excited oxygen produced emissions from $I_2(B^3\Pi(0_u^+))$, $I(^2P_{1/2})$ (denoted as I* in the following), and $O_2(b^1\Sigma^+)$. The reactions responsible for excitation of I* and $O_2(b)$ were correctly identified as

$$O_2(a^1\Delta)+I(^2P_{3/2})\rightarrow O_2(X^3\Sigma^-)+I(^2P_{1/2}) \qquad (1)$$

and

$$O_2(a)+ I(^2P_{1/2}) \rightarrow O_2(b)+ I(^2P_{3/2}) \qquad (2)$$
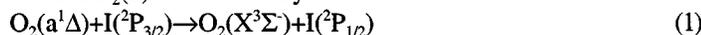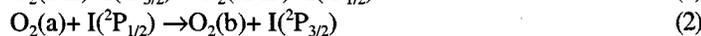
However, Arnold et al.[1] were unable to resolve the question of how I_2 was initially dissociated. The energy levels of O_2, I_2 and I that are relevant to this problem are shown in Fig. 1. As $O_2(a)$ does not carry enough energy to dissociate I_2 in a single collision, Arnold et al.[1] speculated that the first encounter could populate an excited state of I_2, and a second $O_2(a)$ molecule would dissociate this excited species. This can be represented by the sequence

$$O_2(a)+I_2\rightarrow O_2(X)+I_2^\dagger \qquad (3)$$
$$O_2(a)+I_2^\dagger\rightarrow O_2(X)+I+I \qquad (4)$$
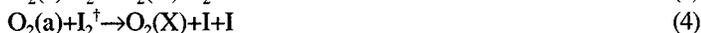
An alternative explanation is that $O_2(b)$ directly dissociates I_2. Arnold et al.[1] demonstrated that $O_2(b)$ could be generated in a flow of $O_2(a)$ by the pooling reaction

$$O_2(a)+O_2(a) \rightarrow O_2(b)+O_2(X) \qquad (5)$$

The dissociation mechanism is a matter of importance for COIL as this process consumes an appreciable amount of energy. In a flow tube study, Alsing et al.[2] found that approximately six $O_2(a)$ molecules were needed to dissociate one I_2 molecule under optimized conditions. For less favorable reagent ratios up to sixteen $O_2(a)$ molecules were needed to dissociate one I_2. In addition to consuming energy, the kinetics of the dissociation process can also influence the power extraction efficiency in a laser system. The time scale for dissociation determines the downstream position at which the maximum concentration of I* will occur. If dissociation takes place too slowly the maximum I* concentration will be achieved after the gas has left the optical cavity. Conversely, if high concentrations of I* are formed before reaching the optical cavity, energy is lost during transport (mostly due to quenching by H_2O from the $O_2(a)$ generator). This leads to a curious situation where the conditions that give maximum power from the laser do not correspond to complete dissociation of I_2[3,4].

Since the seminal work of Arnold et al.[1] there have been several attempts to unravel the details of the dissociation mechanism. A generally accepted model was established in 1988, and optimal values for the most important rate constants were proposed[5,6]. The model was developed using data from kinetic studies of elementary reactions and analyses of device performance characteristics. It has been used for most

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subsequent computational studies of COIL systems. Due to the method of construction, the model does a good job of reproducing the behavior of well-characterized devices. However, it cannot be relied upon to predict the properties of devices running under non-standard conditions (e.g., high pressures and/or novel gas mixing geometries). Consequently, computational predictions for untested conditions or new hardware cannot be trusted. As we will discuss in this article, the problems stem from the fact that we still do not have a complete understanding of the dissociation process.

2. THE FIRST QUANTITATIVE MODEL: DISSOCIATION OF I_2 BY O_2(b)

Derwent and Thrush[7-10] used flow tube techniques to examine the oxygen-iodine system. The kinetics were followed by monitoring emissions from I_2(B) and I*. Arnold et al.[1] had assumed that I_2(B) was formed by I*+I+M recombination, but Derwent and Thrush[7] were able to show that it is produced by sequential excitation of I_2. They proposed the mechanism

$$I_2+O_2(b)\rightarrow I_2(A^3\Pi(1_u))+O_2(X) \qquad (6)$$
$$I_2(A^3\Pi(1_u))+O_2(a) \rightarrow I_2(B)+O_2(X) \qquad (7)$$
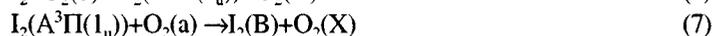
but did not consider the excited states of I_2 to be important in the dissociation process. Their analysis of the kinetics led to the conclusion that I_2 was dissociated by[8]

$$I_2+O_2(b) \rightarrow 2I+O_2(X) \qquad (8)$$

This reaction set, along with the pooling reactions 2 and 5, provided a satisfactory representation of the observed emission signals. Derwent and Thrush[10] also used the equilibrium between reaction 1 and the reverse process

$$I*+O_2(X) \rightarrow I+O_2(a) \qquad (9)$$

to evaluate the radiative lifetime of I*. In considering these data they realized that reaction 1 could sustain CW lasing on the I*$\rightarrow$I transition. The subsequent demonstration of a chemically driven O_2(a)/I* laser[11,12] (as described in the preceding paper by McDermott[13]) stimulated further studies of O_2/I_2 kinetics.

3. THE CHAIN DISSOCIATION MECHANISM AND PROBLEMS WITH THE IDENTITY OF $I_2^\dagger$.

The model proposed by Derwent and Thrush[7,8] required a gas kinetic rate constant ($\sim2\times10^{-10}$ cm^3 s^{-1}) for the removal of O_2(b) by I_2. Using pulsed laser excitation of O_2(b,v=0), Houston and co-workers[14,15] made direct measurements of the removal rate constant. The value they obtained, 2×10^{-11} cm^3 s^{-1}, was too small to account for the flow tube results. Consequently, Heidner et al.[16] performed a careful and systematic reinvestigation of the I_2/O_2(a) kinetics. Fluorescence signals from I_2(B), I_2(A), I*, O_2(b) and O_2(a) were monitored in flowing I_2/O_2(a) mixtures. The dependence of the I_2 dissociation rate on the presence of H_2O was also examined; the motivation being that H_2O was present in the flow from chemical O_2(a) generators, and it was expected to have a deleterious effect on the dissociation rate. Heidner et al.[16] established the most important characteristics of the dissociation process. They found that there was a slow initiation step followed by rapid, branched-chain dissociation of I_2. I* was identified as the chain carrier. Noting that the dissociation rate was dependent on the initial concentration of I_2, they also suggested that an excited state of I_2 was the precursor to atomic iodine. The reaction scheme used to model these observations was as follows. The slow initiation step was attributed to reaction 3. This was followed by the rapid dissociation of $I_2^\dagger$ by reaction 4. I atoms liberated by this sequence are excited by reaction 1, permitting I* to carry the chain via the reaction

$$I*+I_2\rightarrow I+ I_2^\dagger \qquad (10)$$

As expected, the presence of H_2O did slow the dissociation rate. It was known that both O_2(b) and I* were effectively quenched by H_2O, but when Heidner et al.[16] modeled their results they found that these were not the primary reactions influencing the dissociation rate. Instead, the models required gas kinetic (2×10^{-10} cm^3 s^{-1}) deactivation of $I_2^\dagger$ by H_2O

$$I_2^\dagger+H_2O\rightarrow I_2+H_2O \qquad (11)$$

Heidner et al.[16] attempted to define a sub-set of critical rate constants by fitting to their dissociation rate data. Unfortunately, several of the rate constants could not be uniquely determined as they were strongly

correlated. Two limiting rate constant sets were offered as constraints on a yet-to-be-determined set of final values. Three of the rate constants differed by more than an order of magnitude between the two models. Heidner et al.[16] also noted that their models were not completely satisfactory, as they could not find a single set of parameters that could represent all of the data. They did find that the original Derwent and Thrush[8] model gave acceptable results, but concluded that "the agreement with experiment is moderately good, but, based on the direct measurements of Houston and co-workers, such agreement must be fortuitous".

Hediner et al.[16] discussed possible assignments for $I_2^\dagger$. Within the framework of their model there were two plausible alternatives. Either $I_2^\dagger$ was vibrationally excited $I_2(X)$ or the metastable electronically excited species $I_2(A'^3\Pi(2_u))$. There were troubling difficulties with both of these choices. $I_2(A')$ has an excitation energy of 10,042 cm^{-1}, so it cannot be accessed by energy transfer from $O_2(a)$ (T_0=7882 cm^{-1}). Near-resonant transfer from $O_2(a)$ or I^* would populate $I_2(X)$ vibrational levels in the range of v=40-50. Experiments performed by Hall et al.[17] showed that I^* was rapidly quenched by I_2 (k=3.5x10^{-11} cm^{3}s^{-1}), and that vibrationally excited $I_2(X)$ was formed in the process. Van Bentham and Davis[18] later went on to show that vibrationally excited $I_2(X)$ was generated when I_2 was added to a flow of $O_2(a)$. The problem, with regard to assigning $I_2^\dagger$ to vibrationally excited $I_2(X)$, was that Hall et al.[17] reported rapid relaxation of $I_2(X, v=40)$ by Ar. This result appeared to be at variance with Heidner et al.'s[16] observation that the dissociation rate was not influenced by the presence of Ar. This conflict could be resolved by recognizing that several vibrational energy transfer collisions would be needed to relax the initially formed $I_2(X,v\sim40)$ to levels that did not have sufficient energy to be dissociated by a collision with $O_2(a)$ ($I_2(X, v<20)$). Assuming that the vibrational relaxation rate constant measured by Hall et al.[17] corresponded to $\Delta v=-1$ transfer, David et al.[19] used kinetic modeling to show that the vibrational cascade process would not be fast enough to impact the dissociation rate for the conditions of Heidner et al.'s[16] experiments. With this insight it was concluded that $I_2^\dagger$ is the vibrationally excited species, and Heidner et al.'s[16] model 1 rate constants were adopted for subsequent simulations of COIL devices. However, lingering doubts concerning the identity of $I_2^\dagger$ remained. Lilenfeld[20] compared the effects of H_2O, CO_2, and SF_6 on the dissociation rate. He found that H_2O and CO_2 were very effective in deactivating $I_2^\dagger$, while SF_6 was about 8 times less effective than CO_2. It was surprising to find that SF_6 was not the best deactivator, as this molecule has many vibrational modes that can accept vibrational energy from I_2. Based on these observations Lilenfeld[20] favored the notion that $I_2^\dagger$ is the electronically excited species $I_2(A')$. He noted that $O_2(a,v=1)$ has almost enough energy to excite $I_2(A')$, and used EPR spectroscopy to show that $O_2(a,v=1)$ was present in the flow from his singlet oxygen generator.

Several excited states of I_2 could be involved in the process where $O_2(a)$ dissociates $I_2(A')$. Emission from $I_2(B)$ is seen in $O_2(a)/I_2$ flames, and it had been suggested that reaction 7 and $I_2(A')+O_2(a)\rightarrow I_2(B)+O_2(X)$, followed by predissociation of $I_2(B)$ were the source of I atoms. Lilenfeld[20] was able to eliminate these channels by demonstrating that strong magnetic fields, which accelerate the $I_2(B)$ predissociation rate, do not increase the overall dissociation rate.

4. IS $I_2^\dagger$ VIBRATIONALLY EXCITED $I_2(X)$? A CLOSER LOOK.

Lilenfeld[20] and Heidner et al.[16] had drawn attention to the puzzling characteristics of $I_2^\dagger$ deactivation. This species was rapidly removed by H_2O and CO_2, while collisions with He or Ar were less effective by orders of magnitude. For example, in Heidner et al 's[16] model 1 the rate constants for deactivation of $I_2^\dagger$ are (in units of cm^3 s^{-1}) 3x10^{-10} (H_2O), 5x10^{-11} ($O_2(X)$), and 4x10^{-12} (Ar). These trends are more typical of electronic quenching, rather than vibrational relaxation. Heaven and co-workers[21-24] examined the viability of equating $I_2^\dagger$ deactivation with $I_2(X)$ vibrational energy transfer by studying the relaxation process under well-controlled conditions. Individual ro-vibrational levels of $I_2(X)$ in the range 22<v<43 were populated using a pulsed stimulated emission pumping technique. The excited molecules were allowed to make a few collisions with the surrounding bath gas, and then the pulses from a probe laser were used to observe the range of levels populated by energy transfer. Fig. 2 shows results from this type of measurement. In this instance $I_2(X)$ was excited to the v=23, J=57 level (where J is the rotational quantum number). The upper panel in Fig. 2 shows a probe laser spectrum taken under collision free conditions. The J=57 population gives rise to just two spectral lines that obey the $\Delta J=\pm1$ selection rule. The lower panels show the results of colliding $I_2(v=23, J=57)$ with Ar and H_2O. Most of the lines in these traces originate from rotationally inelastic collisions

($\Delta v=0$ transfer). The lines marked with asterisks are the result of $v=23\rightarrow22$ transfer. From these traces it can be seen that the probabilities for vibrational relaxation by H_2O and Ar are comparable. Modeling of these data indicates that vibrational relaxation by H_2O is about a factor of two faster than relaxation by Ar^{24}. The rate constants do not differ by a factor of 75, as required by the models of $I_2^\dagger$ deactivation. The absolute magnitudes of the vibrational relaxation rate constants also pose a problem. For relaxation by H_2O the total removal rate constant was 1.6×10^{-10} cm^3 s^{-1}, and this was dominated by $\Delta v=-1$ transfer. This is only half of the $I_2^\dagger$ deactivation rate constant, without considering the damping effect of the vibrational cascade sequence. Models of $v=40\rightarrow20$ relaxation[24] predict an overall deactivation rate constant for H_2O of 8×10^{-12} cm^3 s^{-1}.

Although the vibrational relaxation rate constants were in gross disagreement with the limiting deactivation rate constants of Heidner et al.[16], this did not mean that the identification of $I_2^\dagger$ as $I_2(X, v>20)$ had necessarily been invalidated. Heidner et al.[16] stated that their rate constant set was not unique. Consequently, Paschkewitz and Heaven[25] explored the possibility of re-optimizing the rate constant package with the $I_2^\dagger$ deactivation rate constants constrained to values that were compatible with the vibrational relaxation rate constant measurements. The model was fit to Heidner et al.'s[16] dissociation rate data. It was found that the value of the H_2O deactivation rate constant could be reduced to a minimum value of 4.8×10^{-11} cm^3 s^{-1}, but this was still too large to be consistent with vibrational relaxation. Other problems with the re-optimized model were that it could not tolerate deactivation by Ar and the dissociation rates predicted for low concentrations of H_2O were in poor agreement with the experimental data[25]. The conclusion drawn from these efforts was that $I_2(X, v>20)$ is not the immediate precursor of atomic iodine. Although $I_2(X, v>20)$ may play an important role in the dissociation mechanism, the deactivation kinetics are governed by a different species.

5. IS $I_2^\dagger$ ELECTRONICALLY EXCITED I_2?

Emission from $I_2(A^3\Pi(1_u))$, $\tau_{rad}=220$ μs) is readily observed from $O_2(a)/I_2$ flames[16,26], but the lowest energy electronically excited state of I_2 $(A'^3\Pi(2_u))$ is very metastable, and cannot be detected by emission spectroscopy. Basics et al.[27] used laser excitation techniques to demonstrate that $I_2(A')$ was generated in $O_2(a)/I_2$ mixtures. They found that $I_2(A')$ and $I_2(X, v>20)$ were present at comparable concentration levels. Barnault et al.[28] proposed that $I_2(A')$ was populated by the process

$$I_2(X, v\approx10)+O_2(a)\rightarrow I_2(A')+O_2(X) \qquad (12)$$
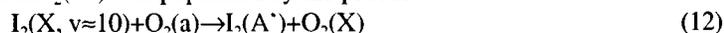
Support for this mechanism was provided by a study of the $I_2(X)$ vibrational population distribution in a flowing $I_2/O_2(a)$ mixture. Barnault et al.[28] observed selective depletion of vibrational levels around $v\approx10$, indicating that this population was being removed by reaction 12. The dissociation mechanism proposed by Barnault et al.[28] was dependent upon vibrational excitation of $I_2(X)$, but the kinetics were controlled by passage through the A' state. Additional kinetic schemes involving $I_2(A')$ were elaborated by Bouvier et al.[29] These models could accommodate the fact that moderate pressures of Ar or He had very little influence on the dissociation rate. Tellinghuisen and Phillips[30] had reported rate constants for removal of $I_2(A')$ by He and Ar of 0.94×10^{-14} and 2.8×10^{-14} cm^3 s^{-1}, respectively. The small rate constants were consistent with removal via collision induced dissociation. Quenching of $I_2(A')$ by molecular collision partners that could accept energy by E-E or E-V transfer was expected to be much more effective. Tellinghuisen and Phillips[30] observed a self-quenching rate constant of 5.5×10^{-11} cm^3 s^{-1}. These trends provided some indication that $I_2(A')$ could be the key intermediate, but data for the quenching of $I_2(A')$ by H_2O and $O_2(X)$ were needed to further explore this possibility. Komissarov et al.[31] measured these rate constants using pulsed laser pump-probe techniques. Quenching rate constants of 6.3×10^{-12} and 3.4×10^{-12} cm^3 s^{-1} were obtained for $O_2(X)$ and H_2O, respectively. Clearly, these collision partners were much more effective quenchers than He or Ar, but the quenching still appeared to be slower than that required for $I_2^\dagger$ deactivation. Furthermore, O_2 was more effective in removing $I_2(A')$ than H_2O, in conflict with the ordering of the deactivation rate constants. Komissarov et al.[31] suggested that the latter problem could be resolved if O_2 quenching of $I_2(A')$ occurred by the process

$$I_2(A')+O_2(X)\rightarrow I_2(X, v\approx10)+O_2(a) \qquad (13)$$
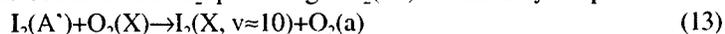
which would minimize the loss of energy and permit facile re-excitation. Conversely, it was assumed that quenching by H_2O caused irreversible deactivation to the lowest vibrational levels of $I_2(X)$. The remaining problem was the low absolute magnitudes of the $I_2(A')$ quenching rate constants. This could be

accommodated in the model by reducing the rate constants for excitation and dissociation of $I_2(A')$, thereby allowing the deactivation processes to compete. The resulting kinetic scheme is illustrated in Fig. 3.

An attempt to derive rate constants for the revised kinetics package was made by modeling the data of Heidner et al.[16] The performance of the revised model was comparable to that of Heidner et al.'s[16] limiting case models. Once again it was found that the available data were not sufficient to define a unique set of rate constants. Komissarov et al.[31] concluded that their model was capable of reproducing the dissociation rate data, and presented one set of physically reasonable rate constants as an example. Subsequently, Bruins et al.[32] and Madden[33] have modeled the performance of COIL devices using the Komissarov et al.[31] rate constants. They found poor agreement with the experimental data, primarily due to underestimation of the I_2 dissociation rate. This failure shows that the rate constant package contains errors, it does not necessarily imply that the mechanism is incorrect. The model has sufficient flexibility that fitting the rate constants to flow tube and COIL performance data would provide a parameterized model that would work as well as the standard model. However, this would be an exercise of questionable value, as it cannot be used to distinguish the true mechanism from functionally equivalent models. Further studies of the elementary reactions are needed to assess the viability of the mechanism proposed by Komissarov et al.[31]

6. IS VIBRATIONALLY EXCITED O_2 IMPORTANT IN THE DISSOCIATION PROCESS?

The crux of the problem with models that are dominated by the kinetics of an $I_2^\dagger$ intermediate is the relative ordering of the deactivation rate constants, $k_{H_2O}^\dagger \approx 6k_{O_2}^\dagger > 75k_{Ar}^\dagger$. The Derwent and Thrush[7,8] model was successful because H_2O is the most efficient quencher of $O_2(b)$. Houston and co-workers had shown that dissociation by $O_2(b, v=0)$ was untenably slow, but alternative mechanisms involving vibrationally excited $O_2(b)$ and $O_2(a)$ have been advanced. As noted above, Lilenfeld[20] detected $O_2(a, v=1)$ in his experiments, and suggested that $I_2(A')$ could be directly excited by this species. More recently, Azyazov et al.[34] observed $O_2(a, v=1)$ in the flow from a jet-type singlet oxygen generator. In these experiments the evidence for the presence of $O_2(a, v=1)$ was provided by detection of the $O_2(a, v=1)$-$O_2(a) \rightarrow O_2(X)$-$O_2(X)$ dimole emission band. Azyazov et al.[34] estimated that about 2% of the $O_2(a)$ in their system was vibrationally excited. They suggested possible roles for vibrationally excited O_2 in the dissociation mechanism that included $O_2(a, v>0)+I_2(X) \rightarrow O_2(X) + I_2(A')$, and gas kinetic dissociation of $I_2(X)$ by $O_2(b, v>0)$. Processes that might generate vibrationally excited O_2 include

$$O_2(a) + O_2(a) \rightarrow O_2(b, v>0) + O_2(X) \qquad (14)$$
$$O_2(a) + I^* \rightarrow O_2(b, v>0) + I \qquad (15)$$
$$O_2(b) + H_2O \rightarrow O_2(a, v>0) + H_2O \qquad (16)$$

Models based on these reactions will no doubt be able to reproduce the flow tube and laser performance data, once the rate constants have been empirically adjusted. As with the previous models, it will not be possible to evaluate the reality of the model as the required rate constants and final state distribution data are not available. Measurements of a few key rate constants should be undertaken to assess the importance of these reactions.

7. CONCLUSION

Thirty six years ago Arnold et al.[1] noted that "A more difficult question is how the I_2 is initially dissociated". Their comment remains valid. Important details of the dissociation mechanism have been gleaned from careful kinetic measurements, but this data set is still far from complete. Models of the dissociation process have been further elaborated and refined by fitting to laser performance characteristics. Unfortunately, the complexity of the process does not allow the mechanism to be determined by this approach. Since the establishment of the standard reaction set and rate constant package used to model COIL devices, investigations of specific reactions have shown that some of the critical rate constants are incorrect, and have called the accepted mechanism into question. At this point the standard model should be regarded as an intelligent parameterization, rather than a correct physical description.

The majority of the data used to establish the COIL kinetics package was recorded more than fifteen years ago. The generation of researchers who revealed the potential of the $I_2/O_2(a)$ system, and mapped the functional characteristics of the I_2 dissociation process, did so through elegant application of a limited set of diagnostic tools. Since that time advanced techniques for characterizing the key species in COIL systems have been developed, as described in the paper by Davis[35]. Application of the full range of diagnostic techniques in new studies of the dissociation mechanism will lead to a final resolution of this long-standing problem. The development of truly predictive computational models for COIL devices will then be in reach.

ACKNOWLEDGMENT

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Energy $(cm^{-1}) \times 10^{-3}$

$I_2\ B(^3\Pi_0^+)$

15

4878

$O_2\ (^1\Sigma)$

$- + - 2I(^2P_{3/2})$

$I_2\ A(^3\Pi_{1u})$

5239

805

$I_2\ A'(^3\Pi_{2u})$

10

$I\ (^2P_{1/2})$

$O_2\ (^1\Delta)$

7603

7882

10042

1.315 μm

5

$I\ (^2P_{3/2})$

$O_2\ (^3\Sigma)$

$I_2\ X(^1\Sigma)$
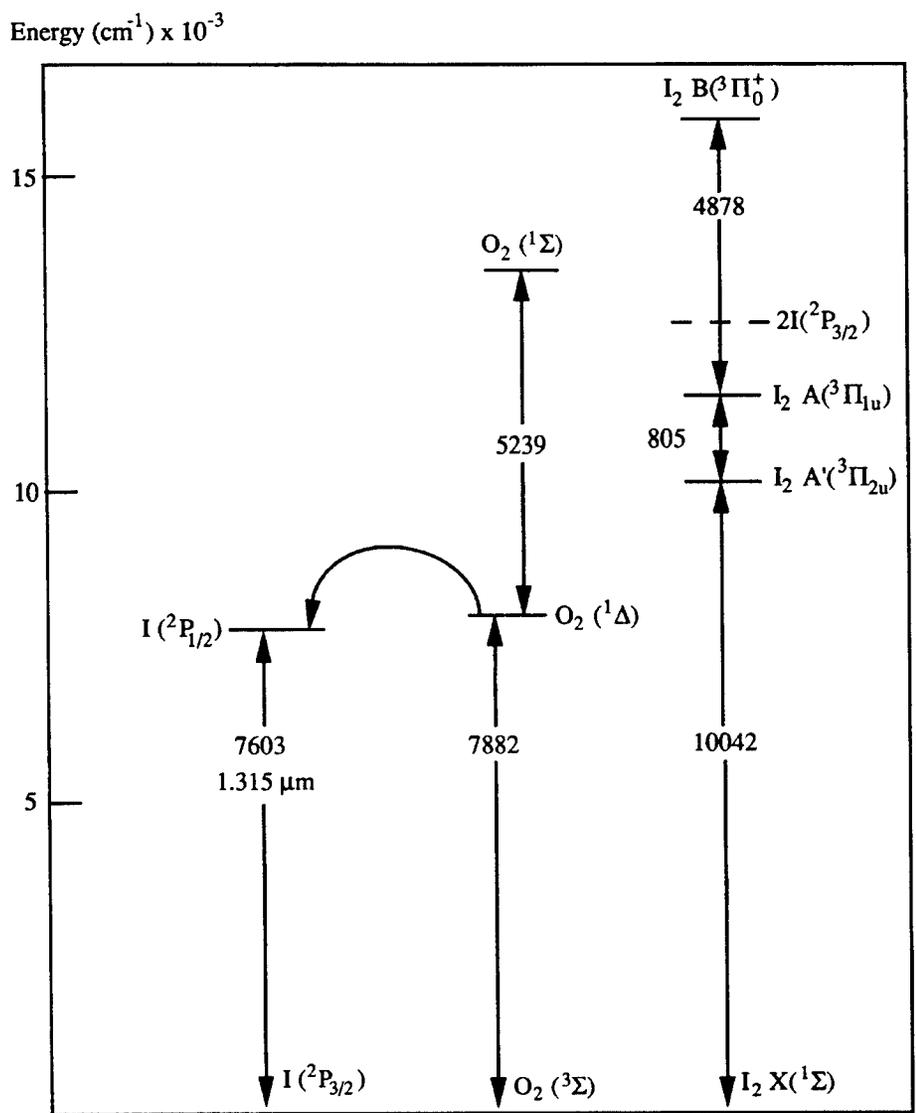
Figure 1. Energy level diagram showing the low-lying states of O_2, I_2, and I
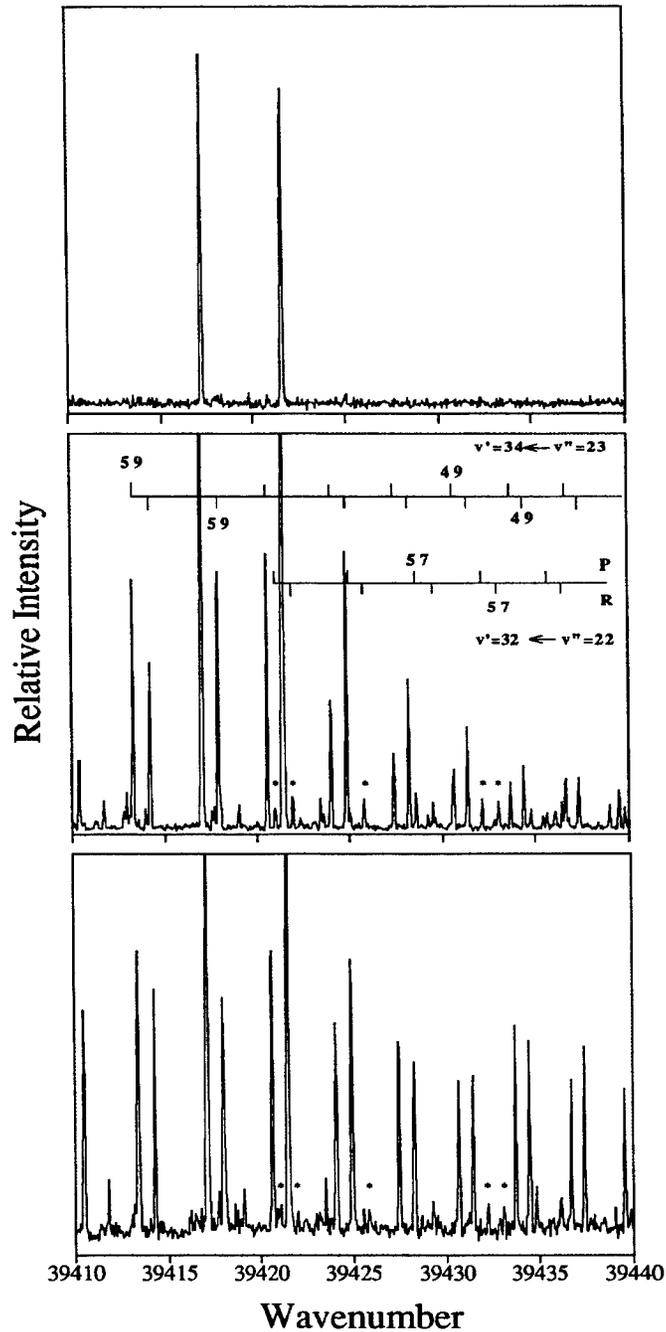
Figure 2. Spectra showing ro-vibrational level state preparation and collisional energy transfer. The upper trace demonstrates clean preparation of the $I_2(X)$ v=23, J=57 level under collision-free conditions. The middle and lower traces show the effects of ro-vibrational energy transfer induced by collisions with H_2O (middle trace) and Ar (lower trace). The peaks marked with asterisks originate from levels populated by vibrational energy transfer.
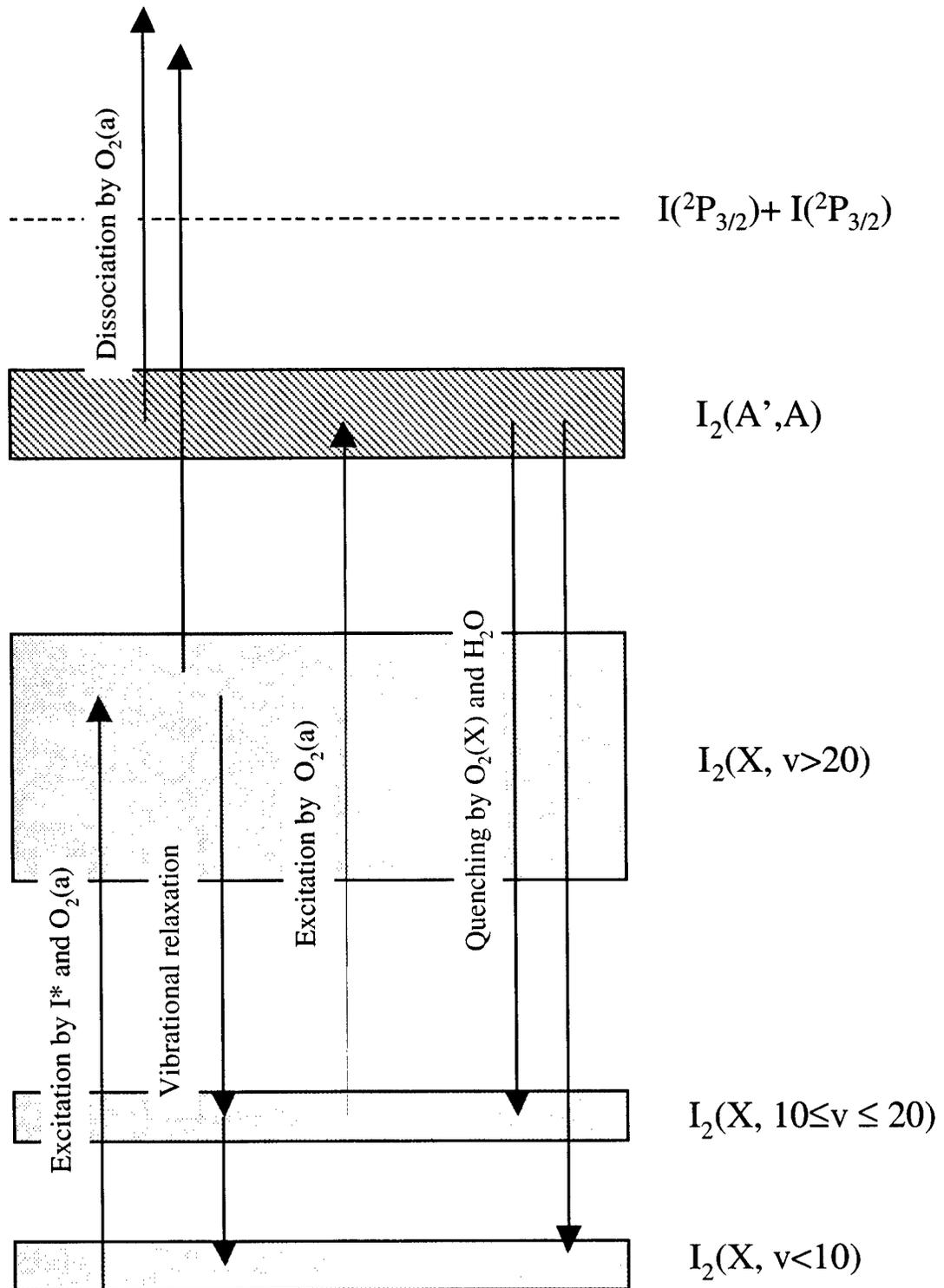
Figure 3. Schematic of the proposed dissociation mechanism proposed by Komissarov et al.[31]