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ABSOLUTE MEASUREMENTS OF THE $I_2(X)$ HIGH VIBRATIONAL LEVELS IN THE OXYGEN-IODINE REACTION

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Abstract - The dissociation with of I_2 by $O_2(^1\Delta_g)$ in a Chemical Oxygen Iodine Laser (COIL) cannot occur a single collision. A two-step model where the excited intermediate species is identified with the vibrational states of $I_2X(O_g^+)$, with V between 30 and 43, has been proposed. The existence of these species has already been checked by using laser fluorescence excitation spectroscopy. The aim of this work is to perform absolute measurements of the iodine vibrational levels populations along the reaction zone in order to have a better understanding of the dissociation mechanism.

1 - Introduction

The dissociation of I_2 by $O_2(^1\Delta_g)$ in a Chemical Oxygen Iodine Laser (COIL) cannot occur with a single collision because the energy of $O_2(^1\Delta_g)$ is far less than the dissociation energy of iodine (figure 1).

A two-step dissociation process where the excited intermediate species are supposed to be the vibrational states of $I_2X(O_g^+)$ has been proposed by several groups^(1,2,3). David and coworkers proposed a model in agreement with this hypothesis⁽³⁾. It is consistent with Heidner's model in which the intermediate species I_2^* is not identified⁽⁴⁾.

According to this model, the dissociation occurs as follows:

1) the excitation by collision with $O_2(^1\Delta_g)$ followed by the vibrational relaxation populates all the levels under $V'' = 43$:

2) dissociation:

Only the levels with V'' between 30 and 43 have an energy sufficient to lead to the dissociation in a single collision with $O_2(^1\Delta_g)$. Another process has been proposed by Nota et al⁽⁵⁾. According to this process, the first step of the dissociation is the same as in references^{1,2,3} mechanism.

The second step is:

As A'_{2u} is a non radiative state, it can be the intermediate species of the dissociation process. Finally, the dissociation would occur as follows:

or

This process requires three collisions with a singlet oxygen molecule. But, in the reaction (4), one of the two iodine atoms is produced in the $^2P_{1/2}$ state the energy of which corresponds to the singlet oxygen energy. So, in this case, it is equivalent to a two-step process if the energy consumption is considered. Previous experimental results have shown that the $\text{I}_2(X, V'' \leq 43)$ levels and the $\text{I}_2(A'_{2u})$ state are significantly populated^(5,6,7). The aim of the present work is to perform absolute measurements of the iodine vibrational level populations along the reaction zone in order to check the existence of the reactions (2) and (3) and to observe their effects.

2 - Experimental

The laser excites the iodine molecules from the vibrational levels with $5 \leq V \leq 43$ of the X-state to levels of the B-state. The B-X LIF can be observed (figure 1). The laser linewidth is about 50 MHz. This is lower than the 700 MHz of the iodine lines. The excitation spectra are obtained by scanning the laser wavelength in a 30 GHz range. Each scan begins at a different wavelength. The theoretical spectra are calculated by assuming an approximate iodine vibrational population distribution and an estimated rotational temperature. These populations are adjusted by a comparison of the experimental spectra and theoretical spectra, using a non linear least squares fit inversion method described in^{2,7,8}. The levels V'' between 17 and 43 are probed with the LDS 821 dye (800 - 850 nm) and the levels $\text{I}_2(X, 5 \leq V'' \leq 25)$ are detected with the DCM dye in the 635 - 680 nm range. The reaction takes place in a $2 \times 2 \times 17 \text{ cm}^3$ movable square glass tube (figure 2). The physical parameters are given in the table I.

Total oxygen pressure (Torr)	% $\text{O}_2(^1\Delta)$	Iodine pressure (Torr)	H_2O pressure (Torr)
1	5 - 10%	$43 \cdot 10^{-3}$	0
1	0	$43 \cdot 10^{-3}$	0
0,170	5 - 10%	$7,3 \cdot 10^{-3}$	0 and $30 \cdot 10^{-3}$

Table I

Experimental conditions used in the laser excitation experiments

3 - Results

The main results presented here have been obtained at an oxygen pressure of 1 Torr and with a iodine concentration of $1,38 \cdot 10^{15} \text{ molecules/cm}^3$. In these conditions, the maximum iodine dissociation rate is about 46% and is reached $2 \cdot 10^{-3} \text{ s}$ after the

iodine injection (figure 3). The figure 4 shows the vibrational population distribution in the reaction zone. It is deduced by joining the vibrational population curves obtained with the DCM and the LDS 821 dyes. Its shape does not change along the reaction zone or with water vapor added in the flow. The absolute concentration measurements of the vibrational levels are possible by comparison with the concentration measurements of the lowest vibrational levels at room temperature. The ratio $[I_2(X, 30 \leq V'' \leq 43)]/[I_2]$ is about $3 \cdot 10^{-4}$, in good agreement with the results of Van Benthem and Davis⁽¹⁾. The figures 5 and 6 show the vibrational levels concentrations versus time obtained respectively with DCM and LDS 821 dyes.

The main new fact is the existence of a concentration depletion for the levels above $V'' = 10$, which occurs simultaneously with the maximum dissociation rate. Now, the $V'' = 11$ level is the first from which the excitation towards A'_{2u} by collision with the singlet oxygen is exoenergetic. So, this depletion can be the consequence of the reaction (3) which is a step of the dissociation mechanism involving the A'_{2u} state.

4 - Conclusion

It can be deduced from the figure 3 that the average dissociation speed during the first millisecond is about $5.8 \cdot 10^{17}$ molecules $\text{cm}^{-3} \text{s}^{-1}$. The dissociation speed calculated with the upper values $[O_2(^1\Delta_g)] = 3.2 \cdot 10^{15} \text{cm}^{-3}$, $k_{\text{diss}} = 3 \cdot 10^{-10} \text{cm}^3 \text{s}^{-1}$,⁽⁴⁾ and $[I_2^*] = 4.13 \cdot 10^{11} \text{cm}^{-3}$, is about $4 \cdot 10^{17}$ molecules $\text{cm}^{-3} \text{s}^{-1}$. So the part of the iodine molecules which are dissociated by collision between $I_2(X, 30 \leq V'' \leq 43)$ and $O_2(^1\Delta_g)$ does not exceed 70%. Moreover, the depletion of the low vibrational levels population agrees with the dissociation from the A'_{2u} state. In our low singlet oxygen concentration conditions, this last mechanism can be dominant, especially if one consider the vibrational relaxation efficiency and the value $[I_2(X, V'' = 10)] = 4 \cdot 10^{12} \text{cm}^{-3}$. These results show that the two processes are in competition. Their relative importance may change with the singlet oxygen concentration (about 60% in the COIL) or with the water vapor concentration and it is difficult to identify the dominant process without a more extensive study.

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Fig. 1 - Transitions involved in the laser excitation experiments.

Fig. 4 - Vibrational population distribution.

Fig. 2 - Experimental set-up.

Fig. 3 - $I_2(B \rightarrow X)$ fluorescence and dissociation rate versus time.

Fig. 5 - Iodine vibrational population $I_2(X, 5 \leq v' \leq 20)$ versus time. DCM dye.

Fig. 6 - Iodine vibrational population $I_2(X, 17 \leq v' \leq 43)$ versus time. LDS 821 dye.