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R. Crozet, R. Bacis, A. Bouvier, S. Churassy, J. P. Pique. THE SINGLET MOLECULAR OXYGEN-IODINE REACTION: POPULATION OF ROVIBRATIONAL LEVELS OF THE IODINE GROUND STATE THROUGH INVERSION OF LASER EXCITED SPECTRA. *Journal de Physique Colloques*, 1987, 48 (C7), pp.C7-385-C7-387. 10.1051/jphyscol:1987792 . jpa-00227097

HAL Id: jpa-00227097

<https://hal.science/jpa-00227097>

Submitted on 4 Feb 2008

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THE SINGLET MOLECULAR OXYGEN-IODINE REACTION : POPULATION OF ROVIBRATIONAL LEVELS OF THE IODINE GROUND STATE THROUGH INVERSION OF LASER EXCITED SPECTRA

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The mechanism for the dissociation of molecular iodine in the presence of $O_2(^1\Delta_g)$ is poorly understood at present. It is of fundamental importance for the comprehension of the mechanism of the chemical oxygen-iodine laser (R. Bacis and S. Churassy, Proceedings of the 6th G.C.L. Conference, Jerusalem, Sept. 8-12, 1986 - Ed. S. Rosenwaks, Springer-Verlag, 1987, p.142-155). It is thought that high vibrational levels of the I_2 ground state, excited by energy transfer from $O_2(^1\Delta_g)$, play an important role in this dissociation of I_2 . A dye laser pumped by a copper vapour laser is used to generate $I_2(B0_v^+ \leftarrow X^1\Sigma_g^+)$ excitation spectra of the $I_2/O_2(^1\Delta_g)$ flame, obtained by mixing heated I_2 vapour with $O_2(^1\Delta_g)$ generated through a microwave discharge (2.45 GHz). The pressure in the flow tube is 0.5 Torr (Fig.1). The vibrational levels of $I_2(X)$ around $v''=40$ are expected to be resonantly populated by collision between I_2 and $O_2(^1\Delta_g)$ or excited iodine atoms. In the experiments, we have recorded excitation spectra (S.P.E.(v)) obtained after the absorption of the laser photons (" $h\nu_{laser}$ ") from the X state to the B state of I_2 , by detecting, with a photomultiplier, the laser induced fluorescence (L.I.F.) $B \rightarrow X$ (Fig.2).

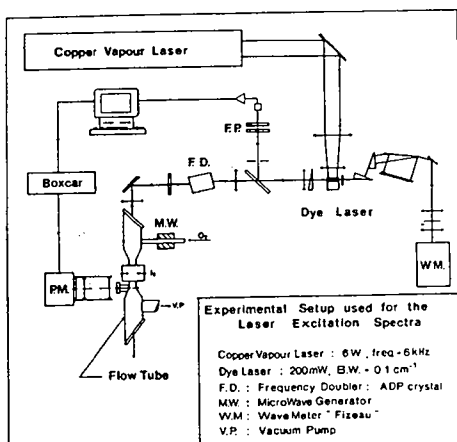


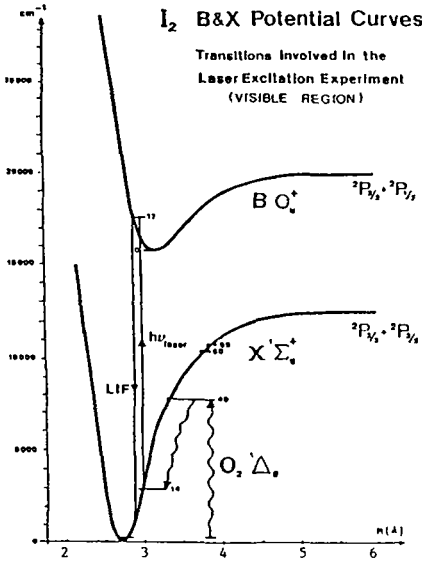
Fig. 1

We have developed a non-linear least squares technique for inverting such spectra and we can obtain accurate vibrational and rotational population data. The theoretical absorption intensity I_v is given by

$$I_v = \text{DET}(v') \cdot X(1) \cdot \nu \cdot \text{FCF}(v',v'') \cdot \text{Pop}(v'') \cdot \exp\{-B_{rot}/X(2)\}$$

$X(1)$: normalisation factor
 $X(2)$: rotational temperature
 $B_{rot} = |B_{v'} - B_{v''}| J'(J'+1) - J''(J''+1)^2 + \dots (hc/k)$

$\text{Pop}(v'')$: population function, the form of which can be approximated by a Boltzmann function or a parabolic function. Every significant $\text{Pop}(v'')$ can also be considered as a separate parameter
 $\text{FCF}(v',v'')$: Franck Condon Factor
 $\text{DET}(v')$: detection function.



A theoretical spectrum (S.P.(ν)) can be obtained by summing all the I_{ν} for the various transitions $\nu'', J'' \rightarrow \nu', J'$ taking into account of the apparatus function A.F., which depends on the excitation source and lineshape

$$S.P.(\nu) = \sum I_{\nu} \cdot A.F.$$

$$(0 \ll J'' \ll 250, 0 \ll \nu'' \ll 70, 0 \ll \nu' \ll 60)$$

We compare this with the experimental intensity S.P.E.(ν) and we minimize

$$\bar{\chi}^2 = \sum [S.P.(\nu) - S.P.E.(\nu)]^2 \quad (\text{Fig. 3}).$$

Fig. 2

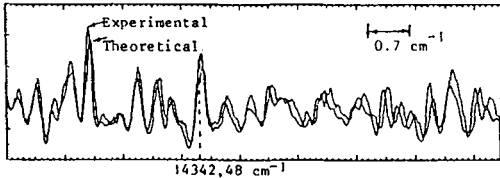


Fig. 3
Excitation spectra of the O₂-I₂ flame by LD 700 dye laser.

We then calculate the best parameters and deduce the statistical error in a given experimental run. The standard error is taken as

$$ERROR = [\bar{\chi}^2 / (n-m)]^{1/2} V_{ii}^{1/2}$$

V : dispersion matrix ; n : number of points used to reconstruct the spectrum ; m : number of parameters.

As example of the results of our measurements we show on Fig.4 the variation of the $\nu''(\bar{X}^2 \Sigma_g^+)$ populations at the end of the reaction region. When the results of separate experiments are brought together, due to various systematic errors, the r.m.s. deviation on the parameters is significantly larger than the statistical error found for individual runs (example : $T_{rot} = 380$ K, standard error = 4 K, r.m.s. = 70 K). Due to multicollisional process the expected maximum population around $\nu''=35-40$ at the beginning of the reaction seem to be degraded to lower ν'' levels through vibrational transfers in the explored region of Fig.4.

Another important point is the possible existence of other electronic lower states acting as reservoirs. The only easy way to discover the populations of these reservoirs states is through laser excitation to ionic states of I₂. Thus in the 3000-3200 Å region, we mainly expect excitation spectra from the 2u and 1u states (Fig.5). A strong excitation

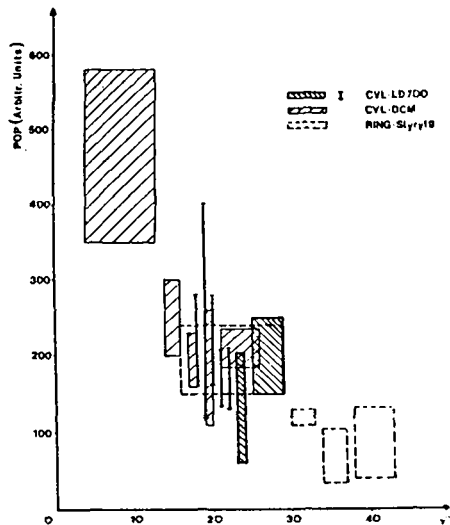


Fig. 4
Full height of a point = 2 r.m.s. deviation

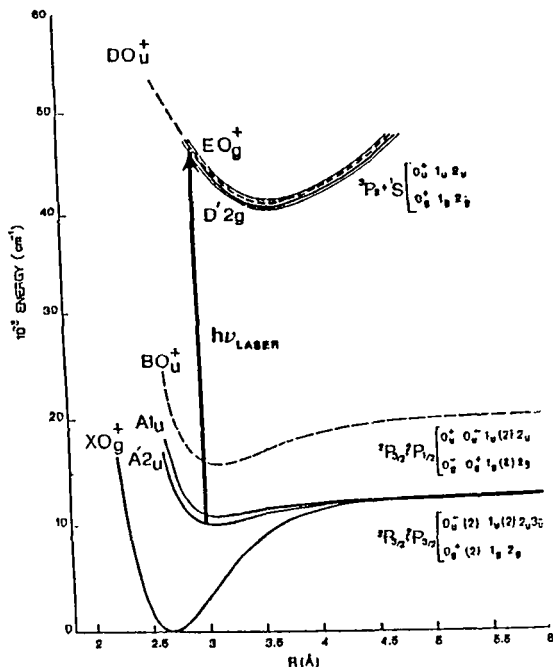


Fig. 5
Frequency doubled dye laser excitation of the ionic states of I_2 detection of L.I.F. in the U.V. region (≈ 300 nm).

signal has recently been recorded (Fig.6). Unfortunately, at the present time spectroscopic studies of the ionic states involved such as $2g$ are not sufficiently developed to enable us either to characterize the states involved in these spectra with certainty or to deduce related populations.

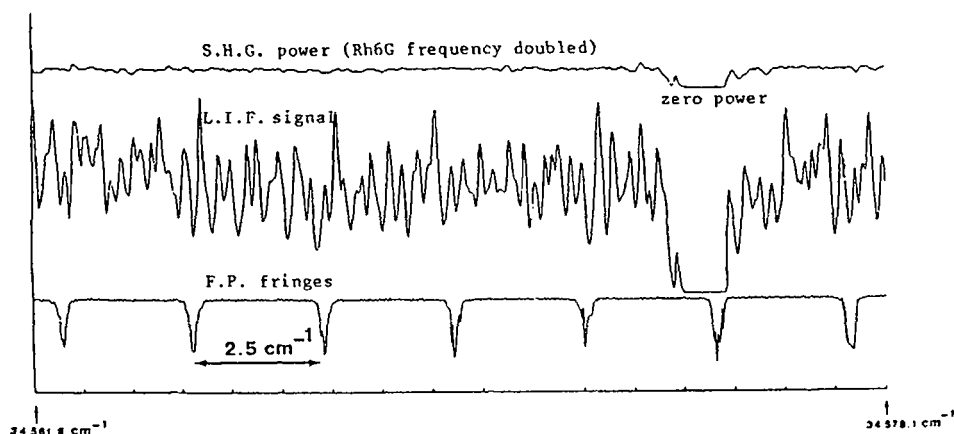


Fig. 6