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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

P. CROZET, R. BACIS, A. BOUVIER, A.J. BOUVIER, S. CHURASSY and J.P. PIQUE

Laboratoire Spectrométrie Ionique et Moléculaire (CNRS UA-171 et Greco Celphyra), Université Lyon I, 43, Bd du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France

*Laboratoire de Spectrométrie Physique (CNRS UA-08 et Greco Celphyra) USM Grenoble, BP 68, F-38402 Saint-Martin-d’Hères, France

The mechanism for the dissociation of molecular iodine in the presence of \( \text{O}_2(1\Delta_g) \) 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 5th 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 \( \text{I}_2 \) ground state, excited by energy transfer from \( \text{O}_2(1\Delta_g) \), play an important role in this dissociation of \( \text{I}_2 \). A dye laser pumped by a copper vapour laser is used to generate \( \text{I}_2(\text{B}_0^0 \rightarrow \text{X}_1^1\Sigma_g^+) \) excitation spectra of the \( \text{I}_2/\text{O}_2(1\Delta_g) \) flame, obtained by mixing heated \( \text{I}_2 \) vapour with \( \text{O}_2(1\Delta_g) \) generated through a microwave discharge (2.45 GHz). The pressure in the flow tube is 0.5 Torr (Fig.1). The vibrational levels of \( \text{I}_2(\text{X}) \) around \( v^\prime=40 \) are expected to be resonantly populated by collision between \( \text{I}_2 \) and \( \text{O}_2(1\Delta_g) \) or excited iodine atoms. In the experiments we have recorded excitation spectra (S.P.E.\((\nu)\)) obtained after the absorption of the laser photons ("\( h\nu_{\text{laser}} \)) from the \( \text{X} \) state to the \( \text{B} \) state of \( \text{I}_2 \), by detecting, with a photomultiplier, the laser induced fluorescence (L.I.F.) \( \text{B} \rightarrow \text{X} \) (Fig.2).

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

\[
I_v = \text{DET}(\nu) \cdot X(1) \cdot \nu \cdot \text{FCF}(\nu',\nu^\prime) \cdot \text{Pop}(\nu^\prime) \cdot \exp\{-B_{\text{rot}}/(X(2))\}
\]

\( X(1) \): normalisation factor
\( X(2) \): rotational temperature
\( B_{\text{rot}} = [B_{\nu^\prime} + J(j^\prime+1) - B_{\nu} + J^2(j^\prime+1)^2 + ...]/(\hbar c/K) \)
\( \text{Pop}(\nu^\prime) \): population function, the form of which can be approximated by a Boltzmann function or a parabolic function. Every significant \( \text{Pop}(\nu^\prime) \) can also be considered as a separate parameter
\( \text{FCF}(\nu',\nu^\prime) \): Franck Condon Factor
\( \text{DET}(\nu) \): detection function.
Erni, BaX Potential Curves

A theoretical spectrum (S.P.\( (v) \)) can be obtained by summing all the \( \Pi_v \) 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

\[
S.P.(v) = \sum \Pi_v \cdot A.F.
\]

\((0 \leq j' < 250, 0 \leq \nu'' \leq 70, 0 \leq \nu' \leq 60)\)

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

\[
\chi^2 = \sum [S.P.(v) - S.P.E.(v)]^2
\]

(Fig. 3).

**Fig. 2**

**Fig. 3**

Excitation spectra of the \( \text{O}_2 \cdot \text{I}_2 \) 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

\[
\text{ERROR} = [\chi^2/(n-m)]^{1/2} \quad \text{V}_{ij}^{1/2}
\]

\( V \): 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 \( \nu''(X^2\Sigma_g^+) \) 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: \( T_{\text{rot}} = 380 \text{ K}, \) 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 \( \nu'' \) 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 \( \text{I}_2 \). Thus in the 3000-3200 Å region, we mainly expect excitation spectra from the \( 2u \) and \( 1u \) states (Fig. 5). A strong excitation...
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. 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).