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Implementation of laser induced fluorescence technique to study the kinetics of radicals generated in the IR multiphoton dissociation of chloroform

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Abstract. In this work we present the design and implementation of an experimental facility for the study of the reaction mechanisms of the CCl2 radicals produced in the Infrared Multiple-Photon Dissociation of CDCl3. The design of this facility was performed by combining two techniques: Laser Induced Fluorescence (LIF) and Infrared Multiple-Photon Dissociation (IRMPD). A TEA CO2 laser and a dye laser were synchronized to couple both techniques. The IRMPD of CDCl3 with a TEA CO2 laser produces CCl2 radicals and DC1 as main products. The dye laser was used for the electronic excitation of the CCl2 radicals. The relaxation of these radicals to the ground level gives rise to the fluorescence signal which is proportional to the radicals’ concentration. The kinetics of the CCl2 radicals was studied by analyzing the fluorescence signal intensity for different delay times between both lasers radiation. We also present the data acquisition system developed, the kinetic model proposed to explain the experimental results and the rate constants values \( k_{O2} \) and \( k_{HCl} \) determined for the reactions of the CCl2 radicals with O2 and HCl.

1. Introduction

The growing interest in isotopically pure materials has brought the attention to the development of new techniques in the field of isotopic separation. The Infrared Multiple-Photon Dissociation (IRMPD) technique has been widely employed to enrich different isotopes using diverse working molecules. When a polyatomic molecule is subjected to an intense IR field coincident with a vibrational band of the electronic ground state, it will sequentially absorb a certain number of photons. When the accumulated energy exceeds the dissociation threshold, the molecule will dissociate. If only one isotopic species is selectively excited and dissociated, isotopically enriched fragments will be produced which can be later removed by conventional techniques. Subsequent to the IRMPD the generated fragments undergo reactions that can strongly affect the selectivity of this technique. Thus, the study of the kinetics followed by these fragments is essential in the development of an isotope enrichment system.

In this work we present the implementation of an experimental facility that couples the Laser Induced Fluorescence (LIF) technique to an IRMPD system. The LIF technique is a highly selective and sensitive detection technique in which the species to be studied are excited to an electronic state upon absorption of laser radiation. The intensity of the fluorescence signal emitted by the excited species as they return to the electronic ground state is dependent on their concentration, the gas
temperature and the total sample pressure. In consequence, this is a powerful technique for quantitative determinations when the species under study are found in trace levels. It can be also used for the determination of the rate constants of the reactions of the generated species with other gases.

The kinetics of the reaction of the CCl₂ radical with O₂ and HCl was studied, as well. The CCl₂ radicals were generated by the IRMPD of CDCl₃, which is a promising working molecule for the laser hydrogen isotopes separation [1-7]. O₂ usually appears as a contaminant in production lines, and its reaction with CCl₂ would strongly affect the selectivity of the IRMPD process [8, 9]. The reaction of CCl₂ radicals with HCl or DCl which is the reverse reaction of the IRMPD process can also affect the selectivity of the process [8]. Even though the reaction rate constants of CCl₂ with CH₄, CF₂Cl₂, C₂H₆, C₂Cl₄, N₂O, CHCl₂ and CH₂Cl₂ have been already determined [9-11], there is little information about the rate constants of the reactions of this radical with many compounds of technological interest. The implementation of the LIF technique allowed the CCl₂ radicals to be monitored in a sensitive and selective way. The reaction rate constants of these radicals with O₂ and HCl were determined.

2. Experimental

Figure 1 shows the design of the experimental set-up used to carry out the LIF experiments. The CCl₂ radicals were generated by the IRMPD of CDCl₃ with a pulsed TEA CO₂ laser with a repetition rate of 0.9 Hz tuned to the 10P(48) emission line. The laser radiation was focused into the center of the reaction cell with a 12 cm focal length Ge lens.

The radicals were excited to the first electronic state with a dye laser pumped by a frequency tripled Nd:YAG laser pulsed at a repetition rate of 9 Hz. The dye laser consisted of an oscillatory stage followed by an amplification stage. The dye used was Cumarina 540, Exciton, and the laser wavelength was tuned to 541 nm and controlled with a spectrometer, Avantes, Ava Spec 3648.

The lasers were introduced into the reaction cell co-linear way through opposite windows and the fluorescence signal was detected at 90° as shown in figure 1. A photomultiplier tube, RCA 1P28, was used for the detection of the fluorescence signal and, at the entrance of the photomultiplier tube, a wavelength longpass interferential filter and an iris were disposed in order to diminish the background signal generated by reflections of the dye laser in the walls of the reaction cell.

The Nd:YAG and TEA CO₂ lasers emissions were externally controlled with a Stanford Research Systems DG 535 delay unit with an internal clock frequency of 9 Hz. An output channel of the delay unit output was used to trigger the TEA CO₂ laser. As shown in figure 1, this output channel was connected to the entrance of a fₚ/10 frequency divider so as to obtain a repetition rate of 0.9 Hz. Another channel was used to trigger the Nd:YAG laser and the total jitter of the system was found to
be 20 ns. The Nd:YAG laser trigger was delayed with respect to that of the TEA CO₂ laser. The fluorescence signals for different delay times as well as the pulse-to-pulse TEA CO₂ and Nd:YAG lasers output energies were acquired with an oscilloscope, Tektronix DPO 7054. A specific program was developed for the control of the whole experiments by a PC.

The samples were prepared in a high vacuum system with a turbomolecular pump (Leybold, Turbovac) pumped by a rotary vane pump (Leybold, Trivac) and introduced in a cylindrical Pyrex glass cell 3 cm diameter and 10 cm long. The CDCl₃ pressure was fixed at 1 Torr and the O₂ and HCl pressures were varied in the 0 - 10 Torr and 10 - 30 Torr ranges, respectively. In the experiments in the presence of O₂, 1 Torr of CHCl₃ was added to the gas mixture in order to determine the amount of CDCl₃ dissociated by the laser.

The output energy of the dye laser was 1.5 mJ. The TEA CO₂ laser output energy was 500 mJ and was registered by a GenTec meter, ED 200.

The intensities of the fluorescence signals acquired for the different delay times were then fitted with a proposed kinetic model and the reaction rate constants for the reactions of CCl₂ radicals with O₂ and HCl were obtained.

2.1 Measurement method

CCl₂ radicals were excited to the first electronic state (A¹B₁ ← X¹A₁) with a dye laser. The amount of excited radicals is proportional to their concentration and, due to the kinetics of the reaction, it is time dependent. The dye laser pulse was delayed with respect to that of the TEA CO₂ laser in order to retard the electronic excitation of the CCl₂ radicals with regard to their generation and thus enable the time dependence of the radical concentration to be studied. Figure 2 shows the measurement and analysis processes.

![Figure 2](image)

**Figure 2.** a) Dye laser pulses at different delay times with respect to the TEA CO₂ laser pulses. b) LIF signals of the CCl₂ radicals excited by the dye laser pulses shown in a). c) LIF intensity corresponding to the maxima of the LIF signals shown in b).

The delay times were varied in a geometric progression between 5 µs and 10 ms in order to give the same relevance to fast and slow processes, as shown in figure 2. The fluorescence intensity was determined from the maxima of the fluorescence signals arising from the decay of the CCl₂ radicals to
the electronic ground state, X1A1. Finally, the rate constants of the reactions of the CCl2 radicals with O2 and HCl were obtained by fitting the experimental time dependence of the fluorescence intensity signals with the theoretical model.

3. Results

3.1 Kinetic reaction model

The CCl2 radicals were generated by the IRMPD of CDCl3 [2]

\[ \text{CDCl}_3 + h\nu \rightarrow \text{CCl}_2 + \text{DCl} \]  

(1)

Subsequent to the dissociation the radicals’ recombination reaction [12]

\[ \text{CCl}_2 + \text{CCl}_2 + \text{M} \rightarrow \text{C}_2\text{Cl}_4 + \text{M} \]  

(2)

and the reaction of the radicals with the buffer gas take place. In the presence of O2, the radicals react with this molecule to produce CCl2O and O [13]

\[ \text{CCl}_2 + \text{O}_2 \rightarrow \text{CCl}_2\text{O} + \text{O} \]  

(3)

and the radicals concentration can be calculated from

\[ \frac{d[\text{CCl}_2]}{dt} = -k_{\text{O}_2}[\text{CCl}_2][\text{O}_2] - 2k_T[\text{M}][\text{CCl}_2]^2 \]  

(4)

In the presence of HCl, CHCl3 is formed [8]

\[ \text{CCl}_2 + \text{HCl} \rightarrow \text{CHCl}_3 \]  

(5)

and the radicals concentration can be calculated from

\[ \frac{d[\text{CCl}_2]}{dt} = -k_{\text{HCl}}[\text{CCl}_2][\text{HCl}] - 2k_T[\text{M}][\text{CCl}_2]^2 \]  

(6)

Equations (4) and (6) evidence that the reaction rates of the radicals are proportional to the buffer gases concentrations. The proportionality constants are the corresponding reaction rate constants \( k_{\text{O}_2} \), \( k_{\text{HCl}} \) and \( k_T \). \( k_{\text{O}_2} \) and \( k_{\text{HCl}} \) are the reaction rate constants of the CCl2 radical with O2 and HCl, respectively, and \( k_T \) represents the termolecular rate constant for the radicals’ recombination reaction.

Theoretical expressions for the fluorescence intensity can be obtained by solving the differential equations (4) and (6) considering that the fluorescence signal intensity is proportional to the radicals’ concentration

\[ S_{\text{O}_2} = \kappa_1 \frac{k_{\text{O}_2}[\text{O}_2]}{2k_T[\text{M}][\text{CCl}_2]^2_0} \frac{[\text{CCl}_2]^0}{e^{k_{\text{O}_2}[\text{O}_2]} \left( \frac{k_{\text{O}_2}[\text{O}_2]}{2k_T[\text{M}][\text{CCl}_2]^2_0} + 1 \right)^{-1}} \]  

(7)

\[ S_{\text{HCl}} = \kappa_1 \frac{k_{\text{HCl}}[\text{HCl}]}{2k_T[\text{M}][\text{CCl}_2]^2_0} \frac{[\text{CCl}_2]^0}{e^{k_{\text{HCl}}[\text{HCl}]} \left( \frac{k_{\text{HCl}}[\text{HCl}]}{2k_T[\text{M}][\text{CCl}_2]^2_0} + 1 \right)^{-1}} \]  

(8)

In equations (7) and (8) \( \kappa_1 \) is an instrumental constant that depends on geometrical parameters of the detection system alignment and on instrumental parameters of the detection system. Equations (7) and (8) were used to adjust the experimental results and the fitting parameters were \( k_T, k_{\text{O}_2}, k_{\text{HCl}} \) and \( \kappa_1 \).
3.2 Samples with O₂
The rate constant for the reaction of CCl₂ with O₂ was determined from the delay time between the
dissociation and excitation pulses dependence of the fluorescence intensity signal.

![Fluorescence intensity vs. time for different O₂ pressures](image)

**Figure 3.** Time delay between lasers pulses dependence of the fluorescence intensity for the different
O₂ pressures. Experimental and fitted results are shown in dotted and solid lines, respectively.

These signals were fitted with equation (7) and the rate constant for the reaction was obtained. The
complete series of data of the fluorescence intensity signals corresponding to the different O₂ pressures
was simultaneously fitted with the model. Figure 3 shows the results of the fit for all O₂ pressures. An
excellent correlation between the experimental and calculated data has been obtained. The resulting
value of the reaction rate constant $k_{O₂}$ obtained from the fit was
$k_{O_2} = 3.4 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \quad (9)$

and for the radical recombination reaction (2)

$k_T = 9.5 \times 10^{-29} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \quad (10)$

To our knowledge, no room temperature data of the recombination reaction rate constant (10) have been reported in the literature. Kumaran et al. [12] have reported the values of this constant in the 1282-1878 K temperature range with Kr as buffer gas. The room temperature value extrapolated from their results is of the same order of magnitude as the value reported in this work in which the buffer gas was the mixture of chloroform and O$_2$.

There is only an upper bound of $3 \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ reported by Tiee et al. [13] for the rate constant of the reaction of CCl$_2$ radicals with O$_2$. In that work the radicals were generated by the laser photolysis of CCl$_4$ at 193 nm (ArF laser) and 248 nm (KrF laser). In the present work we report a value an order of magnitude larger than that bound for the same reaction rate constant. However, in that same work, Tiee et al. have reported an upper bound of $3 \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for the rate constant of the reaction of the CCl$_2$ radicals with C$_2$H$_4$. In later works, much larger values for this reaction rate constant have been reported by different authors. Mereleas et al. [10] and Liu et al. [11] have reported values of $2.4 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and $3.5 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, respectively. In the first work the CCl$_2$ radicals were generated by the IRMPD of CF$_2=CCl_2$ with a TEA CO$_2$ laser while in the second work, the radicals were generated from the photolysis of CCl$_4$ with a frequency fivefolded Nd:YAG laser at 213 nm as in the work of Tiee et al..

3.3 Samples with HCl

The study of the LIF signals in the presence of HCl was similar to that performed in samples with O$_2$.

![Figure 4](image_url)

**Figure 4.** Fluorescence intensity vs. delay time between laser pulses for different HCl pressures. Experimental and fitted results are shown in dotted and solid lines, respectively.

For each HCl pressure, the delay time between laser pulses dependence of the LIF intensity was fitted with equation (8). The complete series of data registered for the different HCl pressures was simultaneously fitted. The results obtained from the fit are shown in figure 4.
The value of $k_T$ obtained from the fit of the experimental data with equation (8) is coincident within experimental error with that obtained in the experiments with $O_2$. There is a range of values of the reaction rate constant $k_{HCl}$ for which the error in the fit remains constant and at its lowest value. This allows an upper bound to be obtained for the reaction rate constant of $CCl_2$ with $HCl$

$$k_{HCl} < 3 \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \quad (11)$$

4. Conclusions

A facility based on the Laser Induced Fluorescence (LIF) and the Infrared Multiple-Photon Dissociation (IRMPD) techniques has been implemented with the objective of studying the reaction kinetics of $CCl_2$ radicals produced by the IRMPD of $CDCl_3$. This study has been carried out to characterize how the reactions of these radicals with $O_2$ and $HCl$ affect the efficiency of the IRMPD of $CDCl_3$. The critical factors found in the implementation of this technique were: an efficient superposition of the excitation laser pulses with the volume in the cell where the radicals are generated and an efficient filtering of the background signal produced by reflections of the excitation laser on the reaction cell walls.

Mechanisms for the reactions of the $CCl_2$ radical with $O_2$ and $HCl$ and for the $CCl_2$ recombination reaction have been proposed. A model for the dependence of the LIF intensity on the lasers pulses time delay has been developed. The experimental data have been fitted with this model and an excellent agreement has been found. The rate constant for the radicals reaction with $O_2$ determined from the fit was

$$k_{O_2} = 3.4 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

The radicals recombination reaction rate constant resulting from the fit was

$$k_T = 9.5 \times 10^{-29} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$$

while an upper bound has been obtained for the rate constant of the radicals reaction with $HCl$

$$k_{HCl} < 3 \times 10^{-15} \text{ cm}^3 \text{ moléculas}^{-1} \text{ s}^{-1}$$

Kumaran et al. [12] have reported values for the $CCl_2$ recombination reaction rate constant in the 1282 - 1878 K temperature range. The extrapolation to room temperature of these values is of the same order of magnitude than the rate constant value determined in this work.

Tiee et al. [13] have established upper bounds for the rate constants of the reactions of $CCl_2$ with $O_2$ and $C_2H_4$. Larger values of the rate constant of the $CCl_2$ reaction with $C_2H_4$ have been found in later works carried out by other authors [14]. These results would support the discrepancies between the values of the rate constant of the reaction of $CCl_2$ with $O_2$ determined in this work and the upper bound given by Tiee et al.

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