

Infrared photochemical properties of sensitized SO₂–O₂ mixtures

R. Alexandrescu, N. Chitica, D.C. Dumitras, I. Morjan, I. Voicu, I.N. Mihailescu

Laser Department, Institute of Atomic Physics, P.O. Box MG-6, Bucharest, Romania

Received 16 May 1995; accepted 11 August 1995

Abstract

Sulphur dioxide photo-oxidation in sensitized SO₂–O₂ mixtures at overall pressures of several hundred Torr was studied in the CO₂ laser emission range on addition of different absorbing gases (SF₆, C₂H₄F₂, C₂HCl₃). The extent of conversion was correlated in each case with the absorption of energy by the specific ternary system under investigation. To explain the high reactivity found in SO₂–O₂–C₂H₄F₂ mixtures irradiated with the 9R24 laser line, the gas temperature inside the laser beam was estimated and a model of the energy transfer processes at different irradiation frequencies was proposed. It is suggested that, complementary to the thermalized chemistry, a vibrational enhancement of SO₂ oxidation can occur when the laser frequency correlates with the energy level structure of the specific molecular system employed.

Keywords: Laser-induced reactions; Sensitized reactions; Molecular energy transfer; SO₂ oxidation; SO₂ photochemistry

1. Introduction

Continued industrialization is generating unexpected pollutant effects and influencing environmental factors due to the atmospheric conversion of trace gases and chemical substances. In airborne toxic compounds, an important role is played by the photoconversion of primary pollutants induced by solar radiation. Sulphur dioxide (SO₂) is a primary pollutant which interferes, through its reaction products, in complex mechanisms such as the formation of acid rain and the large-area acidification of soils and water [1]. The interactions of SO₂ with H₂O and the nucleation of H₂SO₄ have been suggested as important early steps in photochemical smog formation. Extensive effort is currently being directed towards decreasing the SO₂ pollutant level by the lowering of the sulphur content in fuel oil and/or by SO₂ retention in filters and by chemical means [2]. From an economical point of view, SO₂ is of particular interest as the precursor of sulphuric acid in the large-scale chemistry of industrial processes.

Photochemical processes induced by lasers in SO₂- or SO₂[–]-containing mixtures have been reported in the infrared (IR) [3,4] and ultraviolet (UV) [5] spectral regions. It has been demonstrated that excitation by laser light and subsequent chemical reactions can lead to the conversion of SO₂, in a controlled manner, into a useful product [4]. The IR photo-oxidation of SO₂ to SO₃ has been performed in a flow reactor equipped with a trapping system for the physical separation and capture of the reaction product [4].

Although SO₂ is almost transparent in the wavelength region of CO₂ laser emission, gaseous absorbing species can modify the level of absorption of an SO₂-containing mixture by strongly absorbing IR radiation and subsequently exciting the SO₂ component by collisional energy transfer. The majority of studies in nearly thermalized systems (with molecular collision rates much higher than the photon absorption rate per molecule [6]) have dealt with gas mixtures containing sulphur hexafluoride (SF₆) as sensitizer [7–9], although many other absorbing organic (ethylene (C₂H₄), difluoroethane (C₂H₄F₂), trichloroethylene (C₂HCl₃), etc.) and inorganic (tetrafluorosilane (SiF₄), silane (SiH₄)) molecules may be used as energy transfer agents for CO₂-laser-driven chemical reactions. The efficiency of the energy transfer processes in mixtures depends on the molecular characteristics of the components (e.g. the dissociation energy) and on the specific experimental parameters (i.e. pressure, laser intensity, etc.). In addition, the quantity of energy deposited in a gaseous mixture irradiated by an IR laser depends on the concentration of gaseous species which do not absorb the laser radiation directly, but modify the saturation of absorption by collisional effects [4,9].

In this work, we report the SO₂ photo-oxidation by IR laser irradiation of SO₂–O₂ mixtures using different molecular gases (SF₆, C₂H₄F₂, C₂HCl₃) as sensitizers. Some were chosen because they are known pollutants active in different industrial areas, e.g. freons and trichloroethylene (used in ultrasonic cleaning). The correlation between the conversion efficiency and the absorption of energy by each irradiated

ternary gas mixture was studied. In order to explain the high conversion efficiency in $\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$ mixtures irradiated with the 9R24 line, the temperatures inside the beam at two different laser wavelengths (942 and 1081 cm^{-1}) were estimated and a model of the collisional energy transfer processes at these wavelengths is proposed.

2. Experimental details

The experimental apparatus consisted of a tunable continuous wave (cw) CO_2 laser, a transmission cell, a beam splitter, a beam attenuator and two power meters (for the transmitted and reflected beams). In experiments leading to SO_2 photo-oxidation, the laser beam was focused inside the cell, 2 cm from the front window, using a lens with a focal length of 8 cm. The frequency stabilized CO_2 laser (power range, 2–8 W; frequency stability, 3×10^{-8}) was operated on different vibrational–rotational lines in the 9.4 and 10.4 μm bands. The reaction/transmission cell (length, 12 cm) made of Pyrex glass was sealed with ZnSe windows and was equipped with Teflon valves. The experiments were conducted in the static pressure mode with the cell evacuated prior to each run to a base pressure of 10^{-4} Torr. The cell was successively filled with $\text{SO}_2\text{--O}_2$ mixtures in which different concentrations of absorbing gases (SF_6 , C_2HCl_3 , $\text{C}_2\text{H}_4\text{F}_2$), acting as sensitizers, were introduced. Gas sample pressures were measured by a membrane manometer (Wallace & Tiernan). Before introduction into the reaction cell, SO_2 was purified in concentrated sulphuric acid (to eliminate H_2O traces).

The linear absorption coefficients were determined according to the Beer–Lambert law by measuring the beam intensities I_0 and I at one wavelength (empty and filled cells respectively). The absorption coefficients were measured at about 100 Torr total cell pressure.

For laser-induced chemical reactions, the relative concentration of the gaseous components was set at approximately 1:1 to 1:3.5 for $\text{SO}_2\text{:O}_2$ precursors, and from approximately 3:1 to 7:1 for the system $\text{SO}_2\text{:sensitizer}$. For quantitative measurements of the conversion of SO_2 to SO_3 , a sensitive chemical method was employed [4,10]. Briefly, the method allows for the determination of SO_3 in an initial quantity of SO_2 (for a known cell volume and gas pressure). The degree

of conversion (efficiency) η is defined by $\eta(\%) = A/B$, where A is the quantity of SO_2 (g) transformed into SO_3 as a consequence of the photochemical reaction involving an initial quantity B of SO_2 . It should be noted that, as a volumetric method, it implies $\pm (3 \times \eta/100)$ precision and that, in the specific case of SO_3 synthesis, it avoids some of the characteristic difficulties arising when trying to separate SO_3 from SO_2 , namely interference effects, the large solubility of SO_3 and SO_2 in water (79.8 vol. SO_2 in 1 vol. H_2O at 0°C) and the oxidation of SO_2 in the presence of O_2 and water. IR spectrophotometry was used to monitor reactant depletion (i.e. the fraction of SO_2 undergoing reaction) at 1151 cm^{-1} .

3. Results and discussion

Table 1 displays the measured degree of conversion of SO_2 (η) in different ternary mixtures of $\text{SO}_2\text{--O}_2\text{--sensitizer}$ as a function of the irradiation frequency. In all runs, the laser power and irradiation time were maintained constant (6.5 W and 1 h respectively).

It is worth mentioning that, on increasing the radiation intensity, the conversion of SO_2 to SO_3 increases: when mixtures of $\text{SO}_2\text{--O}_2\text{--SF}_6$ were irradiated with a cw medium power CO_2 laser (50 W) emitting at the 10P20 line, η values higher than 6% were obtained [4].

Control tests were also performed to verify the “zero” conversion in the absence of laser radiation: for a binary mixture of $\text{SO}_2\text{:O}_2 = 1:2$ and a total pressure $p = 450$ Torr, an average value $\eta \approx 0.1\%$ was obtained.

The depletion of SO_2 , determined as the difference $\log(1/T_0) - \log(1/T)$ where T_0 and T are the transmittances before and after irradiation respectively, is presented in Table 2. The results indicate efficient SO_2 conversion on irradiation of mixtures containing $\text{C}_2\text{H}_4\text{F}_2$ and SF_6 with the 9R24 and 10P20 laser lines respectively. It should be noted that the data in Tables 1 and 2 are in relatively good agreement.

The reaction rate may be monitored by the reactant depletion, which was measured over the pressure range $p(\text{SO}_2 + \text{O}_2) = 120\text{--}480$ Torr (Fig. 1), by maintaining constant the relative concentration ($\text{SO}_2\text{:O}_2 = 1:2$) and the partial pressure of the sensitizer ($p(\text{C}_2\text{H}_4\text{F}_2) = 22$ Torr). The irradiation conditions were held fixed at 6.5 W of the 9R24 CO_2 laser line. The fraction of SO_2 undergoing reaction

Table 1
The conversion efficiency η of SO_2 by CO_2 laser irradiation of sensitized and pure $\text{SO}_2\text{--O}_2$ mixtures ^a

Mixture composition	Laser line	Frequency (cm^{-1})	Total pressure (atm)	Conversion η (%)
1. $\text{SO}_2\text{:O}_2 = 1:1.88$	9R24	1081.38	0.47	0.83
2. $\text{SO}_2\text{:O}_2\text{:C}_2\text{HCl}_3 = 6:11:1$	10P22	942.64	0.45	1.22
3. $\text{SO}_2\text{:O}_2\text{:C}_2\text{H}_4\text{F}_2 = 3:11:1$	10P22	942.64	0.46	1.43
4. $\text{SO}_2\text{:O}_2\text{:C}_2\text{H}_4\text{F}_2 = 5:10:1$	9R24	1081.38	0.46	2.17
5. $\text{SO}_2\text{:O}_2\text{:SF}_6 = 5:10:1$	10P20	944.45	0.47	2.05

^a Irradiation time, 1 h; laser power, 6.5 W.

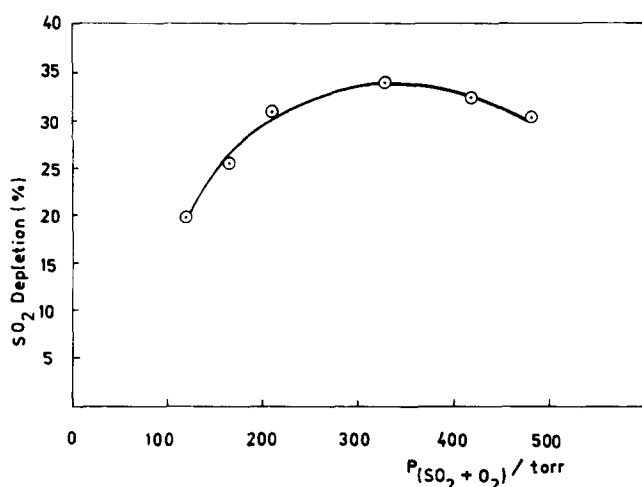


Fig. 1. SO_2 depletion in $\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$ mixtures as a function of the $\text{SO}_2 + \text{O}_2$ total pressure for fixed irradiation parameters ($p(\text{C}_2\text{H}_4\text{F}_2) = 22$ Torr; $\text{SO}_2:\text{O}_2 = 1:2$; $P_{\text{laser}} = 6.5$ W on the 9R24 line).

Table 2

The depletion of SO_2 (monitored in the IR transmission spectrum) on CO_2 laser irradiation of different gas mixtures ^a

Gas mixture	Laser line	Depletion (%)
$\text{SO}_2\text{--O}_2$	9R24	4
$\text{SO}_2\text{--O}_2\text{--C}_2\text{HCl}_3$	10P22	6
$\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$	10P22	14
$\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$	9R24	34
$\text{SO}_2\text{--O}_2\text{--SF}_6$	10P20	32

^a The other experimental parameters (mixture compositions, laser power, etc.) are as listed in Table 1.

increases over this pressure range, reaching a maximum for a pressure $p(\text{SO}_2 + \text{O}_2) \approx 330$ Torr. It has been observed [3] that, in many IR-sensitized reactions, the reaction rate reaches a maximum on increasing the pressure of the buffer (transparent) gas. This behaviour points to a non-thermal mechanism which may result from the competition between collisional vibrational–vibrational (V–V) and vibrational–

translational (V–T) transfers inside the thermal bath of molecules.

The conversion efficiency of SO_2 should depend on the overall quantity of energy deposited by the IR laser radiation into the irradiated gas mixture. The absorption coefficients α (cm^{-1}), determined for the most relevant laser lines absorbed in sensitized $\text{SO}_2\text{--O}_2$ mixtures, are displayed in Table 3. As expected, the measured α value for the binary $\text{SO}_2\text{--O}_2$ system shows that this mixture is a very poor absorber at the 9R24 CO_2 laser line. Also presented are the measured α values for the pure absorbing gases ($\text{C}_2\text{H}_4\text{F}_2$, C_2HCl_3 , SF_6); it can be observed that the addition of buffer (transparent) gases modifies the level of absorption, particularly when the buffer partial concentration is high. A competition between thermal diffusion and collisional processes explains this increased absorption.

Fig. 2 presents the experimentally measured absorption coefficients for $\text{SO}_2\text{--O}_2\text{--SF}_6$ mixtures as a function of the SO_2 partial pressure, maintaining constant the partial pressure of the sensitizer ($p(\text{SF}_6) = 0.1$ Torr), the radiation frequency (the 10P20 laser line) and the relative concentration ($\text{SO}_2:\text{O}_2 = 1:1.2$). It can be seen that the absorption of SF_6 in a mixture with $\text{SO}_2\text{--O}_2$ increases more rapidly between 30 and 60 Torr than between 75 and 130 Torr. This effect is the result of the decrease in the molecular mean free path as the pressure of the transparent gas increases, which leads to reduced thermal diffusion of absorbing molecules out of the beam and an increasing number of collisions.

The evolution of the absorption coefficient α (cm^{-1}) as a function of the radiation frequency (P branch of the $00^0_1\text{--}01^0_0$ band) may be followed in Fig. 3 for $\text{SO}_2\text{--O}_2$ mixtures sensitized with $\text{C}_2\text{H}_4\text{F}_2$ (curve a, $\text{SO}_2:\text{O}_2 = 1:1.2$, $p(\text{SO}_2 + \text{O}_2) = 592$ Torr, $p(\text{C}_2\text{H}_4\text{F}_2) = 10$ Torr) and C_2HCl_3 (curve b, $\text{SO}_2:\text{O}_2 = 1:1.2$, $p(\text{SO}_2 + \text{O}_2) = 592$ Torr, $p(\text{C}_2\text{HCl}_3) = 45$ Torr). A maximum absorption was recorded in both cases for the 10P22 laser line (942.64 cm^{-1}).

A comparison of the results presented in Tables 1 and 3 shows that the high chemical conversion of SO_2 ($\eta = 2.17\%$), obtained on irradiation of $\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$

Table 3

Absorption coefficients α (cm^{-1}) for ternary $\text{SO}_2\text{--O}_2\text{--sensitizer}$ mixtures and for pure absorbing gases

Gases	Sensitizer partial pressure (Torr)	SO_2 partial pressure (Torr)	Mixture total pressure (Torr)	Laser line	α (cm^{-1})
$\text{SO}_2\text{--O}_2$	–	46	98.8	9R24	0.54×10^{-2}
$\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$	5	43	98.8	9R24	3.56×10^{-2}
$\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$	5	43	98.8	10P22	7.12×10^{-2}
$\text{C}_2\text{H}_4\text{F}_2$	5	–	–	9R24	1.98×10^{-2}
$\text{C}_2\text{H}_4\text{F}_2$	5	–	–	10P22	6.34×10^{-2}
$\text{SO}_2\text{--O}_2\text{--C}_2\text{HCl}_3$	5	43	98.8	9R24	0.64×10^{-2}
$\text{SO}_2\text{--O}_2\text{--C}_2\text{HCl}_3$	5	43	98.8	10P22	6.89×10^{-2}
C_2HCl_3	5	–	–	9R24	0.16×10^{-2}
C_2HCl_3	5	–	–	10P22	5.79×10^{-2}
$\text{SO}_2\text{--O}_2\text{--SF}_6$	0.1	44.8	98.8	10P20	6.24×10^{-2}
SF_6	0.1	–	–	10P20	4.42×10^{-2}

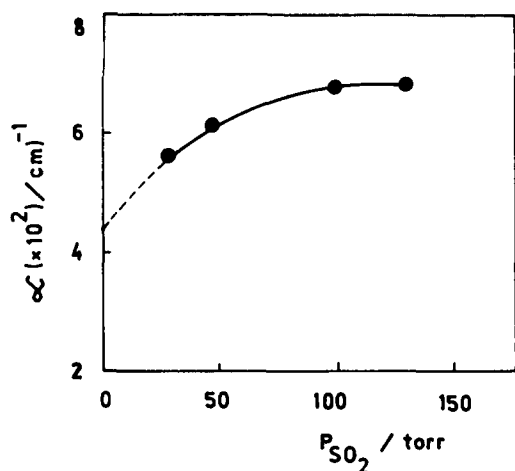
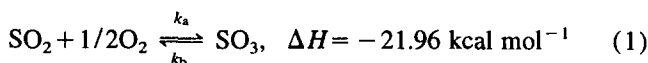


Fig. 2. Absorption coefficient of $\text{SO}_2\text{-O}_2\text{-SF}_6$ mixtures irradiated with the 10P20 line as a function of the SO_2 partial pressure for fixed $\text{SO}_2\text{:O}_2$ relative concentration ($\text{SO}_2\text{:O}_2 = 1\text{:}1.2$) and partial pressure of SF_6 ($p(\text{SF}_6) = 0.1$ Torr).

mixtures with the 9R24 laser line, corresponds to an α value ($\alpha = 3.56 \times 10^{-2} \text{ cm}^{-1}$) which is lower than that of almost the same mixture irradiated with the 10P22 laser line ($\alpha = 7.12 \times 10^{-2} \text{ cm}^{-1}$) for which a lower degree of conversion ($\eta = 1.43\%$) was obtained. This observation deserves further attention and, in the following sections, the $\text{SO}_2\text{-O}_2\text{-C}_2\text{H}_4\text{F}_2$ system on irradiation with both the 10P22 and 9R24 CO_2 laser lines is analysed using thermal and collision-induced transfer approaches. The same is not performed for the $\text{SO}_2\text{-O}_2$ mixtures sensitized with SF_6 and C_2HCl_3 because, in the first case, an analysis was partially performed in Ref. [4], and in the second case, the conversion efficiency was low and in accordance with a lower absorption coefficient.

3.1. Thermal considerations; application to the $\text{SO}_2\text{-O}_2\text{-C}_2\text{H}_4\text{F}_2$ mixture

The reaction used industrially to prepare SO_3 is the exothermic process



where ΔH represents the enthalpy change for the occurrence of reaction (1) and k_a and k_b are the temperature-dependent rate constants.

The equilibrium of reaction (1) is shifted towards the right as the temperature decreases. In order to maintain a high reaction rate at lower temperatures (approximately 693 K), supported catalysts (such as Pt, Pd, Au, Cu, etc.) are used [11].

For the $\text{SO}_2\text{-O}_2$ mixtures sensitized with $\text{C}_2\text{H}_4\text{F}_2$, the temperature in the laser beam may be estimated by considering that the energy deposited in the beam volume is rapidly thermalized by collisions, raising the gas temperature in a cylindrical volume coaxial with the cell, and that heat transfer

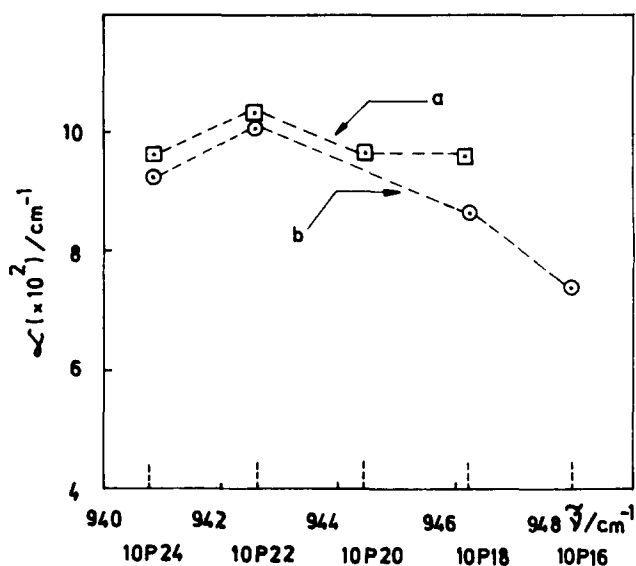


Fig. 3. Absorption coefficient for $\text{SO}_2\text{-O}_2\text{-C}_2\text{H}_4\text{F}_2$ (curve a) and $\text{SO}_2\text{-O}_2\text{-C}_2\text{HCl}_3$ (curve b) as a function of the laser frequency (in the P branch of the $00^0_1\text{-}01^0_0$ band): (a) $p(\text{C}_2\text{H}_4\text{F}_2) = 10$ Torr; (b) $p(\text{C}_2\text{HCl}_3) = 45$ Torr. In both cases, $\text{SO}_2\text{:O}_2 = 1\text{:}1.2$ and $p(\text{SO}_2 + \text{O}_2) = 592$ Torr.

takes place through diffusion. The following relationship has been deduced (see Appendix A)

$$T_s^{3/2} \cong T_w^{3/2} + \frac{3}{4\pi} \frac{\Delta P}{\Delta K_{\text{ef}}} \ln \frac{r_w}{r_s} \quad (2)$$

where T_s , r_s and T_w , r_w are the temperatures and radii for the beam and the cell wall respectively. The thermal diffusivity constant K_{ef} for the gas mixture was estimated by assuming that each component of the mixture behaves like an ideal gas and by using the thermal conductivity data from Ref. [12]. We have obtained $K_{\text{ef}} = 1.4 \times 10^{-3} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1/2}$. The average power dissipated per unit path, $\Delta P / \Delta l$, depends on the effective absorption coefficient α_{ef} at the actual pressure of the $\text{C}_2\text{H}_4\text{F}_2$ absorber. We obtained α_{ef} values of 0.15 cm^{-1} and 0.28 cm^{-1} for the 9R24 and 10P22 laser lines respectively absorbed in the $\text{SO}_2\text{-O}_2\text{-C}_2\text{H}_4\text{F}_2$ mixtures used.

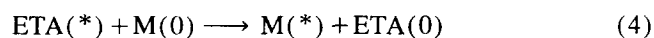
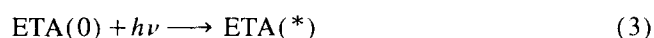
For $P_0 = 6.5 \text{ W}$, $r_w = 15 \text{ mm}$, $r_s = 0.5 \text{ mm}$ and $T_w = 333 \text{ K}$, the average temperatures in the $\text{SO}_2\text{-O}_2\text{-C}_2\text{H}_4\text{F}_2$ mixtures at a distance of 20 mm from the entrance window were estimated to be $T_s \cong 1100 \text{ K}$ and $T_s \cong 1400 \text{ K}$ for irradiation with the 9R24 and 10P22 laser lines respectively.

It is worth mentioning that an estimation of the mean power P_m generated by the exothermic reaction (Eq. (1)) was possible using the reactant depletion during a 1 h experimental run (approximately 10% of the total SO_2 amount, i.e. approximately $5 \times 10^{-5} \text{ mol}$). A value of $P_m \cong 1.5 \text{ mW}$ was found, which could not contribute significantly to the reaction efficiency.

Finally, we may observe that the thermal model proposed above, which uses a cylindrical geometry, is no longer valid for a strong absorber such as SF_6 for which the radiation energy is almost entirely absorbed in a thin gas layer near the entrance window.

3.2. Collisional energy transfer in $\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$ mixtures

Sulphur dioxide is a non-linear symmetric molecule [13] presenting three fundamental vibrational modes (symmetric stretch ν_1 (1150 cm^{-1}), bending ν_2 (518 cm^{-1}) and asymmetric stretch ν_3 (1367 cm^{-1})). CO_2 laser radiation with approximately 942 cm^{-1} energy (10P22 line) is largely off-resonant relative to any of the SO_2 states, and there is no obvious overlap between the ν_3 mode of SO_2 and approximately 1080 cm^{-1} radiation (9R24 line). In such conditions, the sensitizer plays the role of an energy transfer agent (ETA), which absorbs the laser energy and transfers it by collisions with other molecules, according to the general scheme



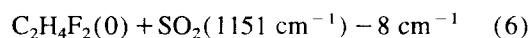
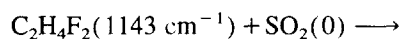
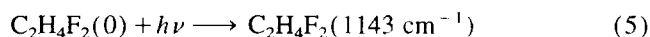
where $\text{ETA}(0)$ and ETA^* are the sensitizing molecules in the fundamental and different excited states respectively and M is the other molecules in the mixture. In the pressure range involved in our experiments (exceeding 100 Torr), collisional relaxation, which redistributes the energy into rotational (R) and vibrational (V) modes, is a highly efficient relaxation channel [9].

In the following, a qualitative model of the energy transfer in $\text{SO}_2\text{--O}_2$ mixtures using $\text{C}_2\text{H}_4\text{F}_2$ as sensitizer is proposed; to our knowledge, data concerning collisional transfer rates for the $\text{C}_2\text{H}_4\text{F}_2$ polyatomic molecule have not been published. Without entering into detail, we should remember that, at low levels of excitation, V–V relaxation is much faster than V–T,R processes, and that if other factors are equal, resonant V–V transfer is more likely than non-resonant transfer [8]. However, a steady state may be established among the vibrational modes of the sensitized system (absorbing/non-absorbing species) which may partly allow, even during long-time irradiation, the establishment of a localized metastable vibrational distribution [14], superimposed on the thermal heating effect.

1,1-Difluoroethane is a slightly asymmetrical top molecule of oblate shape, with C_s planar symmetry. Parallel and perpendicular IR bands are produced by in-plane (species A') and out-of-plane (species A'') vibrations.

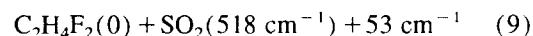
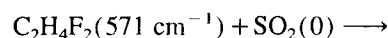
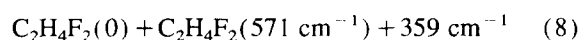
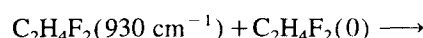
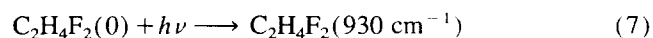
In the wavelength region of the SO_2 ν_1 vibration, there is a rather complex strong absorption band of $\text{C}_2\text{H}_4\text{F}_2$, which is a superposition of the A' fundamentals (at 1143 cm^{-1} and 1129 cm^{-1}) and A'' fundamental (at 1169 cm^{-1}) [15]. These bands were assigned to the symmetric (1143 cm^{-1}) and asymmetric (1169 cm^{-1}) C–F stretching modes [15]. A quasi-resonant V–V energy transfer channel, induced by collisions from $\text{C}_2\text{H}_4\text{F}_2$ molecules, towards the ν_1 mode of SO_2 is probable. Moreover, it was shown [16] that a rapid equilibration of ν_1 and ν_3 SO_2 stretching modes is expected, favoured by an anomalous weak coupling of these modes to the low-lying ν_2 bending mode, thus preventing rapid V–T,R

deactivation processes. We may assume that the 9R24 laser line (at approximately 1081 cm^{-1}) excites $\text{C}_2\text{H}_4\text{F}_2$ in the 1143 cm^{-1} band, followed by near-resonant excitation transfer to the ν_1 mode of SO_2



thus allowing for a metastable, vibrationally ‘hot’, SO_2 stretching mode distribution.

The collisional energy transfer processes involved in $\text{C}_2\text{H}_4\text{F}_2$ excitation with the 10P22 laser line (at approximately 942 cm^{-1}) seem to proceed through the perpendicular band of $\text{C}_2\text{H}_4\text{F}_2$ near 940 cm^{-1} , which is a superposition of the A'' fundamental (at 930 cm^{-1}) and a combination band of the same species (at 939 cm^{-1}). The following energetic scheme may be proposed



where Eq. (8) represents the collisional intermode coupling with the low-lying A' fundamental of $\text{C}_2\text{H}_4\text{F}_2$ at 571 cm^{-1} ; the mechanism expressed by Eq. (9) represents the raising of SO_2 molecules in the ν_2 vibrational mode. We observe that, due to the sequential character of processes (7)–(9), leading to progressive dissipation of the vibrational energy accumulated in $\text{C}_2\text{H}_4\text{F}_2$ molecules, and to the rather large off-resonance of processes (8) and (9), a localization of energy in SO_2 vibrational modes is less probable and thermalization processes seem to prevail. We also note that similar considerations, implying as an intermediate step intermode coupling of SF_6 vibrations, may be applied for the system $\text{SO}_2\text{--O}_2\text{--SF}_6$ irradiated with the 10P20 laser line [4].

It is known that most of the vibrational energy captured by the sensitizers is dissipated through V–T,R processes, feeding the translational heat bath. Once the high temperature Boltzmann equilibrium is reached by the $\text{SO}_2\text{--O}_2\text{--sensitizer}$ systems, the reverse process, i.e. non-specific thermal vibrational excitation, can also occur, raising some SO_2 molecules in low-lying rovibrational levels. The build-up of the overall internal energy may partly reach the activation energy for the formation of SO_3 from $\text{SO}_2 + \text{O}_2$. It has been shown that rovibrational levels of low-lying (below the dissociation threshold) excited electronic states participate in SO_2 photochemical reactions [3].

Eqs. (5) and (6) suggest that, in addition to the normal high temperature steady state reached by collisional energy transfer, a complementary excitation channel may contribute

to the enhanced chemical reactivity of the system $\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$ irradiated by the 9R24 CO_2 laser line. In this system, the high temperature (approximately 1100 K), characterizing to a different extent all the sensitized reactions, allows reaction (1) to occur through thermal vibrational excitation. At the same time, some SO_2 molecules may be excited by the near-resonant processes (5) and (6) and may be continuously raised to their ν_1 mode, thus feeding a vibrationally excited metastable SO_2 distribution and, in addition, increasing the internal free energy of the system. The following observations corroborate this assumption: (i) the lower absorptivity (and temperature) but higher reaction efficiency in mixtures of $\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$ irradiated with the 9R24 CO_2 laser line relative to those irradiated with the 10P22 laser line; (ii) the non-thermal behaviour of the reaction rate with pressure: a pure thermal mechanism would involve an increase with increasing pressure which is contradicted by the laser experiment (SO_2 depletion exhibits a maximum in Fig. 1).

4. Conclusions

The study of the IR photochemical properties of sensitized $\text{SO}_2\text{--O}_2$ mixtures at high overall pressures (hundreds of Torr), in the wavelength range of CO_2 laser emission, shows that the extent of SO_2 oxidation is dependent on the particular photoabsorbing species added. The absorption coefficients exhibit higher values in the presence of transparent (low absorbing) components than in the case of the pure absorbing gases.

In ternary $\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$ mixtures, a higher conversion efficiency was found on irradiation with the 9R24 laser line than with the 10P22 laser line. By performing an estimation of the gas temperature inside the laser beam, it was found that, for this system, thermal considerations only were not sufficient to explain the increased reactivity. A qualitative model of the specific collisional energy transfer processes was proposed, in which, complementary to thermalized chemistry, a vibrational enhancement of SO_2 oxidation occurred when the radiation frequency correlated with the energy level structure of the molecular system.

Acknowledgements

The authors wish to thank Professor Jorg Reuss for many useful suggestions and discussions.

Appendix A

This section is devoted to the derivation of expression (2) for the temperature on the axis of a cylindrical cell. We made the following assumptions: (i) the heat transfer takes place by a diffusion mechanism described by Fourier's diffusion law; (ii) the heat source is a cylinder of radius r_s , placed on

the axis of the cell, and with a constant temperature distribution over its cross-section; (iii) a cylindrical symmetry is applicable. In our experimental conditions, the laser energy is dissipated through an intermediary (the sensitizer molecules) in the volume crossed by the laser beam. Due to the very low mean free path of these molecules, the energy is rapidly and uniformly transferred to the other molecules present in this volume. Thus the heat source can be considered as a solid cylinder. Taking into account the rather low absorptivity of $\text{SO}_2\text{--O}_2\text{--C}_2\text{H}_4\text{F}_2$ mixtures, the heat source may be considered to be quasi-uniform along the axis of the cell and a cylindrical symmetry can be assumed.

At steady state, the following equations are valid

$$j(r) = -\Psi \, dT/dr \quad (\text{A1})$$

$$j(r) = q/(2\pi r) \quad (\text{A2})$$

where j is the density of the heat flux, Ψ is the thermal diffusivity, T is the temperature and q is the dissipated power over a unit path, $q = \Delta P/\Delta l$. The first equation is the heat diffusion equation for the radial component of the flux and the second is derived from the continuity law. For a gas mixture, the thermal diffusivity is a function of the thermodynamic temperature

$$\Psi = K_{\text{ef}} \sqrt{T} \quad (\text{A3})$$

where the proportionality constant K_{ef} is determined by the thermodynamic properties of each constituent of the mixture

$$K_{\text{ef}} = \sum_{i=1}^n \frac{p_i}{p_0} K_i \quad (\text{A4})$$

where K_i and p_i are the K constant and partial pressure respectively for the i th component and p_0 is the total pressure of the gas mixture. We have verified the linear dependence of Ψ on $T^{1/2}$ for each component of our mixture. Taking into account this dependence, the correlation of the temperature on the radius was obtained as

$$T_s(r) = \left[T_w^{3/2} + \frac{3}{4\pi} \frac{q}{K_{\text{ef}}} \ln \frac{r_w}{r} \right]^{2/3}, \quad r \geq r_s \quad (\text{A5})$$

where $q = \Delta P/\Delta l$ was found from the attenuation of the incident power P_0 (corrected for the transmission loss of the entrance window) at a distance l

$$\frac{\Delta P}{\Delta l} \cong 0.68 P_0 \frac{1 - e^{-\alpha \Delta l}}{\Delta l} \quad (\text{A6})$$

References

- [1] P.L. Mayer and M.W. Sigrist, *Rev. Sci. Instrum.*, **61** (1990) 1779.
- [2] D.L. Fox, *Anal. Chem.*, **61** (1989) 12.
- [3] C. Lalo, J. Masanet, F. Lempereur and J. Tardieu de Maleissye, *Chem. Phys. Lett.*, **124** (1986) 447.
- [4] I. Voicu, R. Alexandrescu, I. Morjan, M. Stoica, I. Ursu and V. Jianu, *Infrared Phys.*, **33** (1992) 557.
- [5] D. Fotakis, *Chem. Phys. Lett.*, **82** (1981) 68.

- [6] R.N. Zitter, D.F. Koster and K. Cheung, *J. Phys. Chem.*, **89** (1985) 1401.
- [7] A. Mele, F. Salvetti, E. Molinari and M.L. Terranova, *J. Photochem.*, **32** (1986) 265.
- [8] V.P. Vlahoyannis, N. Presser and R.J. Gordon, *Chem. Phys. Lett.*, **106** (1984) 157.
- [9] J. Deson, C. Lalo, J. Masanet and J. Tardieu de Maleissye, *Chem. Phys.*, **119** (1988) 343.
- [10] E.B. Seidmann, *Anal. Chem.*, **30** (1958) 1680.
- [11] *Nouveau Traité de Chimie Minérale*, Tome XIII, Masson and Co., Paris, 1961, p. 1258.
- [12] J.H. Perry (ed.), *Chemical Engineers' Handbook*, McGraw-Hill, New York, San Francisco, Toronto, London, 1963.
- [13] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, Princeton, 1968.
- [14] J. Shamah and G.W. Flynn, *J. Am. Chem. Soc.*, **99** (1977) 3191.
- [15] D.C. Smith, R.A. Saunders, J.R. Nielsen and E.E. Ferguson, *J. Chem. Phys.*, **20** (1952) 847.
- [16] D. Siebert and G.W. Flynn, *J. Chem. Phys.*, **62** (1975) 1212.