SPATIAL TEMPERATURE DISTRIBUTION IN *CW* CO_2 LASER PHOTOSENSITIZED REACTIONS

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The temperature distribution in gaseous SF_6 and SF_6-inert gas samples under irradiation with *cw* CO_2 laser measured by a thermocouple technique is confronted with the results of a computational procedure neglecting heat convection. The results are helpful in understanding the effect of the inert gas on the distribution of temperature and the size of the reacting "hot" volume in the *cw* laser-photosensitized chemical reactions.

There is rapidly growing interest in the use of infrared lasers in chemistry because these instruments can affect chemical reactions[1,2] in a number of ways. The continuous-wave laser-photosensitized excitation of reactants[3,4], including multiple energy transfer from collisions between excited but stable absorber molecules and reactant molecules, will generate a thermalized system and provide chemist with the possibility to perform thermal reaction in the absence of hot wall heterogeneous effects.

After steady-state conditions are approached in a few milliseconds, the thermalized system of absorbing sensitizer, reactant and a diluent is described by the reactant density and the spatial temperature distributions[4]. The estimation of these quantities is needed for understanding the reaction progress and computing quantitative kinetic data. The temperatures can be estimated by thermocouples[5], as the mean reaction temperature[4], and by more precise techniques such as the interferometric measurement[6] and the calculation from power absorption measurements[7,8]. The calculation method[7,8] succeeded to give[6] correct values when assuming that the laser-induced reaction takes place only in a very narrow region of the laser beam, ignoring the heat convection, and considering that the molecular diffusion is sufficiently rapid to maintain reactant concentration and to remove products. Under similar conditions (total pressures >10 kPa, laser beam density 10^2-10^3 W/cm^2; compare refs[1,6]) the size of the "hot" reacting volume was conceded to be quite uncertain and the heat convection introducing extensive scrambling of reacting "hot" volume with other layers was stressed to be an appropriate explanation of the observed conversions[4]. Because of these controversial views more data on the relative importance of heat conduction and heat convection and also on the size of the reacting "hot" volume are needed.

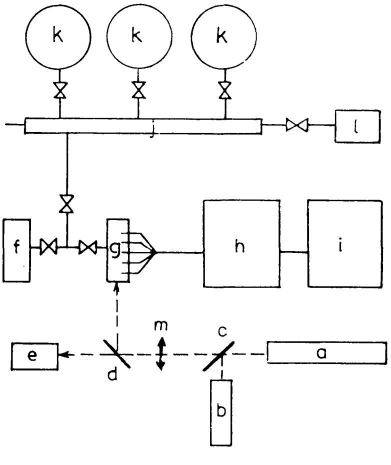
In this note we present spatial temperature distribution in SF_6 and SF_6–He gaseous samples irradiated with a *cw* CO_2 lasser acquired by a thermocouple technique and by the computational procedure neglecting heat convection. The obtained temperature distribution along with some our previous reactivity data are consulted to draw qualitative inferences on the size of the hot reacting volume.

EXPERIMENTAL

The experimental procedure of the measurement of the temperature distribution in the gaseous samples of SF_6 and SF_6–He in a vertically or horizontally placed cylindrical cell irradiated by a *cw* CO_2 laser operated on the *P*(34) line of the 00°1→10°0 transition was performed as illustrated in Scheme I. The experiments were carried out with the cell of 10 cm path length and 3·6 cm inner diameter fitted with NaCl windows and one P.T.F.E. stopcock, equipped with thermocouples (jacket diameter 0·15 mm, Walzwerk Hettstadt) placed 12, 38, 63 and 88 mm (*x*) from the entrance window. The distance of the thermocouples from the laser beam (radial distance, *r*) altered within the range 0—18 mm. The laser beam was focussed with a Ge lens (f. 1. 25 cm) into the middle of the cell, in the case of the vertical cell configuration the laser beam entered its bottom. The settlement of the *cw* CO_2 laser beam in the cell axis was performed by using a coaxial visible beam of the He–Ne laser (HNA 50, Carl Zeiss, Jena). The voltage on the individual thermocouples was recorded at the speed of 10 channels per second by means of the digital center Dynamco Systems (Chertsey) with an accuracy 0·05 mV. The results were fed into punched paper tape and evaluated by the EC 1033 computer. The samples for the laser irradiation experiments were prepared by a standard vacuum line technique and the SF_6 concentration was checked by measuring the IR spectra at 987 cm^{-1} ($\nu_2 + \nu_6$) with an infrared spectrometer (Perkin–Elmer 621).

Sulfur hexafluoride (Montedison Milano, I.E.C. Standard) and helium (Messergriesheim, Gumpoldkirchen) were commercial products.

The calculation of the temperature distribution is made possible through the knowledge of the laser beam intensity, the effective beam radius, the radius of the cell and the temperature



Apparatus for measurement of spatial distribution of temperature. **a** CO_2 laser, **b** He—Ne laser, **c** rectangular NaCl window, **d** revolving chromium coated mirror, **e** coherent model 201 powermeter, **f** reference cell for ir analysis, **g** cell for measurement of temperature, **h** digital center, **i** computer, **j** vacuum line, **k** gas reservoir, **l** manometer, **m** lens

SCHEME 1

of the cell wall and is derived from the steady state heat conduction equation (*1*)

$$\nabla k \,.\, \nabla T = g \;, \tag{1}$$

where g designates a power absorption per unit volume. The calculations have been carried out under the following assumptions: *1*) total neglection of heat convection, *2*) fixed cell-wall temperature 300 K, *3*) either the known heat conductivity of gases for 300 K, or the dependence of the heat conductivity on temperature (*2*)

$$k = k_{300} \cdot (T/300)^{m} \;, \tag{2}$$

where k_{300} relates to thermal conductivity at 300 K (ref.[9]), *4*) the assumption that thermal conductivity of the SF_6-inert gas (in excess) mixture equals to that for the inert gas and *5*) the control of the laser beam absorption by Lambert–Beer's law.

TABLE I

The maximum temperature T_{max}, and the parameters k_{300} and m with the Eq. (*2*) for gaseous SF_6-inert gas mixture[a]

Gas mixture	$k_{300} \,.\, 10^3$ W m^{-1} K^{-1}	m	T_{max} K
$SF_6 + He$	145	0·766	520
$SF_6 + Ne$	49·3	0·631	849
$SF_6 + N_2$	26·0	0·771	1 112
$SF_6 + Ar$	17·7	0·729	1 388
$SF_6 + Kr$	9·4	0·823	1 851
$SF_6 + Xe$	5·6	0·863	2 331

[a] Laser output 1 W, absorptivity of gaseous mixture (1·3 kPa SF_6) $5 \,.\, 10^{-5}$ mm^{-1} Pa^{-1}, effective beam radius 1 mm.

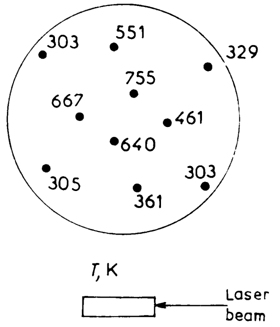


FIG. 1

Experimental temperature distribution at the distance 1·2 cm from the entrance window for the horizontal configuration of the cell filled with 1·3 kPa of SF_6, laser output 4 W

RESULTS AND DISCUSSION

The experimentally obtained temperature distribution in the cell filled with SF_6 is strongly affected by the configuration of the cell.

Fig. 1 depicts the temperatures for the horizontal case at different points 1·2 cm from the entrance window and shows higher temperature in the upper part of the cell. The steady state being acquired after about 3 seconds produced noticeable heating of the upper front part of the cell. These facts favour explanation of the temperature distribution by convection currents.

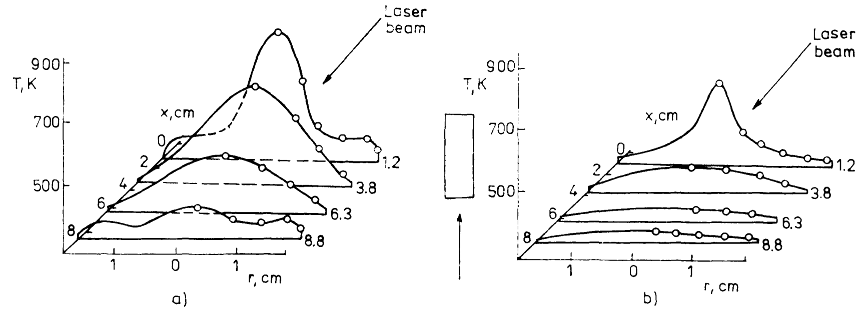


Fig. 2

Experimental temperature distribution for the vertical configuration of the cell filled with 1·3 kPa of SF_6 (*a*) and 1·3 kPa SF_6 and 38·5 kPa He (*b*), laser output 4 W

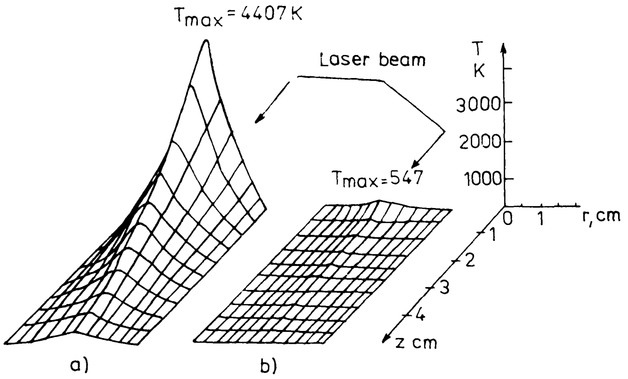


FIG. 3

Theoretical temperature distribution for 1·3 kPa SF_6 (*a*), and 1·3 kPa SF_6 in excess of He (*b*). Laser output 1 W, effective beam radius 1 mm, cell radius 18 mm, heat conductivity of SF_6 and He assumed for 300 K (ref.[14])

In the vertical configuration the SF_6 sample is characterized by a steady state achieved in a shorter time (about 1 second) and by the temperature distribution symmetrical along the laser beam axis (Fig. 2*a*). Here the existence of convection currents is supported by the fact that temperatures at the radial distance from the axis $1{\cdot}5\ \text{cm} > r > 0{\cdot}5$ cm are higher for the distance from the laser input window $x = 3{\cdot}8$ than for $x = 1{\cdot}2$ cm. A similar temperature difference is not obtained with the SF_6–He mixture (Fig. 2*b*); helium increases thermal conductivity of the system and obviously makes molecular diffusion more important. Supportive of these inferences is also temperature distribution obtained by the theoretical treatment neglecting convection – the smooth successive decrease in the temperature along the x for all r (Figs 3*a* and *b*) matches the experimental counterpart for the SF_6–He, but not for the SF_6 alone.

Besides of ensuring rapid thermalization[10] the effect of the addition of an inert gas is generally considered to consist in an increase of the heat capacity of the system which, all other conditions remaining constant, decreases the maximum temperature. The latter effect is seen for helium in Figs 2 and 3 and is consistent with our results on the *cw* CO_2 laser-photosensitized decomposition of oxalyl chloride[11] and 2-nitropropane[12] (2NP), where reaction rate was in each case suppressed upon the addition of He to the sensitizer (SF_6)-reactant mixture.

Nevertheless, the study of the temperature distribution and the decomposition rate of 2NP in the 2NP–SF_6–He and 2NP–SF_6–Ar systems revealed[12] higher temperature and smaller reacting hot volume in the latter system. Additionally, the reaction rate for 2NP decomposition is in 2NP–SF_6–Ar and 2NP–SF_6 systems almost comparable. It thus appears that also heat conductivity of inert gas relative to that of sensitizer has to play a significant role in affecting the temperatures and the size of reacting hot volume in a way that inert gas of a lower heat conductivity makes the maximum temperature higher and the reacting "hot" volume smaller. Such a view is consonant with the data on the maximum temperature in the SF_6-inert gas mixtures gathered in Table I where the increasing maximum temperature is observed when going from He to inert gas with lower heat conductivity and finds also some support from the observation of the rate increase in the *cw* CO_2 laser-photosensitized decomposition of methyl iodide by small admixtures of xenon[13].

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