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FIELD DISTRIBUTION EFFECTS IN LASER DRIVEN DIFFUSION THROUGH METAL CAPILLARIES

BOGDAN DRAGNEA

Laser Department, Institute of Atomic Physics, R-76900, P.O. Box MG-6, Bucharest, Romania

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Abstract—A new approach for the IR laser driven diffusion through metal capillaries is reported in this paper. It reveals the influence of the inner distribution of the electromagnetic field on the resonant character of the diffusion of a mixture of SF_6 (resonant) and N_2 through an Ni capillary under IR irradiation. A waveguide model is proposed for the considered e.m. field–heterogeneous system interaction, an explanation for the persistence of the selective effects even at total pressures as high as 7 Torr being provided. Some spectral differences between the inside-capillary molecules and bulk-phase molecules are pointed out using a simple attenuation measurement method.

1. INTRODUCTION

It is well known that the sticking coefficient for adsorbed molecules depends on the occupation of the energy levels. This behaviour, if used in heterogeneous systems (gas-solid surface) could lead at laser induced selective processes as isotope or substance separation, or at changes in optical properties of the adsorbents (under laser irradiation).[1]

We describe here a list of results concerning laser driven diffusion of a resonant–non-resonant gas mixture through a metal capillary for a range of average pressures from 1 to 7 Torr. These values far exceed those reported in the previous works related with the same topic, 10^{-7} Torr.[2] At those low pressures, it easily held the assumption that, because the mean free path is large enough to exceed the capillary diameter (Knudsen flow regime), an excited molecule has a big chance to arrive at the adsorbant wall in the same state. In general, the molecules pass through a few field zones with different intensity and polarization values, without collisions. This distribution can be obtained by solving the wave equation for a hollow cylinder (the capillary) coupled with an external Gaussian e.m. field. Thereby, the influence of the e.m. field will be averaged, and the field structure will not play an important role in the related diffusion process. On the contrary, at a higher level of pressure, like those used, the mean free path length (m.f.p.l.) is shorter than the capillary diameter. Therefore, the averaging of the field intensity distribution is no longer effective: a molecule between two collisions, may be placed in one or another region of the field. We present here a model of the capillary in terms of a waveguide which describes the observed experimental behaviour concerning the influence of the e.m. field intensity distribution on the resonant diffusion and its effects:

- the persistence of the resonant behaviour at pressures far above the Knudsen regime;
- the observed dependence of the separation coefficient on the pressure.

In the last part of this work we report an experimental investigation concerning the absorptivity for the above mentioned mixture inside the capillary. The experiments were carried out for 10 laser lines (10 μm band of a CO_2, cw, frequency stabilized laser). Some differences between the adsorption of the resonant gas in bulk and in the capillary were revealed; the sensitivity of the method is due, in our opinion, to the superposition between waveguiding effects and the resonant adsorption.

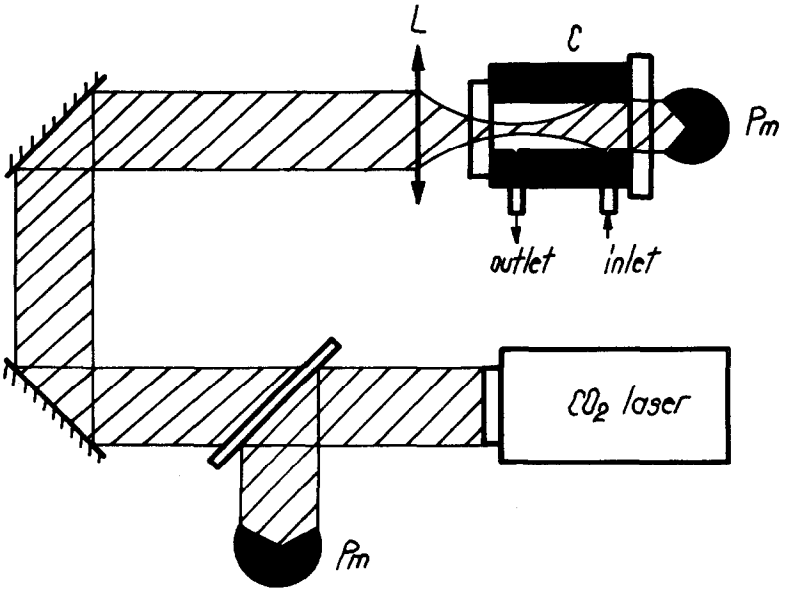

Fig. 1. Experimental set-up. L, ZnSe lens; C, Ni capillary; Pm, powermeter.

2. EXPERIMENTAL

Two kinds of experiments were performed with the experimental set-up from Fig. 1:

(a) experiments that had to point out the influence of the inner field distribution on the resonant effect of diffusion through the capillary;
(b) experiments dedicated to the measurement of the adsorptivity for the inside-capillary gas mixture (SF_6-resonant:N_2-non-resonant) and for the bulk-phase gas mixture (inside a 3-cm dia cell).

For the both sets a Ni capillary (0.5 mm dia, 40 mm length) was used. The capillary was mounted in a metal piece to prevent the heating. For irradiation we used a cw, CO_2, frequency stabilized laser—maximal power: 7W on 10P(20) line. The weight of the Gaussian characteristics in the actual beam was estimated at 76%. This enabled us to consider later the coupling between a Gaussian idealized e.m. field and a waveguide (the capillary).

The laser was focused at the entrance of the capillary with a ZnSe lens (12 mm focal length, at the 950 cm^{-1} wavenumber). In the experiments that were carried out in a gas flow regime, the pressure gradient was pointing in the same direction with the laser (the highest pressure, at the end of the capillary). The outlet was connected at a quadrupole mass spectrometer (QMG-III Balzers). The entrance pressure was chosen in the 0.2–0.4 Torr range for pure SF_6 and 5–7 Torr for 20% SF_6 in mixture with N_2. The incident and emergent power were measured with LM-2 Zeiss powermeters. An IR spectrophotometer SPECORD M80 Zeiss, was used at the absorptivity measurements.

3. RESULTS AND DISCUSSION

While the laser driven resonant diffusion through metal capillaries at low pressures has been the subject of some research in the past,[3,4] we are not aware of any modelling of this phenomena at higher pressures (as 1–7 Torr)—however, the theory describing the laser driven diffusion at low pressures,[5] (that deals with a Knudsen flow regime) is based on the assumption of a mean free path length greater than the capillary diameter. Therefore, the model must be reconsidered if, at

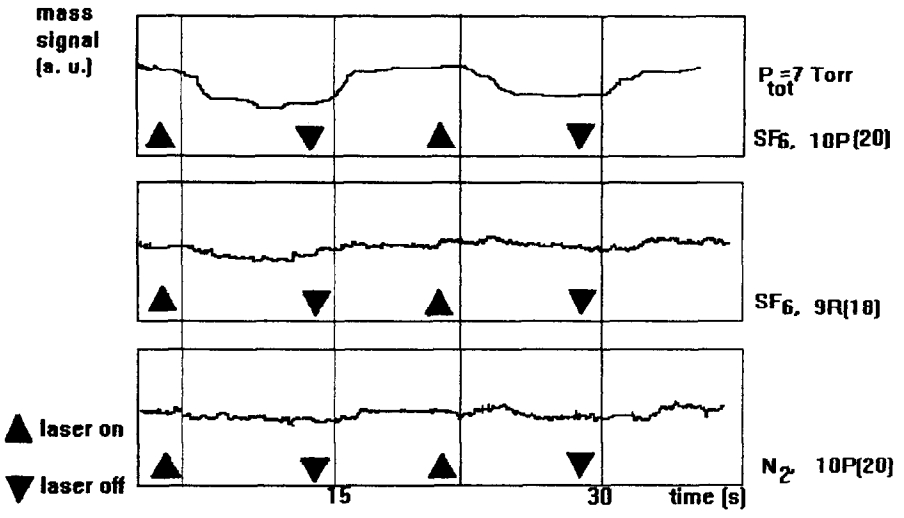

Fig. 2. Mass-spectrometer signal vs time for SF_6 and for N_2.

quite different conditions of pressure (five orders of magnitude) we find a persistence of the resonant diffusion effect.

In Fig. 2 the mass flow dependence on time is presented, as it is recorded on a quadrupolar mass spectrometer, for a mixture of SF_6 (20%) and N_2 under intermitent irradiation and at a total pressure of 7.0 Torr. A dominant thermal effect is present when irradiating either the pure non-resonant component N_2 or when irradiating the initial mixture with a laser line from the R-branch of 10 μm band or from the 9 μm band. A comparatively strong effect is noticed when the gas mixture was irradiated with the laser matched on the 10P (20) line (950 cm^{-1}). SF_6 has an intense absorption band between 953.5 and 936 cm^{-1} corresponding to the ν_3 vibration-rotation band.

In case of low pressures the mechanism of the resonant diffusion may be summarized as follows:[6] when one irradiates the resonant gas, the molecules get into an excited vibrational state. The dipole momentum of the transition interacts with its "image" in the metal wall or with molecular dipoles already adsorbed; in addition, the adsorption potential has a deepening and this cause in a decrease of the global diffusion coefficient of the resonant component through the capillary.[7]

The above description is derived supposing that there are no intermolecular collisions between the instant the molecule is excited and its adherence to the wall. The Knudsen flow regime satisfies indeed this condition because at sufficient low pressures the mean free path length exceeds the capillary diameter, m.f.p.l. $\gg$ D. In our case, this condition is no more fulfilled because, if we use the well-know relation between pressure and m.f.p.l.:

$$\text{m.f.p.l.} = kT/\sqrt{2}\sigma_c p, \tag{1}$$

where T = the temperature; p = the pressure; σ_c = the collision cross section. We notice that m.f.p.l. $\simeq D$ at 0.5 Torr (300 K) or at 1.0 Torr (400 K). We found the pressure distribution inside the capillary supposing a laminar, isothermal flow through a cylindric narrow pipe;[8] thus, the pressure at z value of the axial co-ordinate is:

$$p(z; p_{in}, T) = \sqrt{p_{out}^2 + (P_{in}^2 - P_{out}^2)z/L}, \tag{2}$$

where L stands for the length of the capillary.

Our calculations using formula (2) for the experimental setup from Fig. 1 leads to the conclusion that at pressures above 1.5 Torr at the entrance, there is no Knudsen zone inside the capillary. In the following, we shall prove that the hypothesis of a Knudsen zone is no more necessary if we consider the inner e.m. field structure: it can also be demonstrated that in the wave guided propagation of the field there are zones of high intensity near to the walls, that could supply excited molecules that have to travel a shorter distance to the adsorbing wall than the m.f.p.l. Therefore, the resonant diffusion effect could persist for a range of pressures of 2–7.5 Torr.

In order to evaluate the inner e.m. field intensity distribution we had at first to find the distribution for the existing propagation modes and then, using the superposition of the above modes, we found the final formula for the e.m. field intensity in a cylindric system of coordinates associated with the capillary.

It has been started from the following assumptions:

(a) we deal with an idealized waveguide;
(b) the coupling between the laser and the waveguide takes place as follows: the laser beam (considered in a Gaussian field distribution) is focused behind the front window of the capillary; the power density will be (Fig. 3):[9]

$$\frac{d\mathscr{P}}{d\mathscr{A}} = \frac{\mathscr{P}_0}{\pi v_0^2} \exp[-\rho^2/v^2(z)], \tag{3}$$

where

v_0 = the waist of the focused beam;
$\mathscr{P}_0$ = the incident power;
ρ = the radial coordinate;
$v^2 = v_0^2 + (z/kv_0)^2$;
$k = 950\ \text{cm}^{-1}$ – the wave-number.

The radius of curvature of the spherical wave front, behind the focal point, is given by:

$$R(z) = z + (kv_0^2)^2/z \tag{4}$$

and the angle between the curvature radius of the wave front and the Oz axis, θ', is given by (Fig. 3):[9]

$$\cos\theta' = \sqrt{1 - \rho^2/R^2(z)}. \tag{5}$$

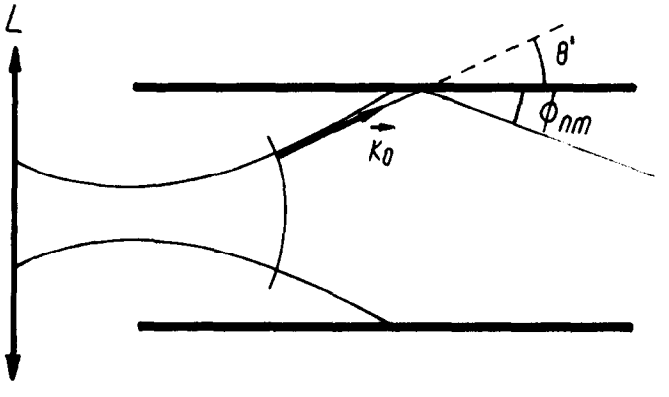

Fig. 3. The Gaussian wave front at the entrance of the capillary. ϕ_{nm} = the incidence angle assigned to the mode labelled (n, m). θ' = the angle between the wave vector and the axis of the capillary (Oz).

On the other hand, it is known that the guide propagation has a formal equivalence in terms of the geometric inner reflection propagation—each mode has, in this equivalence, its own incidence direction on the inner wall. This direction is quantified by the frontier conditions applied to the Helmholtz equation.[10,11] Therefore, we supposed that the coupling of the (n, m) labelled mode (TE or TM) takes place in all the points, (ρ, z), that satisfy:

$$\theta' = \Phi_{nm} \tag{6}$$

or

$$[1 - \rho^2/R^2(z)]^{1/2} = \lambda_0(1/\lambda_0^2 - 1/\lambda/\lambda_{c,nm}^2)^{1/2} \tag{7}$$

where

ρ = the radical co-ordinate;
Φ_{nm} = the angle assigned to the mode labelled (n, m);
λ_0 = the wavelength of the incident radiation;
$\lambda_{c,nm}$ = the cut-off wavelength; from equations (3) and (6) the following system will be obtained:

$$\begin{cases} |E_0|^2 = [2\mathscr{P}_0/\pi v^2(z)\epsilon c] \exp[-\rho^2/v^2(z)] \\ \sqrt{1 - \rho^2/R^2(z)} = \lambda_0(1/\lambda_0^2 - 1/\lambda_{c,nm}^2)^{1/2} \end{cases} \tag{8}$$

The second equation is a curve that represents the geometric place of the points for which exists a match between the direction of the wave vector of the Gaussian incident field and the direction associated with the propagation by reflection of a certain mode (n, m).

We assumed that the energy transfer mainly takes place for the least value of z that still holds on the coupling curve for the given mode. Let z_- be this value and ρ_- its correspondent radial co-ordinate value. Then, for a TE_{nm} or TM_{nm} mode, the initial intensity that is taken over by the guide from the laser e.m. field will be:

$$|E_{0,nm}|^2 = [2\mathscr{P}_0/\pi v^2(z_-)\epsilon c] \exp[-\rho_-^2/v^2(z_-)]. \tag{9}$$

Equation (9) gives the weight of a particular mode of propagation whose intensity distribution will have, for example, the form:

$$\begin{aligned} I \sim |E_{nm}(\rho, \theta)|^2 &= [2\mathscr{P}_0/\pi v^2(z_-)\epsilon c] \exp[-\rho_-^2/v^2(z_-)] \\ &\times \left\{ |\Gamma_{nm}|^2 \left[k_{c,nm}^2 \cdot J_{n-1}^2(k_{c,nm}\rho) \sin^2 n\theta - \frac{2nk_{c,nm}}{\rho} J_{n-1}(k_{c,nm}\rho) J_n(k_{c,nm}\rho) \sin^2 n\theta + \frac{n^2}{\rho^2} J_n^2(k_{c,nm}\rho) \right] \right. \\ &\left. + k_{c,nm}^2 J_n^2(k_{c,nm}\rho) \sin^2 n\theta \right\} \end{aligned} \tag{10}$$

(for a TM_{nm} arbitrary mode) with $\Gamma_{nm}^2 = k_{c,nm}^2 - k_0^2$; the propagation constant.

As concerns the number of propagating modes, it can be noticed that the $R(z)$ function has always a minimum for $z \in [0, \infty]$. This minimum corresponds to a maximum for θ'. Therefore, we have a finite number of modes that are coupled, i.e. the modes that satisfy $\Phi_{nm} \leqslant \theta'_{\max}$. Following this criterion we found that n and m are in $0 \div 3$ and $1 \div 4$ ranges, respectively, for both TM and TE modes.

Taking into account the orthogonality of the normal modes, the resultant intensity of the field inside the capillary is:

$$I(\rho, \theta) = \sum_{\substack{n=1 \\ m=0}}^{3,4} |E_0|^2 I_{nm}(\rho, \theta), \tag{11}$$

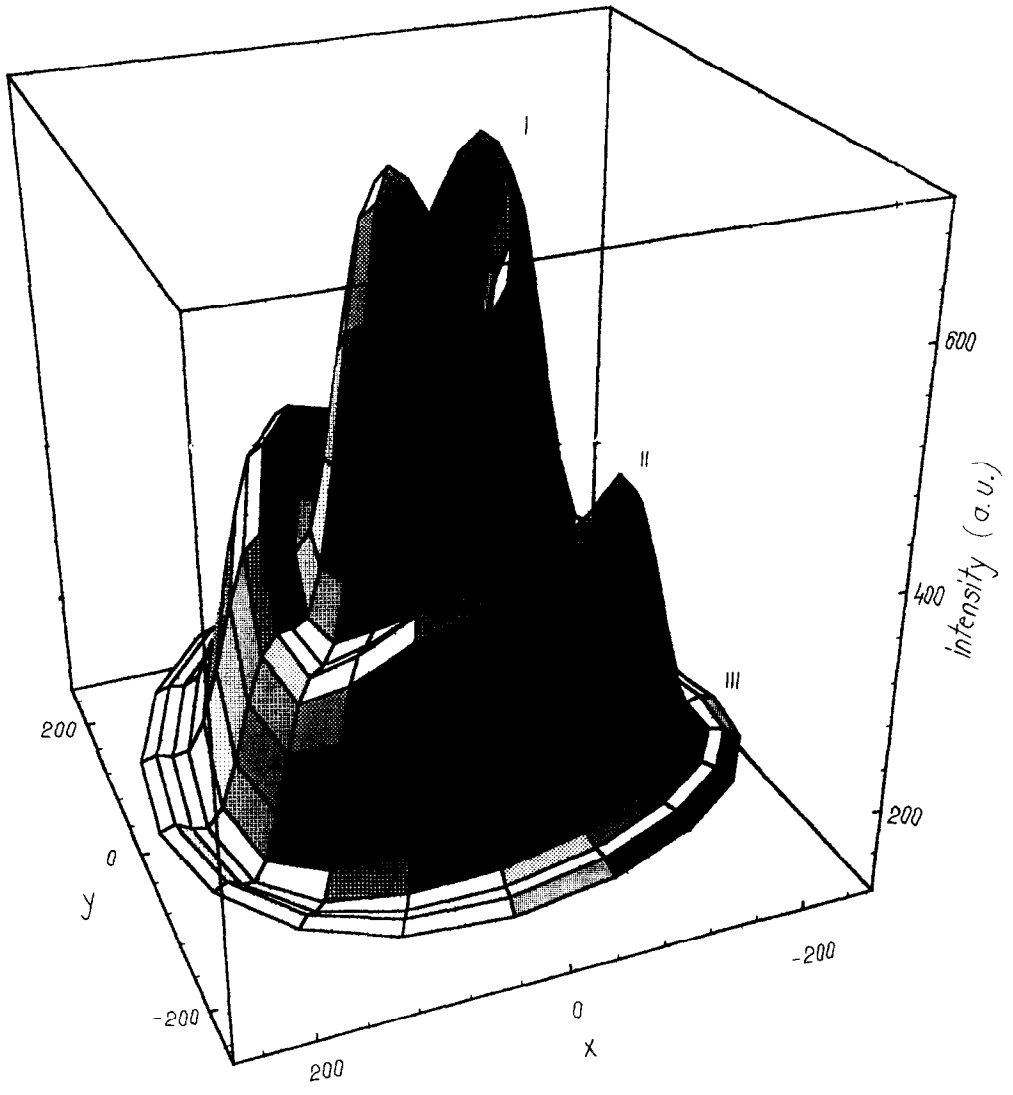

Fig. 4. The plot of the radial distribution of the e.m. field intensity, at the entrance of the capillary, as it results from equation (11). The adsorbed excited molecules are supplied in the most by the three "hot" radial zones, I, II, III. The lack in circular symmetry is due to the finite number of modes that, for the reasons of the calculation time, was limited to the first 10, in the order of their weights.

its graph shown in Fig. 4: it can be observed that there are radial zones of alternate high and low intensity levels of the e.m. field. The highest zones are labelled I, II, and III. Keeping in mind that the concentration of the excited molecules is proportional to the intensity of the field, one supposes that the adsorbed excited molecules are supplied mainly by these three "hot" zones. Therefore