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SUBSTANCE SEPARATION BY THE ACTION OF A PULSED IR LASER RADIATION ON GAS-MIXTURE FLOWS THROUGH CAPILLARIES

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Abstract—New aspects of substance separation by the laser driven diffusion of gaseous mixtures through capillaries are presented. By using the chopped radiation of a low power CO_2 laser, the experimental dependence of the separation coefficient on the pulse frequency in mixtures containing resonant and non-resonant gases was investigated. The induced effects agree with a model in which the number density of adsorbed molecules should be connected to temporal characteristics of the radiation. By avoiding heating effects, a pulsed laser irradiation may provide a new approach related to the practical purposes of substance separation in metal capillaries.

I. INTRODUCTION

Molecular surface diffusion in a laser field is an area of current interest in physics and technology of interface processes. When mixtures of gases, showing different spectral features relatively to the radiation wavelength are diffusing through capillaries, a laser induced separation effect could occur through the enhanced molecular adsorption of the resonant component.[1,2] Although the modification of the adsorption potential (and subsequently, of the diffusion coefficient), should not affect the non-resonant molecules, it was observed that the thermal heating is acting in a specific manner on both resonant and non-resonant components in a mixture flowing through metal capillaries, leading to time-dependent processes and an altered temporal behaviour.[3]

On the other hand, it was observed that, if a resonant gas is diffusing in an electromagnetic field through the capillary, the resonant effects are persistent even at pressures that, are by far exceeding the Knudsen flow regime.[4] Taking into account a waveguided propagation inside the capillary, it was shown,[5] that the molecular mean free path length could still exceed the distance between the capillary surface and the high intensity field zones located near the walls, thus accounting for the maintenance of the induced resonant adsorption effects.

Based on the above-mentioned premises, we have further used the low frequency chopped CO_2 laser radiation in order to investigate the separation capacity of the capillary–gas-mixture system and to maximize the separation coefficient. Optimum pulse frequency values were found for two different mixtures of resonant and non-resonant gases, at intermediate pressures (around 1 Torr), where the separation in a steady state regime of the irradiation begins to fail.

To explain the main features of molecular adsorption, a model was used in which the temporal variation of the pulsed radiation is connected to the number density of adsorbed molecules.

By avoiding heating effects and allowing for long lasting irradiation periods, the use of a pulsed radiation in separation process through capillaries could provide an attractive basis for practical purposes.

II. EXPERIMENTAL

The experimental set-up follows the description given in Ref. (3). It mainly consists of a Ni capillary (4 cm length and 0.5 mm dia), separating the preliminary vacuum system (pressures of

$0.2 \div 1.5$ Torr) and the high-vacuum system (pressures of $10^{-5} \div 10^{-7}$ Torr) provided with a quadrupolar mass spectrometer (Balzers QMG 111) for quantitative determination of the relative flow variations. The radiation of a cw, CO_2 laser [emitting on the 10P(20) line, 15 W power] was mechanically chopped at low frequencies, running from 0.2 to 1.5 Hz (with pulse lengths, Δt, ranging from 1.1 to 0.15 s). The radiation was focused near one end of the capillary (towards the exit of the diffusing gases).

Different gas mixtures were used, containing the non-resonant component CF_4 and the resonant gases SF_6 or $C_2H_4F_2$, respectively, with the relative concentrations: $CF_4:SF_6$ (or $C_2H_4F_2$) = 1:7 or 1:5. These concentrations were chosen in a region where experimental determinations showed an increase in the separation coefficient.[3]

III. RESULTS AND DISCUSSION

Previous results have shown that, when a mixture of gases is flowing through the capillary, there is a sudden lowering of the resonant component flow at the switch-on of the laser radiation.[1-4] There is also a diminishing of the non-resonant component, but gradually, with a much lower temporal slope.[3] In these conditions (continuous irradiation), only for reduced time intervals (few seconds) one may obtain quite important separation coefficients which are very rapidly decreasing towards very low values.

By using a chopped laser irradiation, the mass signal (recording the flow) decreases during the illumination of the capillary and has also a pulsed shape, with different pulse heights and number per second, depending on the chopper frequency.

For the non-resonant flow, even if the frequency is reduced, the height of the mass peaks keeps very low, much lower than for a continuous irradiation (in which the steady state is established after few seconds). On the contrary, for the resonant gas there is a decrease in the height of the mass pulses, as the frequency becomes larger than a certain value. These experimental facts may be followed in Fig. 1, which represents the dependence of the relative flow decrease q^*/q_0 on the chopper frequency, f, in a mixture $CF_4:SF_6 = 1:7$.

The flow values q were calculated by the integration over a given period of pulsed mass signals. q^* and q_0 stand for the flow values during and before the switch-on of the laser radiation, respectively. We note that the steady-state values of flow variation for the two gases are very close (the points on the ordinate). In a pulsed regime, the laser induced flow decrease for the non-resonant gas becomes very small (upper curve on Fig. 1) and maintains almost the same as the frequency increases. For the resonant gas, SF_6, the values of the relative flow decrease are more important, reaching a maximum around a given frequency value ($f = 0.7$ Hz, lower curve in Fig. 1). The minimum in Fig. 1 (which represents the maximum flow decrease of the resonant gas in a pulsed irradiation regime) is due to the interplay of two opposite effects: the number of pulses and their respective heights. Thus, the flow decrease values maintain low both

- when there are few pulses in a given period of time (even if their heights are near a maximum value, reached in a continuous irradiation regime)

and

- when their heights are progressively reduced with increased pulse frequency.

The pressure at the capillary entrance was maintained constant and equal to 0.9 Torr. It is usual to characterize a system aiming to substance separation by the separation coefficient, η, whose

evolution vs the pulse frequency is represented in Fig. 2. Two gas mixtures with the same concentration were used ($CF_4 + SF_6$ and $CF_4 + C_2H_4F_2$, respectively). η is expressed as the ratio between the relative flow composition under and before laser irradiation,

$$\eta = \frac{q^*_{CF_4}/q^*_R}{q^0_{CF_4}/q^0_R}, \tag{1}$$

where $R = SF_6$ or $C_2H_4F_2$.

In a continuous laser irradiation, the separation coefficient keeps very low for both mixtures (the values of η on the vertical axis, in Fig. 2). With increasing chopper frequency there is an increase of η for both mixtures, which reaches a maximum around $f \simeq 0.7$ Hz. The decrease of η that follows an increase in frequency above this value is mainly due to the increased laser effect on the non-resonant CF_4 component (Fig. 1).

The best values obtained for the separation coefficient at the pulse frequency of 0.7 Hz were $\eta_{CF_4/C_2H_4F_2} = 1.016$. These values should be compared with the maximum possible values in the capillary system, which would be obtained if there was no reaction of the non-resonant gas to the laser radiation [$(q^*/q_0)_{CF_4} = 1$)] and if the other experimental conditions (partial concentrations and pressure) were the same: $\eta_{max} = 1.062$ [for $CF_4 + SF_6$, $(q^*/q_0)^{max}_{SF_6} = 0.94$] and $\eta_{max} = 1.043$ [for $CF_4/C_2H_4F_2$, $(q^*/q_0)^{max}_{C_2H_4F_2} = 0.95$]. Note that in continuous irradiation, steady state values of the separation coefficient are much lower (Fig. 2).

Considering now the pressure at the capillary entrance, one may observe that the investigations on separation effects were confined to a pressure value of $p = 0.9$ Torr. This intermediate regime of pressures (situated around 1 Torr) is high enough to allow for a good observation of the laser induced adsorption effect but, at the same time, sufficiently low to minimize the energy transfer between the molecules of the two components.[2-4] With increasing pressure, (above 1 Torr) the relative flow decrease for the resonant component is rising,[2] but the separation coefficient under steady state irradiation maintains very low (lower curve in Fig. 3). On the contrary, a pulsed laser

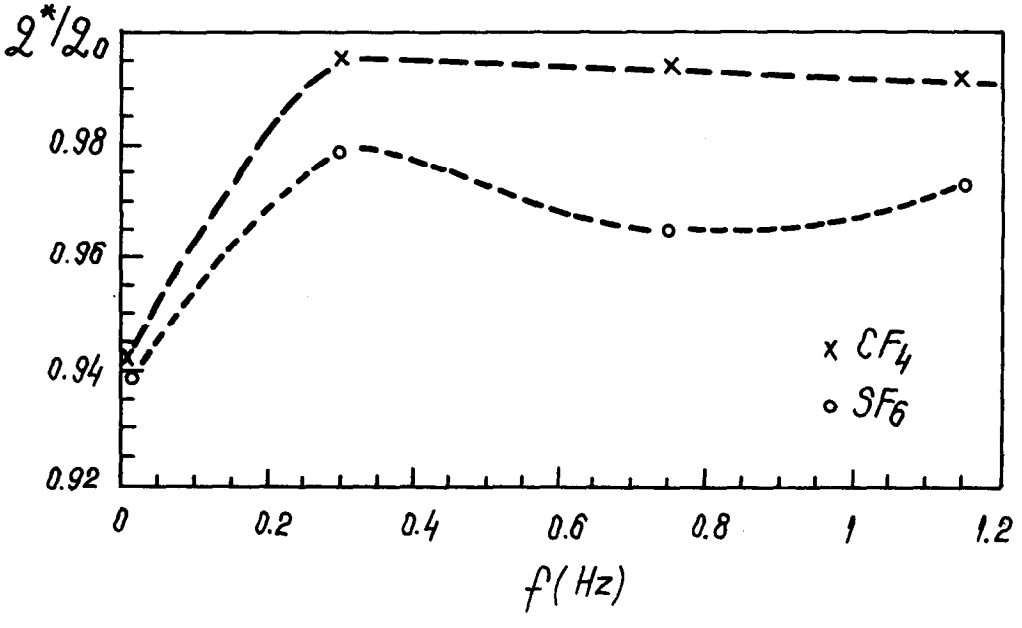

Fig. 1. The dependence of the relative flow, q^*/q_0, on the chopper frequency, f, for a mixture CF_4:SF_6 = 1:7 (x, CF_4; o, SF_6).

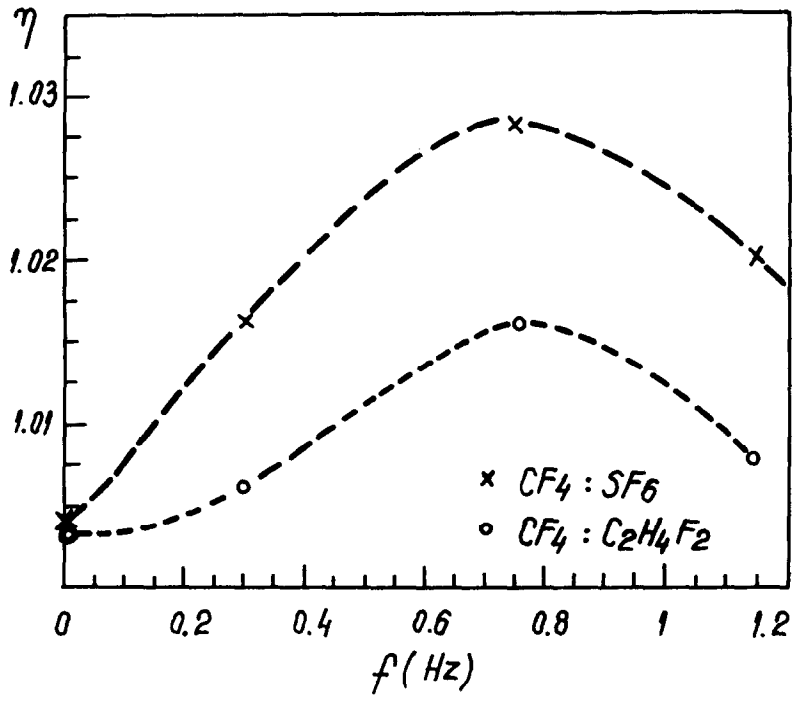

Fig. 2. The separation coefficient, η, vs the pulse frequency. Two gas-mixtures, with the same concentrations, were used (x, CF_4:SF_6, o, CF_4:$C_2H_4F_2$).

regime favours an increasing of η, which has a maximum around 1 Torr. This behaviour may be followed in Fig. 3, for the mixture CF_4:$C_2H_4F_2 = 1:5$ (pulse frequency $f = 0.7$ Hz).

The behaviour of the resonant (and non-resonant) molecular flows with increasing chopper frequency as evolving in Fig. 1 may be explained on the basis of a thermodynamical model,[6] for molecules adsorbed at a surface. At equilibrium, one may define the number, R of molecules arriving at the unit surface per unit time, and the mean residence time, τ_a of adsorbed molecules on the surface, i.e.

$$R = (2\pi mkT)^{-1/2}p, \tag{2}$$

where m, T and p stand for the molecular mass, the temperature and the pressure, respectively, and

$$\tau_a = \frac{1}{\nu_0}\exp(E_a/kT), \tag{3}$$

where E_a represents the adsorption energy, and $\nu_0 = 10^{13}$ Hz. It is supposed that the arriving molecules are all thermally accommodated to the walls and that there are no interactions between adsorbed molecules.

In a dynamical regime, a balance between molecules arriving at the surface and those which are desorbed is described by the equation

$$\frac{dn}{dt} = R - \frac{n}{\tau_a}, \tag{4}$$

where n is the number of the adsorbed molecules on unit surface. If integrated,

$$n(t) = R\tau_a - (R\tau_a - n_0)\exp\left(-\frac{t-t_0}{\tau_a}\right), \tag{5}$$

where $n(t_0) = n_0$, and represents the number of molecules adsorbed in a steady state regime.

If we consider that in a laser field, resonant molecules will exhibit different values for R and τ_a as compared to non-resonant ones, then the following series of equations may describe the behaviour of the number of adsorbed molecules in a simple periodic regime of irradiation:

$$\begin{cases} n_1 = R\tau_a - (R\tau_a - n_0)\exp\left(-\dfrac{\Delta t}{\tau_a}\right) \text{(without irradiation)} \\ n_2 = R^*\tau_a^* - (R^*\tau_a^* - n_1)\exp\left(-\dfrac{\Delta t}{\tau_a^*}\right) \text{(with irradiation)} \\ \cdots \\ n_{2k-1} = R\tau_a - (R\tau_a - n_{2k-2})\exp\left(-\dfrac{\Delta t}{\tau_a}\right) \\ n_{2k} = R^*\tau_a^* - (R^*\tau_a^* - n_{2k-1})\exp\left(-\dfrac{\Delta t}{\tau_a^*}\right) \end{cases} \tag{6}$$

where Δt is the pulse length and the series is developed after the number k of illuminated and dark half-periods (for simplicity taken as equal).

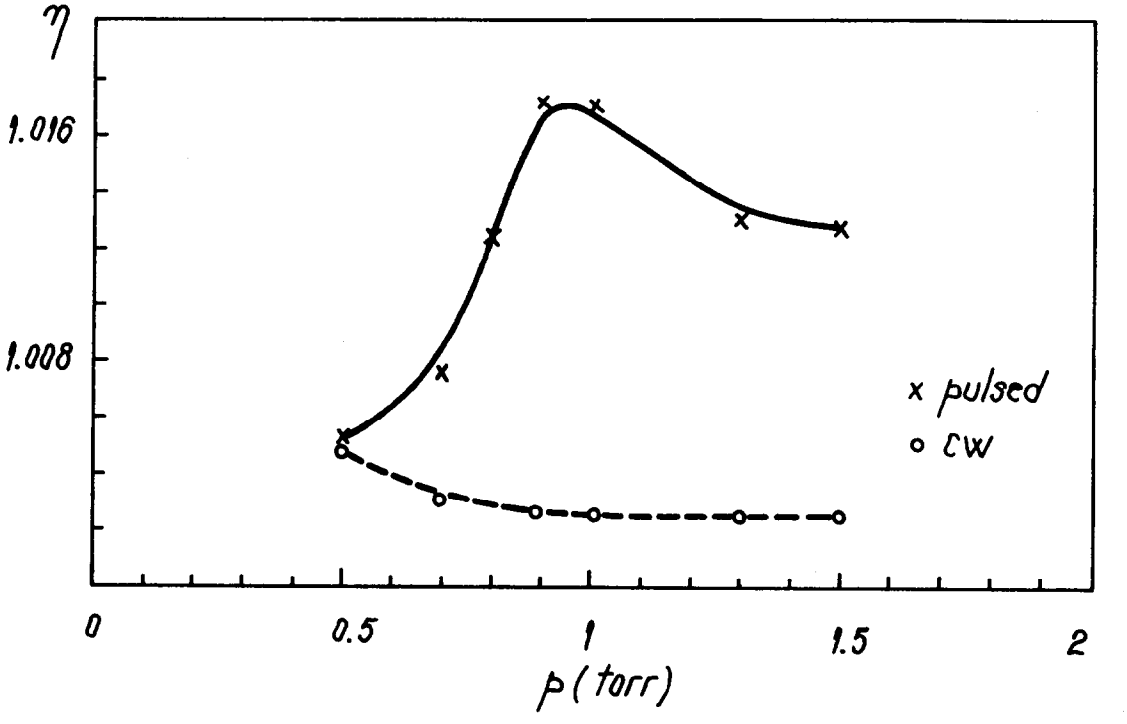

Fig. 3. The pressure dependence of the separation coefficient, η, ($f = 0.7$ Hz), x, pulsed laser; ○, steady irradiation (cw).

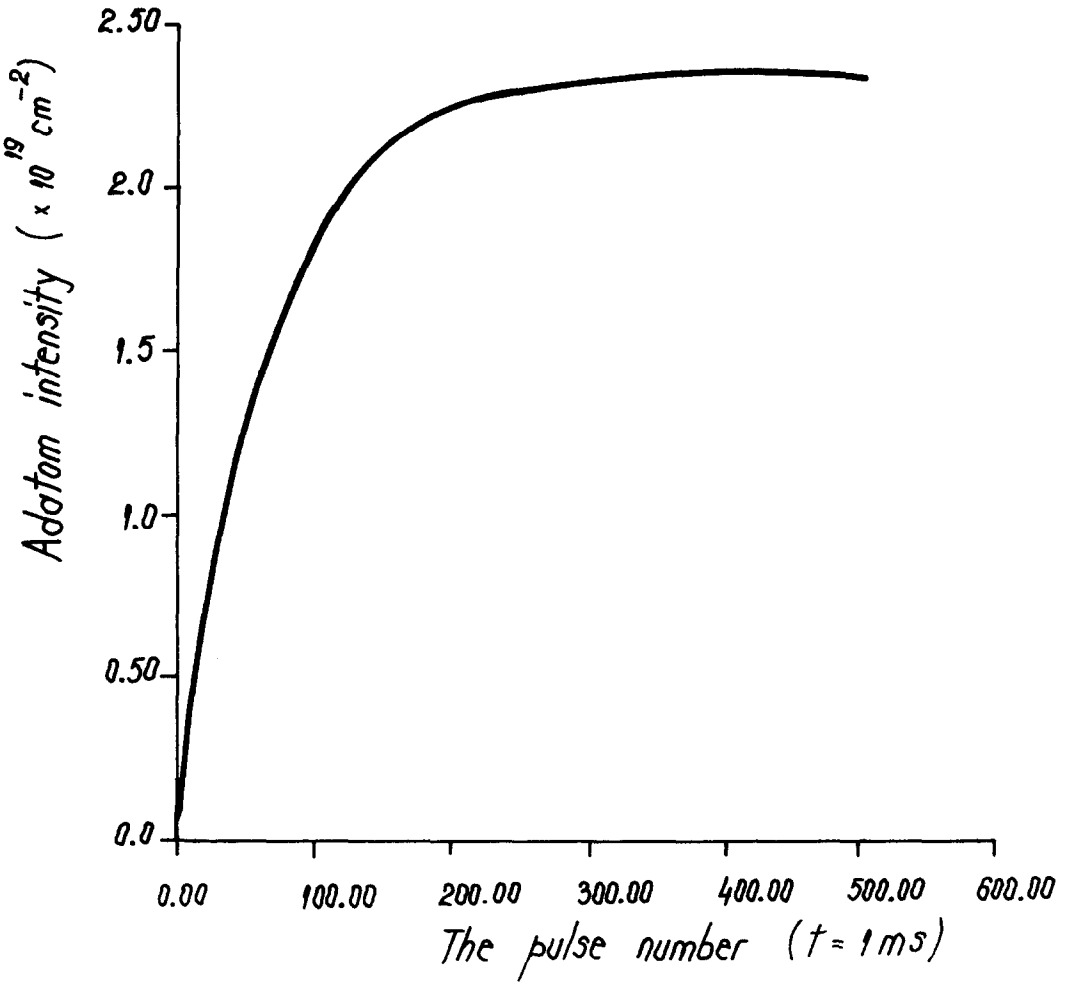

Fig. 4. The plot of the calculated dependence of n_k on the pulse number.

The limit of the above series is:

$$\lim_{k\to\infty} n_k = R\tau_a + \frac{\exp(-\Delta t/\tau_a) - 1}{\exp(\Delta t/\tau_a) - \exp(-\Delta t/\rho_a^*)}(R^*\tau^* - R\tau_a). \tag{7}$$

The numerical calculations show that one can consider $k\to\infty$ for $k \geqslant 200$: in Fig. 4, the dependence of n_k on the number of pulses clearly shows that the rising time of the number density of adsorbed molecules towards an equilibrium [described by equation (7)] subscribes to the characteristic experimental times (typical, several minutes). The density of adsorbed resonant molecules in an alternate irradiation regime may be obtained using equation (7) as:

$$n = \lim_{k\to\infty} n_k, \tag{8}$$

which is plotted in Fig. 5, taking E_a as a parameter. R^* and τ_a^* were calculated taking into account a temperature rise of 50 K [mainly due to the heating of the capillary walls—see Ref. (2) and comments below]. Although running in a wide range of values (in Fig. 5), the values of adsorption energy were chosen around 3000 K which was considered characteristic for steady-state experiments.[1] From Fig. 5 one may easily observe that for different values of adsorption energy, the

number density of the adsorbed molecules presents maxima relatively to the pulse lengths (or, equivalently, to the chopper frequency) in the periodic regime of radiation.

At the same time, for a non–resonant gas ($R^*\tau_a^* \simeq R\tau_a$) we get

$$n = \lim_{k\to\infty} n_k \simeq R\tau_a, \tag{9}$$

which is in agreement with the quasi-independent behaviour on the chopper frequency exhibited by the CF_4 non-resonant component in Fig. 1.

One can conclude that the different dependence of the resonant and non-resonant components on chopper frequency may lead, as it is suggested from formulas (6) and (7), at the maximum for