

# Selective heterogeneous separation of vibrationally excited molecules

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We analyze the possibility of separating selectively excited molecules in selectively occurring heterogeneous processes. We consider the adsorption mechanism of separating a mixture of molecules in an elementary cell—a vessel containing a low-pressure gas and irradiated by a laser. We estimate the efficiency of the adsorption in separation of a mixture of molecules in a chromatographic column with cooled walls in the presence of a laser-radiation field.

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It is well known that the problem of laser separation of molecules having different compositions or structures reduces the problem of separating selectively excited molecules of the required sort from the unexcited molecules. As applied to isotope separation with lasers, the methods proposed were those of light pressure<sup>[1]</sup> and deflection of a beam of vibrationally-excited molecules in an inhomogeneous electric field.<sup>[2]</sup> These methods, as well as the application of collisionless dissociation,<sup>[3]</sup> can be used only when the number of molecules to be separated is small. Two-step photodissociation<sup>[4,5]</sup> is difficult for heavy molecules. In this paper we analyze the possibility of separating selectively-excited molecules in selectively-occurring adsorption processes.

It is known that the probability of detaching a molecule by adsorption on a wall is determined by the specific energy of interaction of the molecule with the wall  $E_0$  and by the molecule energy  $E$

$$p = 1 - c = e^{-E_0/E}, \quad (1)$$

where  $c$  is the coefficient of capture by adsorption. As shown by our analysis of the published experimental data on adsorption of molecules of a gas in thermo-

dynamic equilibrium,<sup>[6]</sup> the quantity  $E$  should include the vibrational energy of the molecule. The constancy of  $E_0$  with changing ratio of the gas and wall temperatures in a wide range gives grounds for assuming that the capture coefficient  $c^*$  in the presence of nonequilibrium vibrational excitation of the molecules is also determined by the relation (1).  $E_0$  remains unchanged in this case, and  $E$  includes the energy  $E_v$  of the vibrational excitation of the molecule. Then the ratio of the probabilities of the detachment of vibrationally excited and equilibrium molecules is given by

$$p^*/p = (1/p)^{E_v/(E_T + E_v)}, \quad (2)$$

where  $E_T$  is the average energy of the equilibrium molecules. At  $E_v \gg E_T$  we have  $p^* \rightarrow 1$  and  $c^* \rightarrow 0$ .

It is obvious that the difference between the detachment probabilities of excited molecules permits a selective separation of these molecules if the excitation is selective.

By way of example, we consider a gas contained in a vessel whose characteristic dimensions are smaller than the mean free path. Then the laser radiation acts only on molecules of one sort. From the rate equations for a two-level system

$$\frac{dn_1}{dt} = (n_2 - n_1)W - c \frac{n_1 - n_0}{\tau} \quad n_1 + n_2 = n \quad (3)$$

$$\frac{dn_1}{dt} = - (n_2 - n_1)W - c^* \frac{n_2}{\tau}$$

( $W$  is the probability of the induced transitions,  $\tau$  is the average time of flight, and  $n_0$  is the equilibrium number of molecules) it follows that under stationary conditions and at saturation ( $n_1 = n_2 = n/2$ ), the number of molecules in the gas phase differs significantly from the equilibrium number

$$n = 2n_0 \frac{c}{c + c^*} \quad (4)$$

and doubles at  $c^* \ll c$ . When writing down Eqs. (3), we took into account the experimental fact that detachment of previously adsorbed molecules occurs in a vibrationally-unexcited state.<sup>[7]</sup> It is also assumed that the temperatures of the gas and of the walls are the same. The power flux necessary for the saturation is determined by the condition  $I > h\nu/\sigma\tau$ , and amounts to 1–10 W/cm<sup>2</sup> for the case of a CO<sub>2</sub> laser and molecules of the BCl<sub>3</sub> type.

The considered example, which pertains in essence to an elementary cell of the discussed separation method, is illustrative in character.

The selectivity of the adsorption of the vibrationally excited molecules can be effectively used when a continuous stream of nonadsorbed gas, to which a small amount of the adsorbable molecules that are to be separated is added, is passed through a cylinder with cooled walls. Under conditions of Poiseuille flow, the concentrations of the excited and unexcited molecules, in the case of saturation by the laser-radiation field, decrease exponentially as the gas flows through, with essentially different damping factors. Such a laser chromatographic column can have high enrichment coefficients at considerable mass flows. The enrichment coefficient at the exit from a column of length  $L$  and radius  $R$ , at a flow velocity  $v_0$  on the axis and at a molecule diffusion coefficient  $D$  in the carrier gas, is equal to

$$\eta = \exp\{(\lambda - \lambda^*) LD/v_0 R\} \quad (5)$$

where  $\lambda$  and  $\lambda^*$  are given by the transcendental equations cited in<sup>[8]</sup>, in which it is necessary, to determine  $\lambda$  and  $\lambda^*$ , to substitute the dimensionless parameters  $G$  and  $G^*$ , respectively, with  $G = [2c/(2-c)]v_T R/4D$  and

$$G^* = \frac{1}{2} \left( \frac{2c}{2-c} + \frac{2c^*}{2-c^*} \right) v_T R/4D,$$

while  $v_T$  is the average thermal velocity of the molecules.

We note that in the case of selective saturation of a multilevel system, the efficiency of separation increases with increasing number of excited levels.

The output flux density of the separated molecules on the column axis

$$\dot{n} = n_0 v_0 e^{-\lambda^* LD/v_0 R} \quad (6)$$

may not differ greatly from the input density  $n_0 v_0$  if  $\lambda^*$  is small and the parameters are judiciously chosen.

For a stream of the gas mixture BCl<sub>3</sub>(10<sup>-2</sup> Torr) + He(10<sup>-1</sup> Torr) at a velocity  $v_0 = 50$  m/sec, a temperature 195°K, a wall temperature 77°K, a tube diameter 1 cm, and a length 2 cm, we can obtain  $\eta = 3.5$  and  $\dot{m}_{\text{BCl}_3} = 0.4$  g/hr at an initial separated-molecule concentration 1:1. The helium flow rate is ~5 g/hr.

Similar results can be obtained by adsorption on the tube walls in the case of free molecular flow of the operated gas without the carrier gas (Knudsen outflow). In addition to physical adsorption, selective heterogeneous separation of vibrationally-excited molecules can be effected by chemisorption, as well as by using the differences of the solubilities of the vibrationally excited molecules in liquids and of the diffusion rates.

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