Methods for selective heterogeneous separation of vibrationally excited molecules

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A demonstration is reported of the possibility of selective heterogeneous separation of a mixture of vibrationally excited molecules with similar but different vibrational quanta. Separation of boron isotopes by adsorption, on a cooled wall, of boron trichloride molecules excited by CO_2 laser radiation is reported. An analysis is made of the possibility of improving the selectivity of the process.

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1. INTRODUCTION

Various aspects of laser separation of multicomponent mixtures of molecules are being investigated intensively.[1–4] The problem of laser separation of isotopes reduces to two tasks, one of which is the selective excitation of molecules of the required kind in the field of laser radiation and the other is the subsequent separation of the selected molecules with the aid of some interaction mechanism which is efficient for the excited molecules. Suggested possible mechanisms of isotope separation include chemical reactions involving the excited molecules or their fragments[2,3] and also the interaction of vibrationally excited molecules with an inhomogeneous electric field.[4]

In our earlier communication[5] we suggested a heterogeneous method for the separation of selectively excited molecules by selective adsorption. The main advantage of this method is that the critical adsorption energy is low compared with the activation energy of homogeneous chemical reactions and this makes the adsorption process highly sensitive to small changes in the excitation energy of the molecules and, therefore, it ensures a high selectivity of separation. Moreover, a distinguishing feature of this method is the possibility of working in a wide range of pressures and the avoidance of subsequent chemical purification.

Excitation conditions are made much easier by the fact that in heterogeneous separation it is sufficient to excite only the first vibrational level of a molecule. Firstly, this means that there is no need to overcome the anharmonicity of the molecule, which is important in the excitation of higher vibrational levels. Secondly, it is possible to carry out separation without elimination of gaskinetic collisions.

Collisions effectively equalize the relative populations of the vibrational levels of molecules of different kind if the isotopic shift is small. A strong influence of even a small difference between the vibrational energies of molecules of different types on the rates of adsorption processes is responsible for the selectivity of heterogeneous separation. Clearly, in contrast to the collisionless case, the separation coefficient of this method is lower and the yield is higher.

Heterogeneous separation of excited molecules from those which are unexcited is possible when the separation coefficient is large at high pressures and the role of the resonant $V-V$ exchange processes is weakened by the addition of a thermalizing monatomic gas (helium).

We shall consider these methods and report experimental tests of the heterogeneous separation of the $B^{10}Cl_3$ and $B^{11}Cl_3$ molecules excited by cw CO_2 laser radiation.

2. ADSORPTION OF VIBRATIONALLY EXCITED MOLECULES

It is known that the rate of adsorption, on a cooled wall, of molecules in a gas at thermodynamic equilibrium is governed by the sticking coefficient

$$C=1-e^{-E_c/E}, \tag{1}$$

where E_c is the critical adsorption energy, which is a function of the temperature of the wall, and E is the energy of the translational motion of the gas molecules.[6] This relationship is in good agreement with the experimental results.[7] However, the data obtained in[7] for several polyatomic molecules at different gas temperatures indicate that the change in the value of C with rising gas temperature can be understood if E is regarded as the total energy of a molecule including vibrational and rotational components. The problem of the dependence of the sticking coefficient C on the degree of vibrational excitation of a molecule under nonequilibrium conditions, when the vibrational temperature differs from the translational value, requires separate discussion. However, the constancy of the value of E_c when the ratio of the gas and wall temperatures is varied over a wide range suggests that even in the presence of nonequilibrium vibrational excitation the sticking coefficient C is still given by Eq. (1) in which the value of E_c remains constant and E includes the energy of the vibrational excitation of the molecule E_v. From this point onward, we shall use the following formula for the sticking coefficient of vibrationally excited molecules

$$C^*=1-\exp[-E_c/(E_v+E_T)]. \tag{2}$$

Our experimental results demonstrate the validity of the above approximation, at least for the BCl_3 molecules when the wall temperature is 160 °K.

3. EXCITATION AND SELECTION OF MOLECULES

Clearly, the selectivity of laser excitation of a mixture of molecules is retained in the absence of gaskinetic collisions between molecules. In this case the heterogeneous separation of excited molecules occurs in a time shorter than the time between collisions. An analysis of this simple model[5] gives

$$n=2n_0C/(C+C^*), \tag{3}$$

where n and n_0 are the concentrations of resonating molecules in the gas phase in the presence and absence of laser radiation, respectively. An increase in the gas pressure results in the loss of the excitation selectivity. However, the influence of the resonant $V-V$ exchange between molecules of different isotopic compositions may be weakened greatly by the additional of a thermalizing monatomic gas (for example, helium).

In fact, in the two-level approximation the system of rate equations for the populations of vibrational levels of molecules of two types can be represented in the form

$$\left.\begin{aligned} dn_2/dt&=W(n_1-n_2)-n_2/\tau+Kn_1N_2-Kn_2N_1,\\ dN_2/dt&=-N_2/\tau+Kn_2N_1-Kn_1N_2,\\ n_1+n_2&=n,\ N_1+N_2=N. \end{aligned}\right\} \tag{4}$$

Here, n_1, n_2, n, N_1, N_2, N are the concentrations of unexcited, excited, and all the molecules of both isotopic modifications under consideration, W is the probability of stimulated transitions, τ is the $V-T$ relaxation time, K is the rate constant of the quasiresonant $V-V$ exchange. In these equations it is assumed that the parameters K and τ are the same for molecules of both types.

Then, under steady-state conditions the ratio of the concentrations of the excited molecules becomes

$$N_2/n_2=KN\tau/(Kn\tau+1). \tag{5}$$

In the case of strong dilution with helium (i.e., when $Kn\tau \ll 1$), we find that $N_2 \ll n_2$, i.e., the concentration of excited nonresonating molecules is relatively small. It is known that the cross section for the quasiresonant $V-V$ exchange of molecules such as BCl_3 with an isotopic shift of 40 cm^{-1} is 2–4 times smaller than the gaskinetic cross section. On the other hand, the cross section of the $V-T$ process in the case of relaxation by interaction with helium is 50–100 times smaller than the gaskinetic cross section. Therefore, in the case of the concentration ratio $B^{10}Cl_3 : B^{11}Cl_3 : He = 1:1:100$, we have $N_2/n_2 \approx 1/30$.

In this case, heterogeneous separation can be carried out conveniently by passing a mixture of gases with helium through a cylindrical tube with cooled walls. The steady-state transport equation describing this process on the assumption that the quasiresonant $V-V$ exchange is negligible is of the form

$$\left.\begin{aligned} V\frac{\partial n_1}{\partial x}&=D\left(\frac{\partial^2}{\partial x^2}n_1+\frac{\partial^2}{\partial r^2}n_1+\frac{1}{r}\frac{\partial}{\partial r}n_1\right)-Wn_1+\left(W+\frac{1}{\tau}\right)n_2,\\ V\frac{\partial n_2}{\partial x}&=D\left(\frac{\partial^2}{\partial x^2}n_2+\frac{\partial^2}{\partial r^2}n_2+\frac{1}{r}\frac{\partial}{\partial r}n_2\right)-\left(W+\frac{1}{\tau}\right)n_2+Wn_1, \end{aligned}\right\} \tag{6}$$

where x and r are, respectively, the longitudinal and radial coordinates, V the flow velocity, and D is the diffusion coefficient of the molecules being separated in the carrier gas. In our case, the boundary conditions on the walls of a cylindrical reactor can be expressed in the form[8]

$$\left.\begin{aligned} \left(D\frac{\partial n_1}{\partial r}\right)_{r=R}&=-\left(\frac{\bar{C}n_1V_T}{4}\right)_{r=R},\\ \left(D\frac{\partial n_2}{\partial r}\right)_{r=R}&=-\left(\frac{\bar{C}^*n_2V_T}{4}\right)_{r=R}, \end{aligned}\right\} \tag{7}$$

where V_T is the average thermal velocity of the molecules and $\bar{C}=C/(1-C/2)$. In the Poiseuille flow case with $V=V_0(1-r^2/R^2)$ and on the assumption of saturation $n_1=n_2=n/2$, we find that, beyond the zone where the concentration is established, in the range $x>R/\alpha$ we can easily derive the expression for the concentration in the axial region

$$n=n_0e^{-\alpha x/R},\quad n_0=n(0,\ r), \tag{8}$$

where the decay constant is $\alpha=\lambda^2D/V_0R$, λ is the solution of a transcendental equation[9]

$$\frac{(^1/_2-\lambda/4-\alpha^2/4\lambda)\,{}_1F_1(^3/_2-\lambda/4-\lambda^2/4\lambda,2,\lambda)}{{}_1F_1(^1/_2-\lambda/4-\alpha^2/4\lambda,1,\lambda)}=\frac{\lambda-G}{2\lambda}, \tag{9}$$

and

$$G=(\bar{C}+\bar{C}^*)V_TR/8D. \tag{10}$$

For the unexcited component of the mixture of concentration N the solution of the steady-state transport equation

$$\left.\begin{aligned} V\frac{\partial N}{\partial x}&=D\left(\frac{\partial^2}{\partial x^2}N+\frac{\partial^2}{\partial r^2}N+\frac{1}{r}\frac{\partial}{\partial r}N\right),\\ \left(D\frac{\partial N}{\partial r}\right)_{r=R}&=-\left(\frac{\bar{C}NV_T}{4}\right)_{r=R},\quad N(0,r)=N_0 \end{aligned}\right\} \tag{11}$$

beyond the zone of establishment of the concentration in the range $x>R/\beta$ again has the form

$$N(x,\ 0)=N_0e^{-\beta x/R}, \tag{12}$$

where, however, the decay constant $\beta=\lambda^2D/V_0R$ has to be found from Eq. (9) assuming that $G=\bar{C}V_TR/4D$. The enrichment coefficient on the axis at the exit from a reactor of length L

$$\eta=\frac{n(L)}{N(L)}\Big/\frac{n_0}{N_0}=e^{-(\alpha-\beta)L/R} \tag{13}$$

is governed by the difference between the decay constants of the concentrations $n(x)$ and $N(x)$.

By way of example, we shall consider the separation of the $N_2^{14}O$ and $N_2^{15}O$ molecules mixed with helium at pressures of 1 and 100 Torr, respectively. If the gas temperature is 195 °K and the temperature of the reactor walls is 77 °K, it follows from[7] that the sticking coefficient is $C_{N_2O} = 0.85$. In the excitation of antisymmetric vibrations of the N_2O molecule it follows from Eq. (2) that $C^*_{N_2O} = 0.21$. If the stream velocity is $V = 100$ m/sec, the radius of the tube is 0.5 cm, and length of the tube is $L = 5$ cm, the enrichment coefficient is $\eta = 20$. If the initial isotopic composition of the mixture is $n_0/N_0 = 1$, the yield of the enriched mixture is 10^{-7} g/sec. The consumption of helium is 0.15 g/sec.

Under the same conditions an estimate for BCl_3 gives $\eta = 3$ and the yield of the enriched mixture is 5×10^{-7} g/sec.

Thus, the use of helium in this isotope separation method is promising. We must bear in mind that the laser power has to be considerably higher in the presence of helium. Moreover, although the separation of helium from the enriched mixture is a fairly simple process, it is desirable to consider a heterogeneous isotope separation method in which the influence of the $V-V$ processes is not excluded.

In the limiting case of a strong $V-V$ exchange we have $Kn\tau \gg 1$ and $N_2/n_2 = N/n$. In this case, heterogeneous separation is due to the difference between vibrational energies of the excited molecules of different isotopic compositions. Then, the gas mixture at the exit from the reactor will be enriched in the molecules whose vibrational level is higher, i.e., with the lighter molecules. The parameters of the separation process will be governed by the isotopic shift.

Under these conditions the enrichment coefficient at the exit from the reactor is again given by Eq. (13) but now the decay constants are $\alpha = \lambda_n^2 D/V_0 R$ and $\beta = \lambda_N^2 D/V_0 R$, and λ_i are the solutions of Eq. (9) where

$$\left.\begin{aligned} G_n &= (\bar{C}_n + \bar{C}_n^*)V_T/8D, \\ G_N &= (\bar{C}_N + \bar{C}_N^*)V_T/8D. \end{aligned}\right\} \qquad (14)$$

In the case of the $B^{10}Cl_3$ and $B^{11}Cl_3$ molecules at $T = 160$ °K and $P = 1.5\times10^{-3}$ Torr, for $R = 0.6$ cm, $L = 30$ cm, $V = 30-100$ m/sec, the enrichment coefficient can reach $\eta = 1.65-1.45$.

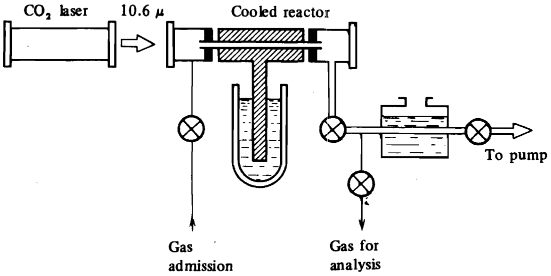

FIG. 1. Schematic diagram of the apparatus.

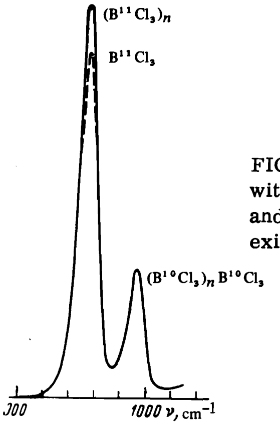

FIG. 2. Absorption spectrum of $(BCl_3)_n$ with a natural proportion of the isotopes and the spectrum of BCl_3 at the reactor exit.

4. EXPERIMENT

Heterogeneous laser isotope separation was achieved experimentally under conditions corresponding to a strong $V-V$ exchange between the $B^{10}Cl_3$ and $B^{11}Cl_3$ molecules.

We used apparatus shown schematically in Fig. 1. Gaseous boron trichloride with a natural proportion of the boron isotopes was admitted through a leak valve into a reactor whose active part was a stainless-steel tube 30 cm long with an internal diameter of 12 mm. The tube was cooled to 160 °K by a massive heat sink. The gas from the reactor was collected (for subsequent analysis) in a liquid-nitrogen-cooled storage tank. The reactor was illuminated with cw CO_2 laser beam of 30 W power which passed through NaCl windows. The density of the CO_2 laser radiation flux needed to achieve saturation of the populations of the vibrational levels ν_3 in the BCl_3 molecules was less than 10 W/cm^2. The gap between the beam of 10.6 μ wavelength and the internal tube wall was ~1 mm. An analysis of the isotopic composition of the accumulated gas was made on the basis of infrared spectra recorded at different pressures in the gas. Typical absorption spectra of the gas at the entry and exit from the reactor are shown in Fig. 2. Figure 3 gives the results of measurements of the ν_3 vibrational absorption peaks of the $B^{10}Cl_3$ and $B^{11}Cl_3$ molecules at different pressures. The relative content of the $B^{10}Cl_3$ and $B^{11}Cl_3$ molecules was determined from the slope of the tangent to the curve at the origin (the curve was extrapolated to low pressures). A standard computer program was used in the analysis of the experimental results.

We achieved experimentally an enrichment of boron trichloride in $B^{10}Cl_3$ and the enrichment coefficient was $\eta = 1.57 \pm 0.2$, which was in good agreement with the results of the above estimates. The amount of the enriched BCl_3 accumulated in 2 h was 2.2 mg. The gas pressure at the exit from the reactor was 1.5×10^{-3} Torr when the flow rate was 8 liter/sec and this pressure was ensured by varying the exit pressure during the experiment from

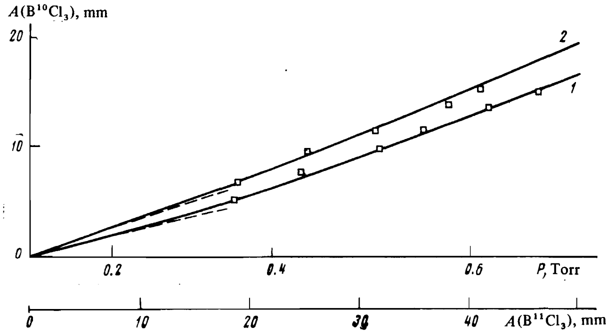

FIG. 3. Amplitudes of the absorption peaks A of the ν_3 vibration in the $B^{10}Cl_3$ and $B^{11}Cl_3$ molecules in a natural mixture (1) and at the exit from the reactor (2) plotted for different pressures P of the gas in the cell used to measure the infrared spectra.

1.2 to 1.7×10^{-2} Torr. Before the experiments, the reactor was evacuated to 10^{-4} Torr.

Control experiments were carried out using a laser beam which glanced along the reactor walls and also in the absence of laser radiation, keeping the other conditions constant. The control experiments showed no change in the isotopic composition of the gas, which was to be expected in accordance with the experimental results[10,11] according to which the separation coefficient of the boron isotopes in the case of equilibrium evaporation at $T = 160$ °K was only $N(B^{10}Cl_3)/N(B^{11}Cl_3) = 1.0035$. At temperatures above 208 °K the more volatile component was $B^{11}Cl_3$. A control experiment carried out using laser radiation but keeping the reactor walls at room temperature showed that the isotope separation by chemical sorption was negligible.

5. CONCLUSIONS

We demonstrated thus the possibility of using adsorption in heterogeneous selective separation of vibrationally excited molecules. Clearly, it would be interesting to utilize other heterogeneous processes such as chemisorption, solubility of gases in liquids, diffusion in porous adsorbents, and relaxation of gases interacting with aerosols.

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