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**DISCUSSIONS OF BULK ATOMIC
OR MOLECULAR SEPARATIONS
BY RESONANT RADIATION PRESSURE**

Edgar A. Rinehart
Jeffery H. Richardson
Lawrence W. Hrubesh

May 29, 1975

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DISCUSSIONS OF BULK ATOMIC OR MOLECULAR SEPARATIONS BY RESONANT RADIATION PRESSURE

Abstract

Resonant radiation pressure has been produced by the transfer of photon momentum to an atom or molecule during resonant absorption of photon energy. We believe that this pressure is large enough to induce atomic and molecular separations when a laser is used as a source. We developed a model to describe the motion of molecules (or atoms) with a diffusion-limited mobility, under the influence of laser-induced resonant radiation pressure. The time dependency of the

process was examined for a cw laser in the bulk movement of a one-component gas. Thermodynamic calculations showed that the process should be efficient and substantial. Preliminary experimental results were not conclusive. Two additional experimental techniques have been examined: the use of a pulsating laser source; and the use of periodic withdrawals and replenishings of the mixture within the system. Applications in the bulk separations of isotopic mixtures and optical isomers are discussed.

Introduction

Considerable attention is being given to methods of inducing physical separations of atoms or molecules which normally exist in mixed composites. Particular emphasis is placed on isotopic separation, although chemical separations of any kind find many applications in present technology. One interesting approach to achieve atomic or molecular separations, especially because of the potential use of lasers, is by resonant radiation pressure. Resonant radiation pressure is produced by the transfer of photon momentum to an atom or molecule during resonant absorption of photon energy. Ashkin¹ has calculated that this pressure can indeed be large enough to induce atomic separation

when a laser is used as a source, and proposed that it might be used to separate isotopes. The principle has in fact been used by several experimentors²⁻⁴ to deflect resonant atoms from a beam. Although these experiments suggest the feasibility of this technique for separation, they all have used beams which considerably limit the yield of separated material. We will consider in this paper the possibility of separation of much larger quantities by applying resonant radiation pressure in a bulk process.

We will develop a model which describes the motion of molecules (a similar case exists for atoms) under the influence of the resonant radiation pressure and a

"mobility" which is diffusion limited. A similar description of radiation induced pressure on a bulk gas was given recently by Gelbewachs and Hartwick.⁵ The time dependence of the process will be examined for the case where cw laser radiation supplies the radiation pressure. Thermodynamic calculations are made for a binary mixture to predict the equilibrium state of

such a system. We describe a set of experiments designed to produce and observe the actual separation of gases and isotopes by this method. We discuss the optimization of experimental conditions and parameters, and describe in detail a novel application of a pulsed laser which should produce highly efficient laser-induced separation in the bulk.

Model of Resonant Radiation Induced "Mobility"

We consider an ideal, equilibrated gas, confined to a long cylindrical tube of narrow cross-section at a reduced pressure, with a concentration of n_0 molecules/cc.

Suppose we could apply a force (F) uniformly over the cross-sectional area of the tube in the longitudinal (\hat{x}) direction which would affect the motion of a certain number (n) of the molecules in the tube. In the absence of a restoring force, we would expect a net molecular flux through an element of area directed along \hat{x} given by

$$j_x = n\bar{v}_x \quad (1)$$

where \bar{v}_x is the average drift velocity of the n molecules in the \hat{x} direction.

Opposing this molecular flux would be a flux in the opposite direction operating under a diffusional force. This flux can be given by

$$j_{-x} = -D \partial n / \partial x \quad (2)$$

where D is the self-diffusion constant and $\partial n / \partial x$ is the molecular gradient in the \hat{x} direction.

After a sufficient time, a steady state would be reached at which

$$j_x = j_{-x} \quad (3)$$

or

$$-D \partial n / \partial x = n\bar{v}_x \quad (4)$$

The steady-state solution of this equation is

$$n(x) = n_0 \exp(-\bar{v}_x x / D) \quad (5)$$

which is similar to that written by Ashkin.¹ It implies that if the force is sufficiently large to impart a large mean drift velocity to the molecules in the \hat{x} direction, the distribution of molecules within the tube along the \hat{x} direction becomes exponential. Thus, as long as the applied force is maintained, molecules can be "pushed" toward one end of the tube and held there.

The force referred to above can be supplied by the time rate of momentum transferred from a photon beam to molecules absorbing the photons during the resonant absorption process. Because only certain molecules can absorb those photons, they alone receive the preferential force, thus providing a mechanism to "push" certain molecular species to one end of the tube. This phenomenon is called resonant radiation pressure or photon pressure.

For a more detailed understanding of the force produced by resonant radiation,

consider a molecular system whose energy levels are defined by a two-manifold vibrational-rotational structure. The resonant radiation is going to change the lower state (n_1) and excited state (n_2) populations of some transition within the manifold. The system's response will be determined by a combination of rates of stimulated absorption, radiative momentum transfer, collisional deactivation, and the relaxation of the excited state by spontaneous emissions. The effective radiation pressure force per molecule produced during resonant absorption is given by the product of the momentum per photon and the number of quanta absorbed per molecule per second. Thus,

$$F_{\text{eff}} = (h/\lambda) (\gamma I / \Delta n) \quad (6)$$

where h/λ is the momentum per photon, γ is the unsaturated coefficient of absorption of the gas made up of n molecules/cc, Δn is the difference in populations of the two states involved, and I is the radiation intensity (expressed in units of quanta per second per unit cross-section of area). The term $(\gamma I / \Delta n)$ represents an effective deactivation rate of the upper state of the transition so that we can define an effective lifetime (τ_{eff}) for the upper state as

$$\tau_{\text{eff}} = (\gamma I / \Delta n)^{-1}. \quad (7)$$

The effective force per molecule then becomes

$$F_{\text{eff}} = (h/\lambda) \tau_{\text{eff}}^{-1}. \quad (8)$$

We may consider the molecules to have a "mobility" under the action of the effective force F_{eff} given by

$$\mu = v_x / F_{\text{eff}} \quad (9)$$

where v_x is the drift velocity defined above. From kinetic theory, the "mobility" is also defined by the "Einstein relation,"

$$\mu = D/kT \quad (10)$$

where D is the diffusion coefficient. Using the equipartition principle and the definition of D from kinetic theory

$$\mu = \tau_k / M \quad (11)$$

where τ_k is the mean time between collisions which transfer kinetic energy from the excited molecules and M is their molecular weight. Then, from Eqs. (8), (9) and (11),

$$v_x = (h/M\lambda) (\tau_k / \tau_{\text{eff}}) \quad (12)$$

which defines the drift velocity imparted to the molecules in the \hat{x} direction in terms of the collisional and radiative lifetimes of the excited molecular state. From Eq. (5), maximization of the drift velocity v_x optimizes the attainable spatial separation within the tube. Thus, to affect large separations, τ_{eff} should be made as small as possible (i.e., the deactivation of the upper state should be enhanced).

Time-Dependent Solutions

An estimate of the time-dependence for molecular separation may be made by studying the case for a one-component

gas subject to resonant radiation pressure and self-diffusion. Consider a cylindrical tube of length L and cross-section A to

be filled with a given gas at initial concentration (C_0) and temperature (T). Assume that the laser beam fills the tube and that the photon flux is sufficiently high so that the rate-limiting step for absorption is the relaxation rate from the excited state to the ground state. Then, as previously defined, a drift velocity v_x can be associated with the absorbing gas:

$$v_x = (h/M\lambda) (\tau_k/\tau_{eff}) \quad (13)$$

Under isothermal conditions and neglecting radial diffusion and wall effects (i.e., the mean free path is much less than the tube diameter), the concentration $C(x, t)$ is given by the solution to

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2} - v_x \frac{\partial C(x, t)}{\partial x} \quad (14)$$

Two additional assumptions are made:

(1) an ideal gas is assumed, and (2) D , the diffusion coefficient, is assumed to be constant. Note that Eq. (14) is analogous to that of forced diffusion for a single gas mixture.⁶

Equation (14) can be solved by separation of variables subject to the following boundary conditions:

- 1) as t approaches infinity, $C(x, t)$ approaches the steady-state solution, i.e.,

$$\frac{\partial^2 C(x, t)}{\partial x^2} - \frac{v_x}{D} \frac{\partial C(x, t)}{\partial x} = 0 \quad (15)$$

- 2) for the steady-state solution, $\langle C \rangle = C_0$
 3) at $t = 0$, $C(x, t) = C_0$ for $0 \leq x \leq L$.

In addition, in order to obtain a closed analytical solution, one of the following two assumptions must be made:

- 4) $C = 0$ at $x = 0, L$ for $t = 0$ or

- 5) $\frac{\partial C}{\partial x} = 0$ at $x = 0, L$ for $t = 0$.

Assumption (4) leads to the following expression for the concentration

$$C(x, t) = \exp(2\beta x) + \sum_{n=0}^{\infty} A_n \sin \frac{n\pi x}{L} \exp(\beta x) \exp(-\lambda_n^2 Dt) \quad (16)$$

where

$$E = \frac{2\beta LC_0}{\exp(2\beta L) - 1} \quad (17)$$

$$\beta = v_x/2D \quad (18)$$

$$A_n = \begin{cases} \frac{2n\pi [C_0 (1 + \exp(-\beta L)) - E (1 + \exp(\beta L))]}{\beta^2 L^2 + n^2 \pi^2} & n \text{ odd,} \\ \frac{2n\pi [C_0 (1 - \exp(-\beta L)) - E (1 - \exp(\beta L))]}{\beta^2 L^2 + n^2 \pi^2} & n \text{ even,} \end{cases} \quad (19)$$

$$\lambda_n^2 = (n\pi/L)^2 + \beta^2 \quad (20)$$

This solution is more properly limited to the region $0 < x < L$. As it approaches infinity, C approaches the steady-state solution $E \exp(2\beta x)$. This exponential variation of the concentration with distance was shown in Eq. (5) and previously obtained.^{5,6} (Note that β has the dimension (length)⁻¹.) The concentration approaches the steady-state solution with a time constant proportional to $(\lambda_n^2 D)^{-1}$.

The alternate boundary condition, assumption (5), leads to the following expression for C :

$$C(x, t) = E \exp(2\beta x)$$

$$+ \sum_{n=0}^{\infty} \left[(A_n + B_n) \cos \frac{n\pi x}{L} + i(A_n - B_n) \sin \frac{n\pi x}{L} \right] \exp(\beta x) \exp(-\lambda_n^2 Dt) \quad (21)$$

where E and λ_n^2 are defined as before. The steady-state solution falls out as a special case of the time dependent solution. Note that both boundary conditions lead to identical expressions for the time dependence. This would be expected from comparison with other diffusion problems.⁶

The concentration must be real; a special case would be to require $A_n = B_n^*$, leading to the following expression for $C(x, t)$:

$$C(x, t) = E \exp(2\beta x)$$

$$+ \sum_{n=0}^{\infty} A_n \cos \frac{n\pi x}{L} \exp(\beta x) \exp(-\lambda_n^2 Dt) \quad (21a)$$

where

$$A_n = \begin{cases} \frac{C_0 \{1 - \exp(-\beta L)\} + E \{1 - \exp(\beta L)\}}{2\beta L}, & n = 0 \\ \frac{2\beta \{C_0 \{1 - \exp(-\beta L)\} + E \{1 - \exp(\beta L)\}\}}{L (\beta^2 + n^2 \pi^2 / L^2)}, & n \text{ even, } > 0 \\ \frac{2\beta \{C_0 \{1 + \exp(-\beta L)\} + E \{1 + \exp(\beta L)\}\}}{L (\beta^2 + n^2 \pi^2 / L^2)}, & n \text{ odd, } > 0 \end{cases}$$

The most general solution is, of course, when $A_n = B_n^*$ (i.e., complex conjugates). However, closed analytical expressions for the coefficients cannot be obtained in that case.

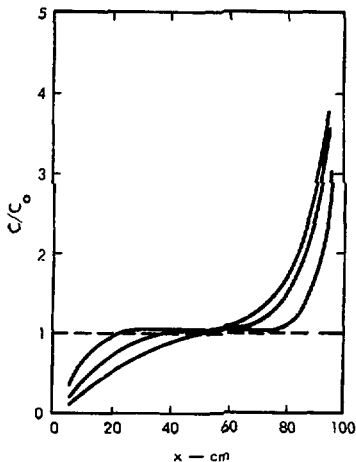


Fig. 1. Graphed solution to Eq. (16) (sin solution).

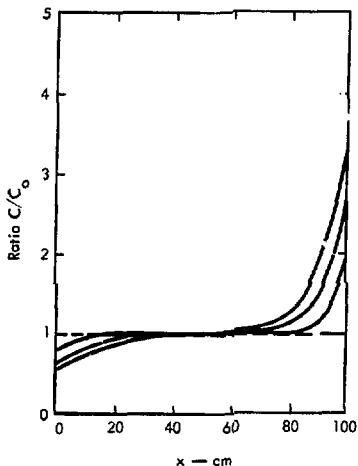


Fig. 2. Graphed solution to Eq. (21a) (cos solution).

Figures 1 and 2 illustrate the two different expressions for $C(x,t)$ [Eqs. (16) and (21a) respectively]. For illustrative purpose the following values were used for the constants: $D = 0.2 \text{ cm}^2/\text{sec}$, $V_x = 0.01 \text{ cm/sec}$, $L = 100 \text{ cm}$, and $C_0 = 1$. The first 5000 terms were evaluated in the infinite sum; Eq. (21a) converges faster because of its $1/n^2$ dependence. Although the expressions for the time dependence are identical, for this particular example Eq. (16) approaches the steady-state solution faster because L is small and all the terms for $n = 0$ vanish.

Figure 3 represents the separation ratio 1 cm from the end of a 1 m tube. It is seen that the rate of separation decreases with time. For $0 < t < \infty$ the time varying

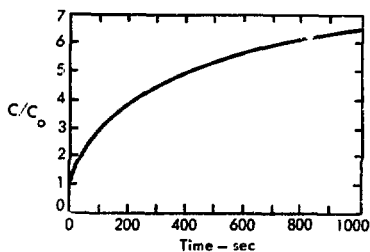


Fig. 3. Separation ratio at end of tube.

part of the solution does not integrate to zero. The data in Fig. 3 have been accordingly renormalized; for a 1 m tube the maximum total error is about 25% at 5000 seconds.

Thermodynamic Calculations

The degree of separation for a binary mixture can be estimated by considering the thermodynamics of mixing in a constant volume system. It will be apparent that the situation is similar to that of osmosis. Assume A molecules are being separated by a laser from B molecules in a tube of volume $2V$. As an initial simplification, assume that the laser changes the distribution function of A from a constant to a step function. Assume also that the experiment is performed under isothermal conditions. Initially both A and B molecules have a uniform distribution (Fig. 4a). After the laser is turned on, all the A molecules are in the right hand side (Fig. 4b). The free energy $G(T)$, is a state function, and hence the path chosen to reach equilibrium will have no effect on the equilibrium distribution.

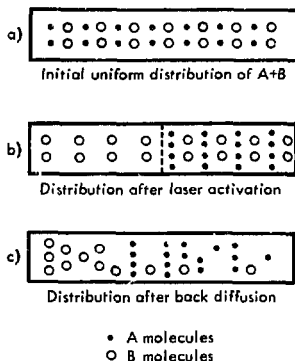


Fig. 4. Schematic representation of binary mixture separation. (a) Initial uniform distribution of A and B . (b) Distribution after laser activation. (c) Distribution after back diffusion.

The question we wish to answer is which way and to what extent will the B molecules diffuse?

The change in free energy (ΔG) is a function of the chemical potential, μ , temperature, and pressure:

$$dG = -Sdt - VdP + \sum \mu_j dn_j. \quad (22)$$

We have assumed a distribution function for A which is determined by the work being done on A by the laser. At equilibrium therefore, $dG = 0$ and is a function of μ_B^L , μ_B^R , and VdP .

$$\begin{aligned} dG = 0 = VdP + \mu_B^L dn_B^L + \mu_B^R dn_B^R \\ \mu_B^L = \mu_B^0 + RT \ln P_B^L \\ \mu_B^R = \mu_B^0 + RT \ln P_B^R \\ \mu_B^0 + RT \ln P_T^R + RT \ln X_B \end{aligned} \quad (23)$$

where X_B is the mole fraction of B, dn_B^L the increase in moles of B on the left, equals $-dn_B^R$, and $dP = P^L - P^R$. Note that $\mu_B^L = \mu_B^R$, hence there will be no tendency for B to separate due to a difference in chemical potential. This differs from osmosis, which normally applies to condensed phases and constant pressure. Assuming ideal gas behavior and substituting, Eq. (23) simplifies to the following:

$$2 n_A - 2 dn_B^L = \ln \left(\frac{n_{B,i} + dn_B^L}{n_{B,i} - dn_B^L} \right) dn_B^L \quad (24)$$

where $n_{B,i}$ is the initial concentration of B. For a 1-liter tube at a total pressure of 2 Torr, equimolar mixture of A and B, $dn_B^L/n_{B,i} = +70\%$. Hence B will back diffuse, further enhancing the degree of

separation in an attempt to equalize the pressure (Fig. 4c).

Equation (24) can be generalized to our specific case, assuming the steady-state one-component solution for $C_A(x) = \text{Exp}(2\beta x)$.

$$\begin{aligned} 2 \left[\text{Exp}(2\beta x) - 2dc_B^L(x) \right] \\ = \ln \left\{ \frac{C_{B,i} + dc_B^L(x)}{C_{B,i} - dc_B^L(x)} \right\} dC_B^L(x). \end{aligned} \quad (25)$$

This expression can be solved numerically to yield $C_B(x)$ (Fig. 5).

A calculation for the energy needed to overcome the entropy of mixing for a fully separated binary mixture shows that ideally (no energy lost in the process) 1720 J/mole are required to fully separate a binary mixture.

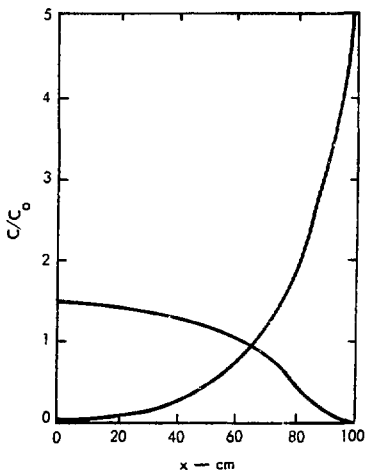


Fig. 5. Binary equilibrium distribution.

Experimental Aspects

The ideal cw experiment to test for separation of molecular species would utilize a very short wavelength to maximize the drift velocity, sufficient power to saturate the transition to the point of maximum power absorption, a buffer gas which would rapidly remove molecules from the upper state, and, for initial tests, a gas with a very small diffusion coefficient. These conditions obviously cannot all be optimized. Ashkin¹ has selected, for purposes of illustration, sodium vapor buffered by helium. Others⁵ have calculated the separation efficiencies for several spectral regions and a few small molecules. Separation efficiencies should not be based on input laser power, but on total expended energy. From that standpoint, the CO₂ laser would be a reasonable choice for large numbers of cheap photons because it is the most efficient laser available today. Since many molecules have an absorption near one of the CO₂ wavelengths, the concept would appear worthy of test.

Two slightly different approaches have been used in preliminary investigations. The results of the time-dependence solution in the proposed model, as shown in Fig. 3, suggest an approach which we will call the interrupted cw method. Recent results⁷ of studies of transient absorption of radiation suggest a pulsed technique, which will be discussed separately.

CW EXPERIMENTS

Very preliminary experiments at the University of Wyoming and more recent studies at J.L. have utilized a CO₂ laser operating in the cw mode at a power output

of 10 to 20 W. The output beam irradiates a long tube containing a gaseous mixture at pressure of 0.1 to 100 Torr. In the earlier experiments, no wavelength selection was used, and the glow discharge (of 1 m length) was produced by a neon sign transformer. In these experiments, the copper absorption cell was 3.81 m long and 0.95 cm i.d. The laser produced a beam of approximately 1.5 cm diam and filled the cross-section of the tube. In the later series of tests, a stabilized, wavelength selected laser was used, also of 1 m active length. A filtered dc supply was used to excite the discharge. The stainless steel cell length was 3.65 m and 0.95 cm in diameter. The beam diameter was approximately 0.5 cm.

The procedure in both sets of experiments was similar: a small amount of an absorber was admitted, and a larger amount of some buffer was added. After allowing time for the mixture to reach equilibrium, the laser was turned on for a time which varied from 15 min to 4 hr. Sample bottles at each end of the tube were then valved off and the samples analyzed by either microwave spectroscopy or mass spectroscopy.

The test gases used were ¹⁴NH₃, ¹⁵NH₃, and CH₂Cl-CH₂Cl with N₂, air, and SO₂ used as buffer gases. In the experiments discussed here, one or more reference samples were taken before irradiation to serve as a standard for analysis. These experiments have served primarily as indicators of experimental problems.

In an earlier experiment a binary mixture consisting of equal amounts of NH₃ and SO₂ was admitted to the absorption

Table 1. Microwave spectrometric analysis of test samples.

	NH ₃		SO ₂	
	$\frac{\text{Signal}}{\text{Pressure}}$	Partial pressure ratios NH ₃ in sample	$\frac{\text{Signal}}{\text{Pressure}}$	SO ₂ Partial pressure ratio
	$\frac{\text{mv}}{\text{m Torr}}$		$\frac{\text{mv}}{\text{m Torr}}$	
Reference	0.639	1	3.14	1
Near sample	0.117	0.184	3.564	1.044
Far sample	0.428	0.671	3.557	1.042

cell at a total pressure of 0.4 Torr. A reference sample (125 cc) was taken, and laser irradiation proceeded for 30 min at approximately 12 W with no wavelength selection.

A summary of observed results, using microwave spectrometric analysis, is shown in Table 1. The loss of NH₃, apparently to the walls, indicates one serious experimental pitfall. In another earlier experiment, the reference sample was not used, but the experiment was repeated, without irradiation, as a control. In this case 1-2 dichloroethane was used with air as a buffer. A summary of the microwave spectrometric analysis is shown in Table 2. The signal/pressure ratio is proportional to the concentration in the spectrometer. The experimental error in reading the pressure gauge used in this experiment is

Table 2. Reference samples taken without irradiation in binary separation experiment of 15 m Torr C₂Cl₂H₄ and 3 Torr air.

	20 min irradiation ($\mu\text{V/m Torr}$)	20 min wait with no irradiation ($\mu\text{V/m Torr}$)
Near sample	3.11	8
Far sample	48	3.4

sufficient to account for the inequality of the second set of ratios.

The second series of experiments, at LLL, followed a similar procedure with important differences. The reference samples were taken for analysis from both the near and far ends before irradiation commenced. This was to ensure that thorough mixing of the gases had occurred. A second difference was that the sample bottles were of much larger volume than the active region.

The results of the second series of experiments were inconclusive due to difficulties in achieving complete mixtures, and in obtaining sufficient sample quantities for analysis. The small beam diameter and relative volumes of active and inactive regions are both believed to be detrimental. The abortive attempts at separation indicate a need for considerably greater sophistication in the apparatus and care in analytical measurements.

A new experiment has been designed to alleviate these difficulties, and to test the model presented above. The new experiment, shown schematically in Fig. 6, will use a 3.65 m cell with the inactive volume reduced to almost zero. Small samples will be withdrawn from each end

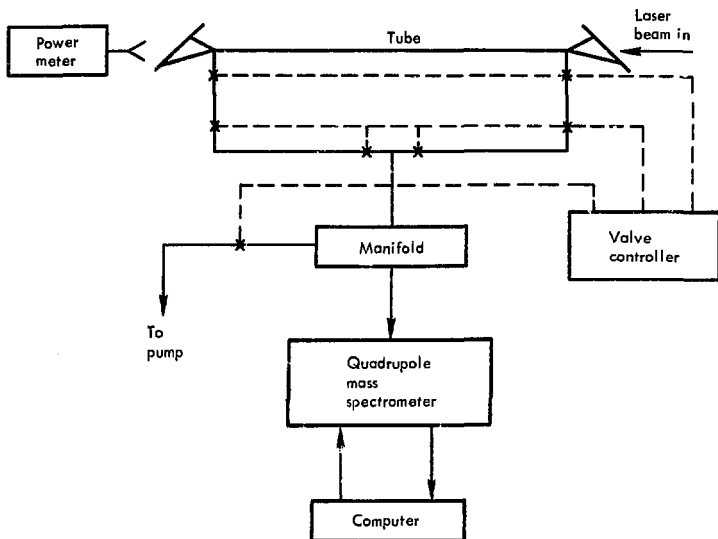


Fig. 6. Experimental apparatus for laser separation of binary gas samples.

simultaneously and analyzed on-line in a computer-controlled mass spectrometer. A new laser with ≈ 2 cm beam diam has been constructed so the test cell will be filled by the beam. Approximately 100 W cw is expected to be available. Premixed gases will be used. It has been shown⁸ that the Q(12, 2) line of the $\nu_3(1 \leftarrow 0)$ band of $^{12}\text{CH}_3\text{F}$ lies within 44 MHz of the P(20) line of the 9.4μ band of the CO_2 laser. This transition has been chosen for initial tests. However, it has been shown⁹ that the relaxation from the upper state of this transition is rather slow; in fact, higher levels are rapidly populated where fluorescence occurs. We propose to use N_2O as a buffer gas and use the 100 state of N_2O as a resonance relaxation pathway

from the $2\nu_3$ state of $^{12}\text{CH}_3\text{F}$. In this case $\tau_{\text{eff}}(\text{CH}_3\text{F})$ should be greatly enhanced by the very large number of relaxation pathways through the rotational sublevels of N_2O . Since laser action is known to occur from this vibrational level of N_2O , some enhancement may be derived from the subsequent stimulated emission in N_2O . These gases are well behaved in regard to wall adsorption and clarity of mass spectra.

In order to test the theoretical model which we have presented, the following procedure will be followed. Samples of less than 1 cm^3 volume will be drawn off simultaneously from both ends before irradiation. After a suitable equilibrium time, when these samples show constant

mass ratios of CH_3F and N_2O at both ends, irradiation will commence. Samples will be drawn off at short intervals at first, and longer intervals later, in order to test the time dependence shown in Fig. 3. The valve and sampling controller in Fig. 6 will insure that pumpout and sampling procedures are repeated exactly for each sample. Each sample will then be analyzed several times in the mass spectrometer. In tests of the analytical procedure, expected variations in measured ratios have been found to remain less than 0.1%.

PULSED EXPERIMENTS

Several recent studies^{7,10,11} of transient effects in the infrared and microwave spectral regions have produced results of interest. In particular, the expression for the population difference, ΔN , between two levels for transient absorption is given by Eq. (30) of Ref. 10 as:

$$\Delta N(t) = \Delta N_0 / \Omega^2 [(\Delta\omega)^2 + k^2 E^2 \cos^2 \Omega t] \quad (25)$$

where $\Delta\omega = (\omega - \omega_0)$ is the difference between the exciting and resonant absorption frequencies,

$$\Omega = [k^2 E^2 + (\Delta\omega)^2]^{1/2}, \quad k = 2 | \langle a | \mu | b \rangle | \hbar \quad (25a)$$

and E is the electric field intensity of the exciting radiation. When the pulse length (T) is such that

$$\int_0^T \Omega dt = \pi \quad (26)$$

then $\Delta N(T) = -\Delta N_0$ and the populations are exactly inverted. This suggests that the use of the " π " pulse allows the opportunity of involving essentially all the molecules in the lower state in the momen-

tum transfer process. If, in addition, the " π " pulse is immediately reflected back up the tube, stimulated emissions would revert the populations back to equilibrium and result in the transfer of two quanta of momentum to each molecule. This would also make possible the recovery and reuse of the energy contained in the " π " pulse.

Under these conditions, one may arrive at a molecular flux in analogy with the $N_0 \cdot V_x$ used above. In this case the flux may be arrived at as the product of the number of molecules absorbing radiation per second and the average distance each moves per absorption. The number of molecules involved is $\Delta N_0 \cdot r$, where r is the pulse rate. The average distance each moves per pulse is

$$V_x t_k \text{ or } 2 h \tau_k / M \lambda.$$

Then:

$$\phi_\pi = \frac{2 \Delta N_0 r h \tau_k}{\lambda M}.$$

In order to compare this with the cw experiment we may arrive at a ϕ_{cw} in a similar manner.

The number of absorptions per second is merely the power absorbed divided by hc/λ or

$$N_0 = W_{cw} [1 - \exp(-\gamma \ell)] \frac{\lambda}{hc}$$

for the unsaturated case, so

$$\phi_{cw} = W_{cw} \frac{[1 - \exp(-\gamma \ell)] \tau_k}{Mc}$$

and we then have

$$\frac{\phi_\pi}{\phi_{cw}} = \frac{2 \Delta N_0 r hc}{W_0 [1 - \exp(-\gamma \ell)] \lambda}.$$

Recognizing that the average power, W_π , absorbed in the " π " pulse experiment is

$$W_{\pi} = \Delta N_0 r hc/\lambda$$

we have

$$\frac{\phi_{\pi}}{\phi_{cw}} = \frac{2 W_{\pi}}{W_{cw} [1 - \exp(-\gamma \ell)]}$$

Assuming that the same average power is available for both experiments, and the length and conditions of saturation have been optimized for the cw experiment so that essentially all of the cw power is absorbed, we have $\phi_{\pi}/\phi_{cw} = 2$. However, one important difference exists. In particular, it is possible to recover the energy present in the " π " pulse since, after reflection, the pulse will grow due to the inverted absorber population. This energy then becomes reusable some number of times (N) with the laser input making up the losses. The advantage then is 2N.

INTERRUPTED CW METHOD

The proposed model suggests, as shown in Figs. 2 and 3, that relative concentration will change rapidly near the ends of the absorption cell. This indicates that a

sample consisting of a short length of the modified mixture may be drawn off at short time intervals. Since the mixture has not been modified at the center, the total quantity of mixture may be replenished at that point without disturbing the system. We propose that efficiency would be greatly enhanced by withdrawing the partially separated mixture at short intervals, in contrast to a static system where little further improvement in concentration ratios occurs at the ends with extended exposure. From Fig. 2 we see that for a 1-m tube the ratio of concentration at the far end to that at the near end is predicted to be 4.25 after 1000 sec. However, the same figure shows a ratio of 2.33 after only 200 sec, a factor of less than 2 improvement with a factor of 5 increase in time. Cascading two cells would result in a ratio of 4.67 in the shorter time. Since efficiency depends directly upon the separation rate, it would be greatly enhanced by removing the separated molecules near the end at very short intervals and relying upon external pumping to move the mixture into and out of the cascaded cells.

Applications

The application of radiation-pressure-induced separations receiving the greatest recent attention is isotope separation. However, other applications are also of great importance, particularly that of isomer separation. One may also speculate concerning the possibility of removal of the products of a reversible chemical reaction, thus driving the reaction in the desired direction. One may also influence the concentration of particular molecular

states near one end of the tube, again modifying reaction rates, or producing particular states for other studies.

Isotopic mixtures would be an obvious application of bulk molecular separation by radiation pressure. In a 1-m tube, an enrichment factor of over 10 would be achieved in less than 30 min with the cw laser and twice that for a pulsed laser. Furthermore, this could be accomplished using several Torr of material; i.e.,

m moles per hour could be easily separated. We expect that, at least for the lighter elements, the whole procedure would be physically simpler and less costly than conventional separation schemes.

Another important application would be the separation of optical isomers. Current technology involves either complex stereo-specific synthesis, starting from natural products, or synthesis of diastereomers followed by laborious physical separation. Many organic com-

pounds of potential interest in synthetic and biochemical applications have sufficient vapor pressure and a different dichroic absorption to be amenable to a bulk separation by radiation pressure. For this application, the shorter lifetime and greater momentum transfer associated with visible and uv radiation would be advantageous, while the elimination of strict monochromaticity and tunability would make such a process feasible even with conventional light sources.

Summary

We have considered the feasibility of obtaining physical separations of large quantities of gas by the application of resonant radiation pressure through a bulk sample. Preliminary experimental attempts at producing and detecting such separations, while not conclusive, have stimulated further investigation and have provided information for more optimal experimental conditions.

The model developed in this paper shows that molecular motion in a closed tube under the influence of an applied force

is similar in many respects to electron "mobility" in a conductor. Thermodynamic calculations show that the process should be efficient and substantial.

Refined experiments have been suggested which should prove the feasibility for bulk separations of an absorbing molecular species from a nonabsorbing buffer. These experiments could then be extended directly to separating isotopes and isomers. Some interesting adaptations of this technique have been considered which could lead to large, efficient separations.

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