

Light-induced drift and separation of the components of the mixture $^{13}\text{CH}_3\text{F} + ^{12}\text{CH}_3\text{F}$ in a continuous IR-radiation field

V. N. Panfilov, V. P. Strunin, P. L. Chapovskii, and A. M. Shalagin

Institute for Automation and Electrometry, USSR Academy of Sciences, Siberian Branch and Institute of Chemical Kinetics and Combustion, USSR Academy of Sciences, Siberian Branch

(Submitted 2 December 1980)

Pis'ma Zh. Eksp. Teor. Fiz. **33**, No. 1, 52–55 (5 January 1981)

A light-induced drift was produced as a result of continuous CO_2 -laser radiation on a mixture of isotopic molecules $^{13}\text{CH}_3\text{F} + ^{12}\text{CH}_3\text{F}$. An isotopic effect with a separation coefficient of ≈ 1.2 was recorded. The variation of the transport cross section as a result of vibrational excitation of molecules was measured quantitatively for the first time. It was found to be equal to 6×10^{-3} for CH_3F .

PACS numbers: 33.80. — b, 82.80.Di

The light-induced drift¹ (LID) of gas particles, which resonantly absorb radiation and are mixed with a buffer gas, was predicted theoretically.¹ This effect can have wide use in physical problems and in application (for example, for isotope separation) and, therefore, it requires a detailed study. Although the theory of this effect has been developed fairly completely,^{2–6} there is a paucity of data which to date have appeared in only two publications.^{7,8} The existence of the effect in Na vapors was shown at the qualitative level in Ref. 7, but no measurements were made because of the masking influence of adsorption. The second experiment⁸ was performed with a molecular material (SF_6). Here, too, at least two factors prevented a quantitative comparison with theory. The first factor was the absence of the effect in the continuous irradiation regime. The second factor was that the isotopic effect was too small as compared with the large overall effect. The reason for the inadequacies apparently lies in the fact that higher vibrational states are excited for pulsed irradiation; however, this complicates a reliable theoretical description because of the complexity of the test material.

The purpose of our investigation was to select optimum conditions for the experiment so that we could conduct it at a quantitative level. The CH_3F molecule, which possesses a whole series of advantages from the viewpoint of the stated problem, was chosen as the object for the experiment. The $P(32)$ line of the $9.6\text{-}\mu\text{m}$ radiation band of the CO_2 laser lies near the resonance (on the high-frequency side) with the isolated $R_Q(4,3)$ line of the ν_3 vibration of the $^{13}\text{CH}_3\text{F}$ molecule. The resonance detuning $\Omega = 24$ MHz (Ref. 9) comprises one-half of $k\bar{v}$ —the Doppler half-width. The absorption coefficient of the radiation in this line is high¹⁰ ($0.3\text{ cm}^{-1}/\text{mm Hg}$). Finally, the CH_3F molecule is not corrosive and is not adsorbed on the walls.

As follows from the theory, the LID effect increases with increasing rate of vibrational relaxation; this can be done by using molecules with similar vibrational quantum as the buffer gas. In addition, the resonance exchange by excitation with such a gas results in an effective increase of the difference of the transport cross sections.⁶ On the basis of these considerations, we chose the isotopic molecules $^{12}\text{CH}_3\text{F}$ as the buffer molecules. Experiments were performed in the continuous regime, which guaranteed excitation of only one vibrational state.

The CO_2 -laser radiation [up to 15 W in the $P(32)$ line of the $9.6\text{-}\mu\text{m}$ band] was focused in a copper tube (inside diameter of 4 mm and 1 m in length) with good filling of the cross section. A portioning valve, which remove samples for gas-composition analysis in a mass spectrometer, has mounted at the entrance (for the radiation) end of the cell. The exit end of the tube was connected to a ballast volume.

The experiment involved repeated comparison, by means of the mass spectra, of the steady-state ratios of the concentrations (N and N_B) of the isotopic molecules $^{13}\text{CH}_3\text{F}$ and $^{12}\text{CH}_3\text{F}$ with and without long-term (5–10 min) irradiation. It was observed that the CO_2 -laser radiation increases significantly the relative concentration of the $^{13}\text{CH}_3\text{F}$ molecules at the entrance of the tube. The separation coefficient $\eta = K_{\text{irr}}/K$ (K_{irr} and K are the concentration ratios N/N_B with and without irradiation) reached a value of 1.19 ± 0.02 under optimum conditions. A detailed examination of this effect indicates that we are dealing with LID.

We performed a series of experiments to prove that there were no other reasons for the change in the isotopic composition. In particular, the influence of laser thermal diffusion¹¹ was checked. Its contribution was determined by the degree of excitation and by the temperature gradient. It was established that an additional heating of the entrance end of the tube or its middle portion by $50^\circ\text{--}60^\circ\text{C}$ in both cases reduced η by 1–2%. This result, which is in qualitative agreement with LID, cannot be accounted for by thermal-diffusion along the longitudinal temperature gradients. In addition, if the radiation that passes through the tube is reflected and transmitted through it in the opposite direction, then η will also be reduced. This does not occur if the enrichment were caused by the excitation of one component of the mixture. On the other hand, a decrease of η as a result of addition of the radiation in the opposite direction is characteristic of LID, which is sensitive to the direction of the wave vector.

The results of the measurement of η under different conditions are given in Table I. P (mm Hg) is the total pressure of the mixture and ΔS (W/cm^2) is the variation of the energy flux density when the cell is traversed. The accuracy of the measurement of η is 2%.

TABLE I

| K | P | ΔS | η |
|-------|------|------------|--------|
| 0.53 | 0.26 | 34 | 1.11. |
| 0.25 | 0.23 | 20.6 | 1.11 |
| 0.25 | 0.68 | 68.7 | 1.15 |
| 0.25 | 0.24 | 14 | 1.12 |
| 0.25 | 0.24 | 18 | 1.12 |
| 0.25 | 0.68 | 73 | 1.19 |
| 0.067 | 0.7 | 38 | 1.17 |

Preliminary measurements of the time of establishment of the steady-state concentrations showed that it is about 15 seconds and is approximately the same as the diffusion-equalization time.

Under our conditions the theoretical relation, which determines the concentration variation ΔN of the absorbing component along the cell length, has the form

$$\Delta N = \frac{\nu_m - \nu_n}{\nu_n} \frac{2 \Delta S}{\hbar \omega \bar{\nu}} \frac{\Omega}{k \bar{\nu}}, \quad (1)$$

where ν_n and ν_m are the gas-kinetic collision frequencies in the ground state and excited vibrational state and ΔN is related to the separation coefficient by the relation

$$\Delta N = N \frac{\eta - 1}{1 + K_{\text{irr}}}. \quad (2)$$

All of the values in Eqs. (1) and (2) are either known or were measured in the experiment, except for the factor $(\nu_m - \nu_n)/\nu_n$, which for the condition $N \ll N_B$ is determined only by the interaction of isotopic molecules. Its value, determined from Eqs. (1) and (2) and from all measurements, is $(5.7 \pm 1) \times 10^{-3}$. Only the random measurement error is shown here. Its small value indicates that the agreement between the results of the experiment and theory is good.

According to Eq. (1), ΔN depends linearly on ΔS , which is confirmed by the results of the experiment. This dependence remains valid until the field broadening is

equal to the Doppler broadening. This corresponds to energy flux densities of $\sim 10^5$ W/cm². Consequently, the LID effect obtained in this experiment can be increased by 3–4 orders of magnitude.

In conclusion, we note that the results obtained here can serve as the basis of a new isotope separation method.^{1,6} The radical difference between this method and all other laser methods is that the collisions with excitation exchange between the isotopic components do not impede the effect, but rather are responsible for it.

The authors thank S. G. Rautian for useful discussions of the results of this investigation.

¹We use the more appropriate term "drift," suggested by Dykhne, instead of the term "diffusion," which was used in Ref. 1.

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Translated by Eugene R. Heath

Edited by S. J. Amoretty