Light-induced drift of CH_3F molecules

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Experimental studies are reported of light-induced drift of CH_3F molecules in helium, hydrogen, and another isotopic modification of CH_3F molecules. The ^{13}C-enrichment that has been achieved was about 70%. The magnitude of the effect was measured as a function of the laser radiation frequency, homogeneous transition width, and absorbed power density. The observed relationships were compared with theoretical predictions. The relative change in the frequency of Maxwellizing collisions of the CH_3F molecule after its vibrational excitation has been measured.

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In 1979, Gel'mukhanov and Shalagin[1] predicted theoretically an interesting phenomenon, namely, light-induced drift (LID) of particles in the field of a traveling electromagnetic wave. This effect gives rise to a macroscopic current of atoms (or molecules) that interact resonantly with the radiation, but the current appears only in the presence of a buffer gas. Its direction is parallel to the direction of the light beam, and is opposite to the current of the buffer particles. This presents us with the possibility of spatial separation of particles with different absorption spectra, including atoms, molecules, their isotopic or spin modifications, and so on. The scope of possible practical applications of the effect is still not clear, but it is already possible to exploit the phenomenon in physical investigations, for example, in studies of molecular (atomic) collisions.

Theory predicts that the effect should be a maximum in atoms.[2,3] However, most of the research performed so far has been concerned with the LID of molecules. This has been due to a number of factors that make experiments with molecules much simpler and more readily accessible. Such experiments are concerned with the LID effect based on vibrational-rotational transitions in molecules. The LID effect based on electronic transitions in molecules is, of course, interesting, and is at present even more complicated than the study of LID in atoms. The relative simplicity of molecular LID is due, as was correctly noted in Ref. 4, to the availability of powerful infrared lasers whose radiation is at resonance with strong absorption lines of many molecular gases.

At present, the bibliography of experimental work on LID can be summarized as follows. The atomic effect has been investigated in sodium[5] and neon.[6] The list of papers concerned with molecules is substantially greater. Experiments with SF_6 have been reported,[7–10] but it must be concluded that the effect has not, in fact, been detected in this material.[9,10] On the other hand, a pronounced LID effect has been recorded for CH_3F molecules.[11,12]

The present paper is devoted to light-induced drift of CH_3F. The main objective was quantitative verification of the theory of the effect.

1. GENERAL DESCRIPTION OF THE PHENOMENON

We shall consider the interaction between a traveling electromagnetic wave and moving two-level particles present with low relative concentration in a buffer gas, so that collisions between the absorbing particles can be neglected. We now introduce velocity distributions for particles in the excited $[\rho_m(\mathbf{v})]$ and unexcited $[\rho_n(\mathbf{v})]$ states. The laser radiation that is in resonance with the transition is assumed to be monochromatic. As a result of the Doppler effect, particles with velocity components in the direction of the wave vector ($\mathbf{k}$) of the radiation that are close to $v_x = \Omega/k$ will interact with the radiation, where $\Omega = \omega - \omega_{mn}$ is the detuning of the radiation frequency from the center of the line emitted as a result of the transition. Let N be the concentration of absorbing particles and p the probability per unit time that they will be excited. In steady state, the number of excited molecules with velocity components close to $v_x = \Omega/k$, will exceed the Maxwell number by Np/ν'_m, where ν'_m is the frequency of collisions involving excited molecules that remove them from the particular velocity interval. In the lower state, there is a deficiency Np/ν'_n in the same velocity interval, where ν'_n is the corresponding collision frequency for the state n. These are the well-known Bennett peak and dip. The difference between the distributions $\rho_m(\mathbf{v})$ and $\rho_n(\mathbf{v})$, on the one hand, and the equilibrium distributions, on the other, leads to the appearance of currents of excited and unexcited molecules. It is readily seen that these currents are, respectively, equal to $Np\Omega/k\nu'_m$ and $-Np\Omega/k\nu'_n$. The resultant current of absorbing molecules is thus $(\nu'_n - \nu'_m)Np\Omega/k\nu'_n\nu'_m$ and is nonzero only for $\nu'_n \neq \nu'_m$.

Even these very qualitative considerations exhibit an important feature of the phenomenon, namely, the antisymmetric dependence of the direction of the current on frequency Ω. The effect is absent at the center of the absorption line ($\Omega = 0$). Without going into the many other properties of the effect that follow from the foregoing qualitative considerations, we must now proceed to a quantitative description of the phenomenon.

2. THEORY OF LIGHT-INDUCED DRIFT OF MOLECULES

LID is relatively simple to describe in terms of the strong collision model.[13] Applications of this model to the LID problem can be found in the literature.[4,14] In accordance with the assumptions of the strong collision model, we introduce the frequencies of rotational (ν_{mR}, ν_{nR}) and translational (ν_{mT}, ν_{nT}) relaxation in states m and n. Since the rate of departure of the CH_3F molecules to neighboring rotational levels (which determines the homogeneous width of the transition) in their own gas is much greater than the rate of translational relaxation, we assume that rotational relaxation is not accompanied by a change in the translational velocity of the molecules. Next, we assume that vibrational relaxation (frequency ν_{mv}) is accompanied by the establishment of equilibrium distributions over velocities and rotational states.

Under stationary conditions, the equations for the distributions of the molecules over the velocities and the rotational levels in the upper ($\rho_{mJ}(\mathbf{v})$) and lower ($\rho_{nJ}(\mathbf{v})$) states are as follows:

$$\mathbf{v}\nabla\rho_{mJ}(\mathbf{v})+\nu_m\rho_{mJ}(\mathbf{v})=Np(\mathbf{v})\delta_{JJ_0}+\nu_{mR}\rho_m(\mathbf{v})W_B(J)+\nu_{mT}\rho_m W(\mathbf{v})W_B(J), \tag{1a}$$

$$\mathbf{v}\nabla\rho_{nJ}(\mathbf{v})+\nu_n\rho_{nJ}(\mathbf{v})=-Np(\mathbf{v})\delta_{JJ_0'}+\nu_{nR}\rho_n(\mathbf{v})W_B(J)+\nu_{nT}\rho_n W(\mathbf{v})W_B(J)+\nu_{mv}\rho_m W(\mathbf{v})W_B(J), \tag{1b}$$

$$Np(\mathbf{v})=\frac{2|G|^2\Gamma}{\Gamma^2+(\Omega-\mathbf{kv})^2}[\rho_{nJ_0'}(\mathbf{v})-\rho_{mJ_0}(\mathbf{v})], \tag{1c}$$

where $G=Ed_0/2\hbar$, $\nu_m=\nu_{mR}+\nu_{mT}+\nu_{mv}$, $\nu_n=\nu_{nR}+\nu_{nT}$, E, ω, $\mathbf{k}$ are, respectively, the amplitude, frequency, and wave vector of the radiation, Γ, d_0 is the homogeneous halfwidth and the dipole moment of the transition mJ_0-nJ_0', $W(\mathbf{v})$ is the Maxwell velocity distribution, and $W_B(J)$ is the Boltzmann distribution over the rotational levels. The quantities $\rho_i(\mathbf{v})$, ρ_i ($i=m,n$) are given by

$$\rho_i(\mathbf{v})=\sum_J\rho_{iJ}(\mathbf{v});\qquad \rho_i=\int\rho_i(\mathbf{v})\,d\mathbf{v}\qquad (i=m,n). \tag{2}$$

We now give the expressions for the currents of excited ($\mathbf{j}_m$) and unexcited ($\mathbf{j}_n$) particles. From (1a) and (1b) we have, after summation over J,

$$\mathbf{j}_m=\int\mathbf{v}\rho_m(\mathbf{v})\,d\mathbf{v}=\frac{1}{\nu_{mT}+\nu_{mv}}\int\mathbf{v}[Np(\mathbf{v})-\mathbf{v}\nabla\rho_m(\mathbf{v})]\,d\mathbf{v},$$
$$\mathbf{j}_n=\int\mathbf{v}\rho_n(\mathbf{v})\,d\mathbf{v}=-\frac{1}{\nu_{nT}}\int\mathbf{v}[Np(\mathbf{v})+\mathbf{v}\nabla\rho_n(\mathbf{v})]\,d\mathbf{v}. \tag{3}$$

In steady state, and under the conditions of our experiment, the resultant current of absorbing molecules is $\mathbf{j}_m+\mathbf{j}_n=0$. When this is used in conjunction with (3), we obtain

$$-\Delta\nu N\int p(\mathbf{v})\mathbf{v}\,d\mathbf{v}-(\nu_{mT}+\nu_{mv})\int\mathbf{v}(\mathbf{v}\nabla N(\mathbf{v}))\,d\mathbf{v}+\Delta\nu\int\mathbf{v}(\mathbf{v}\nabla\rho_m(\mathbf{v}))\,d\mathbf{v}=0, \tag{4}$$

where $\Delta\nu=\nu_{mT}+\nu_{mv}-\nu_{nT}$ and $N(\mathbf{v})=\rho_m(\mathbf{v})+\rho_n(\mathbf{v})$.

For the CH_3F molecules with which we are concerned here, the difference between the frequencies of Maxwellizing collisions $\nu_{mT}+\nu_{mv}$ and ν_{nT} in the two vibrational states is small. The spatial derivatives are therefore also small, as can be seen from (4). We shall solve (4) assuming that the functions $p(\mathbf{v})$, $N(\mathbf{v})$, and $\rho_m(\mathbf{v})$ satisfy approximately Eqs. (1a)–(1c) without the terms containing the spatial derivatives.

Solving (1) in this approximation, we obtain

$$N(\mathbf{v})=-\frac{\Delta\nu Np(\mathbf{v})}{(\nu_{mT}+\nu_{mv})\nu_{nT}}+NW(\mathbf{v})\left[1+\frac{\Delta\nu p}{(\nu_{mT}+\nu_{mv})\nu_{nT}}\right]$$
$$\rho_m(\mathbf{v})=\frac{Np(\mathbf{v})}{\nu_{mT}+\nu_{mv}}+NW(\mathbf{v})p\left[\frac{1}{\nu_{mv}}-\frac{1}{\nu_{mT}+\nu_{mv}}\right]$$
$$p=\int p(\mathbf{v})\,d\mathbf{v}=\frac{W_B(J_0')Y(\Omega)}{\tau_1[1+1/\varkappa+Y(\Omega)\tau_2/\tau_1]};\qquad \varkappa=2|G|^2\tau_1/\Gamma \tag{5}$$
$$p(\mathbf{v})=\frac{\Gamma_B^2\varkappa W(\mathbf{v})}{\tau_1(1+\varkappa)[\Gamma_B^2+(\Omega-\mathbf{kv})^2]}[W_B(J_0')-p\tau_2].$$

The function $Y(\Omega)$, which depends on the frequency Ω and the homogeneous halfwidth of the transition $\Gamma_B=\Gamma(1+\varkappa)^{1/2}$, is given by

$$Y(\Omega)=y'\pi^{1/2}\,\mathrm{Re}\,[w(z)];\; z=x'+iy';\; v_0=(2kT/M)^{1/2},$$
$$w(z)=e^{-z^2}\left[1+\frac{2i}{\pi^{1/2}}\int_0^z e^{t^2}\,dt\right];\qquad x'=\Omega/kv_0;\qquad y'=\Gamma_B/kv_0. \tag{6}$$

The times τ_1 and τ_2 are given by the following expressions:

$$\tau_1=\frac{1}{\nu_n}+\frac{1}{\nu_m}+W_B(J_0')\left[\frac{1}{\nu_{nT}}-\frac{1}{\nu_n}\right]+W_B(J_0)\left[\frac{1}{\nu_{mT}+\nu_{mv}}-\frac{1}{\nu_m}\right],$$
$$\tau_2=W_B(J_0')\left[\frac{1}{\nu_{mv}}-\frac{1}{\nu_{nT}}\right]+W_B(J_0)\left[\frac{1}{\nu_{mv}}-\frac{1}{\nu_{mT}+\nu_{mv}}\right]. \tag{7}$$

Substituting $N(\mathbf{v})$ and $\rho_m(\mathbf{v})$ from (5) in (4), and neglecting small terms containing both $\Delta\nu/\nu$ and the spatial derivatives, we obtain

$$-\frac{\Delta\nu}{\nu}N\int p(\mathbf{v})\mathbf{v}\,d\mathbf{v}=\int\mathbf{v}(\mathbf{v}\nabla NW(\mathbf{v}))\,d\mathbf{v}, \tag{8}$$

where $\nu=\nu_{nT}\approx\nu_{mT}+\nu_{mv}$. In the one-dimensional case, we find that for the function $W(\mathbf{v})$ that is independent of position,

$$-\frac{\Delta\nu}{\nu}N\int p(v_x)v_x\,dv_x=\frac{v_0^2}{2}\frac{dN}{dx}, \tag{9}$$

where x is the position coordinate along the axis of the cylindrical cell (and increases in the direction of the beam). The integral on the left-hand side of this equation can be expressed[14] in terms of p and the function $w(z)$ [see (5) and (6)]:

$$\int p(v_x)v_x\,dv_x=pv_0\,\mathrm{Re}[zw(z)]/\mathrm{Re}[w(z)]\equiv pv_0\varphi(\Omega).$$

Since the product $\hbar\omega Np$ determines the power absorbed by the gas per unit volume, integration of (9) with respect to x gives [assuming that $\varphi(\Omega)$ is independent of x]

$$\Delta N=\frac{\Delta\nu}{\nu}\frac{2\Delta S}{\hbar\omega v_0}\varphi(\Omega), \tag{10}$$

where ΔN and ΔS is the drop in concentration and power

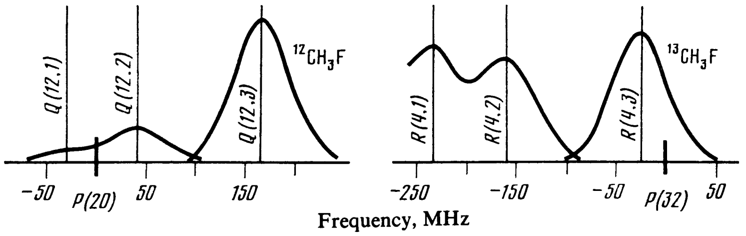

FIG. 1. Sections of the absorption spectra of $^{12}CH_3F$ and $^{13}CH_3F$ molecules near the $P(20)$ and $P(32)$ generation lines in the 9.6-μm band of the CO_2 laser.[17]

density absorbed by the gas along the length of the cell, respectively. Equation (10) was first obtained in Ref. 14 and provides us with a simple way of determining the relative change in the frequencies of Maxwellizing collisions during molecular excitation from the experimental conditions.

3. PARAMETERS OF THE CH_3F MOLECULE

Precision measurements of the molecular constants of CH_3F were reported in Ref. 15 which was devoted to the Stark spectroscopy of the molecule. These data enable us to calculate with sufficient precision the frequencies of the vibrational-rotational transitions. The relative intensities of the absorption lines are found from well-known formulas for the absorption coefficients of symmetric-top molecules.[16]

There are two strong resonances in the spectrum of the CH_3F molecule and the CO_2 laser radiation. The laser radiation generated by the $P(32)$ transition in the 9.6-μm band is absorbed by the $R(4,3)$ transition of the ν_3 vibration in the $^{13}CH_3F$ molecule (absorption coefficient ~ 0.3 cm^{-1}/Torr and $\Omega = 25.8$ MHz). This resonance produces absorption in the orthomodification of the molecule.

In the second resonance, radiation from the $P(20)$ transition in the 9.6-μm CO_2 band is absorbed by two lines of the $^{12}CH_3F$ molecules, namely, $Q(12,2)$ and $Q(12,1)$ of the ν_3 vibration. These two absorption lines belong to the paramodification of the molecule. The frequency deviations of the centers of the absorption lines from the center of the $P(20)$ line of CO_2 are 44.2 MHz [$Q(12,2)$] and 28.4 MHz [$Q(12,1)$].

Figure 1 shows the sections of interest of the absorption spectra[17] of $^{13}CH_3F$ and $^{12}CH_3F$ molecules. The Doppler profiles correspond to 300 K ($kv_0 \simeq 39$ MHz). Their relative intensities were calculated on the assumption of an equilibrium distribution of molecules over the vibrational levels.

To calculate the magnitude of the effect from (10), we must have information on the saturation parameter ($\varkappa$), the times τ_1 and τ_2, and the collisional broadening. Let us first consider data on the homogeneous halfwidth Γ. This quantity has frequently been measured both for rotational[18] and vibrational-rotational[19] transitions in CH_3F. These data are listed in Table I for $^{12}CH_3F$ in its own gas. The table also gives our measurements of the broadening of the $R(4,3)$ line belonging to the ν_3 vibration of $^{13}CH_3F$ in a gas of buffer $^{12}CH_3F$ molecules. The somewhat lower broadening (18.3 MHz/Torr) that we have obtained may have been due to a deterioration of resonance during collisions between $^{13}CH_3F$ and $^{12}CH_3F$ as compared with the collisions between $^{12}CH_3F$ and $^{12}CH_3F$ molecules. Henceforth we shall use the broadening 18.3 MHz/Torr in our calculations of the LID effect in mixture of the isotopic molecules $^{13}CH_3F$ and $^{12}CH_3F$. The transfer of vibrational energy between the molecules $^{13}CH_3F$, $^{12}CH_3F$ and their ortho-paramodifications have been investigated by double infrared resonance.[17] These measurements showed that the frequency ν_{mv} describing the transfer of a vibrational quantum in collisions between $^{13}CH_3F$ and $^{12}CH_3F$ is about 5×10^5 s^{-1}/Torr and depends little on the orthoparamodification of the colliding particles. We shall assume, in accord with the model with three relaxation constants, that assume that $\Gamma = (\nu_m + \nu_n)/2$. Since $\nu_m \approx \nu_n = \bar{\nu}$, we have $\bar{\nu} \approx \Gamma$. Using the observed absorption coefficient [according to our measurements, 0.45 cm^{-1}/Torr at the center of the $R(4,3)$ line] to determine the transition dipole moment, we can readily calculate the parameter $\varkappa$ for all three transitions in CH_3F that are in resonance with the CO_2-laser radiation. At 1 Torr (CH_3F) and at a radiation power density 1 W/cm^2, we find that $\varkappa(R(4,3)) = 0.53 \cdot 10^{-2}$, $\varkappa(Q(12,1)) = 9.6 \cdot 10^{-5}$, and $\varkappa(Q(12,2)) = 3.8 \cdot 10^{-4}$. According to (7), the times τ_1 and τ_2 are $\tau_1 \approx 1.7 \cdot 10^{-8}$ s and $\tau_2/\tau_1 \approx 0.87$.

4. EXPERIMENTAL METHOD

Since the LID effect results in the spatial separation of the components of a gas mixture, the most convenient meth-

TABLE I. Collisional broadening of transitions in the CH_3F molecule

Molecule	Transition $(\nu_3,J,K,M) \leftarrow (\nu_3,J',K',M')$	Perturbing molecule	Broadening, MHz/Torr	Reference
$^{12}CH_3F$	$(2,3,1,-1) \leftarrow (0,1,1,-1)$	$^{12}CH_3F$	21.05±0.5	[19]
		He	3.15±0.15	[19]
$^{12}CH_3F$	$(2,3,1,-3) \leftarrow (0,1,1,-1)$	$^{12}CH_3F$	20.35±0.5	[19]
		He	3.00±0.15	[19]
$^{12}CH_3F$	$(0,1,0,M) \leftarrow (0,0,0,M')$	$^{12}CH_3F$	20	[18]
$^{13}CH_3F$	$(1,5,3,M) \leftarrow (0,4,3,M')$	$^{12}CH_3F$	18.3	*

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*Our measurements.

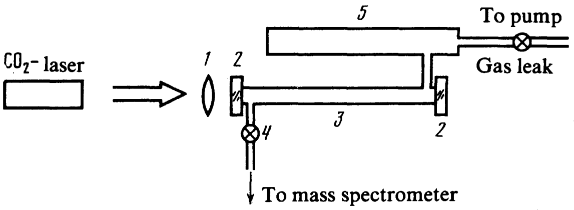

FIG. 2. Experimental arrangement: 1—lens, 2—NaCl end windows, 3—cylindrical cell, 4—batching valve, 5—ballast volume.

od of investigating it is mass spectroscopy of the gas. In contrast to determination of the size of the effect by measuring the concentration of a particular component of the gas mixture (for example, by optical methods), the mass-spectroscopic approach practically excludes effects connected with the heating of the sample cell by the laser radiation.

A block diagram of the apparatus is shown in Fig. 2. The gas was excited by continuous radiation from a low-pressure CO_2 laser, using a diffraction grating as a rotational-line selector. The laser was operated in the single-mode regime, using lines belonging to the 9.6-μm vibrational band ($00^01 - 02^00$ transition in CO_2). The laser radiation was plane-polarized (power up to 15 W) and was focused by a lens (focal length 50 cm) into a cylindrical specimen cell. The cell length was 1 m and its internal diameter was 4 mm (copper) or 1 mm (glass). NaCl end windows were inserted into the copper cell almost at right angles to the tube axis, whereas, in the glass cell, they were mounted at the Brewster angle. Radiation losses in the absence of the absorbing gas in the copper and glass cells were 20% and 50%, respectively. The gas composition was analyzed in a large number of experiments at entry (relative to the beam) to the cell. A gas sample (0.2–1 cm^3) was leaked into the mass spectrometer after the stationary state had been reached in the system. The exit end of the cell was connected to a ballast volume. The cell was in thermal contact with a radiator along its entire length. These two cells enabled us to investigate the effect in the laser power-density range between about 10 W/cm^2 and about 10^3 W/cm^2.

The measurement of the effect of the laser radiation on gas composition consisted of repeated comparisons of the mass spectra of the gas with and without the incident radiation. A small amount of a reference gas (argon) was added in a number of these experiments, for example, in the case of CH_3F drift in helium or hydrogen, to increase the precision of the measurements. This enabled us to observe variations smaller than 1% in the component concentration ratios. Special steps were taken to verify that thermal effects had no influence on the gas composition. For example, heating of the cells to 50–60 °C (even nonuniform heating) produced no appreciable change in the composition of the gas in a test volume.

5. MANIFESTATIONS OF THE EFFECT UNDER OPTIMUM CONDITIONS

It was convenient in our experiments to measure the ratio of the concentration of the absorbing isotopic component (N) to that of the buffer component with (K_{ill}) and without (K) the incident radiation. We introduce the enrichment coefficient $\beta = K_{\text{ill}}/(K-1)$. If the total concentration of the gas particles can be assumed to be constant along the cell, we have

$$\beta=\frac{\Delta N}{N}(1+K)\bigg/\left(1-\frac{\Delta N}{N}K\right). \tag{11}$$

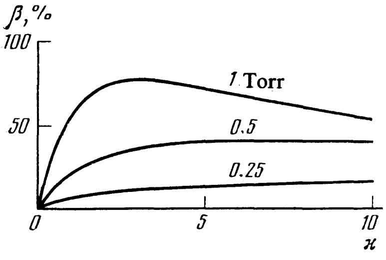

FIG. 3. Theoretical dependence of the enrichment coefficient (β) on the saturation parameter ($\varkappa$) for a number of buffer-gas pressures ($^{13}CH_3F$ and $^{12}CH_3F$ mixture).

To determine the optimum conditions for the observation of isotopic enrichment, we must turn to (9). The drop in the concentration of the absorbing component along the length l of the cell is given by

$$\Delta N=N_0-N_l=N_l\left[\exp\left(\int_0^l\frac{\Delta\nu}{\nu}\frac{2p\varphi(\Omega)}{v_0}dx\right)-1\right]. \tag{12}$$

The enrichment coefficient β can readily be found from (11) and (12) at low concentrations of the absorbing component ($K\rightarrow 0$), when p and $\varphi(\Omega)$ are independent of position. The dependence of β on the saturation parameter $\varkappa$ is shown in Fig. 3 for several buffer-gas (CH_3F) pressures. In our calculations, we used the value $\Delta\nu/\nu = 1.04\cdot10^{-2}$ which follows from measurements of the frequency dependence of the effect, described below.

Figure 4 shows an example of the gas mass spectra before and after irradiation. The intensity (minus the mass-spectrum background) of the $M/e = 35$ line, recorded with higher sensitivity, is proportional to the $^{13}CH_3F$ concentration. The intensities of the $M/e = 33$ and 34 lines are largely determined by the $^{12}CH_3F$ concentration (the contribution of $^{13}CH_3F$ to these lines is, respectively, 5.7 and 0.5%). Thus, the change in the ratio of the peak heights in Fig. 4 clearly shows the change in the gas composition as a result of LID. The ^{13}C enrichment in this particular experiment was $69 \pm 0.9\%$.

The procedure used to determine the parameter $\varkappa$ and the absorbed power density ΔS from the experimental data requires some explanation. Let W be the radiation power, ΔW the radiation power absorbed by the gas, and s the cross section of the cell. Good agreement between calculation and measurement is achieved for $\Delta S = \Delta W/s$. The values of the parameter $\varkappa$, determined for power density $S = W/s$, had to be increased by a factor of two. This correction factor is evidently due to the nonuniform distribution of the field over the cross section of the cell and to the approximate nature of the estimate $\bar{v}\approx\Gamma$.

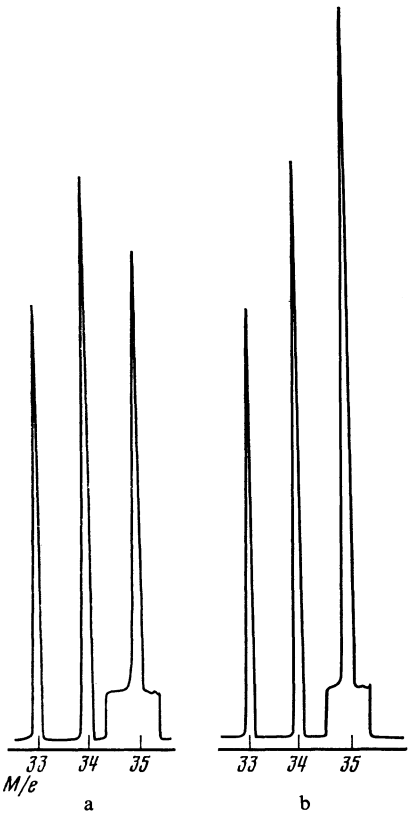

FIG. 4. Light-induced change in the isotopic composition of the mixture $^{13}CH_3F$:$^{12}CH_3F$ = 1:15. Pressure 1 Torr. $^{13}CH_3F$ molecules are excited (a—before illumination; b—after illumination).

6. DEPENDENCE OF THE MAGNITUDE OF THE EFFECT ON FREQUENCY

The first derivative of the frequency dependence of the emitted laser power was used to stabilize the laser frequency, both at the center of the line and at the shifted value. The frequency shift was determined, in final analysis, by the change in the cavity length. Pulling effects could conveniently be taken into account by introducing a small (18%) linear stretching of the frequency scale. The observed frequency difference between the center of the $P(32)$ line of the CO_2 laser and the center of the $R(4,3)$ absorption line of the $^{13}CH_3F$ molecule was then found to be in agreement with precision measurements.[15]

Equations (10) and (11) give the enrichment as a function of the frequency difference. In our particular experiment, ΔS was a complicated function of Ω because of the frequency dependence of the laser power and the absorption coefficient. The enrichment normalized to the absorbed power density $\beta/\Delta S$ should repeat the frequency dependence $\varphi(\Omega)$ for small values of K. Measurements of the specific enrichment $\beta/\Delta S$ are shown in Fig. 5 together with the corresponding theoretical curve. The figure also shows our measurements of the linear absorption coefficient as a function of frequency. It is clear that the measured values of $\beta/\Delta S$ and of the absorption coefficient are in good agreement both with the theoretical $\beta/\Delta S$ curves and with the previously known spectroscopic data (Fig. 1). As predicted by the theory, the effect vanishes at the center of the absorption line, although the absorbed power is not at all small and exceeds the corresponding value at $\Omega = 50$ MHz by a factor of about three.

Our laser could be tuned over a range of about 50 MHz. Frequency scanning within this range turned out to be insufficient to produce reversal of the sign of the effect which, according to theory, should occur when the sign of Ω is reversed. However, the reversal was observed upon excitation of the other isotopic molecule ($^{12}CH_3F$). The position of its absorption lines relative to the center of the $P(20)$ line of the CO_2 laser is shown in Fig. 1.

Two types of experiment with the $^{12}CH_3F$ molecules were performed. They differed by whether the buffer particles promoted the resonance transfer of excitation ($^{13}CH_3F$) or did not do so (He, H_2). Measurements of enrichment in the $^{12}CH_3F$:$^{13}CH_3F$ = 1:4 mixture (the $^{12}CH_3F$ molecules were excited) yielded the following results. At gas pressures of 0.68 Torr and absorbed power density $\Delta S = 19$ W/cm^2, the ^{12}C enrichment was $\beta = -(5.6 \pm 0.7)\%$. The sign of the effect was in accordance with spectroscopic data (Fig. 1), and is discussed below. In experiments of the second type, we again observed effects of different sign: $\beta = 19 \pm 1\%$ for the mixture $^{13}CH_3F + H_2$ and $\beta = (-4.5 \pm 0.5)\%$ for the mixture $^{12}CH_3F + H_2$. These data are discussed in detail in Sec. 8.

The data of Fig. 5a are satisfactorily approximated by the theoretical curve (solid line) calculated for $\Delta\nu/\nu = 1.04 \cdot 10^{-2}$ (this value will be used below). The calculations were performed without taking field broadening into account since, in this experiment, the saturation parameter was small ($\varkappa \lesssim 0.1$), but collisional broadening, which was large for the CH_3F transitions, was taken into account. We note that the approximate expression $\varphi(\Omega) \approx \Omega/kv_0$, obtained on the assumption that $\Gamma \ll kv_0$, was employed in Ref. 12.

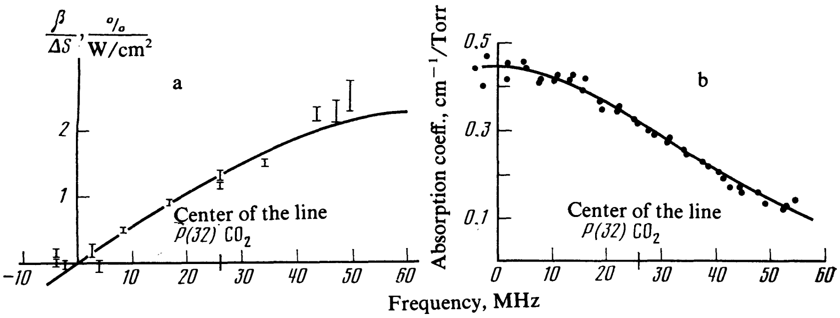

FIG. 5. Dependence of the LID effect and the absorption coefficient on frequency: a—1.6 Torr, solid line—calculation for $\Delta\nu/\nu = 1.04 \times 10^{-2}$, b—0.7 Torr, broadening 18.3 MHz/Torr.

Let us now calculate the factor $\Delta v/v$ from data on the drift of the $^{12}CH_3F$ molecules in the medium of the $^{13}CH_3F$ buffer particles. The CO_2-laser radiation is absorbed in this case as a result of two transitions in the $^{12}CH_3F$ molecule, namely, $Q(12,1)$ and $Q(12,2)$, where the corresponding detunings from the center of the $P(20)$ line of CO_2 are, respectively, + 28.4 and − 44.2 MHz. Since the dipole moments of these transitions are sufficiently small, they were not field-saturated in this experiment. The absorbed power ratio for these transitions with p given by (5) is

$$r=W_B(J_{01}')Y(\Omega_1)\varkappa_1/W_B(J_{02}')Y(\Omega_2)\varkappa_2, \tag{13}$$

where subscripts 1 and 2 identify quantities referring to the $Q(12,1)$ and $Q(12,2)$ transitions, respectively. In our case, $r\simeq 0.42$. Since the signs of effects observed for these absorption lines are opposite, the resulting concentration drop is given by

$$\Delta N=\frac{\Delta\nu}{\nu}\frac{2\Delta S}{\hbar\omega v_0}\left[\frac{r\varphi(\Omega_1)}{1+r}-\frac{\varphi(\Omega_2)}{1+r}\right]. \tag{14}$$

It is then readily shown that the enrichment $(-5.6\pm 0.7)\%$ recorded in this experiment corresponds to $\Delta v/v=(1.16\pm 0.15)\cdot 10^{-2}$. This value agrees to within experimental error with $\Delta v/v=1.04\cdot 10^{-2}$, determined for the $R(4,3)$ transition in the $^{13}CH_3F$ molecule.

Allowance for other absorption lines in the Q branch of $^{12}CH_3F$ has little effect on the factor $\Delta v/v$. Calculations performed for the three absorption lines $Q(12,1)$, $Q(12,2)$, and $Q(12,3)$ yield $\Delta v/v=(1.09\pm 0.14)\times 10^{-2}$.

7. COLLISIONAL AND FIELD BROADENING

We now turn again to (10) which gives the concentration drop ΔN. The effect of collisional and field broadening on $\Delta N/\Delta S$ is determined by the dependence of the function $\varphi(\Omega)$ on the homogeneous transition width $\Gamma_B=\Gamma(1+\varkappa)^{1/2}$. It is therefore convenient to consider these two effects together and classify the experimental conditions according to values of Γ_B. Figure 6 shows measurements and calculations based on (10) and (11). Once again, we have good agreement between theory and experiment. This is, in fact, a convincing illustration of the important advantage[14] of (10), namely, all relaxation processes in the molecular gas are included in the absorbed power, which is readily measured. On the other hand, it is very difficult to calculate its value with sufficient accuracy from molecular constants.

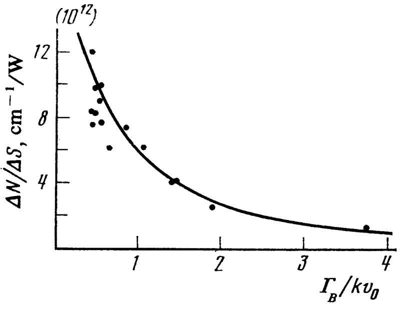

FIG. 6. Specific concentration drop as a function of the homogeneous width of the transition (solid line—calculation for $\Delta v/v=1.04\times 10^{-2}$).

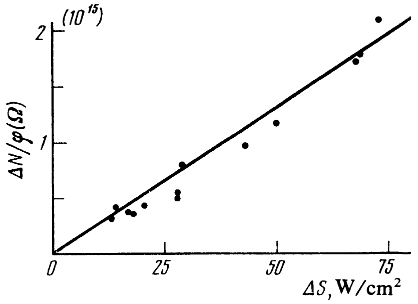

FIG. 7. Magnitude of the LID effect as a function of absorbed power density. Solid line—calculated for $\Delta v/v=1.04\times 10^{-2}$.

Let us now investigate the dependence of the effect on the absorbed power density ΔS. Theory predicts that this relationship should be linear at constant values of the other parameters, namely, $\varkappa$, Γ_B, Ω. In the experiment, changes in ΔS are due to changes in gas pressure or incident power, and are accompanied by changes in $\varkappa$ and Γ_B. It is therefore natural to compare the quantity $\Delta N/\varphi(\Omega)$ with the measured values, since this ratio depends only on ΔS. The measurement and calculation results are shown in Fig. 7.

8. DRIFT MOTION OF CH_3F IN HELIUM AND HYDROGEN

The role of the buffer particles in the LID effect is largely determined by two factors. First, the parameter $\Delta v/v$, which is important for the LID effect, depends on the species of the buffer particle, since it is specific to the colliding pair. Second, the absorption probability and, in the final analysis, the absorbed power density ΔS, depend on the type of buffer particle.

We have investigated the drift of $^{13}CH_3F$ and $^{12}CH_3F$ molecules in He and H_2. These results are listed in Table I. We shall confine our attention to the estimation of $\Delta v/v$ for the pair $^{13}CH_3F$ and He. Consider experiment No. 2 in Table II. The collisional broadening of CH_3F transitions in helium[19] is about 3 MHz/Torr. The resulting collisional halfwidth (with allowance for broadening in its own gas) is about 7.2 MHz, and the saturation parameter is $\varkappa\simeq 3.4\cdot 10^{-2}S$ (S is in units of W/cm^2). In this experiment, vibrational relaxation is largely determined by vibrational relaxation of the molecules in their own gas and by the diffusion of excitation to the cell walls, since bulk relaxation on helium[20] is only $0.65\times 10^3\ s^{-1}\ Torr^{-1}$. Estimates show that $\nu_{mv}\simeq 2\cdot 10^5\ s^{-1}$, $\tau_1\simeq 4.4\cdot 10^{-8}$ s, and $\tau_2/\tau_1\simeq 1.8$. If we use these parameters, we find that experimental data yield $\Delta v/v\simeq 4.5\cdot 10^{-3}$.

9. EFFECT OF OTHER FACTORS

The effect of radiation on the translational motion of atoms and molecules has been investigated for a considerable time, and several of the physical factors controlling the motion of gas particles are now known. We must now estimate the effect of these factors on the above measured quantities. We begin with light pressure. The current of absorbing particles due to light pressure is given by[21] $\mathbf{J}_{l.p.}\simeq Np\hbar\mathbf{k}/vM$. The current ratio $(J_{LID}/J_{l.p.})$ is equal to $(\Delta v/v)\varphi(\Omega)Mv_0/\hbar k$.

TABLE II. Collisional broadening of transitions in the CH_3F molecule

№	Composition of mixture	Total pressure, Torr	Absorbed power dentity, W/cm^2	Enrichment, %
1	$^{13}CH_3F : Ar : H_2 = 1 : 0.44 : 30{,}6$	3.2	17	19±1
2	$^{13}CH_3F : Ar : He = 1 : 0.44 : 16{,}5$	1.8	8	10
3	$^{12}CH_3F : Ar : H_2 = 1 : 0.44 : 17{,}8$	1.7	5.6	−4.5±0.5

In our case, $\Delta v M v_0 / v \hbar k \approx 3 \cdot 10^3$ and light pressure can be neglected. This conclusion is confirmed by the observed dependence of the effect on frequency (Ω).

Strictional forces likewise provide a small contribution to the observed current. The ratio of currents due to LID and striction effects is approximately determined by the factor[3] $g = \Delta v M v_0 L / v\hbar$, where L is the characteristic length over which the field changes. In our case, $g \sim 2 \times 10^9$. The radiation intensity gradient along the beam varied from about 0.1 to about 10 W/cm^3 in our experiments. Analysis then shows that the observed concentration drops are due entirely to the LID effect. The contribution of striction forces is absent to within experimental uncertainty.

Illumination of the gas by the laser beam has practically no heating effect on the cell walls. The heating of the gas itself is determined by vibrational relaxation of the absorbing molecules within the sample. Estimates show that, in our experiments, no less than 90% of the vibrationally excited molecules relaxed on the walls, and the vibrational relaxation within the sample corresponded to the release of less than 0.01 W/cm within the cell. This can raise the temperature of the gas (CH_3F) at the center of the cell by not more than 4 K. As noted in Sec. 4, an increase in the temperature by an amount ten times greater than this figure produced no appreciable effects.

10. CONCLUSIONS

Thus, studies of light-induced drift of CH_3F molecules demonstrate good agreement between experiment and the theory of the LID effect. This applies, in particular, to the dependence of the magnitude of the effect on collisional and field broadening, absorbed power density, and frequency detuning. Our experimental conditions and the method used to record and observe the effect in the isotopic mixture preclude other factors from contributing to the effect. The factors include laser thermodiffusion, light pressure, striction forces, nonuniform heating, and convective and thermal currents.

The values of $\Delta v / v$ given above are quoted with random measurement uncertainties and are valid only to within a certain factor because of possible systematic uncertainties. Our estimates show that this factor may differ from unity by not more than 30%. This must be taken into account when the values of $\Delta v / v$ reported here are compared with theoretical calculations or measurements performed by other methods.

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