Observation of light-induced drift of ammonia molecules

A. K. Folin and P. L. Chapovskiĭ
Institute of Automation and Electrometry, Siberian Branch of the USSR Academy of Sciences

(Submitted 28 September 1983)
Pis'ma Zh. Eksp. Teor. Fiz. **38**, No. 9, 452–454 (10 November 1983)

Light-induced drift of ammonium molecules is observed. In a mixture of molecules $^{15}NH_3 + {}^{14}NH_3$, enrichment with the ^{15}N isotope reaches 97%. It is determined that the excitation of the ν_2 mode of $^{15}NH_3$ molecules decreases their frequency of thermalizing collisions with the buffer gas particles.

PACS numbers: 28.60. + s, 51.20. + d

The experimental investigation of light-induced drift (LID), predicted theoretically by Gel'mukhanov and Shalagin,[1,2] is currently attracting a great deal of attention. From the experimental point of view, it turns out that it is most convenient to study the effect in molecules. The theory of LID of molecules is developed in Refs. 3 and 4. The appearance of the effect in CH_3F molecules has been observed experimentally and investigated.[5–8]

In this paper we report the observation of LID of NH_3 molecules. As in the experiments with CH_3F molecules,[5–7] we studied the light-induced change in the isotopic composition of the mixture (in our case the mixture $^{15}NH_3 + {}^{14}NH_3$) with mass-spectrometrical measurement of the gas composition. This experimental procedure essentially excludes spurious signals associated with laser heating of the gas. In the experiments we used ammonia with the natural isotopic composition $^{15}NH_3$:$^{14}NH_3 = 1{:}270$. The transition aR (6,0) of the ν_2 vibration of the $^{15}NH_3$ molecule was excited. This absorption line is situated near (on the high-frequency side) the generation line 9R10 of the CO_2 laser. The detuning of the laser frequency was $\Omega = -125$ MHz.[9]

CO_2 laser radiation was focused with a spherical mirror ($f = 50$ cm) into a cylindrical copper cell (inside diameter 3 mm and length 1.5 m) with NaCl windows, positioned at the Brewster angle. The radiation density in the cell $\lesssim 200$ W/cm^2. A dispensing valve, which permits extracting gas specimens for analysis on the mass spectrometer, is installed at the input (relative to the beam) end of the cell. The output end of the cell is connected to a ballast volume.

The investigation of LID of ammonia has two peculiarities, greatly complicating the experiment. First, the weak line of $^{15}NH_3$ in the mass spectrum is situated near the H_2O^+ background. The distance between them is 0.013 amu. It was possible to obtain a reliable measurement of the intensity of the $^{15}NH_3$ line with mass spectrometer resolution ~ 3000. Secondly, the significant molecular absorption on the surface of the vacuum system required repeated "washing" of the entire system during the analysis of the isotopic composition of the gas with the specimens of the analyzed gas, so that the ratio of the background intensities of the $^{15}NH_3$ and $^{14}NH_3$ peaks would be equal to their ratio in the analyzed gas specimen.

The experiments showed that irradiation of the mixture $^{15}NH_3 + {}^{14}NH_3$ leads to enrichment of the gas composition with respect to the isotope ^{15}N at the input end of the cell. The maximum enrichment achieved in the experiment was 97%. (We define enrichment as $\beta = K_{\text{light}}/K - 1$, where K_{light}/K is the ratio of the densities of absorbing molecules to the buffer gas molecules with and without illumination, respectively.) As follows from the theory of the effect and the relative position of the frequency of the absorption line and of the laser frequency, the enrichment corresponds to a decrease in the frequency of thermalizing collisions of $^{15}NH_3$ molecules with buffer gas molecules that accompany the excitation of the vibration mode ν_2.

The results of measurements of enrichment (β) under different conditions are presented in Table I. Here P is the total pressure of the mixture (Torr); ΔS is the laser radiation density absorbed by the gas (W/cm^2); $\Delta\nu/\nu$ is the relative change in the frequencies of thermalizing collisions accompanying excitation of the molecule.

The theory of LID of molecules[4] gives an expression for the drop in the concentration of the absorbing component of the gas at the ends of the cell:

$$\Delta N = \frac{\Delta\nu}{\nu}\frac{2\Delta S}{\hbar\omega\upsilon_0}\varphi(\Omega). \tag{1}$$

The function $\varphi(\Omega)$ is expressed[4] in terms of the probability integral and can be calculated if the detuning Ω and the homogeneous line width Γ_B are known. Expression (1) and the data in the table permit calculating the quantity $\Delta\nu/\nu$. Enrichment in the case of small relative concentrations of absorbing molecules is related simply to ΔN: $\beta = \Delta N/N$, where N is the concentration of absorbing molecules. Unfortunately, a number of circumstances interfere at the present time with making these calculations exact. Because the system with the gas being analyzed must be "washed" frequently, the measurement procedure was drawn out over 1–2 hours. Over this time, the radiation intensity changed, which led to an appreciable error in the measurements of ΔS. In addition, there are no data in the literature on the broadening and shift of the

TABLE I.

P	ΔS	β, %	$\Delta\nu/\nu$ (10^{-2})
2.2	~ 1.3	26	− 4.5
2.2	~ 1.8	26	− 3.3
4.6	10.0	70	− 4.6
6.4	17.0	97	− 6.5
9.6	33.0	93	− 6.6
9.6	41.0	94	− 5.4
18.0	78.0	60 − 80	− 6.8 − − 9.4
9.6[1)]	25.0	− 49	− 4.6

[1)]The direction of propagation of the radiation is reversed.

transition used in this work. For this reason, we shall limit ourselves here to estimates under the following assumptions. We shall assume that the collision broadening is 10 MHz/Torr. This value is apparently close to the real value, as may be concluded from Ref. 10. In the estimates, we shall ignore the collisional line shift and the field-induced broadening. The results of the estimates of $\Delta\nu/\nu$ are presented in Table I. It is evident that the experiments performed under strongly differing conditions (for example, according to the absorbed intensity, by almost two orders of magnitude) are described well by the LID theory. The change in the sign of the effect accompanying the change in the direction of the wave vector of the radiation (the last line in the table) also agrees completely with the theory of LID. The contribution of thermal diffusion to the observed effect, on the contrary, is small, since the thermal diffusion constant is only 0.01,[11] while the heating of the gas by the laser radiation was $\lesssim 10$ °C.

The most reliable measurements are the measurements of $\Delta\nu/\nu$ at pressures of 4.6–9.6 Torr, when field-induced broadening and the collisional line shift are estimated to be small. Thus the value of the factor $\Delta\nu/\nu$ turns out to lie in the range $-(4.6\text{–}6.6)\times 10^{-2}$. This value is appreciably larger (in modulus) than the analogous quantity for CH_3F molecules: $+1\times 10^{-2}$.

The decrease in the collision frequency in the excited state agrees with the data on the structure of the ammonia molecule: when the molecule $^{15}NH_3$ is excited the state $v_2 = 1$, the dipole moment decreases significantly [by 16% (Ref. 12)].

In conclusion, we thank S. G. Rautian, A. M. Shalagin, V. N. Panfilov, V. P. Strunin, and L. N. Krasnoperov for supporting this work and for many useful discussions.

[1]F. Kh. Gel'mukhanov and A. M. Shalagin, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 773 (1979) [JETP Lett. **29**, 711 (1979)].
[2]F. Kh. Gel'mukhanov and A. M. Shalagin, Zh. Eksp. Teor. Fiz. **78**, 1672 (1980) [Sov. Phys. JETP **51**, 839 (1980)].
[3]A. M. Dykhne and A. N. Starostin, Zh. Eksp. Teor. Fiz. **79**, 1211 (1980) [Sov. Phys. JETP **52**, 612 (1980)].
[4]V. R. Mironenko and A. M. Shalagin, Izv. Akad. Nauk SSSR, Ser. Fiz. **45**, 995 (1981).
[5]V. N. Panfilov, V. P. Strunin, P. L. Chapovskiĭ, and A. M. Shalagin, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 52 (1981) [JETP Lett. **33**, 48 (1981)].
[6]V. N. Panfilov, V. P. Strunin, and P. L. Chapovskiĭ, Zh. Eksp. Teor. Fiz. **85**, 881 (1983) [Sov. Phys. JETP, to be published].
[7]P. L. Chapovsky, A. M. Shalagin, V. N. Panfilov, and V. P. Strunin, Opt. Commun. **40**, 129 (1981).
[8]H. Riegler, M. Tacke, H. G. Haefele, and E. Skok, Opt. Commun. **46**, 195 (1983).
[9]G. D. Willenberg, Opt. Commun. **45**, 60 (1983).
[10]G. Baldacchini, S. Marchetti, V. Montelatici, G. Buffa, and O. Tarrini, J. Chem. Phys. **76**, 5271 (1982).
[11]S. Chapman and T. Cowling, The Mathematical Theory of Non-Uniform Gases, Cambridge University Press, N. Y., 1970.
[12]K. Shimoda, Y. Ueda, and J. Iwahori, Appl. Phys. **21**, 181 (1980).

Translated by M. E. Alferieff
Edited by S. J. Amoretty