

Photoinduced-drift separation of the *o*- and *p*-modifications of CH₃F

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A spatial separation of the nuclear-spin modifications of CH₃F has been detected during the photoinduced drift of molecules in the beam from a cw CO₂ laser.

The photoinduced drift predicted in 1979 by Gel'mukhanov and Shalagin¹ has been used²⁻⁴ to separate isotopic modifications of CH₃F and NH₃ molecules. It has also been used to separate nuclear-spin modifications of molecules.⁵ Our purpose in the present study was to observe this effect experimentally.

The spins of equivalent nuclei of molecules have an indirect effect on the term system of the molecule.⁶ The CH₃F molecules with a resultant hydrogen nuclear spin of 3/2 and 1/2 (the *o*- and *p* modifications, respectively), for example, have rotational levels with unequal quantum numbers *K*. Because of the weak coupling of the nuclear spins with the electrons, these states should have long lives.⁶

As in Refs. 2 and 3, we observed the effect by using the beam from a cw CO₂ laser. The 9*P*(32) output line of the laser is absorbed by the isolated transition *R*(4.3) of the ν_3 vibration of the molecule ¹³CH₃F. This transition corresponds to the *o*-modification of the molecule. The laser frequency is 25.8 MHz higher than the frequency at the center of the absorption line.⁷ The molecule ¹²CH₃F absorbs the laser emission in the 9*P*(20) line by means of two transitions, *Q*(12.1) and *Q*(12.2) of the vibration ν_3 , which belongs to the *p*-modification of the molecule. The intensities and positions of

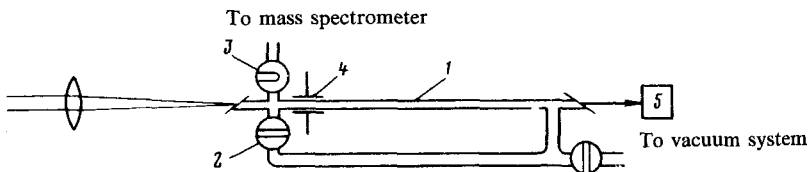


FIG. 1. The experimental arrangement. 1—Cell; 2—bypass valve; 3—sampling valve; 4—electrodes for Stark modulation; 5—photoresistor.

these absorption lines are such that the photoinduced drift has the sign opposite that for the $^{13}\text{CH}_3\text{F}$ molecule.³

The beam from a CO_2 laser which is frequency-stabilized at the intrinsic center of the line is focused into a glass cell 1 m long with an inside diameter of 1 mm (Fig. 1). A ballast volume (200 cm^3) is continuously connected to the end of the cell where the beam exists, and it is also connected through a bypass valve to the entrance end. An alternating (50 -kHz) electric field is applied to a small part (1 or 4 cm long) of the tube near the entrance end of the cell for measuring the concentrations of the spin modification of the molecules which is interacting with the beam. The Stark modulation of the absorption coefficient of the gas in this region gives rise to an alternating component at twice the modulation frequency in the beam transmitted through the cell. After synchronous detection, the amplitude of the alternating component (J) is recorded on a chart recorder. The concentration of the isotropic modification of the molecules is determined by a mass-spectrometry method for a sample of the gas withdrawn with the help of a sampling valve at the entrance end of the cell.

In the experiments, the cell is continuously bombarded by the laser beam. To detect a separation of the spin modifications of the molecules, we measure the changes in the readings of the mass spectrometer and the value of J with the bypass valve open and shut. We note that the position of the valve has essentially no effect on the thermal conditions in the cell because of the very low thermal conductivity of the gas in comparison with that of the cell material. Clearly, with the bypass valve open there should be no separation of the gas components, while with the valve closed a separation should occur if the "*o-p*-conversion" time is not too short in comparison with the characteristic time for separation of the gas components in the apparatus (50 s in our experiments).

To observe the separation of the *o*- and *p*-modifications of the $^{12}\text{CH}_3\text{F}$ molecules, we filled the cell with gaseous CH_3F of natural isotopic composition (98.9% $^{12}\text{CH}_3\text{F}$ + 1.1% $^{13}\text{CH}_3\text{F}$) at a pressure of 0.33 torr. The power density of the laser beam in the cell was 550 W/cm^2 ; the power density absorbed by the gas was 100 W/cm^2 . Figure 2a demonstrates the effect of the bypass valve on the value of J (the amplitude of the electric field for the Stark modulation was $E_0 = 110\text{ W/cm}$). The average change in J upon the shutting of the valve was $-(8.6 \pm 0.4)\%$. When the bypass valve was closed, we also observed a change in the concentration of $^{12}\text{CH}_3\text{F}$ molecules, by $-(0.8 \pm 0.3)\%$. Here and below, the indicated error is the standard deviation of the average value.

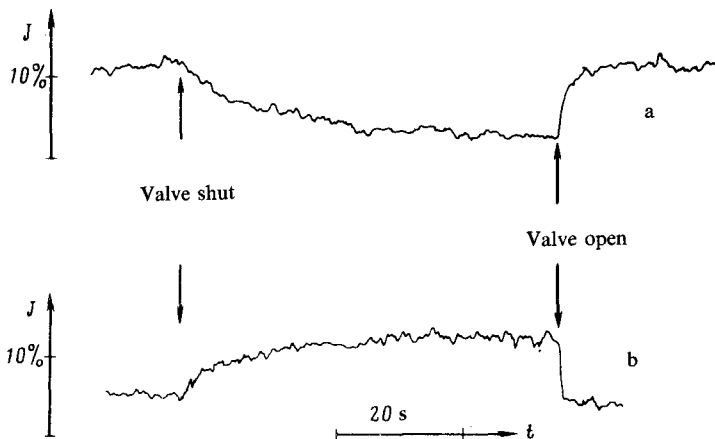


FIG. 2. Effect of closing (opening) the bypass valve on the amplitude (J) of the alternating component of the laser beam transmitted through the cell. a—Experiment with $^{12}\text{CH}_3\text{F}$ molecules; b—with $^{13}\text{CH}_3\text{F}$ molecules.

The separation of the *o*- and *p*-modifications of the $^{13}\text{CH}_3\text{F}$ molecules was observed under similar conditions. The cell was filled with gaseous CH_3F with an isotopic composition of 92% $^{13}\text{CH}_3\text{F}$ + 8% $^{12}\text{CH}_3\text{F}$ at a pressure of 0.33 torr. The laser power density in the cell was 530 W/cm^2 , and the power density absorbed by the gas was 330 W/cm^2 . In this case, shutting the bypass valve increases J by $7.5 \pm 0.3\%$ (an illustrative result is shown in Fig. 2b, for $E_0 = 37 \text{ V/cm}$), and it increases the concentration of $^{13}\text{CH}_3\text{F}$ molecules by $2.6 \pm 0.4\%$. In each case, the sign of the change in J is the same as the sign of the photoinduced drift in Refs. 2 and 3.

The increase in the concentration of $^{13}\text{CH}_3\text{F}$ molecules at the entrance end of the cell in the latter experiment can be explained in part by means of a photoinduced separation of $^{13}\text{CH}_3\text{F}$ and $^{12}\text{CH}_3\text{F}$ molecules (by analogy with Refs. 2 and 3). Our measurements put the enrichment at $\sim 18\%$ in this case. Under these experimental conditions, this enrichment would increase the $^{13}\text{CH}_3\text{F}$ concentration by 1.3%. The rest of the increase in the $^{13}\text{CH}_3\text{F}$ concentration (1.3%) can be attributed to a photoinduced separation of $^{13}\text{CH}_3\text{F}$ molecules and some uncontrolled impurity gas. The residual gas plays a similar role in the experiments with the $^{12}\text{CH}_3\text{F}$ molecules.

We see that the relative change ($\Delta J/J$) in the optical signal when the bypass valve is opened (or shut) is significantly larger in each case than the relative change in the concentration of the absorbing isotopic modification of the CH_3F molecules. It can be shown that the relative change in the optical signal ($\Delta J/J$) can only be smaller than the relative change in the concentration of the absorbing spin modification of the molecules because of several effects (vibrational saturation of the CH_3F molecules and the change in the absorption of the alternating component of the beam due to a redistribution of the absorbing component of the gas). The difference will be seen to different extents in the cases of the $^{12}\text{CH}_3\text{F}$ and the $^{13}\text{CH}_3\text{F}$. These experiments thus demonstrate a spatial separation of the nuclear-spin modifications of CH_3F as a result of a photoinduced drift.

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