

Anomalously large isotopic effect observed in the conversion of different nuclear-spin modifications of CH₃F molecules

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A large difference (≈ 2 orders of magnitude) has been found experimentally in the conversion times for the different nuclear-spin modifications of ¹³CH₃F molecules (≈ 90 s) and ¹²CH₃F molecules (≈ 3 h).

CH₃F molecules are known to exist in two long-lived states differing in the resultant spin of the equivalent nuclei. Following the terminology of Ref. 1, we will call the CH₃F molecules with a resultant spin $I = 3/2$ of the hydrogen nuclei the "ortho-modification" (*o*-CH₃F), while the molecules with $I = 1/2$ are the "para-modifications" (*p*-CH₃F).

These spin modifications of the molecule are present in essentially equal concentrations under equilibrium conditions at room temperature. The equilibrium can be disrupted (and the different modifications will become spatially separated) by a photoinduced drift,² as was demonstrated in Ref. 3.

The conversion of the nuclear-spin modifications of the ¹²CH₃F molecules was studied in Ref. 4. The conversion time turned out to be ≈ 2 h. In the present letter we report a study of the conversion of the spin modifications of the ¹³CH₃F and ¹²CH₃F molecules. We have found a large difference (≈ 2 orders of magnitude) in their conversion times. This unexpected result is interesting, since other known isotopic effects are much smaller.

The experimental arrangement is shown in Fig. 1. The measurements are carried out with a gas of the natural isotopic composition, ¹³CH₃F:¹²CH₃F = 1:89. The beam from a high-power CO₂ laser (≈ 10 W) causes a photoinduced drift in cell 1. If the laser is working on the 9P20 line, the photoinduced drift results in a decrease in the concentration of the *p*-¹²CH₃F molecules at the entrance end of the cell.¹⁾ When the high-power laser is instead working on the 9P32 line, the photoinduced drift increases the concentration of *o*-¹³CH₃F molecules.

The change in the concentration of molecules due to the photoinduced drift is detected by an optical method. The absorption coefficient is Stark-modulated at 28 kHz in the test cell. The beam from a probing laser (a CO₂ waveguide laser stabilized at the center of the nearest CH₃F absorption line) is also modulated at 300 Hz. The beam which is transmitted through the test cell thus contains alternating components at 28 kHz and 300 Hz. The signal at 28 kHz (u_1) is proportional to the concentration of absorbing molecules, while the signal at 300 Hz (u_2) is proportional to the intensity and is used for a normalization. The signals u_1 and u_2 are converted to digital form by

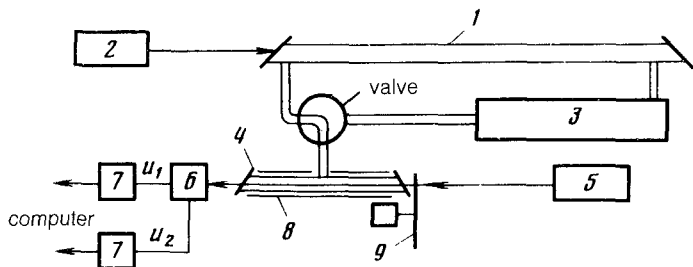


FIG. 1. The experimental arrangement. 1—cell for the separation of the mixture components (1.4 mm in diameter, 141 cm long); 2—high-power CO₂ laser; 3—ballast volume; 4—test cell; 5—waveguide CO₂ laser; 6—detector and frequency filters; 7—voltage-to-frequency converter and pulse counter; 8—electrodes for the Stark modulation; 9—shutter.

two voltage-to-frequency converters (sensitivity of 20 kHz/V) and pulse counters and then processed by computer.

The conversion time of the nuclear-spin modifications is measured in the following way. The test cell is connected by a valve to cell 1. The beam from the high-power CO₂ laser enters cell 1, and the photoinduced drift changes the concentration of either the *p*-¹²CH₃F molecules or the *o*-¹³CH₃F molecules in the test cell by $\approx 10\%$. This change in the concentration of *o*-¹³CH₃F molecules is produced in ≈ 150 s, while that for the *p*-¹²CH₃F molecules takes ≈ 5 min. The test cell is then disconnected from cell 1, and the conversion time is determined from the dynamics of Stark signal u_1 (actually, it is determined from the dynamics of u_1/u_2 in order to reduce the noise). For this purpose a least-squares fit of the function $A \exp(-t/\tau) + B$, with unknown parameters A and B and conversion time τ , is made to the time dependence of u_1/u_2 .

The result of these measurements of importance for the present letter is as follows. The conversion times of the spin modifications of the ¹²CH₃F molecules turn out to be 3.4 ± 0.15 h at a gas pressure $p = 0.58$ torr and 2.8 ± 0.34 h at $p = 0.24$ torr. These times are close to the value of 2 h measured previously⁴ for the same molecules.

The conversion time of the nuclear-spin modifications of the ¹³CH₃F molecules turns out to be significantly shorter: 77 ± 14 s at $p = 0.58$ torr and 103 ± 10 s at $p = 0.24$ torr.

We do not know the conversion mechanism under our conditions or the reason for such a large difference in conversion times. We can only suggest that the conversion is heterogeneous and that the difference in times stems from the existence of a spin and a magnetic moment of the ¹³C atom.

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¹See Ref. 5 for more details on the photoinduced drift of CH₃F molecules.

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⁵V. N. Panfilov, V. P. Strunin, and P. L. Chanovskii, *Zh. Eksp. Teor. Fiz.* **85**, 881 (1983) [*Sov. Phys. JETP* **58**, 510 (1983)].

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