Level-Crossing Resonances in Nuclear Spin Conversion of Molecules

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(Received 5 September 1996)

The first observation of level-crossing resonances in ortho-para conversion is presented. A sharp increase in the conversion rate of gaseous $^{13}CH_3F$ is observed when an applied electric field produces crossing of molecular ortho and para levels. The experimental results are described well by the spin conversion theory based on intramolecular ortho-para state mixing. The results provide direct identification of the levels being mixed and the interaction responsible. The observed spectrum may be considered as an example of Doppler-free spectroscopy. [S0031-9007(96)01812-1]

PACS numbers: 34.30.+h, 33.15.Pw, 33.50.−j

The study of nuclear spin isomers of molecules has a long history which started in the late 1920s after the discovery of ortho and para hydrogen [1]. Despite many attempts, the study of the hydrogen spin isomers was not, until recently, followed by experimental investigations of nuclear spin isomers of other molecules. The main reason was the lack of practical methods to separate spin isomers of molecules heavier than H_2 and D_2. In recent years a few convenient methods of spin isomer separation have been developed which have opened up a new field of research. We would like to mention here especially the separation methods based on light-induced drift [2] and on rotational-state-selective condensation [3].

The investigation of spin isomers is still in an early stage of development. This can be illustrated by the fact that so far there is only one example of spin isomer conversion in a gaseous (nonmagnetic) environment [4–6], viz., nuclear spin conversion in CH_3F molecules. These molecules have two nuclear spin isomers: ortho-CH_3F (total spin of the three protons $I = 3/2$) and para-CH_3F ($I = 1/2$). As follows from the quantum mechanical relation between spin and statistics, ortho-CH_3F molecules can have only $K = 0, 3, 6, \ldots$ (K refers to the projection of the angular momentum on the molecular symmetry axis). For para molecules $K = 1, 2, 4, 5, \ldots$ are allowed.

Experiments on CH_3F molecules yielded some intriguing results. First, the conversion rate of gaseous $^{13}CH_3F$ was found to be almost two orders of magnitude larger than for $^{12}CH_3F$ [4]. Second, collisions with the paramagnetic O_2 were found to be less efficient for conversion of $^{13}CH_3F$ than collisions with CH_3F itself [5]. An explanation was proposed [4] which is based on intramolecular ortho-para state mixing [7]. We feel that this nontraditional type of relaxation (which may be called *quantum relaxation* [8]) has a general physical significance which goes beyond the spin isomer conversion itself. The purpose of the present paper is to provide an experimental verification of the role of quantum relaxation in nuclear spin conversion.

The essence of nuclear spin conversion by quantum relaxation can be explained as follows. The CH_3F molecule has two subspaces of rotational states: one referring to ortho and one to para. Let us assume that there is a small *intramolecular* perturbation $\hat{V}$ in addition to the main Hamiltonian $\hat{H}_0$, that can mix the pure ortho and para states. Two properties of the environment surrounding the test molecules are assumed. First, collisions cannot directly provide transitions between the ortho and para states. Second, collisions destroy the coherence between ortho and para molecular states.

Suppose that the test molecules are initially in the ortho state and that, for simplicity, the perturbation $\hat{V}$ can mix only two states, m and n, from the ortho and para subspaces, respectively. If, as a result of a collision, a test molecule ends up in the state m, then during the free flight following this collision, the time evolution of the molecular wave function will result in the mixing of m and n states because the m state is not an eigenstate of the total molecular Hamiltonian. Because of this mixing the next collision will have a nonzero probability to project the molecular state on the pure para state. Consequently, the ortho molecules will "funnel" through the m-n level pair to the para-subspace until the equilibrium ratio of the two spin isomers densities (1:1 in the case of CH_3F molecules) is established.

A rigorous treatment of this process allowing more level pairs to be mixed can be given [4], using the kinetic equation for the density matrix ρ. In the representation of pure ortho and para states, this equation reads

$$\dot{\rho}_{\alpha\alpha'} = S_{\alpha\alpha'} - i[\hat{V}, \rho]_{\alpha\alpha'}, \tag{1}$$

where $S_{\alpha\alpha'}$ is the collision integral and α, α' represent the set of molecular quantum numbers.

The properties of the environment can be expressed in terms of the collision integral. First, collisions obey particle conservation in each spin state:

$$\sum_{\alpha\in\text{ortho}} S_{\alpha\alpha} = \sum_{\alpha\in\text{para}} S_{\alpha\alpha} = 0\,.$$

Experimental and theoretical evidence for these relations can be found in [5,6,9].

As a second assumption concerning collisions in our system, we assume that the nondiagonal elements of the collision integral $S_{\alpha\alpha_1}(\alpha \in \text{ortho}, \alpha_1 \in \text{para})$ contain only the loss term: $S_{\alpha\alpha_1} = -\Gamma_{\alpha\alpha_1}\rho_{\alpha\alpha_1}$, where $\Gamma_{\alpha\alpha_1}$ is the decay rate of the nondiagonal density-matrix element $\rho_{\alpha\alpha_1}(\alpha \in \text{ortho}, \alpha_1 \in \text{para})$. Note that $\Gamma_{\alpha\alpha_1}$ is proportional to the gas pressure.

The first-order solution of Eq. (1) gives an exponential decay of the nonequilibrium spin isomer concentration (e.g., ortho): $\delta\rho_o(t) = \delta\rho_o(0)e^{-\gamma t}$ with relaxation rate

$$\gamma = \sum_{\alpha \in o, \alpha_1 \in p} \frac{2\Gamma_{\alpha\alpha_1} \mid V_{\alpha\alpha_1} \mid^2}{\Gamma^2_{\alpha\alpha_1} + \omega^2_{\alpha\alpha_1}} [W(\alpha) + W(\alpha_1)], \quad (2)$$

where $\omega_{\alpha\alpha_1}$ is the energy gap between the states α and α_1; $W(\alpha)$ is the Boltzmann factor of the α state. The summation in Eq. (2) is over all pairs of ortho-para levels.

At low pressures, where Γ is much smaller than ω, the conversion rate is strongly dependent on the energy gap between the mixed ortho and para levels, as can be seen from Eq. (2). This dependence is at the heart of the experimental approach used in the present paper. As was proposed in Ref. [10], a homogeneous electric field can be used to vary the level gaps. Because of the first-order Stark effect in CH_3F, the molecular levels are split and at some values of the electric field crossing of ortho and para levels will occur. This should cause a strong increase in the conversion rate according to Eq. (2).

In the case of crossings of ortho and para levels, Eq. (2) should be used with care. Indeed, if $\omega = 0$, the conversion rate γ is seen to be inversely proportional to Γ and thus inversely proportional to pressure. If $\Gamma \to 0$, this would lead to a conversion rate $\gamma \to \infty$. This is in contradiction with the expectation because the limit $\Gamma = 0$ corresponds to the case of isolated molecules which cannot undergo conversion. As has been shown in Ref. [8], the first-order solution (2) is valid only if $4\Gamma|V|^2/\nu \ll \max\{\omega^2; \Gamma^2\}$, where ν is the rotational relaxation rate inside each of the two nuclear spin subspaces. Thus, for very low pressures the solution (2) should be modified, and the modified version indeed gives zero conversion rate in the limit $\Gamma \to 0$. Because the gas pressure in the present experiment was sufficiently high, the solution (2) can be used in a straightforward way also in the case of level crossings.

It is useful at this point to consider the spacing $\omega_{\alpha\alpha_1}$ between the ortho and para levels in $^{13}CH_3F$. In these molecules only two close pairs of ortho-para levels are expected to contribute considerably to the spin conversion rate [12]. The energy gaps and the calculated contributions to the conversion rate γ are given in Table I.

An important question is the origin of the perturbation $\hat{V}$. There are two sources of such perturbation in CH_3F molecules considered so far: magnetic dipole-dipole interaction between the molecular nuclei [12] and spin-rotation interaction [13]. Since the closest and most important pair of (J, K) levels $(11, 1)$-$(9, 3)$ has $\Delta J = 2$, the spin-rotation interaction does not mix these levels and only dipole-dipole interaction contributes. The spin-rotation interaction does contribute to the mixing of the second closest pair of levels $(21, 1)$-$(20, 3)$ [14]. However, since its contribution to this less important level pair is calculated to be only 10%, we will henceforth neglect the level mixing by spin-rotation interaction.

TABLE I. Pairs of energetically close para (primed) and ortho (unprimed) rotational levels in the ground vibrational state of $^{13}CH_3F$ and the calculated spin conversion rates γ at zero electric field.

(J', K')-(J, K)	Energy Difference $\omega_{\alpha\alpha_1}/2\pi$ [a] (MHz)	γ/p [b] (s^{-1}/Torr)
$(11, 1)$-$(9, 3)$	130.014	7.76×10^{-3}
$(21, 1)$-$(20, 3)$	-352.003	4.41×10^{-3}
		12.2×10^{-3} [c]

[a] Rotational level energies were calculated using the molecular parameters from [11].

[b] Contribution to the conversion rates caused by mixing of the given pairs of rotational levels. Calculations were performed using $\Gamma = 1.75 \times 10^8$ s^{-2}/Torr which is an adjusted value to reproduce the overall experimental conversion rate at zero electric field [6], see the text.

[c] Overall spin conversion rates induced by all pairs of rotational levels having $J, K \leq 50$.

We used in our experiment pure $^{13}CH_3F$ gas (isotopic purity 99%). The enrichment of the spin isomers of CH_3F molecules was achieved by light-induced drift similar to our previous studies (see Ref. [6] and references therein). The experimental setup (Fig. 1) was the same as the one used in [6], the only addition being a Stark cell attached to

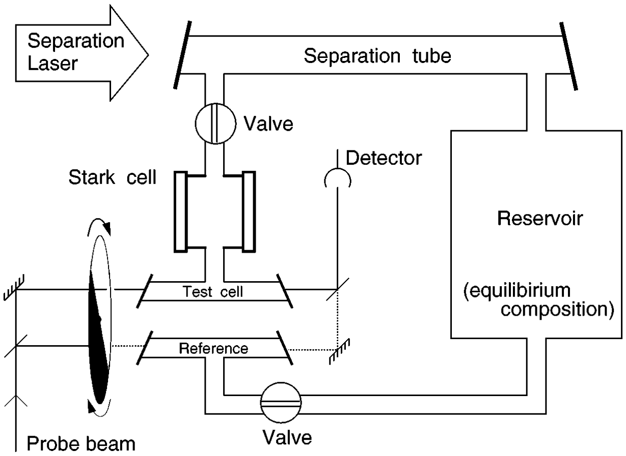

FIG. 1. Schematics of the setup. The separation CO_2 laser (5–10 W) is tuned into the blue Doppler wing of the $R(4, 3)$ absorption line in the ν_3 fundamental vibrational band. After closing the two valves, the back conversion to the equilibrium abundance ratio is monitored by a differential absorption measurement, using a probe laser locked on the $R(4, 3)$ absorption peak. For details see Refs. [5,6].

the test cell. The Stark cell was made of a glass cylinder (diameter 19 mm and height 4.18 mm). The two cylinder ends were parallel to within 1 μm. The cylinder was closed by two optical-quality glass plates coated by gold which served as the internal Stark electrodes.

The measurement procedure was as follows. We started with the equilibrium spin isomer composition in the test cell and two valves open (Fig. 1). After a few percent enrichment was achieved by light-induced drift in the separation tube, both valves were closed and the electric field in the Stark cell was switched on. The subsequent relaxation of the enriched gas to the equilibrium composition was then measured directly by monitoring the absorption decay in the test cell, using the $R(4,3)$ absorption line in the ν_3 fundamental band of ^{13}CH$_3$F. Note that the $R(4,3)$ absorption line belongs to ortho-^{13}CH$_3$F, because $K = 3$. The measurements were repeated at various electric fields. Special care was taken to ensure the absence of electric discharge through the Stark cell.

All data were taken at a pressure of 0.2 Torr. This is a rather convenient pressure for the present experiment; at much higher pressure the resolution is limited by pressure broadening (see Ref. [10]), and at much lower pressure the absorption becomes too weak to perform accurate measurements. The fast diffusion at this low pressure eases the correction for the "dead" volume outside the Stark field. Since the fraction of the time that the molecules spend in the Stark cell is proportional to its volume, the conversion rate $\gamma(E)$ in the Stark field is found from the measured rate γ_{meas} by

$$\gamma(E) = \gamma_{\text{meas}} + \frac{V_0}{V_{\text{Stark}}}(\gamma_{\text{meas}} - \gamma_0), \qquad (3)$$

where γ_0 is the field-free conversion rate and V_0/V_{Stark} is the ratio (3.59 in our case) of the volumes outside and inside the electric field.

The results for $\gamma(E)$ are given in Fig. 2. It is seen that below 500 V/cm the conversion is hardly affected by the field, whereas a sharp rise in the conversion rate occurs at 600 V/cm, followed by distinct and well-resolved peaks. The theoretical curve was calculated according to the model given in Ref. [10], taking as the perturbation $\hat{V}$ only the magnetic dipole-dipole interaction between the molecular nuclei. All $\Gamma_{\alpha\alpha_1}$ were chosen equal for the two pairs of levels (11,1)-(9,3) and (21,1)-(20,3), as well as for all allowed M'-M subpairs. By using this assumption, Γ can be taken out of the sum in Eq. (2), and the model contains only one free parameter, Γ. This parameter was adjusted to fit the ^{13}CH$_3$F isomer conversion rate measured at zero electric field: $(12.2 \pm 6) \times 10^{-3}$ s^{-1}/Torr [6]. Such a fit yields $\Gamma = 1.75 \times 10^8$ s^{-1}/Torr, which is close to the population decay rate 1×10^8 s^{-1}/Torr in the ground state of ^{13}CH$_3$F [15].

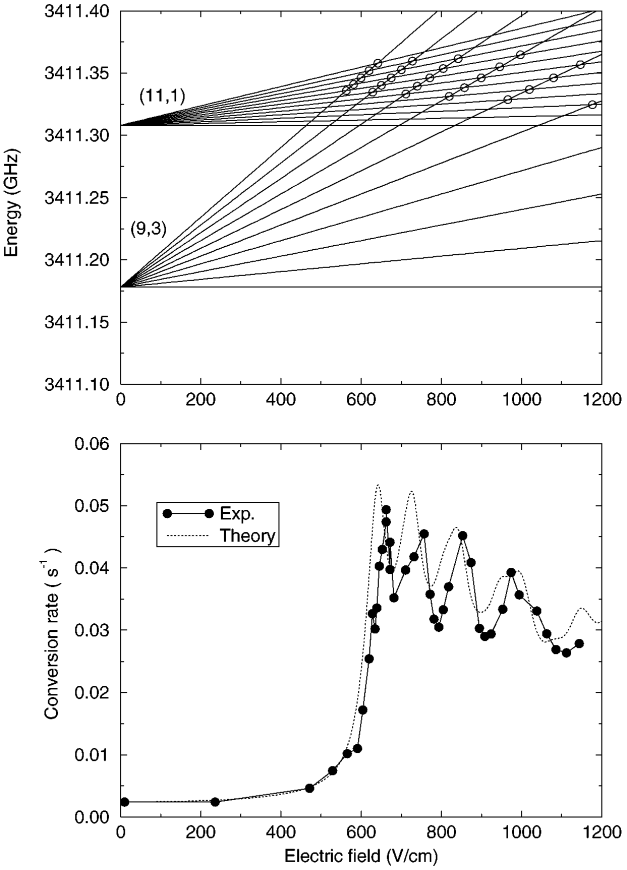

FIG. 2. Upper panel: Splitting of the levels by electric field. Crossings which should contribute to the conversion rate are marked. Lower panel: Experimental and theoretical spin conversion rates $\gamma(E)$ in ^{13}CH$_3$F molecules as a function of the electric field strength. Gas pressure is 26.6 Pa (0.200 Torr). The experimental points are connected to guide the eye.

After the rate Γ is fixed, there are no additional free parameters in the model. The ^{13}CH$_3$F permanent dipole moment was taken to be 1.86 D (or 6.2×10^{-30} C m) [16]. The amplitudes of the individual resonances produced by the crossings of the particular M', M levels are different in height and only part of them have a big amplitude (see Ref. [10]). Consequently, the structure in the spectrum remains despite the high density of the crossings.

As can be seen from Fig. 2, the overall behavior of the experimental data agrees convincingly well with the theoretical model. This includes agreement between calculated and observed positions of the peaks to within a few percent. The small difference between the amplitudes of the measured and calculated spectra may be attributed to the crudeness of the modeling of the relaxation rates $\Gamma_{\alpha\alpha_1}$ which were simply assumed equal for all level pairs involved.

In conclusion, we have demonstrated that crossing of ortho and para energy levels in ^{13}CH$_3$F molecules produces a sharp increase in the nuclear spin conversion rate. The dependence of the conversion rate on the electric field used for creating the level crossings is consistent with the description of the phenomenon given by the quantum relaxation theory with the intramolecular dipole-dipole interactions between the nuclei being responsible for the mixing of the ortho and para states. The measured positions of the resonances give a direct indication of which particular ortho and para levels in $^{13}CH_3F$ are efficiently mixed, being responsible for the nuclear spin conversion. We would like to point out that the conversion spectrum presented in this paper is unaffected by the thermal motion of the molecules, having pressure broadening only. Therefore, this spectrum may be considered as an example of Doppler-free spectroscopy.

The authors are indebted to Jan Beenakker, Eric R. Eliel, Gerard Nienhuis, and Quirin Vrehen for helpful discussions and critical comments. This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM) and was made possible by financial support from the Netherlands Organization for Scientific Research (NWO).

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