Quantum Zeno Effect Induced by Collisions

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(Received 2 May 1997)

It is proven experimentally that the ortho-para conversion of the nuclear spin isomers of $^{13}CH_3F$ molecules can be slowed down by increasing the gas pressure. The observed "freezing" of the molecular quantum states can be considered as an example of the quantum Zeno effect induced by collisions.   [S0031-9007(97)04332-9]

State-to-state molecular relaxation in the gas phase is of fundamental importance. To the authors' knowledge, in all experiments performed so far in this area the role of the environment surrounding the test particles had always one general property, namely, the environment was always able to induce state-to-state molecular transitions directly. However, the role of the environment can also be completely different, as will be experimentally illustrated in the present paper, using the specific example of nuclear spin conversion (ortho para) in molecules.

The problem which we are going to address in this paper can be formulated in a rather general form [1]. Let us consider multilevel test particles embedded in an infinitely large environment. Suppose that the Hilbert space of the particles' quantum states is divided into two subspaces in which the observable $\hat{O}$ has eigenvalues f and s (Fig. 1). Suppose that the test particles are placed initially, say, in subspace f. How will they subsequently relax to an equilibrium distribution over the two subspaces?

One can see here two fundamentally different options. In the first one, the environment can produce direct transitions between subspaces f and s, having scattering amplitude $F(s\,|\,f) \neq 0$. In this familiar situation the relaxation can be characterized by the relevant cross sections. One can call this type of relaxation *classical,* despite the fact that in the calculation of the cross section itself quantum mechanics can be heavily involved.

In the alternative case, which is the subject of the present paper, collisions of the test particle with the environment do not directly produce transitions between f and s subspaces: $F(s\,|\,f) = 0$. Even so, relaxation can take place in this situation if the states $|f\rangle$ and $|s\rangle$ are mixed by the particle's own Hamiltonian. Because of the purely quantum mechanical nature of this process one may call it *quantum relaxation* [1]. The reader should be aware that this type of relaxation is closely related to processes having alternative names in the literature like mixing of states [2], quantum Zeno effect [3], blocking of states [4], inhibition [5,6], or quantum damping [7].

The original model of the quantum Zeno effect [3] is based on the decoherence of states due to frequent measurement. There is one observation of a closely related effect, viz., the inhibition of radiation-induced transitions by perturbations caused by short radiation pulses [8]. This paper stimulated an intensive discussion
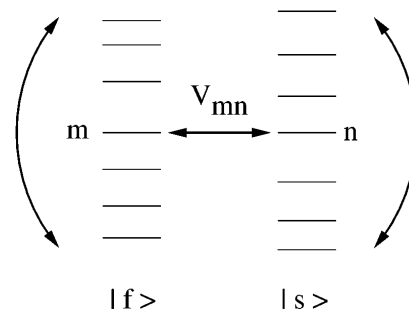

FIG. 1. Two Hilbert subspaces of the multilevel particle. Bent arrows indicate the transitions inside each subspace produced directly by collisions with the environment.

in the literature (see [9], and references therein) as to what extent the perturbation used in [8] constitutes a measurement. On the other hand, the decoherence of states itself can be considered as the main ingredient of the quantum Zeno effect [9–12]. The decoherence can be caused, e.g., by frequent radiation pulses [8,9], or by collisions [11] as is illustrated below.

In paper [1] the relaxation of the nuclear spin isomers of CH₃F molecules was proposed as a convenient system to study the phenomenon of quantum relaxation experimentally. The present paper is devoted to the observation of the most striking feature of this process, viz., the slowing down of the relaxation rate in case of rapid perturbations.

A useful qualitative picture of the quantum relaxation can be drawn using the wave function formalism. Let us split the Hamiltonian of a free particle into two parts:

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{1}$$

where $\hat{H}_0$ is the part of the particle's Hamiltonian for which the states in subspaces f and s are eigenstates (Fig. 1); $\hat{V}$ is the *intramolecular* perturbation able to mix two states m and n, belonging to the f and s subspaces, respectively. Suppose that at time $t = 0$ the particle is placed in state m. Because this state is not an eigenstate of the particle's total Hamiltonian, the wave function of the particle will undergo the following time evolution during the particle's free flight:

$$\Psi(t) = \{[\cos(\omega t/2) - i\cos\theta \sin(\omega t/2)]\varphi_m \\ - i\sin\theta \sin(\omega t/2)\varphi_n\}e^{-i(H_{mm}+H_{nn})t/2}. \tag{2}$$

Here the angle θ determines the efficiency of the state mixing: $\tan\theta = 2|V_{mn}|/(H_{mm} - H_{nn})$ and $\omega = (H_{mm} - H_{nn})\sqrt{1 + \tan^2\theta}$. We assume the Hamiltonian to be written in frequency units.

Wave function (2) gives the probability P_n for the particle to be found in the state n:

$$P_n = \sin^2\theta \sin^2(\omega t/2). \tag{3}$$

It is clear that we do not have *relaxation* so far. Our particle is shuttling between the states m and n and there is no irreversible transition from one subspace to another. For relaxation to take place it is necessary to take into account the interaction with the environment. This can be done in the present qualitative description by assuming that collisions just remove the particle from the state m (or n) thus interrupting the quantum oscillations between these states (see Fig. 1). If the m-n level pair is assumed to be the only mixed pair, the particles can "funnel" through that pair from one subspace to the other.

The relaxation rate (inverse relaxation time) can be easily estimated in two limiting cases. Suppose that $\omega \gg \Gamma$, where Γ is the rate of the level population decay by collisions. Note that Γ is proportional to the gas pressure. In this case the probability P_n, averaged

over time, equals $\overline{P}_n = (\sin^2\theta)/2$. Consequently, the relaxation rate (which is P_n multiplied by the relevant collision frequency Γ) is proportional to $2\Gamma|V_{mn}|^2/\omega^2$, i.e., proportional to pressure. In this limit the relaxation behaves as the ordinary, classical type.

In the opposite case ($\omega \ll \Gamma$), $\sin^2(\omega t/2)$ in Eq. (3) has to be substituted by $\omega^2/2\Gamma^2$ which results from the averaging of $(\omega t)^2$ with the Poisson distribution of free flight intervals. The relaxation rate is then proportional to $2|V_{mn}|^2/\Gamma$, i.e., inversely proportional to pressure. Henceforth we will refer to this slowing down of the relaxation rate as the "$1/p$" dependence.

Let us turn now to the relaxation of the nuclear spin isomers of CH₃F molecules. As a consequence of the restrictions established by spin-statistics relations, the CH₃F molecules have two nuclear spin isomers: ortho and para which have a total spin of three protons $I = 3/2$ and $I = 1/2$, respectively (see, for example, [13]). The ortho molecules can have only K values (quantum number referring to the projection of the molecular angular momentum on the molecular symmetry axis) divisible by 3: $K = 0, 3, 6 \dots$. For para only $K = 1, 2, 4, 5 \dots$ are allowed. The ortho and para states of CH₃F should be identified with the subspaces f and s in the general picture discussed above.

A rigorous treatment of the ortho-para relaxation in CH₃F should be performed in the framework of the density matrix formalism. The result of such calculations in first order perturbation theory is the following [14]. If at time $t = 0$ a nonequilibrium concentration of, e.g., the ortho molecules $\delta\rho_o(0)$ is created, the system will relax exponentially to equilibrium: $\delta\rho_o(t) = \delta\rho_o(0)e^{-\gamma t}$, with the relaxation rate

$$\gamma = \sum_{\alpha'\in p, \alpha\in o} \frac{2\Gamma_{\alpha'\alpha}|V_{\alpha'\alpha}|^2}{\Gamma_{\alpha'\alpha}^2 + \omega_{\alpha'\alpha}^2}(W_{\alpha'} + W_\alpha). \tag{4}$$

Here the states $|\alpha\rangle$ are the total molecular states, being antisymmetric under exchange of any two molecular protons. The summation is performed over all ortho-para level pairs, since mixing is not confined to a single pair in general; $\Gamma_{\alpha'\alpha}$ is the relaxation rate of the nondiagonal density matrix element $\rho_{\alpha'\alpha}$ ($\alpha' \in$ para; $\alpha \in$ ortho); $V_{\alpha'\alpha}$ is the *intramolecular* perturbation which mixes the molecular ortho and para states, $\omega_{\alpha'\alpha}$ is the energy gap between the states $|\alpha'\rangle$ and $|\alpha\rangle$ in units of frequency; W_α is the Boltzmann factor of the state $|\alpha\rangle$.

The solution (4) was obtained under the assumption that the collisions of the test molecule with the environment conserve the number of molecules in each spin state, as should be the case for quantum relaxation. This can be expressed through the diagonal terms of the collision integral ($S_{\alpha\alpha}$) as

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

The second assumption underlying solution (4) was that the nondiagonal element of the collision integral has only the decay term

$$S_{\alpha'\alpha} = -\Gamma_{\alpha'\alpha}\rho_{\alpha'\alpha} \qquad (\alpha' \in \text{para}; \ \alpha \in \text{ortho}).$$

Here $\rho_{\alpha'\alpha}$ is the nondiagonal element of the density matrix.

Solution (4) gives, consistently with the previous qualitative consideration, the two opposite pressure dependences for small and big Γ, i.e., for low and high pressure. If $\Gamma \ll \omega$, the rate Γ can be neglected in the denominator of Eq. (4) and the spin conversion rate γ is proportional to pressure. This part of the pressure dependence was observed in our previous experiments [14,15]. In the opposite limit ($\Gamma \gg \omega$), ω can be neglected and the rate γ will be inversely proportional to pressure.

One way to observe the $1/p$ dependence would be to perform the experiment for $^{13}\text{CH}_3\text{F}$ at pressures such that $\Gamma \gtrsim \omega$. The closest ortho-para level pair ($J' = 11$, $K' = 1$) $-$ ($J = 9$, $K = 3$), which appeared to be the most important for the nuclear spin conversion in $^{13}\text{CH}_3\text{F}$, has a frequency gap of 130 MHz [16]. Consequently, the experiment has to be performed at pressures well above 10 Torr (because $\Gamma \approx 1.75 \times 10^8$ s^{-1}/Torr [17]). Performance of such an experiment proved not to be easy, mainly because our method of separating the ortho and para CH_3F isomers based on light-induced drift becomes inefficient at such high pressures due to the broadening of absorption lines.

Instead, a different approach was chosen in the present experiment. Using a homogeneous electric field we split the molecular levels by the Stark effect and decreased the energy gaps between the relevant $^{13}\text{CH}_3\text{F}$ ortho and para states. This decrease of the ortho-para level gaps should allow us to have a $1/p$ dependence already at low pressures (since $\omega \ll \Gamma$) where the performance of the experiment is much easier.

Splitting of the molecular magnetic sublevels produces crossings between the ortho and para states at some electric field values. To observe the $1/p$ dependence we choose the "resonant" electric field at which the highest peak in the level-crossing spectra occurs (see [17]). This peak is due to the crossing between the magnetic sublevels $M' = 11$ and $M = 9$ which belong to the rotational states ($J' = 11$, $K' = 1$) and ($J = 9$, $K = 3$), respectively. (M refers to the projection of the molecular angular momentum on the electric field direction.) This crossing is found to occur at an electric field of 652.8 V/cm.

Which particular M'-M level crossings contribute to the conversion rate and what the amplitude of the particular peaks is depends on the type of the intramolecular perturbation ($\hat{V}$) responsible for the ortho-para state mixing. The levels ($J' = 11$, $K' = 1$), and ($J = 9$, $K = 3$) are mixed by the magnetic dipole-dipole interaction between the $^{13}\text{CH}_3\text{F}$ nuclei [16]. This type of interaction imposes the selection rule for M: $|\Delta M| \leq 2$.

If the mixing of only one level pair is dominant and if we have $\omega = 0$ for this pair, the spin relaxation rate is inversely proportional to pressure [see Eq. (4)]. The price to pay for this simplification of the situation is that the contributions from the other M'-M level pairs, which have $\omega \neq 0$, are still linear in pressure. Consequently, the sharp slowing down of the conversion rate upon increasing the gas pressure will continue only as long as the nuclear spin conversion is determined mainly by the mixing of the degenerate ortho-para level pair. We will come back to this point later.

The experimental setup is shown in Fig. 2. It is essentially the same as was used in Ref. [17]. As in our previous studies, an enrichment of ortho $^{13}\text{CH}_3\text{F}$ molecules in the test cell was achieved using the light-induced drift effect created by the strong radiation (5– 10 W) of a CO_2 laser operating on the $P(32)$ line from the 9.6 μm band of CO_2. Such radiation is absorbed by the $R(4, 3)$ transition which belongs to the ν_3 fundamental vibrational band of $^{13}\text{CH}_3\text{F}$.

The concentration of ortho molecules in the test cell was measured using the weak probe beam from an additional waveguide CO_2 laser operating on the $9P(32)$ line. This laser was power stabilized and had its radiation frequency locked to the line center of the $R(4, 3)$ absorption line of $^{13}\text{CH}_3\text{F}$.

To avoid possible confusion, we want to stress that the measurement of the ortho-CH_3F concentration decay was performed in a cell separated from the strong CO_2 laser beam. One should also realize that the absorption transition $R(4, 3)$ does not include the state ($J = 9$, $K = 3$), which is mixed with the para molecular state ($J = 11$, $K = 1$).
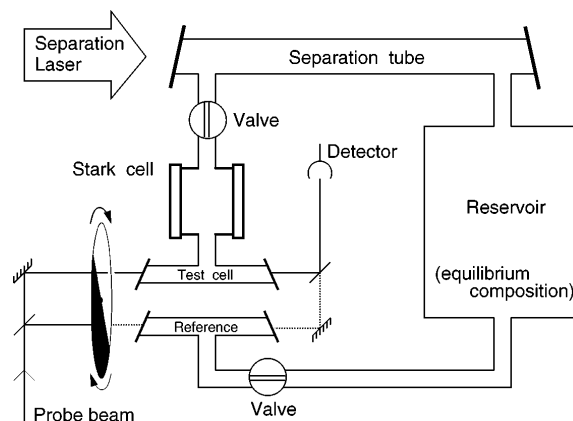

FIG. 2. Schematics of the setup. The separation CO_2 laser (5–10 W) is tuned into the blue Doppler wing of the $R(4, 3)$ absorption line in the ν_3 fundamental vibrational band of $^{13}\text{CH}_3\text{F}$. After isolating an enriched sample by closing the valves, back conversion to the equilibrium abundance ratio is monitored by a differential absorption measurement, using a probe laser locked on the $R(4, 3)$ transition in $^{13}\text{CH}_3\text{F}$. For details, see Refs. [15,17].

The measurement procedure was as follows. After a few percent of enrichment was achieved, the test cell was sealed off by closing the valves. Slow equilibration to the natural abundance ratio (1:1 in the case of CH_3F molecules) in the test cell began. After a few seconds, the electric field was switched on in the Stark cell. A typical decay curve is shown in the inset in Fig. 3. The measurements were repeated at various pressures. The processing of the decay curve to obtain the spin relaxation rate was similar to that used in [17].

The results of the measurements are shown in Fig. 3. It is seen that the CH_3F nuclear spin conversion rate is indeed going down when pressure is increased. The existence of the plateau near 0.5 Torr is the consequence of the neighboring M'-M level pairs which have nonzero frequency gaps at the electric field chosen for the experiment. The intramolecular mixing of these level pairs by the same spin-spin interaction produces a relatively small contribution to the conversion rate at low pressures. But their contribution is linear in pressure and above 0.5 Torr it becomes important. If it were possible to go to much higher pressures, the conversion rate should go down again as $1/p$. Of course, this slowing down will not continue indefinitively. The spin conversion due to the direct collisional transitions (the origin and rate of which we do not yet know) will finally take over because such a mechanism, as any *classical* relaxation, has a contribution to the conversion rate which is linear in pressure.

The experimental results are in fair agreement with the theory given by Eq. (4) (solid line in Fig. 3). The calculations were done assuming $\Gamma = 1.75 \times 10^8$ s^{-1}/Torr for all $(J' = 11, K' = 1, M')$-$(J = 9, K = 3, M)$ level

pairs [17]. As the perturbation $\hat{V}$, which mixes the ortho and para states, the magnetic dipole-dipole interaction between the molecular nuclei was taken [16]. At high pressures the theory fits well to the experimental data. At the low pressures some deviation is observed. This difference can be attributed to the saturation effect in the nuclear spin conversion [18].

To conclude, we have shown that the ortho-para nuclear spin conversion in $^{13}CH_3F$ molecules can provide an example of a peculiar gas phase relaxation having a rate which decreases when the gas pressure is increasing. To our knowledge, this is the first observation of "freezing" of molecular quantum states by collisions in the gas phase. Using an alternative terminology, the observed effect may be considered as the quantum Zeno effect induced by collisions.

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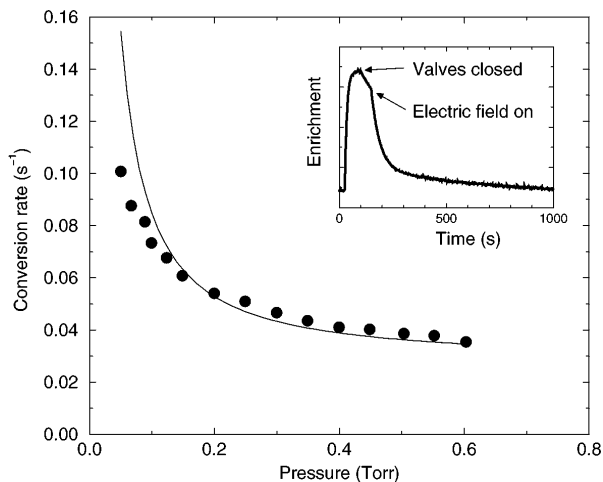

FIG. 3. The ortho-para conversion rate in $^{13}CH_3F$ molecules as a function of pressure: experiment ($\bullet$) and theory (–). The electric field in the Stark cell is chosen such that the $M' = 11$ and $M = 9$ magnetic sublevels of the levels $(J' = 11, K' = 1)$ and $(J = 9, K = 3)$ become degenerate. The inset shows a typical decay curve