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Nonstationary behavior of a high-spin molecule in a bifrequency alternating current magnetic field

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An interaction of a high-spin molecule with a bifrequency ac magnetic field, occurring at times much shorter than the molecule relaxation times, has been considered. The molecule is subjected to a dc magnetic field perpendicular to the easy anisotropy axis of the molecule. The bifrequency ac field is a superposition of two ac fields, one of which is perpendicular to the easy anisotropy axis and causes resonant transitions between the lower states of the fundamental and first excited doublets. The other ac field is parallel to the easy anisotropy axis and has a frequency much smaller than the frequency of the first ac field. It has been shown that, first, the molecule can absorb or emit energy, depending on the frequency of the low-frequency ac field, second, the bifrequency ac magnetic field induces tunneling of the molecule magnetization with the Rabi frequency. The conditions of observation of the effects predicted are discussed.

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I. INTRODUCTION

Among a number of works devoted to quantum coherence and quantum tunneling of magnetization in high-spin molecules [1,2], the papers in which the absorption of an ac magnetic field is studied are of special interest because experiments with ac fields allow one to obtain information about the spectrum and relaxation times of magnetic molecules. In particular, the imaginary part of the high-frequency susceptibility, connected with transitions between two states of the fundamental doublet of a high-spin molecule, was investigated in [3–5]. The measurements carried out in [3,4] demonstrated a nonlinear effect, namely, a large decrease of the imaginary part of the susceptibility with increasing the amplitude of the ac field. In Ref. [5] the dependence of the imaginary part of the susceptibility on temperature was measured (the nature of the obtained dependence is discussed in [5,6]).

In the cited works, the stationary processes (i.e., the processes at large times as compared to the relaxation times characterizing transitions between the states of the fundamental doublet) were considered. In Ref. [7] the nonstationary behavior of a magnetic molecule under the action of an ac field was studied. The ac field frequency was assumed to be resonant for transitions between the lower states of the fundamental and first excited doublets. It has been shown that, in this case, due to oscillations of magnetization with the Rabi frequency, the time required for the magnetization tunneling between two opposite directions is much shorter than the time of tunneling in the absence of an ac magnetic field (for the first time, the influence of a resonant ac electric field on electron tunneling in a double quantum well formed in a semiconductor heterostructure was discussed by Holthaus [8]).

In the present paper, we study a nonstationary process of interaction of a high-spin molecule (or a rare-earth-metal ion) with a bifrequency ac field at times much shorter than the relaxation times. We assume that the molecule doublets are split due to a dc magnetic field perpendicular to the easy anisotropy axis of the molecule, or due to a dc magnetic field and the transverse anisotropy simultaneously. The bifrequency ac field is a superposition of two ac magnetic fields, one of which is perpendicular to the easy anisotropy axis and resonant for transitions between the lower states of the fundamental and first excited doublets. The other ac field is parallel to the easy anisotropy axis, markedly weaker than the first ac field, and has a frequency that is much smaller than the frequency of the first ac field. We will show that the molecule can absorb the energy of the low-frequency ac field or emit it, depending on the frequency of this field. The frequencies at which the resonant interaction of the molecule with the weaker ac field occurs do not coincide with the natural transition frequencies, but depend on the amplitude of the stronger ac field.

We will also show that the bifrequency ac field induces tunneling of the molecule magnetization with the Rabi frequency determined by the stronger ac field. It should be noticed that, in Ref. [7], the initial state of the molecule corresponded to a definite projection of the molecule magnetization on the easy anisotropy axis, i.e., at the initial moment the molecule was not in equilibrium. Now we consider the nonstationary behavior of the molecule in the case in which the molecule is in equilibrium at the initial moment, i.e., the mean value of the projection of the molecule magnetization on the easy anisotropy axis is equal to zero. However, in this case, oscillations of magnetization, associated with tunneling and being analogous to those in Ref. [7], occur in the presence of two mutually perpendicular ac magnetic fields.

Describing the magnetic molecule, we take into account the longitudinal and transverse anisotropy energy and neglect the dipolar-dipolar interactions between magnetic molecules,

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and the coupling between magnetic molecules and nuclear spins (hyperfine interactions). Such a model seems reasonable due to the following facts.

(i) Generally speaking, the dipolar-dipolar and hyperfine interactions influence the magnitude of the doublet splitting (see, for example, Refs. [9,10] in which the splitting of doublets in the clusters of Fe_8 and rare-earth-metal ions Dy^{3+} is discussed). Nevertheless, the influence of a dc magnetic field perpendicular to the easy anisotropy axis on the doublet splitting is more essential (according to [11], the splitting in Fe_8 can be changed by several orders as a result of an insignificant increase of the dc magnetic field).

(ii) Despite the dipolar-dipolar interactions between magnetic molecules and the hyperfine interactions decrease the relaxation times of a magnetic molecule (or a rare-earth-metal ion), it has been established [10] that such a nonstationary process as tunneling-state echoes in high-spin rare-earth-metal ions can be observed.

Furthermore, we assume that the sample temperature is very low so that, in the absence of ac fields, the molecules occupy the ground state or the states of the fundamental doublet. In this case, just the two lowest doublets of the molecule are of our interest.

It should be noticed that, in fact, three levels of a magnetic molecule are involved in the processes considered below. The problem of interaction of a three-level system with electromagnetic fields has been studied for a long time (see, for example, [12,13] and references therein). In particular, the application of a three-level system subject to a bifrequency electromagnetic field (the so-called Λ-type system) for lasing without inversion and obtaining electromagnetically induced transparency is widely discussed currently [14–16].

II. MOLECULE AT ZERO TEMPERATURE

Let us consider a magnetic molecule (for example, Mn_{12} acetate, Fe_8 or CrNi_6) or a rare-earth-metal ion subject to a dc magnetic field and two crossed ac magnetic fields with different frequencies. The dc field and one of the ac fields are perpendicular to the easy anisotropy axis of the molecule. The second ac field is parallel to this axis. As we have mentioned, we take into account the longitudinal and transverse anisotropies and write the molecule Hamiltonian in the form

$$\hat{H}=-D\hat{S}_z^2+\hat{H}_{tr}-g\mu_B\hat{S}_x(H_0+H_x\sin\omega_x t)-g\mu_B\hat{S}_zH_z\sin\omega_z t, \tag{1}$$

where z is the easy anisotropy axis; $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$ are the x, y, and z projections of the spin operator; $\hat{H}_{tr}$ is the operator of the transverse anisotropy energy; D, g, μ_B are the longitudinal anisotropy energy constant, the Landé factor, and the Bohr magneton, respectively; $\mathbf{H}_0$ is the dc magnetic field (we suppose the direction of this field to coincide with the x axis); H_x (H_z) and ω_x (ω_z) are the amplitude and angular frequency of the ac field parallel to x (z) axis. For a rare-earth-metal ion we should write the operator of the total angular momentum instead of the spin operator, but for brevity we use the notation $\hat{\mathbf{S}}$ in all cases.

For Mn_{12} acetate the operator of the transverse anisotropy energy is of the form $\hat{H}_{tr}=C(\hat{S}_+^4+\hat{S}_-^4)$, where C is the transverse anisotropy constant, $\hat{S}_\pm=\hat{S}_x\pm i\hat{S}_y$ [17]. The transverse anisotropy of Fe_8 clusters is characterized by two axes (medium and hard) perpendicular to the easy anisotropy axis. If the direction of the dc field (i.e., the x axis) coincides with the medium axis, the transverse anisotropy energy is $\hat{H}_{tr}=E\hat{S}_y^2$, where E is a positive constant [18] (it should be noticed that in experiments carried out in Ref. [11] the interaction of Fe_8 clusters with an ac field parallel to the easy axis was most effective precisely in the case in which a dc field was parallel to the medium axis). For rare-earth-metal ions in a dysprosium-doped glass, as a rule, the transverse anisotropy energy is not taken into account, however, the authors of Ref. [10] state that better agreement between their theory and experimental results has been achieved by using the transverse anisotropy energy $\hat{H}_{tr}=-K\hat{S}_x^2$ with $K/D\simeq0.6$. According to [4], taking into account the transverse anisotropy for magnetic molecules of CrNi_6 in the form analogous to that for rare-earth-metal ions Dy^{3+} ensures better agreement between the theory and experimental results. In Mn_{12} acetate the transverse anisotropy is inessential because $C/D\simeq5\times10^{-5}$ [19]. On the contrary, the transverse anisotropy of Fe_8 clusters is more essential ($E/D\simeq0.3$ [18]). However, it should be emphasized that, for all molecules and ions mentioned above, the transverse anisotropy can be regarded as a small perturbation with respect to the longitudinal anisotropy.

In all cases mentioned above, the molecule levels form doublets which are split due to the dc magnetic field or due to the transverse anisotropy and the dc magnetic field simultaneously. The phenomena we discuss below do not depend on the nature of the doublet splitting.

Just the two lowest doublets of the molecule are of our interest. The levels belonging to them are [20,21]

$$E_m^\pm\simeq-Dm^2\pm\tfrac{1}{2}\Delta E_m \quad (m=S,S-1). \tag{2}$$

Here $S\gg1$ is the molecule (ion) spin; ΔE_m is a small tunneling splitting of the mth doublet. If the transverse anisotropy is negligible and the splitting is caused by the dc field that is comparatively weak $(g\mu_BH_0/(DS)\ll1)$, one can use the expression [20,21]

$$\Delta E_m\simeq\frac{2D(S+m)!}{[(2m-1)!]^2(S-m)!}\left(\frac{g\mu_BH_0}{2D}\right)^{2m}. \tag{3}$$

The wave functions corresponding to E_m^-, E_m^+ are symmetric and antisymmetric ones. If we regard the transverse anisotropy and the dc field as small perturbations, we can assume that

$$\psi_m^{(s)}\simeq\frac{1}{\sqrt{2}}(\psi_m+\psi_{-m}), \quad \psi_m^{(a)}\simeq\frac{1}{\sqrt{2}}(\psi_m-\psi_{-m}), \tag{4}$$

where $\psi_{\pm m}$ are eigenfunctions of the operator $\hat{S}_z$ ($\hat{S}_z \psi_{\pm m} = \pm m \psi_{\pm m}$). For brevity we designate $\varepsilon_0 = E_S^-$, $\varepsilon_1 = E_S^+$, $\varepsilon_2 = E_{S-1}^-$, $\varepsilon_3 = E_{S-1}^+$, $\varphi_0 = \psi_S^{(s)}$, $\varphi_1 = \psi_S^{(a)}$, $\varphi_2 = \psi_{S-1}^{(s)}$, $\varphi_3 = \psi_{S-1}^{(a)}$ and introduce the transition frequencies $\omega_{jk} = (\varepsilon_j - \varepsilon_k)/\hbar$ $(0 \leqslant k < j \leqslant 3)$.

We suppose that the ac field perpendicular to the easy anisotropy axis is exactly resonant for transitions between the levels ε_0 and ε_2, i.e., $\omega_x = \omega_{20}$. The frequency ω_z of the other ac field is much lower than ω_x. Both ac fields are weak, but the amplitude of the ac field parallel to the easy anisotropy axis is small as compared to the amplitude of the ac field perpendicular to this axis, $H_z \ll H_x$.

In this section we consider the interaction of the molecule (ion) with the bifrequency ac field at zero temperature ($T = 0$) during the time which is much shorter than the relaxation time τ_φ of the wave-function phase. Therefore we can describe the behavior of the molecule by a Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi. \tag{5}$$

Due to the condition $H_z \ll H_x$, we can seek a solution of the Schrödinger equation (5) in the form

$$\psi(t) \simeq \sum_{k=0}^{3} [C_k^{(0)}(t) + C_k^{(1)}(t)]\varphi_k \exp(-i\varepsilon_k t/\hbar), \tag{6}$$

where $C_k^{(0)}(t)$ $(k=0,1,2,3)$ are time-dependent coefficients in the absence of the ac field with the frequency ω_z; $C_k^{(1)}(t)$ are the corrections of the first order in the amplitude H_z.

First of all, we find the coefficients $C_k^{(0)}(t)$. Let the initial state of the molecule be the state φ_0, then $C_0^{(0)}(0) = 1$, $C_k^{(0)}(0) = 0$ $(k = 1,2,3)$. Under the action of the resonant ac field, the coefficients $C_0^{(0)}(t)$, $C_2^{(0)}(t)$ change essentially, whereas $C_1^{(0)}(t)$, $C_3^{(0)}(t)$ can be neglected. The transitions between the levels ε_0, ε_2 are described by the resonant perturbation theory [22] according to which

$$C_0^{(0)}(t) \simeq \cos \Omega_R t, \quad C_2^{(0)}(t) \simeq -\sin \Omega_R t, \tag{7}$$

where

$$\Omega_R = \frac{g\mu_B H_x}{2\hbar} \langle \varphi_2 | \hat{S}_x | \varphi_0 \rangle = \frac{g\mu_B H_x \sqrt{S}}{2\sqrt{2}\,\hbar} \tag{8}$$

is the Rabi frequency. The resonant perturbation theory and therefore the expressions (7) are valid under the condition $\Omega_R \ll \omega_{20}$. Below we shall suppose that the Rabi frequency is comparatively high, namely, $\Omega_R \gg \omega_{10}, \omega_{32}, 1/\tau_\varphi$. Thus, the amplitude H_x has to be such that the condition

$$\omega_{20} \gg \Omega_R \gg \max\{\omega_{10}, \omega_{32}, 1/\tau_\varphi\} \tag{9}$$

holds.

We substitute Eqs. (6) and (7) into Eq. (5), retain the terms of the first order in H_z, and obtain expressions for $dC_k^{(1)}(t)/dt$ $(k = 1,3)$. Integrating these expressions over time with the initial conditions $C_1^{(1)}(0) = C_3^{(1)}(0) = 0$, retaining the terms which can be resonant, and taking into account that $\langle \varphi_1 | \hat{S}_z | \varphi_0 \rangle = S$, $\langle \varphi_3 | \hat{S}_z | \varphi_2 \rangle = S - 1$, we come to

$$C_1^{(1)}(t) \simeq -\frac{g\mu_B S H_z}{4\hbar} \left(\frac{\exp[i(\omega_{10} + \Omega_R - \omega_z)t] - 1}{i(\omega_{10} + \Omega_R - \omega_z)} - \frac{\exp[i(\omega_{10} - \Omega_R + \omega_z)t] - 1}{i(\omega_{10} - \Omega_R + \omega_z)} \right), \tag{10}$$

$$C_3^{(1)}(t) \simeq -i\frac{g\mu_B (S-1) H_z}{4\hbar} \left(\frac{\exp[i(\omega_{32} + \Omega_R - \omega_z)t] - 1}{i(\omega_{32} + \Omega_R - \omega_z)} + \frac{\exp[i(\omega_{32} - \Omega_R + \omega_z)t] - 1}{i(\omega_{32} - \Omega_R + \omega_z)} \right). \tag{11}$$

The first fraction in the big parentheses in Eq. (10) describes transitions of the molecule from the quasienergy level $\varepsilon_0 - \hbar\Omega_R$ to the higher level ε_1, accompanied by absorption of a quantum $\hbar\omega_z$. The second fraction in the big parentheses in Eq. (10) describes transitions of the molecule from the quasienergy level $\varepsilon_0 + \hbar\Omega_R$ to the lower level ε_1, accompanied by emission of a quantum $\hbar\omega_z$ [$\varepsilon_0 + \hbar\Omega_R > \varepsilon_1$ due to the inequality (9)]. Analogously, the first fraction in the big parentheses in Eq. (11) describes transitions of the molecule from the quasienergy level $\varepsilon_2 - \hbar\Omega_R$ to the higher level ε_3, accompanied by absorption of a quantum $\hbar\omega_z$, whereas the second fraction in these parentheses describes transitions from the quasienergy level $\varepsilon_2 + \hbar\Omega_R$ to the lower level ε_3, accompanied by emission of a quantum $\hbar\omega_z$. According to the interpretation given above, the molecule absorbs the energy of the ac field $H_z(t) = H_z \sin \omega_z t$ most effectively (resonantly) at the frequencies $\omega_z = \Omega_R + \omega_{10}$, $\omega_z = \Omega_R + \omega_{32}$ and emits the energy most effectively at the frequencies $\omega_z = \Omega_R - \omega_{10}$, $\omega_z = \Omega_R - \omega_{32}$. The interpretation given in this paragraph will be confirmed by a straightforward calculation of the power absorbed and emitted by the molecule [see Eqs. (16)–(18)].

The perturbation theory used for derivation of Eqs. (10) and (11) is valid if the coefficients $C_{1,3}^{(1)}(t)$ are much smaller than unity. At the resonant frequencies $\omega_z = \Omega_R \pm \omega_{10}$, $\omega_z = \Omega_R \pm \omega_{32}$, this means that $g\mu_B S H_z t/(4\hbar) \ll 1$. This condition certainly holds if the inequality

$$H_z \ll 4\hbar/(g\mu_B S \tau_\varphi) \tag{12}$$

is satisfied.

A. Rabi's oscillations

First, let us find the mean value of the z projection of the spin

$$\langle S_z(t) \rangle = \langle \psi(t) | \hat{S}_z | \psi(t) \rangle = 2S\, \mathrm{Re}[C_0^{(0)*}(t) C_1^{(1)}(t) e^{-i\omega_{10}t}] + 2(S-1)\mathrm{Re}[C_2^{(0)*}(t) C_3^{(1)}(t) e^{-i\omega_{32}t}]. \tag{13}$$

The symbol $\mathrm{Re}(\cdots)$ means the real part of the number $(\cdots)$. Substitution of Eqs. (10) and (11) into Eq. (13) yields a rather cumbersome expression. However, at the combinative frequencies $\omega_z = \Omega_R \pm \omega_{10}$, $\omega_z = \Omega_R \pm \omega_{32}$, at which the interaction of the molecule with the ac field $H_z(t)$ is resonant, we have

$$\langle S_z(t) \rangle |_{\omega_z = \Omega_R \pm \omega_{10}} \simeq \mp \frac{1}{2\hbar} g \mu_B S^2 H_z t \cos \omega_{10} t \cos \Omega_R t, \tag{14}$$

$$\langle S_z(t) \rangle |_{\omega_z = \Omega_R \pm \omega_{32}} \simeq \frac{1}{2\hbar} g \mu_B (S-1)^2 H_z t \sin \omega_{32} t \sin \Omega_R t. \tag{15}$$

Since we assume that $\Omega_R \gg \omega_{10}, \omega_{32}$, we can interpret Eqs. (14) and (15) as describing Rabi's oscillations (i.e., oscillations with the Rabi frequency) of the z projection of the molecule spin (magnetization). The amplitude of these oscillations is time dependent. We remind that Eqs. (14) and (15) are valid at times $t \ll \tau_\varphi$.

To observe the predicted effect of Rabi's oscillations, it is appropriate to use 0.1% dysprosium (Dy^{3+})-doped glasses because, at least, they are characterized by the sufficiently long relaxation time τ_φ in the case in which just the levels of the fundamental doublet are involved in the process. We emphasize that in these glasses tunneling-state echoes have been observed [10]. According to the experimental data [10], for these glasses $S = 15/2$, $DS^2 \simeq 10^2$ K, $g \simeq 4/3$, $\tau_\varphi \sim 10^{-5}$ s. In the processes under our consideration the levels of the first excited doublet are involved, therefore the relaxation time may have a smaller value. Unfortunately, this value is unknown. We admit the quantity τ_φ to have the value of order 10^{-7} s which is typical for magnetic ions in crystals. Supposing $H_0 = 70$ kOe, we find that $\omega_{10} \simeq 0.5 \times 10^6$ s^{-1}, $\omega_{20} \simeq 3.5 \times 10^{12}$ s^{-1}, $\omega_{32} \simeq 3.9 \times 10^8$ s^{-1}. Therefore the inequalities (9) and (12) yield 34 $\mathrm{Oe} \ll H_x \ll 10^5$ Oe, $H_z \ll 0.5$ Oe. Really the upper restriction on H_x is not important because it is a great problem to excite such a strong ac field. It should be noticed that the inequalities $\omega_{10}\tau_\varphi \ll 1$, $\omega_{32}\tau_\varphi \gg 1$ are valid. Below we shall use these inequalities.

If the resonant interaction of the molecule with the weaker ac field just at the frequencies $\omega_z = \Omega_R \pm \omega_{10}$ is of our interest, the right-hand side of the inequality (9) has to be replaced by $\max\{\omega_{10}, 1/\tau_\varphi\}$. As a consequence, the estimate $H_x \gg 34$ Oe (see above) can be replaced by $H_x \gg 3$ Oe.

In Fe_8 clusters tunneling-state echoes have not been observed. Probably, this means that in these clusters the relaxation time τ_φ is very small and therefore it is not easy to observe Rabi's oscilations. Nevertheless, let us estimate typical frequencies and amplitudes of the bifrequency field, conjecturing that $\tau_\varphi \sim 10^{-8}$ s. For Fe_8 clusters $S = 10$, $D \simeq 0.31$ K, $g \simeq 2$, therefore $\omega_{20} \simeq 7.7 \times 10^{11}$ s^{-1}. Using the numerical results given in Ref. [11], we find that $\omega_{10} \simeq 2\pi \times 10^6$ s^{-1} at $H_0 = 13$ kOe. We restrict ourselves to the case of the resonant interaction at the frequencies $\omega_z = \Omega_R \pm \omega_{10}$. Then the amplitudes of the ac fields should satisfy the inequalities 5 $\mathrm{Oe} \ll H_x \ll 3.9 \times 10^4$ Oe, $H_z \ll 2.3$ Oe.

It should be noticed that the conditions of experiments carried out in [5] are not favorable for observing Rabi's oscillations in Mn_{12} acetate molecules because the frequency $\omega_{10} = 2\pi \times 6.8 \times 10^8$ s^{-1} used in [5] puts a severe restriction on the amplitude of the stronger ac field ($H_x \gg 220$ Oe).

B. Absorbed and emitted power

To calculate the mean power P_{ω_z} absorbed by the molecule at the frequency ω_z, it is convenient to use the formula [23]

$$P_{\omega_z} = -g \mu_B \overline{\langle S_z(t) \rangle \frac{dH_z(t)}{dt}}. \tag{16}$$

The line over the right-hand side of Eq. (16) means averaging over a time interval which is much smaller than the relaxation time τ_φ, but larger than the characteristic periods of oscillations.

Substituting Eqs. (14) and (15) into Eq. (16) and supposing $\omega_{10}\tau_\varphi \ll 1$, we obtain at the resonant frequencies $\omega_z = \Omega_R \pm \omega_{10}$ for large t ($1/\Omega_R \ll t \ll \tau_\varphi$),

$$P_{\omega_z = \Omega_R \pm \omega_{10}} \simeq \pm \frac{1}{4\hbar} (\Omega_R \pm \omega_{10}) (g \mu_B H_z S)^2 t. \tag{17}$$

Analogously, for $1/\omega_{32} \ll t \ll \tau_\varphi$,

$$P_{\omega_z = \Omega_R \pm \omega_{32}} \simeq \pm \frac{1}{8\hbar} (\Omega_R \pm \omega_{32}) [g \mu_B H_z (S-1)]^2 t. \tag{18}$$

One can see that $P_{\omega_z} < 0$ at the frequencies $\omega_z = \Omega_R - \omega_{10}$, $\omega_z = \Omega_R - \omega_{32}$, therefore at these frequencies the molecule, indeed, does not absorb, but emits energy.

Up to now we have assumed that the easy anisotropy axis of any magnetic molecule is perpendicular to the dc field $\mathbf{H}_0$. Really such an alignment is unfeasible. A random deflection of the easy anisotropy axis of a molecule from the direction perpendicular to $\mathbf{H}_0$ destroys the resonant interaction between the molecule and the ac field. Therefore the possibility of the observation of the effects we discuss depends on the part of the molecules whose easy anisotropy axis is almost perpendicular to the field $\mathbf{H}_0$. Such a problem arose when the absorption of an ac field, the frequency of which was resonant for transitions between the states of the fundamental doublet, was observed [3–5,11]. Analogously, a random deflection of the medium axis (for example, in a Fe_8 cluster) from the direction of $\mathbf{H}_0$ decreases the interaction between the molecule and the ac field. However, the experiments [3–5,11] confirmed that the sample misalignment was not fateful despite the part of the molecules involved in the process was being small (of the order of 10^{-3} for Mn_{12} acetate [5] and 10^{-6} for Fe_8 [11]).

The influence of a strong light field on the absorption of a weak electromagnetic wave by an ordinary atom has been well known [24]. Rabi's oscillations induced by the strong light field cause a shift of the frequency at which the atom resonantly absorbs the weak wave. The specific character of a magnetic molecule as compared to the atom is that the Rabi frequency (multiplied by $\hbar$) of the magnetic molecule can be much larger than the splitting of the molecule doublets, whereas the Rabi frequency (multiplied by $\hbar$) of the atom, as a rule, is essentially smaller than the spacing between the atom levels. As a result, the atom can only absorb the weak electromagnetic wave, whereas the magnetic molecule can absorb and emit energy.

III. MOLECULE AT FINITE TEMPERATURE

To describe the behavior of the molecule at finite temperature, we use the equations for the density matrix $\hat{\rho}$ [12]. These equations have the form

$$\frac{d\rho_{kj}}{dt}+\frac{i}{\hbar}(\varepsilon_k-\varepsilon_j)\rho_{kj}+\frac{i}{\hbar}[\hat{H}_{int},\hat{\rho}]_{kj}=-\frac{1}{\tau_{kj}}\rho_{kj}\quad (k\neq j), \tag{19}$$

$$\frac{d\rho_{jj}}{dt}+\frac{i}{\hbar}[\hat{H}_{int},\hat{\rho}]_{jj}=\sum_{k=0}^{2}(w_{kj}\rho_{kk}-w_{jk}\rho_{jj}). \tag{20}$$

Here $k,j=0,1,2$ (in this section we restrict ourselves to the case where just three lowest levels are involved in the process; such a case is easily realizable from the experimentalist's point of view); ρ_{kj} is a density matrix element;

$$\hat{H}_{int}=-g\mu_B(\hat{S}_xH_x\sin\omega_xt+\hat{S}_zH_z\sin\omega_zt) \tag{21}$$

is the operator of interaction of the molecule with the bifrequency ac field; τ_{kj} is the relaxation time of the phase of the matrix element ρ_{kj}; w_{kj} is the rate of transition from the kth level to the jth one. Instead of the transition rate w_{kj}, it is usual to introduce the time T_{kj} of relaxation of the population where $w_{kj}=T_{kj}^{-1}\rho_{jj}^{(0)}$, $\rho_{jj}^{(0)}$ is an element of the equilibrium density matrix. It should be noticed that $T_{kj}=T_{jk}$. The matrix elements $(\hat{H}_{int})_{kj}$ different from zero can be found if one takes into account that

$$\langle\varphi_0|\hat{S}_z|\varphi_1\rangle=S,\quad \langle\varphi_0|\hat{S}_x|\varphi_2\rangle=\sqrt{S/2}. \tag{22}$$

The initial condition for Eqs. (19) and (20) is $\rho_{kj}(t=0)=\rho_{kk}^{(0)}\delta_{kj}$. We suppose the temperature to be low enough ($T\ll\hbar\omega_{20}/k_B$ where k_B is the Boltzmann constant) that we can assume $\rho_{00}^{(0)},\rho_{11}^{(0)}\neq 0$, $\rho_{22}^{(0)}\simeq 0$.

Since the amplitude H_z is very small as compared to H_x, we seek the solution of Eqs. (19) and (20) in the form $\rho_{kj}\simeq\tilde{\rho}_{kj}+\delta\tilde{\rho}_{kj}$, where $\tilde{\rho}_{kj}$ is the solution corresponding to $H_z=0$ and $\delta\tilde{\rho}_{kj}$ is the correction of the first order in H_z. The matrix $\tilde{\hat{\rho}}$ obeys the normalization condition $\mathrm{Tr}\,\tilde{\hat{\rho}}=1$. We consider the case of exact resonance, $\omega_x=\omega_{20}$, and use the approach analogous to the resonant perturbation theory for the Schrödinger equation in the case in which the levels ε_0, ε_2 are resonant [22]. Then for small t,

$$t\ll\tilde{\tau}_{20}=\min\{\tau_{20},T_{20}\}, \tag{23}$$

we obtain

$$\tilde{\rho}_{00}=\rho_{00}^{(0)}\cos^2(\Omega_Rt), \tag{24}$$

$$\tilde{\rho}_{22}=\rho_{00}^{(0)}\sin^2(\Omega_Rt), \tag{25}$$

$$\tilde{\rho}_{02}=\frac{1}{2}\rho_{00}^{(0)}\sin(2\Omega_Rt)\exp(i\omega_{20}t), \tag{26}$$

$$\tilde{\rho}_{11}=\rho_{11}^{(0)},\quad \tilde{\rho}_{01}=\tilde{\rho}_{12}=0. \tag{27}$$

The resonant perturbation theory predicting Rabi's oscillations is valid if the condition $\omega_{20}\gg\Omega_R$ holds. It makes sense to speak of Rabi's oscillations if $\Omega_R\gg 1/\tilde{\tau}_{20}$. As in the preceding section, below we will suppose that the amplitude H_x is not very small, namely, $\Omega_R\gg\max\{\omega_{10},1/\tilde{\tau}_{20}\}$. Thus, the double inequality

$$\omega_{20}\gg\Omega_R\gg\max\{\omega_{10},1/\tilde{\tau}_{20}\} \tag{28}$$

has to hold.

Substituting expressions (24)–(27) into Eqs. (19) and (20) and neglecting the relaxation terms, we find in the first order with respect to H_z for small t (we give only one matrix element determining the mean value of the z projection of the spin)

$$\begin{aligned}\delta\tilde{\rho}_{01}=i\sum_{p,q=\pm1}q\frac{g\mu_BSH_z}{8\hbar(\omega_{10}-p\Omega_R-q\omega_z)}\exp(iq\omega_zt)\\ \times[\exp i(\omega_{10}-p\Omega_R-q\omega_z)t-1][3\rho_{00}^{(0)}-2\\ +\rho_{00}^{(0)}\exp(ip2\Omega_Rt)].\end{aligned} \tag{29}$$

Equation (29) is valid under the conditions

$$t\ll\tau=\min\{\tau_{10},T_{10},\tau_{20},T_{20},\tau_{21},T_{21}\}, \tag{30}$$

$$|\delta\tilde{\rho}_{01}|\ll 1. \tag{31}$$

A. Rabi's oscillations

Now we can calculate the mean value of the z projection of the spin

$$\langle S_z(t)\rangle=\langle\varphi_0|\hat{S}_z|\varphi_1\rangle 2\,\mathrm{Re}\,\rho_{01}=2S\,\mathrm{Re}\,\delta\tilde{\rho}_{01}. \tag{32}$$

One can verify that $\mathrm{Re}\,\delta\tilde{\rho}_{01}=0$ and therefore $\langle S_z(t)\rangle=0$ if $\omega_{10}=0$. Hence, in order to induce an ac magnetization of the molecule along the easy anisotropy axis, it is necessary not only to apply an ac magnetic field parallel to this axis, but also to have a splitting of the fundamental doublet.

Substitution of Eq. (29) into Eq. (32) yields at resonant combinative frequencies $\omega_z=\Omega_R\pm\omega_{10}$,

$$\begin{aligned}\langle S_z(t)\rangle|_{\omega_z=\Omega_R\pm\omega_{10}}\simeq\mp\frac{g\mu_BS^2H_z}{4\hbar}t\{(3\rho_{00}^{(0)}-2)\cos[(\Omega_R\\ \pm\omega_{10})t]+\rho_{00}^{(0)}\cos[(\Omega_R\mp\omega_{10})t]\}.\end{aligned} \tag{33}$$

In particular, if the temperature satisfies the condition

$$\hbar\omega_{10}\ll k_BT\ll\hbar\omega_{20}, \tag{34}$$

the matrix element $\rho_{00}^{(0)}$ is close to 1/2, and Eq. (33) amounts to

$$\langle S_z(t)\rangle|_{\omega_z=\Omega_R\pm\omega_{10}} \simeq -\frac{1}{4\hbar} g\mu_B S^2 H_z t \sin\omega_{10} t \sin\Omega_R t. \tag{35}$$

For very low temperature ($k_B T \ll \hbar\omega_{10}$), the matrix element $\rho_{00}^{(0)}$ is close to unity, and, as one could expect, Eq. (33) reduces to Eq. (14). Thus, at finite temperature we come to Rabi's oscillations of the z projection of the molecule spin again.

The relaxation times, except τ_{10}, are unknown, therefore we do not know τ. If this quantity is such that $\omega_{10}\tau \ll 1$ (we assume this case to be the most probable), the amplitude of Rabi's oscillations is proportional to t^2 for temperatures belonging to the interval (34) [see Eqs. (30) and (35)] and proportional to t for very low temperatures [see Eq. (14)]. The latter case is more preferable for observation of Rabi's oscillations than the former one.

At the resonant frequencies, the condition (31) of validity of Eq. (29) certainly holds if

$$H_z \ll 8\hbar/(g\mu_B S\tau). \tag{36}$$

B. Absorbed and emitted power

To calculate the mean power P_{ω_z} absorbed by the molecule at the frequency ω_z, we use the formula (16) once again, but now $\langle S_z(t)\rangle$ is described by Eq. (33). We restrict ourselves to the case in which $\omega_{10}\tau \ll 1$. Carrying out the averaging procedure, we obtain at the resonant frequencies for $t \gg 1/(\Omega_R \pm \omega_{10})$,

$$P_{\omega_z=\Omega_R\pm\omega_{10}} \simeq \pm\frac{1}{4\hbar}(\Omega_R\pm\omega_{10})(g\mu_B S H_z)^2(2\rho_{00}^{(0)}-1)t. \tag{37}$$

One can see that $P_{\omega_z=\Omega_R+\omega_{10}}$ is positive (i.e., the molecule absorbs the energy), whereas $P_{\omega_z=\Omega_R-\omega_{10}}$ is negative (i.e., the molecule emits the energy).

At temperatures defined by the inequalities (34), the matrix element $\rho_{00}^{(0)}$ is close to 1/2 and therefore absorption and emission of energy are negligible. At very low temperatures ($k_B T \ll \hbar\omega_{10}$), the matrix element $\rho_{00}^{(0)}$ is close to unity, and we come to the expression (17).

IV. CONCLUSION

We have studied a nonstationary process of interaction of a magnetic molecule (or a rare-earth-metal ion) with a bifrequency ac magnetic field. The latter is a superposition of two ac fields with different frequencies and polarizations. The ac field with a comparatively low frequency is parallel to the easy anisotropy axis of the molecule and essentially weaker than the ac field which is perpendicular to this axis and has a higher frequency. It has been shown that the bifrequency ac field induces Rabi's oscillations of the magnetization projection on the easy anisotropy axis. The amplitude of these oscillations is time dependent. Under the action of a stronger ac field, the molecule can resonantly not only absorb the energy of the weaker ac field, but emit the energy at the frequency of the weaker ac field as well.

Though our results are approximate and imply that the transverse anisotropy and the dc magnetic field are treated as small perturbations with respect to the longitudinal anisotropy, we believe, however, that this approach catches the physics of the phenomena we have considered.

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