Enrichment of nuclear spin isomers of molecules by bichromatic field

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Abstract. A theoretical model for the enrichment of nuclear spin isomers of molecules by two electromagnetic fields is developed. The fields are resonant with the rotational transitions in the ground electronic and vibrational state of the molecule. Numerical calculations reveal a complicated dependence of the isomer enrichment on the radiation frequencies that consists of three peaks with different shapes, widths and amplitudes.

1. Introduction
Molecules with identical nuclei exist in Nature in the form of nuclear spin isomers [1]. This is a consequence of the quantum statistics that determine the symmetry of the molecular wave function under permutations of identical nuclei: bosons or fermions. The isomers have almost identical physical properties and appear to be extremely stable. The best known example is ortho and para H\textsubscript{2} which was comprehensively studied in the 1930s (see, for example, [2]) and found to have a lifetime of several months at ambient pressure and temperature [2]. Most of the studies of these isomers have been devoted to their enrichment and conversion under various conditions. The isomer enrichment appears to be easy to perform by the deep cooling of hydrogen gas. This unique property of hydrogen isomers results from the anomalously large rotational constant of H\textsubscript{2} and consequently large energy gap (170 K) between the ground states of the ortho and para H\textsubscript{2}, which is significantly larger than the hydrogen boiling point, 20.4 K.

Polyatomic molecules with identical nuclei also have nuclear spin isomers. Since their structure is more complicated than that of diatomic molecules, polyatomic molecules can have two or more types of spin isomers. For example, CH\textsubscript{3}F has two isomers (ortho and para) whereas methane has three and ethylene has four isomers. Enrichment of the isomers of polyatomic molecules appears to be much more difficult to perform than that of the hydrogen isomers. Nevertheless, a few methods for isomer enrichment have been developed. First, enrichment of the spin isomers of polyatomic molecules (\textsuperscript{12}\text{CH}\textsubscript{3}F and \textsuperscript{13}\text{CH}\textsubscript{3}F) was performed using the light-induced drift effect [3]. Later, enrichment of the spin isomers of formaldehyde by UV photolysis was demonstrated [4]. Recently, the nuclear spin isomers of water and methane were separated using magnetic focusing of the cold molecular beams [5], and the spin isomer enrichment of ethylene was performed by catalyzed chemical synthesis [6].
Spin isomers have found important applications in NMR-based techniques due to their ability to significantly enhance the NMR signals. Thus, enhancement of more than three orders of magnitude was achieved with the help of enriched samples of hydrogen spin isomers [7, 8]. The NMR signal enhancement by the enriched isomers of ethylene was demonstrated recently [6]. There are also interesting applications of nuclear spin isomers in astrophysics where the spin isomer abundance in the cosmos is used to investigate the conditions of molecular formation and the properties of interstellar medium. The latest information on spin isomers in astrophysics can be found in the website of the Workshop: Nuclear Spin Effects in Astrochemistry, Goteborg, Sweden, June 9-11, 2014.

The applications of spin isomers rely on our knowledge of the isomers physics and on the available techniques for isomer enrichment. New access to isomer physics and enrichment can be based on the use of resonant electromagnetic fields. It was proposed in [9] that isomer enrichment can be performed by a resonant electromagnetic field that affects the population of the rotational states of the molecule. This idea was generalized in [10] where it was shown that isomer enrichment is affected not only by the level populations but also by the coherences induced by the radiation.

In laser spectroscopy, it is well-known that the use of two resonant electromagnetic fields instead of one significantly increases the variety of the field-induced modifications of the level populations and coherences [11]. For example, coherent population trapping (CPT) [12] has been demonstrated in a Λ system consisting of two lower levels that are close in energy (Zeeman sublevels or hyperfine levels) and an excited electronic level. Two laser fields interact with transitions from the lower levels to the excited level creating a coherence between the lower levels where all the population is trapped. This leads to a transparency window in the absorption spectrum at two-photon resonance. The existence of these dramatic effects motivated us to investigate isomer control by two fields instead of one. The paper is organized as follows. In section 2, we explain the essence of the specific type of isomer relaxation, quantum relaxation. This relaxation process is a key ingredient in the control of isomer conversion by radiation. In section 3, we formulate a theoretical model of isomer control by a bichromatic field in the Π-scheme. In sections 4 and 5, we present the 0th and 1st order perturbation theory of the problem. In section 6, we present the results of the numerical calculations of the isomer enrichment by a bichromatic field. In section 6 we draw conclusions.

2. Quantum relaxation of spin isomers

First, we note that direct electromagnetic transitions between the ortho and para states of the molecule are strongly forbidden [1]. Our approach to isomer control by electromagnetic radiation is not based on the direct ortho-para transitions and is applicable to the isomers whose relaxation is governed by the specific process first suggested in the theoretical paper by Curl et al. [13]. This process was later named quantum relaxation [14].

The essence of quantum relaxation can be explained as follows. Suppose that the Hamiltonian of the molecule under consideration can be divided into two parts,

\[ \hat{H} = \hat{H}_0 + \hbar \hat{V}, \]

(1)

where \( \hat{H}_0 \) is the main part of the Hamiltonian. The eigenstates of \( \hat{H}_0 \) form two Hilbert subspaces of pure ortho and para molecular states, see Fig. 1. \( \hat{V} \) is a small perturbation that creates coherent superpositions of the ortho and para states. The interaction of the molecule with the environment causes transitions of the molecule inside each ortho and para subspace but not between them.

The quantum relaxation of the isomers consists in the following. Suppose that initially the molecule was placed in the ortho subspace. Because of the interaction with the environment, the
molecule starts to shuttle along the ladder of ortho states. It will continue to do so until, after a collision, the molecule arrives at the state $|m\rangle$. During the free flight after this collision, the intramolecular perturbation admixes the state $|\alpha\rangle$ from the para subspace with the state $|m\rangle$. Consequently, the next collision will have some probability to transfer the molecule to other para states thereby completing the relaxation process.

**Figure 1.** Quantum relaxation of spin isomers. Due to the interaction with the environment, the molecule undergoes relaxation inside the ortho and para rotational states in the ground electronic and vibrational state (indicated by the vertical bent arrows). Perturbation $\hat{V}$ mixes the $|m\rangle$ and $|\alpha\rangle$ states.

The quantum relaxation can be described alternatively using the notion of coherences between the molecular states. The intramolecular perturbation $\hat{V}$ creates the off-diagonal ortho-para density matrix element $R_{ma}$. The ortho-para relaxation appears due to the interaction of the intramolecular perturbation $\hat{V}$ with the coherence $R_{ma}$. Thus, ortho-para relaxation can be controlled by all the processes that affect $R_{ma}$. These include molecular collisions that cause the decay of $R_{ma}$, heating or cooling the gas thereby affecting the level populations, and Stark and Zeeman effects that change the molecular energy levels. It can also be done by resonant external electromagnetic fields that affect both the level populations and the mixing of ortho-para states by the perturbation $\hat{V}$.

The quantitative treatment of isomer relaxation in the framework of the density matrix formalism is given in [15]. For example, the nonequilibrium concentration $\delta n_o(0)$ of ortho isomers created at $t = 0$ decays exponentially,

$$\delta n_o(t) = \delta n_o(0) \exp(-\gamma_0 t),$$

with the rate

$$\gamma_0 = \frac{2\Gamma|V_{ma}|^2}{\Gamma^2 + \omega_{ma}^2}(W_m + W_\alpha),$$

in the case of just one ortho-para level pair mixed by the intramolecular perturbation $\hat{V}$, as in Fig. 1. In Eq. (3), $\Gamma$ is the decay rate of the coherence between the states $m$ and $\alpha$, created by the perturbation $\hat{V}$, $\omega_{ma}$ is the frequency gap between the states $m$ and $\alpha$, and $W_m$ and $W_\alpha$ are the Boltzmann factors of the corresponding states. The equilibrium concentrations of ortho ($\pi_o$) and para ($\pi_p$) molecules are determined by the relations,

$$\pi_o = N\frac{W_\alpha}{W_m + W_\alpha}, \quad \pi_p = N\frac{W_m}{W_m + W_\alpha},$$

where $N$ is the total concentration of molecules. Note, that the equilibrium concentrations of ortho and para molecules (4) do not depend on $V_{ma}$ and $\omega_{ma}$.

In a series of studies (see, for example, [16, 17]) it was shown that the ortho-para mixing of states is performed by the intramolecular hyperfine interactions: nuclear spin-spin and spin-rotation. The quantum relaxation of spin isomers is a counter-intuitive process. Note, that each
collision with the environment has the energy $k_B T \sim 10^{12} \text{ Hz}$ at room temperature. Nevertheless, the isomer relaxation is governed by the hyperfine intramolecular coupling that is smaller than $k_B T$ by seven orders of magnitude.

The goal of the present paper is to consider the isomer control by two electromagnetic fields. We have chosen the simplest cases: pure rotational excitation in the ground electronic and vibrational state of the molecule. We have performed the calculations for the three types of radiation schemes presented in Fig. 2. The most interesting results were found for the Π-scheme. This particular case will be considered in more detail below.

3. Isomer control in Π-scheme.

The Π-scheme is presented in Fig. 2c. The molecular states are labeled by Roman or Greek letters for ortho and para states, respectively, or by numbers, as specified in Fig. 2c. The molecular Hamiltonian now consists of three parts,

$$\hat{H} = \hat{H}_0 + \hbar \hat{G} + \hbar \hat{V},$$

where the terms $\hat{H}_0$ and $\hat{V}$ have the same meaning as in Eq. (1). The term $\hbar \hat{G}$ describes the molecular interaction with the bichromatic external field,

$$\hbar \hat{G} = -\mathbf{E}_1 \cdot \hat{\mathbf{d}} \cos \omega_1 t - \mathbf{E}_2 \cdot \hat{\mathbf{d}} \cos \omega_2 t,$$

where, $\mathbf{E}_1$ and $\mathbf{E}_2$ are the amplitudes of the two electromagnetic fields and $\hat{\mathbf{d}}$ is the molecular electric dipole-moment operator. Further, we will assume that the field $\mathbf{E}_1$ interacts only with the transition $1 \rightarrow 2$, and the field $\mathbf{E}_2$ interacts only with the transition $3 \rightarrow 4$. We will use the standard rotating-wave approximation. This leads us to the following nonzero matrix elements of $\hat{G}$,

$$G_{21} = -g_{21} \exp(-i\Omega_1 t), \quad g_{21} = \mathbf{E}_1 \cdot \hat{\mathbf{d}}_{21}/2\hbar, \quad \Omega_1 = \omega_1 - \omega_{21},$$

$$G_{43} = -g_{43} \exp(-i\Omega_2 t), \quad g_{43} = \mathbf{E}_2 \cdot \hat{\mathbf{d}}_{43}/2\hbar, \quad \Omega_2 = \omega_2 - \omega_{43}.\quad (7)$$

Here, $\omega_{21}$ and $\omega_{43}$ are the frequencies of the corresponding transitions, $g_{21}$ and $g_{43}$ are the Rabi frequencies and the $\hat{\mathbf{d}}_{21}$ and $\hat{\mathbf{d}}_{43}$ are the time-independent dipole moments of the corresponding transitions.

The quantum kinetic equation for the density operator $\hat{R}$ reads [18]

$$\partial \hat{R}/\partial t = \hat{S} - i[\hat{G} + \hat{V}, \hat{R}],$$

$$\partial \hat{R}/\partial t = -i \left[ \hat{H}, \hat{R} \right] + i \left[ \hat{V}, \hat{R} \right] - \frac{1}{\hbar} \left[ \hat{G}, \hat{R} \right],$$

$$\partial \hat{R}/\partial t = 0.$$
where $\hat{S}$ is the collision integral and the rectangular brackets denote the commutator.

In our theory, we will use the strong collision model for the collision integral matrix, $S$. This model gives the diagonal terms of $S$ in the form,

$$S_{ii} = -\nu R_{ii} + \nu n_o W_i, \quad n_o = \sum_i R_{ii},$$  \hspace{1cm} (10)$$

$$S_{\alpha\alpha} = -\nu R_{\alpha\alpha} + \nu n_p W_{\alpha}, \quad n_p = \sum_\alpha R_{\alpha\alpha}.$$  \hspace{1cm} (11)$$

Here, $\nu$ is the rotational relaxation rate, and $n_o$ and $n_p$ are the total concentrations of ortho and para molecules, respectively. The collision integrals in the form of (10) and (11) give the Boltzmann distributions of the molecular level populations at equilibrium. Note, that our collision integral conserves the densities of ortho and para molecules,

$$\sum_i S_{ii} = 0, \quad \sum_\alpha S_{\alpha\alpha} = 0.$$  \hspace{1cm} (12)$$

The off-diagonal elements of $S$ are assumed to have only decay terms:

$$S_{ii}' = -\Gamma R_{ii}', \quad S_{\alpha\alpha}' = -\Gamma R_{\alpha\alpha}', \quad S_{i\alpha} = -\Gamma R_{i\alpha},$$  \hspace{1cm} (13)$$

where the decay rate $\Gamma$ is independent of the states involved.

Using the properties of the collision integral and the kinetic equation (9) one can deduce the equations of change of the ortho and para densities. Thus, for example, for para molecules one has

$$\partial n_p/\partial t = 2\text{Re}(iR_{42}V_{24}).$$  \hspace{1cm} (14)$$

This equation is derived on the assumption that the interaction $\hat{G}$ has no ortho-para matrix elements. Because of the conservation of the total molecular density, $\partial n_o/\partial t = -\partial n_p/\partial t$. We see from Eq. (14) that the ortho-para relaxation is determined by the ortho-para coherence $R_{42}$ and the intramolecular mixing, $\hat{V}$.

We assume that the intramolecular perturbation $\hat{V}$ is weak in comparison with $\hat{G}$ and solve the kinetic equation (9) by perturbation theory. The density matrix is approximated by the sum,

$$\hat{R} \simeq \hat{\rho} + \hat{\epsilon},$$  \hspace{1cm} (15)$$

where $\hat{\rho}$ and $\hat{\epsilon}$ are the 0th and 1st order terms of $\hat{R}$, respectively. The kinetic equations for $\hat{\rho}$ and $\hat{\epsilon}$ read

$$\partial \hat{\rho}/\partial t = \hat{S}^{(0)} - i[\hat{G}, \hat{\rho}],$$  \hspace{1cm} (16)$$

$$\partial \hat{\epsilon}/\partial t = \hat{S}^{(1)} - i[\hat{G}, \hat{\epsilon}] - i[\hat{V}, \hat{\rho}].$$  \hspace{1cm} (17)$$

4. The 0th order perturbation theory

In the 0th order perturbation theory, the ortho and para molecular subspaces are completely independent and one needs to solve the standard problem of the radiation interaction with the molecular rotational transition. Let us define the normalized density matrices, for ortho ($\rho'$) and para ($\rho''$) molecules, as

$$\rho_{ii'} = n_o \rho_{ii'}, \quad \rho_{\alpha\alpha'} = n_p \rho_{\alpha\alpha'}.$$  \hspace{1cm} (18)$$

The solution for $\rho'$ was given in [10]. The diagonal elements of $\rho'$ are given by

$$\rho_{ii}' = W_i + (W_1 - W_2) \frac{2\Gamma}{\nu \Gamma_o + \Omega_1^2} |\gamma_{21}|^2 (\delta_{i2} - \delta_{i1}), \quad \Gamma_o = \Gamma \sqrt{1 + |\gamma_{21}|^2/\Gamma \nu}.$$  \hspace{1cm} (19)$$
Here, we introduced the power-broadened line width of the $1 \rightarrow 2$ transition, $\Gamma_p$. Note that this broadening is caused by the finite decay rate $\Gamma$ of the molecular coherence and the rotational level population relaxation rate $\nu$.

The field $\mathbf{E}_1$ creates a nonzero off-diagonal matrix element on only the transition $1 \rightarrow 2$. This is given by

$$\rho_{21} = \overline{\rho}_{21} \exp(-i\Omega_1 t), \quad \overline{\rho}_{21} = ig_{21}(W_1 - W_2) \frac{\Gamma + i\Omega_1}{\Omega_2^2 + \Omega_1^2}. \tag{20}$$

The matrix elements of $\rho''$ can be obtained from the expressions for the matrix elements of $\rho'$ by the following index substitutions: $i \rightarrow \alpha, \ \ 1 \rightarrow 3, \ \ 2 \rightarrow 4$. Thus, one has the diagonal elements,

$$\rho_{\alpha\alpha}'' = W_{\alpha} + (W_3 - W_4) \frac{2\Gamma}{\nu} \frac{|g_{43}|^2}{\Omega_2^2 + \Omega_1^2} (\delta_{\alpha 4} - \delta_{\alpha 3}), \quad \Gamma_p = \Gamma \sqrt{1 + 4|g_{43}|^2 / \Gamma \nu}. \tag{21}$$

Here, $\Gamma_p$ is the power broadened line width of the $3 \rightarrow 4$ transition. The off-diagonal element is given by

$$\rho_{43}'' = \overline{\rho}_{43} \exp(-i\Omega_2 t), \quad \overline{\rho}_{43}'' = ig_{43}(W_3 - W_4) \frac{\Gamma + i\Omega_2}{\Omega_2^2 + \Omega_1^2}. \tag{22}$$

5. The 1st order perturbation theory

In first-order perturbation theory one has to solve the kinetic equation (17). One can check that in the first-order perturbation theory, the densities of the ortho and para molecules remain unchanged because of the relations

$$\frac{\partial}{\partial t} \left( \sum \epsilon_{ii} \right) / \partial t = \frac{\partial}{\partial t} \left( \sum \epsilon_{\alpha\alpha} \right) / \partial t = 0. \tag{23}$$

Changes in the isomer densities $n_p$ and $n_o$ appear in the second-order approximation in $\hat{V}$ because they are now determined by the equations,

$$\frac{\partial n_p}{\partial t} = 2Re(i\epsilon_{42} V_{42}), \quad \frac{\partial n_o}{\partial t} = -\frac{\partial n_p}{\partial t}. \tag{24}$$

The density matrix element $\epsilon_{42}$ can be calculated from the system of four equations that follows from the 1st order kinetic equation (17),

$$\begin{align*}
\partial \epsilon_{42} / \partial t + \Gamma \epsilon_{42} + i(G_{43}\epsilon_{32} - \epsilon_{41}G_{12}) &= -i n_o \rho_{22}' V_{12} + i n_p \rho_{44}' V_{42}, \\
\partial \epsilon_{41} / \partial t + \Gamma \epsilon_{41} + i(G_{43}\epsilon_{31} - \epsilon_{42}G_{21}) &= -i n_o \rho_{21}' V_{12}, \\
\partial \epsilon_{32} / \partial t + \Gamma \epsilon_{32} + i(G_{34}\epsilon_{42} - \epsilon_{31}G_{12}) &= i n_p \rho_{34}' V_{42}, \\
\partial \epsilon_{31} / \partial t + \Gamma \epsilon_{31} + i(G_{34}\epsilon_{41} - \epsilon_{32}G_{21}) &= 0.
\end{align*} \tag{25}$$

In isomer relaxation we have a clear separation in time scales: fast equilibration inside the ortho and para subspaces and slower, by many orders of magnitude, ortho-para relaxation. This allows us to eliminate the fast time-dependence in Eqs. (25) by the following substitutions:

$$\begin{align*}
V_{42} &= \overline{V}_{42} e^{i\omega_{42} t}, \quad \epsilon_{42} = \overline{\epsilon}_{42} e^{i\omega_{42} t}, \quad \epsilon_{41} = \overline{\epsilon}_{41} e^{i(\omega_{42} - \Omega_1) t}, \\
\epsilon_{32} &= \overline{\epsilon}_{32} e^{i(\omega_{42} + \Omega_2) t}, \quad \epsilon_{31} = \overline{\epsilon}_{31} e^{i(\omega_{42} - \Omega_1 + \Omega_2) t}.
\end{align*} \tag{26}$$

Here, the overlined terms are the time-independent factors. For the matrix elements $\overline{\tau}_{42}, \overline{\tau}_{41}, \overline{\tau}_{32}, \overline{\tau}_{31}$ one has a system of four algebraic equations that can be written in a compact matrix form as

$$A \tilde{\epsilon} = -i\overline{V}_{42} n_o B' + i\overline{V}_{42} n_p B'', \tag{27}$$
where we introduced the matrix $A$,

$$A = \begin{pmatrix}
    \Gamma + i\omega_{42} & i\rho_{12} & -i\rho_{43} & 0 \\
    i\rho_{21} & \Gamma + i(\omega_{42} - \Omega_1) & 0 & -i\rho_{43} \\
    -i\rho_{34} & 0 & \Gamma + i(\omega_{42} + \Omega_2) & i\rho_{12} \\
    0 & -i\rho_{34} & i\rho_{21} & \Gamma + i(\omega_{42} - \Omega_1 + \Omega_2)
\end{pmatrix}, \quad (28)
$$

and the vectors,

$$\vec{\epsilon} = (\epsilon_{42}, \epsilon_{41}, \epsilon_{32}, \epsilon_{31})^T, \quad B' = (\rho_{22}, \rho_{21}, 0, 0)^T, \quad B'' = (\rho_{44}', 0, \rho_{34}', 0)^T. \quad (29)$$

The matrix element $\epsilon_{42}$ that determines the isomer conversion can be calculated from Eq. (27),

$$\epsilon_{42} = -i\tilde{V}_{42}n_o(A^{-1}B')_1 + i\tilde{V}_{42}n_p(A^{-1}B'')_1. \quad (30)$$

Substitution of $\epsilon_{42}$ into Eq. (24) gives

$$\frac{\partial n_p}{\partial t} = n_o|\tilde{V}_{42}|^2F_o - n_p|\tilde{V}_{42}|^2F_p,$$

$$F_o = 2Re(A^{-1}B')_1, \quad F_p = 2Re(A^{-1}B'')_1. \quad (31)$$

Because of the conservation of the total molecular density $N$, one has $n_o = N - n_p$ which allows us to transform Eq. (31) into its final form,

$$\frac{\partial n_p}{\partial t} = -|\tilde{V}_{42}|^2(F_o + F_p)n_p + |\tilde{V}_{42}|^2F_oN. \quad (32)$$

Here, we have assumed equal Boltzmann factors $W_2$ and $W_4$ and, consequently, equal equilibrium densities of ortho and para molecules, $n_o(0) = n_p(0) = N/2$, at $t = 0$, when the external field was switched on. The solution to Eq. (32) can be written as the sum of the time-independent part $\pi_p$ and the time-dependent part $\delta n_p(t)$,

$$\pi_p = \frac{F_o}{F_o + F_p}N; \quad \delta n_p(t) = \left(\frac{N}{2} - \pi_p\right)e^{-\gamma t}, \quad (33)$$

where the isomer conversion rate,

$$\gamma = |\tilde{V}_{42}|^2(F_o + F_p). \quad (34)$$

The steady state enrichment of the para molecules produced by the bichromatic field reads

$$\beta_p = 2\pi_p/N - 1. \quad (35)$$

It should be noted that the isomer enrichment (35) does not depend on $\tilde{V}$. This is a consequence of the assumption made in the model that there is only one channel of ortho-para tunneling.

6. The isomer enrichment

The resonant bichromatic field affects the densities of the ortho and para molecules and the conversion rate, $\gamma$. Below we will present the results of numerical calculations of the radiation-induced enrichment of the isomers. Where possible, the numerical parameters of the model will be chosen in such a way as to mimic the typical cases of isomer conversion in polyatomic molecules (see, for example, [16]). We will use the following set of parameters,

$$\Gamma = 3 \text{ MHz}, \quad \nu = 0.1\Gamma, \quad \tilde{V}_{24} = 0.01 \text{ MHz}, \quad g_{21} = g_{34} = 10 \text{ MHz}, \quad \omega_{42} = 200 \text{ MHz}, \quad W_2 = W_4 = 1 \cdot 10^{-2}, \quad W_1 = W_3 = 1.2 \cdot 10^{-2}. \quad (36)$$
The values chosen for $\Gamma$ and $\nu$ correspond to the particular case of CH$_3$F molecules at the gas pressure 0.1 Torr. The free conversion rate $\gamma_0$ (without an external field) calculated with the help of Eq. (3) using the parameters (36) is equal to $2 \cdot 10^{-3}$ s$^{-1}$. This value is close to the conversion rate of $^{13}$CH$_3$F isomers at the gas pressure 0.1 Torr.

The dependence of the enrichment of para molecules on the frequency $\Omega_1$ at various frequencies $\Omega_2$ is presented in Fig. 3. For all values of $\Omega_2$ (except for the particular case $\Omega_2 = -200$ MHz, shown in Fig. 4), the dependence consists of three peaks. The wide peak at $\Omega_1 = 0$ can be associated with the population change of level $|2\rangle$ produced by the field $E_1$. Population of this ortho state is transferred to the para state $|4\rangle$ by the intramolecular perturbation $\hat{V}$. The width of the wide peak is 55 MHz (HWHM). It is close (but not equal) to the power-broadened transition width $\Gamma_o = 63.3$ MHz. On the other hand, we have checked that the absorption line width of the field $E_1$ in our model is equal to $\Gamma_o$.

There are two narrow peaks in the curves of Fig. 3. Their physical nature can tentatively be explained as follows. The field $E_1$ ($E_2$) splits the level $|2\rangle$ ($|4\rangle$) into two sublevels having the energies [18],

\begin{equation}
E_{2,\pm} = E_2 + \frac{\hbar}{2} \left( \Omega_1 \pm \sqrt{\Omega_1^2 + 4|g_{21}|^2} \right),
\end{equation}

and

\begin{equation}
E_{4,\pm} = E_4 + \frac{\hbar}{2} \left( \Omega_2 \pm \sqrt{\Omega_2^2 + 4|g_{43}|^2} \right).
\end{equation}

Crossing of the level $E_{2,+}$ with the levels $E_{4,+}$ and $E_{4,-}$ produces the two narrow peaks in the isomer enrichment shown in Fig. 3. The width of the peak at $\Omega_1 \simeq \omega_{42}$ is 10 MHz. The width
of the peak at $\Omega_1 \simeq \omega_{12} + \Omega_2$ is $\simeq 4.3$ MHz. For the chosen parameters (36), the sign of this peak is positive (that is enrichment of para molecules) at $\Omega_2 > -\omega_{12}/2$, but becomes negative (depletion of the para molecules) at $\Omega_2 < -\omega_{12}/2$. For the case where $\Omega_2 = 0$ shown in Fig. 3, we can see from Eqs. (37) and (38) that the Stark split doublet appears at $\Omega_1 = \omega_{12} \pm |g_{43}|$.

A special case takes place at $\Omega_2 = -200$ MHz, Fig. 4. Here, there are only two peaks. The peak at $\Omega_1 = 0$ has a narrow triangular shape whereas the peak at $\Omega_1 = 200$ MHz has a width equal to $\simeq 4.3$ MHz. A similar triangular shape has been reported but in a different context [19]. It was fitted to an arctan function.

![Graph](image)

Figure 4. Dependence of the enrichment of para molecules $\beta_p$ on the frequency of the first field $\Omega_1$ at the frequency of the second field $\Omega_2 = -200$ MHz.

7. Conclusions
We have proposed a theoretical model for molecular spin isomer enrichment produced by two electromagnetic fields resonant with the molecular rotational transitions. Numerical calculations revealed richer enrichment spectra than in the case of one field [10]. In addition, our model predicts the existence of more narrow peaks in the enrichment spectra than in the case of one field excitation.

The maximum enrichment of the para molecules achieved for the parameters (36) is $\simeq 8\%$. This enrichment appears to be of the same order of magnitude as that created by one field. Thus there seems to be no advantage in using two fields rather than one for getting greater isomer enrichment. The main difference between the schemes explored here and those studied in atomic laser physics is that, in those systems, all the population can be trapped in the lower levels even although the electromagnetic fields are resonant with the one-photon transitions. In the molecular spin isomers considered here, the rotational levels that interact with the electromagnetic fields are part of a large manifold of levels and the rotational relaxation produces fast thermalization of the rotational level populations.

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