Rotational master equation for cold laser-driven molecules

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The equations of motion for the molecular rotation are derived for vibrationally cold dimers that are polarized by off-resonant laser light. It is shown that, by eliminating electronic and vibrational degrees of freedom, a quantum master equation for the reduced rotational density operator can be obtained. The coherent rotational dynamics is caused by stimulated Raman transitions, whereas spontaneous Raman transitions lead to decoherence in the motion of the quantized angular momentum. As an example the molecular dynamics for the optical Kerr effect is chosen, revealing decoherence and heating of the molecular rotation.

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I. INTRODUCTION

Nonlinear optics, as commonly understood, describes the effects of nonlinear media on the optical field via susceptibilities, that are derived by a perturbative approach [1]. It is assumed in this context, that the medium can be treated as being stationary, which is well justified for thermalized samples. The medium may be specifically composed of atoms, molecules or may be implemented as a solid-state device, such as a semiconductor. The change of the quantum state of that physical system during the light–matter interaction is however largely neglected in the nonlinear optics literature, naturally since the focus lies on the properties of the light. Clearly the treated problem is a coupled one, where a description by susceptibilities is the outcome of a decoupling of medium and quantum system under the influence of the applied laser field [2]. In the latter case the scattered radiation is of minor importance, only its effect on the atomic dynamics by absorption and subsequent stimulated and spontaneous emissions of photons is taken into account. Thus the ancillary medium of nonlinear optics becomes the central issue.

Focusing on the atomic or molecular dynamics however requires a treatment of physical conditions that are more general than those usually considered in nonlinear optics. For instance, if significant dynamics emerge, non-stationary initial quantum states and/or sufficiently strong coherent laser drives prevail. For atoms such situations have been reached in several implementations, the majority of them by providing low temperatures and atom–light coupling strengths comparable or larger than spontaneous decay rates. Prominent examples are atoms in high-Q microwave [3, 4, 5] or optical [6] cavities and single ions in radio-frequency traps [7, 8].

Recent advances in trapping and cooling of atomic [6, 10, 11, 12, 13] and molecular [14, 15, 16, 17, 18] gases, progressively give access to the quantum-statistical properties and quantum dynamics of the manipulated gases. The question therefore arises as to how the quantum state of molecular gases, for example, can be manipulated by nonlinear optical interactions or how some of its properties can be revealed from the nonlinear optical spectra. For this purpose it is necessary to go beyond standard calculations of nonlinear optics, in order to treat not only the optical-field dynamics, but to focus on the dynamics of the molecular system.

A first step towards such considerations is the study of the rotational dynamics of molecules that interact with off-resonant laser fields. Since dimers have no permanent dipole moment, they are infrared inactive and thus the rotational dynamics is expected to be to large extent undamped. However, the polarizability of the molecule enables two-photon transitions and it will be shown here that these may in fact lead to decoherence in the rotational dynamics.

Another aspect makes this issue particularly interesting. Consider ultracold molecules in a trap that is based on off-resonant optical fields, such as a dipole trap [15]. Assuming the molecules are cool enough to form a degenerate Bose gas, the lifetime of this peculiar quantum state is of major interest. As we will see here, off-resonant laser fields lead to a decoherence in the rotational quantum state, meaning that after some time the initial rotational quantum state evolves into a statistical mixture of differing angular-momentum states. In that case one may expect that also the degenerate condensate state of molecules will be destroyed.

In this paper we derive the basic equations of motion that describe the molecular rotational dynamics. We will focus on homonuclear, diatomic molecules interacting with both weak, off-resonant laser fields and electromagnetic vacuum modes. In such a configuration, besides the typical elastic Rayleigh scattering, stimulated and spontaneous Raman scattering processes occur that affect the molecular, ro-vibrational quantum state and may lead to decoherence. We derive a master equation that includes these processes for studying rotational decoherence, which may play an important role in the context of recent experiments with ultracold molecules [18]. The theory is applied to the optical Kerr effect, for which we solve the master equation by means of quantum trajectories.

The paper is structured as follows: In Sec. I the physical situation under study is explained and the basic equations for
the molecule-light interaction are given. Sec. III is devoted to the adiabatic elimination of electronically excited states. In Sec. IV the trace over the vibrational degree of freedom is performed, leading to the reduced rotational master equation. It is solved in Sec. V for the case of an optical Kerr interaction and the damping and decoherence effects in the rotational degree of freedom are illustrated. Finally in Sec. VI a summary and conclusions are given.

II. MOLECULE-LIGHT INTERACTION

We consider a cold, homonuclear molecule interacting with a light pulse detuned from possible resonances connected with electronic-state transitions of the type $^1\Sigma \leftrightarrow ^1\Sigma$. More precisely, the molecule is assumed to be initially in its electronic ground-state potential with a given distribution of populations among the ro-vibrational states. The laser field is then considered to be off-resonant, if all allowed ro-vibrational transitions from this distribution to excited electronic states are off-resonant, cf. Fig. 1. In this way two-photon Raman transitions dominate the dynamics and we consider in the following stimulated as well as spontaneous Raman processes.

Since electronic, vibrational and rotational transition frequencies are different from each other by orders of magnitude, 

$$\omega_{eg} \gg \omega_\nu \gg B, \quad (1)$$

the dynamics reveals a separation of timescales. In Eq. (1) $\omega_{eg}$ is the bare transition frequency between the ground and nearest (dipole-allowed) excited electronic potential minima. The frequencies $\omega_\nu$ and $B$ are the typical vibrational frequency and the rotational constant, respectively. To avoid vibrational Raman transitions the spectral width $\Delta \omega$ of the laser pulse obeys then the requirement

$$\Delta \omega \ll \omega_\nu, \quad (2)$$

and is typically of the order of rotational frequencies: $\Delta \omega \sim B$. Typically we may think of the laser field as being bichromatic for addressing particular rotational transitions, though also more general spectra are possible. Note, that condition (2) is contrary to the situation in vibrational wavepacket creation by ultrashort laser pulses [25].

We assume the molecule being located at a fixed position and omit its center-of-mass coordinate. Thus with respect to its center of mass a point-like molecule is considered. However, our derivations can in principle be extended to include the quantum mechanical center-of-mass motion of the molecule. This extension would apply for describing molecular beam deflection [19, 20] and would extend the purely coherent treatment [21] by including spontaneous processes.

We start with the general dynamical equations of a molecule interacting with a generic laser field and spontaneously emitting photons into the vacuum electromagnetic reservoir. The master equation for the density operator of electronic, vibrational and rotational degrees of freedom $\hat{\rho}$ can be written as

$$\dot{\hat{\rho}} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] + \hat{L}_s \hat{\rho}. \quad (3)$$

The time-dependent Hamiltonian reads

$$\hat{H}(t) = \hat{H}_M + \hat{H}_{ML}(t), \quad (4)$$

where $\hat{H}_M$ is the free Hamiltonian of the molecule and $\hat{H}_{ML}(t)$ describes the interaction of the molecule with the applied classical laser field.

The Hamiltonian of the molecule can be written in the form

$$\hat{H}_M = \sum_g \hbar \omega_g |g\rangle \langle g| + \sum_e \hbar \omega_e |e\rangle \langle e|, \quad (5)$$

where $|g\rangle$ and $|e\rangle$ are short-hand notations for ro-vibrational energy eigenstates in the ground and excited electronic potentials, respectively,

$$|g\rangle = |g, \nu_g, j_g, m_g\rangle, \quad |e\rangle = |e, \nu_e, j_e, m_e\rangle. \quad (6)$$

Our derivation applies to general molecular energy spectra. Only the ro-vibrational coupling needs to be neglected here. This coupling has been shown to lead to a decohering effect in the vibrational motion [22, 23] and thus can be expected to produce decoherence also in the rotational degree of freedom. It appears, however, on a much larger timescale compared with the rotational frequencies and can be neglected if the molecule is and stays vibrationally cold during the interaction. Spontaneous Raman processes lead to a diffusion in the vibrational state, which may heat the vibrational degree of freedom. The diffusion rate, however, is small enough.
for being neglected. In simplest approximation, for example, assuming a harmonic inter-nuclear vibration and taking into account only lowest-order rotational contributions, the eigen-
frequencies could be given as

\[ \omega_g = s \omega_{e,g} + B_g j_g (j_g + 1), \]
\[ \omega_e = s \omega_{e,g} + B_e j_e (j_e + 1). \]

Here \( \omega_{e,g} \) are the vibrational frequencies in the ground and excited electronic potential, and \( B_g, B_e \) are the rotational constants in these electronic states.

Turning back to Eq. (4), the interaction of the molecule with the applied laser field \( \mathbf{E}(t) \) reads

\[ \dot{H}_{\text{int}}(t) = -\mathbf{d} \cdot \mathbf{E}(t), \]

where \( \mathbf{d} \) is the dipole operator of the single molecule. The laser field can be decomposed into slowly varying positive and negative frequency components \( \mathbf{E}^{(\pm)}(t) \) by using the ansatz

\[ \mathbf{E}(t) = \mathbf{E}^{(+)}(t) e^{-i \omega_0 t} + \mathbf{E}^{(-)}(t) e^{i \omega_0 t}, \]

where \( \omega_0 \) is the mid frequency of the laser pulse. Then the vector amplitudes \( \mathbf{E}^{(\pm)}(t) \) oscillate only at a maximum frequency given by the spectral width \( \Delta \omega \), which is of the order of rotational frequencies.

The incoherent part of the master equation (3) describes spontaneous emissions of photons into the vacuum electromagnetic reservoir and is given by the Liouville operator \( \hat{L}_\text{a} \).

For the interaction with an off-resonant laser pulse the laser field can be decomposed into slowly varying positive and negative frequency components \( \mathbf{E}^{(\pm)}(t) \) by using the ansatz

\[ \dot{\hat{L}}_\text{a} \dot{\hat{\sigma}} = \sum_{i=1}^3 \sum_{ab} \sum_{a'b'} |a\rangle \langle b| \delta(\omega_{ab} - \omega_{a'b'}) \times \left[ (a|\gamma_i|a') \langle b'|\gamma_i|b \rangle - \frac{1}{2} (a|\gamma_i^2|a') \langle b'|\gamma_i^2|b \rangle - \frac{1}{2} (a'|\gamma_i^2|b') \langle b|\gamma_i^2|a \rangle \right]. \]

The function \( \delta(\omega - \omega') \) is a quasi delta function that ensures energy conservation \( \omega \approx \omega' \) for optical frequencies,

\[ \delta(\omega) = \begin{cases} 1 & \text{for } |\omega| \ll \omega_0, \\ 0 & \text{else.} \end{cases} \]

It selects resonant terms resulting from the performed secular approximation. Furthermore, the notation

\[ \omega_{ab} = \omega_a - \omega_b \]

denotes transition frequencies between the ro-vibronic molecular states \( |a\rangle \) and \( |b\rangle \) \((a, b = g, e)\).

The operators \( \gamma_i \) reflect the spontaneous emission of a photon due to molecular dipole moment pointing into direction \( i \). That is, \( i \) labels the polarization of the spontaneously emitted photon. These operators are defined as

\[ \gamma_i = \kappa \hat{d}_i, \]

where \( \kappa \) is a vector component of the dipole moment and

\[ \kappa = \sqrt{\frac{\omega_{e,g}^3}{3\pi c^2 \epsilon_0 \hbar}}. \]

For Eq. (15) tiny modifications due to ro-vibrational frequencies have been neglected, since they are much smaller than the bare (optical) electronic transition frequency \( \omega_{e,g} \).

Note that the Liouville operator (11) looks different from the usual cases considered in standard quantum-optical systems, such as two-level atoms. This is only due to the energetic degeneracy with respect to the rotational quantum number \( m \). To properly account for this degeneracy we have to allow for subtle coherent effects: Starting from a ro-vibronic state \( |e, \nu_e, j_e, m_e \rangle \), the spontaneous emission of a photon of frequency \( \omega \) may leave the molecule in a coherent superposition of ro-vibronic quantum states \( |g, \nu_g, j_g, m_g \rangle \) with a unique value for \( \nu_g \) and \( j_g \) but multiple values \( m \in [-j_g, j_g] \) according to the selection rules.

Given the dynamical equation (6) of the molecule interacting with the off-resonant laser pulse, in the following sections we will derive a master equation for the reduced rotational density operator \( \hat{\sigma} \), of the form

\[ \dot{\hat{\sigma}} = i \frac{\hbar}{\mathcal{L}} [\hat{H}_\text{in} + \hat{H}_\text{R}, \hat{\sigma}] + \hat{L}_{\text{rad}} \hat{\sigma}. \]

The effective two-photon Hamiltonian \( \hat{H}_\text{R} \) will contain the coherent drive due to optically stimulated rotational Raman transitions. It contains the polarizability tensor of the molecule and the classical laser field. The incoherent effects due to spontaneous Raman scattering will be described by the Liouville operator \( \hat{L}_{\text{rad}}(t) \).

## III. ELIMINATION OF EXCITED ELECTRONIC STATES

For the interaction with an off-resonant laser pulse the molecule is hardly driven from the ground electronic potential surface into the excited one. This applies, given that not too high vibrational levels are populated, which is the case for cold molecules as considered here. Thus the electronically excited states \( |e\rangle = |e, \nu_e, j_e, m_e \rangle \) can be adiabatically eliminated to second-order in the molecule-light coupling. For this purpose we start with the coupled equations of motion of density-matrix elements, derived from the master equation (3)

\[ \dot{\rho}_{gg'} = -i \omega_{gg'} \rho_{gg'} + i \sum_e \left[ \Omega_{eg} \rho_{ee'} e^{i \omega_0 t} - \rho_{ee'} \Omega_{eg}^* e^{-i \omega_0 t} \right] + \sum_{i} \sum_{ee'} \gamma_{i,ge} \rho_{ee'} \gamma_{i,ge'}^*, \]

\[ \dot{\rho}_{ee'} = -i \omega_{ee'} \rho_{ee'} + i \sum_g \left[ \Omega_{eg} \rho_{ee'} e^{i \omega_0 t} - \rho_{ee'} \Omega_{eg}^* e^{-i \omega_0 t} \right] - \Gamma \rho_{ee'}, \]

\[ \dot{\rho}_{eg} = -i \omega_{eg} \rho_{eg} + i \sum_{g'} \Omega_{eg} \rho_{g'g} e^{i \omega_0 t} - i \sum_{e'} \Omega_{eg} \rho_{ee'} e^{-i \omega_0 t} - \frac{1}{2} \Gamma \rho_{eg}, \]
and \( \hat{q}_{ge} = \hat{q}_{eg}^\ast \). Here \( \hat{q}_{ab} \) are the matrix elements of the density operator in energy eigenstates

\[
\hat{q}_{ab} = \langle a | \hat{q} | b \rangle = \langle a, \nu_a, j_a, m_a | \hat{q} | b, \nu_b, j_b, m_b \rangle \quad (a, b = g, e),
\]

and \( \gamma_{i,ge} \) are the matrix elements of the spontaneous-emission operators \( \hat{\gamma}_i \):

\[
\gamma_{i,ge} = \langle g | \hat{\gamma}_i | e \rangle.
\]

Furthermore, in Eqs (18) and (19) the total decay rate \( \Gamma \) is defined as

\[
\Gamma = \sum_i \sum_g \gamma_{i,ge}^\ast \gamma_{i,ge} = \kappa^2 d^2 = \frac{d^2 \omega_{eg}^3}{3 \pi e^3 c_0 \hbar},
\]

with \( d \) being the matrix element of the dipole moment of the considered electronic transition (cf. App. A). Finally, the time-dependent single-photon Rabi frequencies \( \Omega_{eg}(t) \) are defined as

\[
\Omega_{eg}(t) = \frac{1}{\hbar} \langle e | d | g \rangle \cdot \mathbf{E}(+) (t).
\]

They are slowly varying at frequencies given by the spectral width \( \Delta \omega \) of the laser pulse.

We now formally integrate the equation of motion for the electronic coherences, Eq. (19), from an initial time \( t' \) to a later time \( t \), that obey the condition

\[
\frac{1}{\Delta} \ll t - t' \ll \frac{1}{\Omega}, \frac{1}{\Gamma},
\]

and insert the obtained solutions into the equation of motion for the ground-state populations, Eq. (17). We consistently keep only terms up to second-order in the molecule-light interaction. Defining the slowly varying density-matrix elements \( \tilde{q}_{ab}(t) \),

\[
\tilde{q}_{ab}(t) = \tilde{q}_{ab}(t) e^{-i \omega_{0,t}^g t},
\]

the approximation \( \tilde{q}_{ab}(t - \tau) \approx \tilde{q}_{ab}(t) \) can be performed for times \( \tau \) within the integration interval \( t - t' \). From this procedure the equation of motion for the electronic ground-state manifold is obtained,

\[
\begin{align*}
\hat{q}_{gg'} &= -i \omega_{gg'} q_{gg'} + \sum_{i, e} \sum_{e'} \gamma_{i,ge}^\ast \bar{q}_{ee'} \gamma_{i,e'g'} + \left\{ \sum_{e' u} \Omega_{e'g'}^u(t) \left[ \sum_{e'} \hat{r}_{e'e''}^u(t) e^{-i \omega_{e''} t} \int_0^{t-t'} d\tau \, \Omega_{e''g'}^u(t-\tau) e^{i (\omega_{0,t} - \omega_{e''}) t} \frac{\Delta^2}{\Gamma^2} \right] e^{i (\omega_{0,t} - \omega_{e''}) t} - (c.c. and g \leftrightarrow g') \right\} .
\end{align*}
\]

The time dependent Rabi frequencies \( \Omega_{eg}(t) \) oscillate much slower than the molecular vibrational frequencies since \( \Delta \omega \ll \omega_{\nu,g/e} \). They are slowly varying as compared to the oscillating exponentials in the integrals, that on average oscillate with the bare laser detuning defined by

\[
\Delta = \omega_0 - \omega_{eg}.
\]

Thus \( \Omega_{eg}(t - \tau) \approx \Omega_{eg}(t) \) for the time integrations and therefore the Rabi frequencies can be taken outside the integral. After performing the remaining integrations and neglecting all remaining terms that oscillate with frequencies of the order of the detuning \( \Delta \) or the vibrational frequency \( \omega_{\nu,g/e} \), we obtain

\[
\begin{align*}
\hat{q}_{gg'} &= -i \omega_{gg'} q_{gg'} + \sum_{e g'} \left[ q_{gg'} \delta_{\nu_g \nu_{g'}} \Omega_{eg'}^\ast(t) \Omega_{eg}(t) \Delta^2 \left( -i \Delta - \frac{1}{2} \Gamma \right) + (c.c. \text{ and } g \leftrightarrow g') \right] \\
&\quad + \sum_{e e'} \left[ \sum_{g g'} \gamma_{i,ge}^\ast \gamma_{i,e'g'} + \delta_{\nu_{g} \nu_{e'}} \right] \Omega_{eg}^\ast(t) \Omega_{e'g}(t) \Delta^2 \left( -i \Delta - \frac{1}{2} \Gamma \right) .
\end{align*}
\]

Here \( \nu_g \) and \( \nu_e \) are the numbers of vibrational quanta in the ground and excited electronic potentials, respectively, and the Kronecker delta \( \delta_{\nu_g \nu_{g'}} \) and \( \delta_{\nu_{e} \nu_{e'}} \) result as resonances from the rotating-wave approximation. This rotating-wave approximation with respect to vibrational frequencies holds here because we will consider from now on only density-matrix elements diagonal in the vibrational quantum numbers (in Eq. (28) \( \nu_g = \nu_{g'} \)). Those matrix elements do not freely os-
cillate with vibrational frequencies and since also the electric-field spectrum is narrower, they evolve on a slow timescale given by the Raman drive. Moreover, we have neglected small variations of the detuning due to ro-vibrational frequencies, since in the far off-resonant case considered here we may safely assume the condition

$$\Delta \gg \omega_{g/e} B_{g/e}. \tag{29}$$

Considering a laser pulse that is well off-resonant to the electronic transition means also that the bare detuning is larger than the natural linewidth of the dipole transition by orders of magnitude, i.e.,

$$\Delta \gg \Gamma. \tag{30}$$

Since for the case of a homonuclear molecule typically $B_{g/e} \gg \Gamma$, for the matter of consistency the original denominators in Eq. (28) have been further approximated by use of $[\Delta^2 + (\Gamma/2)^2]^{-1} \approx \Delta^{-2}$.

Equation (28) is still coupled to the electronically excited states $\rho_{ee'\nu}$. Thus, the manifold of density-matrix elements of electronically excited states is required. Performing the same procedure as for arriving at Eq. (28) for the electronically excited states, we obtain from Eqs (18) and (19),

$$\rho_{ee'\nu} = \sum_{gg'} \rho_{gg'} \sigma_{\nu g' \nu} \frac{\Omega_{e g}(t) \Omega_{e g'}(t)}{\Delta^2} \cdot \tag{31}$$

Again this result is accurate to second-order in the molecule-light interaction and is valid for matrix elements diagonal in the vibrational degree of freedom ($\nu_e = \nu_{e'}$). This term represents the excitation of the excited state from the electronic ground-states by absorption of a laser photon.

Inserting (31) into (28) and omitting terms of order higher than second in the molecule-light coupling, we arrive at the master equation for the consistently decoupled electronic ground-state manifold ($\nu_g = \nu_{g'}$)

$$\dot{\rho}_{gg'} = -i\omega_{g g'} \rho_{gg'} + \sum_{e e'} \rho_{gg'} \sigma_{\nu e \nu} \frac{\Omega_{e g}(t) \Omega_{e g'}(t)}{\Delta^2} \left(-i\Delta - \Gamma \right) + (c.c. \text{ and } g \leftrightarrow g') + \sum_i \sum_{e e'} \rho_{gg'} \sigma_{\nu e \nu} \frac{\Omega_{e g}(t) \Omega_{e g'}(t)}{\Delta^2} \gamma_{i,e} \gamma_{i,e'} \cdot \tag{32}$$

This equation of motion describes the effects of spontaneous and stimulated Raman scattering processes on the dynamics of the ro-vibrational quantum state of the molecule. It represents a consistent approximation to second-order in the molecule-light coupling and preserves the trace of the density operator of the ground-state manifold:

$$\sum_g \dot{\rho}_{gg} = \sum_{\nu_{e_j}, m_g} \langle g, \nu_{g}, j_g, m_g | \dot{\rho} | g, \nu_{g}, j_g, m_g \rangle = 0 \cdot \tag{33}$$

Note, that the eigenfrequencies $\omega_{g}$, that appear in Eq. (32) as transition frequencies $\omega_{gg'} = \omega_{g} - \omega_{g'}$, only depend on the quantum numbers $\nu_{g}$ and $j_{g}$, i.e.,

$$\omega_{g} \rightarrow \omega_{\nu_{g} j_{g}}, \tag{34}$$

which is due to the energetic degeneracy with respect to the rotational quantum number $m_{g}$.

IV. ELIMINATION OF INTER-NUCLEAR VIBRATION

Now the vibrational degree of freedom has to be eliminated to obtain the reduced dynamics of the molecular rotation. We intend to obtain an equation of motion for the reduced rotational density operator $\hat{\sigma}$, with matrix elements

$$\sigma_{j m, j' m'} = \langle j m | \hat{\sigma} | j' m' \rangle, \tag{35}$$

by tracing the electronic ground-state density matrix $\rho_{gg'}$ over the vibrational degree of freedom,

$$\sigma_{j m, j' m'} = \sum_{\nu_{g}} \langle g, \nu_{g}, j, m | \rho | g, \nu_{g}, j', m' \rangle \cdot \tag{36}$$

For notational convenience we have omitted here the electronic-ground-state subscript $g$ for the rotational quantum numbers: $j_g, m_g \rightarrow j, m$.

In Franck–Condon approximation the dipole operator is independent of the inter-nuclear distance and therefore does not act in the Hilbert space of the vibrational degree of freedom. Then the Franck–Condon factors, being overlap integrals of vibrational wavefunctions in the ground and excited electronic potentials $\langle \nu_{g} | \nu_{e} \rangle$, will naturally emerge. Whereas, due to the narrow spectrum of the laser pulse, the stimulated Raman process only drives rotational transitions, spontaneous Raman scattering is accompanied by all possible vibrational Franck–Condon transitions. However, performing in Eq. (32) the trace over the vibrational quantum number $\nu_{g}$ ($\nu_{g'} = \nu_{g}$), it comes out that completeness relations of vibrational states can be used, so that combinations of Franck–Condon factors are summed over to result as unity. Thus it is possible to obtain an equation of motion for the rotation alone, that is no longer coupled to the vibrational dynamics.

After having performed the sum over the number of vibrational quanta, the resulting master equation for the reduced
rotational density matrix can be written in the following Lindblad form
\[
\dot{\sigma} = \frac{i}{\hbar} [\hat{H}_M + \hat{H}_R(t), \sigma] + \sum_i \left[ \hat{S}_i(t) \sigma \hat{S}_i(t) - \frac{1}{2} \hat{S}_i(t) \dot{\sigma} \hat{S}_i(t) - \frac{1}{2} \dot{\sigma} \hat{S}_i(t) \hat{S}_i(t) \right],
\]
represented by Eq. (37), that describes the stimulated rotational Raman transitions, inherent in the master equation (37), is fixed with the ratio
\[
\frac{\nu}{\nu_e} = \frac{\nu}{\nu_e} \frac{\sigma}{\sigma_e}.
\]
This shows that the ratio of spontaneous and stimulated Raman processes via the time dependent spontaneous Raman operator
\[
\hat{S}_i(t) = \frac{\kappa}{\hbar \Delta} \sum_{j_e, m_e} \hat{d}_j |j_e, m_e \rangle \langle j_e, m_e| \hat{d}_j \cdot \hat{E}^{(+)}(t),
\]
with \(\kappa\) being defined in Eq. (38). From the derivation of Eq. (39) it comes out that the Raman Hamiltonian (38) and the operator (39) are related by
\[
\sum_i \hat{S}_i(t) \hat{S}_i(t) = -\frac{\Gamma}{\hbar \Delta} \hat{H}_R(t).
\]
This shows that the ratio of spontaneous and stimulated Raman processes, inherent in the master equation (37), is fixed by the ratio \(\Gamma/\Delta\) and is independent of the laser intensity. Thus the laser field must be detuned by several natural linewidths from the electronic resonance to diminish spontaneous processes compared to stimulated ones.

A critical issue for the validity of our approach is given by the fact that we assume a far off-resonant laser field. Clearly spontaneous Raman scattering will lead to a diffusive broadening of the vibrational statistics that will slowly populate higher lying vibrational states. For our calculation to be valid, we do not have to assume that this process is negligible during the laser pulse duration. But we have to assume that this process will not populate higher lying vibrational states, that may eventually be subject to resonant transitions into an electronically excited state.

For estimating the increase of vibrational excitation during the laser interaction, a rate equation for the vibrational populations \(P_\nu\) can be derived by omitting the rotational degrees of freedom. It reads
\[
\dot{P}_\nu = \frac{\Omega_R \Gamma}{\Delta} \sum_{\nu'} P_{\nu'} \left( \sum_{\nu_e} |\langle \nu|\nu_e \rangle\langle \nu_e|\nu'\rangle|^2 - \delta_{\nu\nu'} \right),
\]
where the laser-coupling strength is determined by the two-photon Raman Rabi frequency,
\[
\Omega_R = \frac{|\mathbf{d} \cdot \mathbf{E}^{(+)}|^2}{\hbar^2 \Delta}.
\]
The Franck–Condon factors \(\langle \nu'|\nu_e \rangle\) for transitions between vibrational state \(|\nu\rangle\) and \(|\nu_e\rangle\) of the ground and excited electronic states, respectively, determine the strengths of spontaneous Raman scatterings between vibrational states in the electronic ground-state potential.

For vibrationally cold molecules, the internuclear potentials in the ground and excited electronic states may be approximated by harmonic potentials, whose centers are shifted by \(\Delta x\). Neglecting further the difference of vibrational frequencies in ground and excited electronic states, the Franck–Condon factors simplify to overlap integrals of shifted vibrational eigenstates. Starting from the vibrational ground state, the average vibrational excitation and variance can then be found from Eq. (41), as \(\nu(t) = gt\) and \(\Delta\nu^2(t) = \langle g^2(t) + \frac{1}{\eta^2}\rangle\), where \(g = \frac{\xi}{\eta^2} \Omega_R \Gamma/\Delta\) and \(\eta = \Delta x \sqrt{2 \mu \omega / \hbar}\) is the ratio of \(\Delta x\) to the width of the vibrational ground-state, \(\mu\) being the reduced mass.

From the condition \(\omega_E [\tilde{\nu}(t) + \Delta\tilde{\nu}(t)] < \Delta\), which must be fulfilled in order that no resonant single-photon vibronic transitions occur, the valid dimensionless interaction times \(\tau = Bt\), in units of rotational cycles \(B^{-1}\), can be obtained as \(\tau < [B \Delta^2/(\Gamma \omega_E \Omega_R)]\eta^{-2}\). In the weak-field regime, \(\Omega_R < B\), and for large detuning \(\Delta\), the first factor is rather large. Numerical values of \(\eta\) for alkali molecules are from 3.7 for \(^7\text{Li}_2\) up to 8.6 for \(^{133}\text{Cs}_2\). Thus, also the last factor \(\eta^{-2}\) does not severely restrict the range of valid interaction times for our approximations.

V. ROTATIONAL DECOHERENCE IN OPTICAL KERR INTERACTIONS

As an example for the decoherent effects of spontaneous Raman processes and as a first application of the master equation derived here, let us consider a cw monochromatic laser field propagating along the z direction with linear polarization in x direction. This configuration implements an optical Kerr interaction, where \(\sigma_+\) and \(\sigma_-\) polarized field components pick up different phase shifts depending on the rotational state of the molecule. The field is then subject to a rotation of its linear polarization while propagating through the molecular medium. Typically in the treatment of this optical effect the molecular medium is considered as being in a stationary (thermal) state, whereas here we focus on the actual dynamics of the molecule and do not consider the effects on the light field.

Using the quantum-trajectory method, as described in App. [38], we have numerically calculated the dynamics of the
rotational degree of freedom. We start with an initial rotational quantum state that corresponds to an average angular momentum pointing in $y$ direction. It is given by a coherent angular-momentum state, defined as

$$|j, \theta, \phi\rangle = \sum_{m=-j}^{j} \left(\frac{2j-m}{m}\right)^{\frac{1}{2}} [\cos(\theta/2)]^{|j+m|} [\sin(\theta/2)]^{|j-m|} \times e^{im\phi} |j, m\rangle. \quad (43)$$

We take the quantization axis corresponding to the quantum number $m$ as the $z$ axis. For an average angular momentum pointing in $y$ direction we then choose $\theta = \pi/2$ and $\phi = \pi/2$, which are the spherical angles of the average angular momentum. The quantum number $j$ is chosen to be $j = 2$, as an example for a rotationally cold molecule that has been weakly excited.

The numerically solved temporal evolution of the $y$ component of the average angular momentum is shown in Fig. 2. The laser coupling strength is specified here by the two-photon Raman Rabi frequency $\Omega_R$, cf. Eq. (42), which is chosen in units of the rotational constant $B$ as $\Omega_R/B = 0.1$. Moreover, the ratio of detuning to natural linewidth is chosen as $\Delta/\Gamma = 100$, so that electronic transitions for a vibrationally cold molecule are widely suppressed. Nevertheless, rarely occurring spontaneous Raman transitions are important for understanding the origin of decoherence effects, as demonstrated for a Raman-driven trapped ion [26].

Neglecting the spontaneous processes ($\Gamma = 0$) one obtains an oscillation of the average angular momentum as depicted by the dotted line in Fig. 2. In that case the average angular momentum has no projections on the $x$ and $z$ axes, so that a coherent one-dimensional oscillation is observed. The angular momentum changes from positive to negative $y$ projections and vice versa via the $z$ direction. This can be seen in its fluctuations, as shown for the dotted lines in Fig. 3. Whereas, the variance in $x$ direction stays at a constant minimal value, a synchronized exchange of noise is observed in the variances of the angular-momentum projections in $y$ and $z$ directions.

Taking into account the spontaneous Raman scattering of
the laser light that is detuned by 100 natural linewidth, coherent processes are progressively suppressed, cf. solid lines in Figs. 2 and 3. The oscillation of the average angular momentum in \( y \) direction is damped, see Fig. 2. But it should be noted that no average components in \( x \) and \( z \) directions emerge throughout the evolution. Thus the overall coherent dynamics of the average angular momentum remains a one-dimensional oscillation, but it is eventually damped to zero.

On the other hand, fluctuations in overall increase with progressing time and therefore the average free rotational energy, being proportional to \( \langle \hat{J}^2 \rangle \), increases. This heating is caused by the spontaneous emissions of photons with random polarizations and at random times. It is given by the sum of all three variances shown in Fig. 3. Whereas the oscillation depth of the noise in \( y \) and \( z \) directions gradually decreases with a compensating overall decrease of noise in \( y \) and increase of noise in \( z \) directions, there appears a monotonous increase of noise in the \( x \) direction. The latter is due to spontaneous Raman transitions that excite angular momentum in \( x \) direction, but with vanishing mean. Thus the overall rotational energy is subject to heating and increases as shown in Fig. 4.

The decoherence effect of the spontaneous processes can be observed in the purity of the temporally evolving rotational density operator, see Fig. 5. Since any single (experimental) realization of the time evolution is interrupted by spontaneous emissions of photons with random polarizations and at random times, the ensemble average, describing the properties that can be expected from a typical experiment, gradually develops from an initially pure state into a statistical mixture.

VI. SUMMARY AND CONCLUSIONS

In summary we have derived a reduced master equation for the rotation of a small homonuclear molecule for the case of off-resonant laser excitation with pulse lengths larger than the period of the internuclear vibration. Several approximations have been justified and applied for obtaining the sought equations of motion. First the electronically excited states have been adiabatically eliminated by assuming off-resonant laser fields for vibrationally cold molecules. Second the vibrational degree of freedom has been traced over, based on the Franck-Condon approximation.

The obtained rotational master equation describes in its coherent part the interaction of the laser field with the orientation-dependent polarizability tensor of the molecule. This interaction is generated by stimulated Raman processes. The incoherent part, on the other hand, describes the spontaneous Raman processes. The latter lead to a damping of the motion of the angular momentum of the molecule and, more importantly, cause substantial decoherence in the rotational quantum state.

Our resulting master equation is of Lindblad form and can thus be efficiently solved by use of quantum trajectories. For the spontaneous rotational Raman transitions three different quantum jumps can occur, depending on the polarization of the spontaneously emitted photon. The importance of these spontaneous processes has been illustrated for the example of an optical Kerr interaction. Both damping of the rotational motion and quantum decoherence in the rotational state could be shown.

Our results are relevant for ultracold molecules that are to be manipulated by off-resonant laser fields. An example is the interaction of the molecular rotational degree of freedom with the off-resonant laser fields in a dipole trap [14, 15]. One may expect that even for trapping purposes decoherence appears in the rotational quantum state. Considering trapped molecules, our results hold for non-degenerate, non-interacting molecular gases. One may however guess, that the decoherence effects derived here will also emerge for degenerate molecular gases, where a full quantum-field theory applies. In that case one may expect a finite lifetime of, for example, molecular Bose–
Einstein condensates due to off-resonant laser interaction with the molecular rotation, being at the lowest energetic scale.

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APPENDIX A: TOTAL DECAY RATE

For obtaining the total decay rate \( \Gamma \), we start with the calculation of

\[
\Gamma_{ee'} = \sum_i \sum_g \gamma_i^e \gamma_i^{e'} = \sum_i \sum_g \langle e | \hat{d}^\dagger | g \rangle \langle g | \hat{d} | e' \rangle. \tag{A1}
\]

Using the definition \( \| \) we obtain

\[
\Gamma_{ee'} = \kappa^2 \sum_i \sum_g \langle e | \hat{d}^\dagger | g \rangle \langle g | \hat{d} | e' \rangle. \tag{A2}
\]

For a (homonuclear) molecule having no permanent dipole moment, \( \langle g | \hat{d} | g \rangle = \langle e | \hat{d} | e \rangle = 0 \) and thus the replacement,

\[
\sum_g \langle g | g \rangle \rightarrow \sum_g \langle g | g \rangle + \sum_e \langle e | e \rangle = \hat{I},
\]

can be performed, \( \hat{I} \) being the identity operator, to obtain

\[
\Gamma_{ee'} = \kappa^2 \langle e | \hat{d} \cdot \hat{d} | e' \rangle. \tag{A4}
\]

In Franck–Condon approximation the dipole operator does not depend on the internuclear coordinate. Moreover, \( \hat{d} \cdot \hat{d} \) is a scalar that does not affect the rotational degrees of freedom. Therefore, we obtain

\[
\Gamma_{ee'} = \kappa^2 d^2 \delta_{\nu,e} \delta_{j_e,j_{e'}} \delta_{m_e,m_{e'}} = \Gamma_{\nu,e,e'}, \tag{A5}
\]

where \( d \) is the matrix element of the dipole moment of the considered electronic transition \( | g \rangle \leftrightarrow | e \rangle \). The total decay rate \( \Gamma \) reads

\[
\Gamma = \kappa^2 d^2 = \frac{d^2 \omega_{eg}^3}{8 \pi c^3 e_0 \hbar}, \tag{A6}
\]

which is independent of the ro-vibrational state, \( | \nu_e, j_e, m_e \rangle \), in the excited electronic potential.

APPENDIX B: QUANTUM TRAJECTORIES

From Eqs. (38) and (40) an effective non-Hermitian Hamiltonian can be defined as

\[
\hat{H}_{\text{eff}}(t) = \hat{H}_M + \left( 1 + \frac{i}{2 \Delta} \right) \hat{H}_R(t). \tag{B1}
\]

Using this definition the reduced rotational master equation (37) can be rewritten as

\[
\dot{\hat{\sigma}} = -\frac{i}{\hbar} \left[ \hat{H}_{\text{eff}}(t) \hat{\sigma} - \hat{\sigma} \hat{H}_{\text{eff}}(t) \right] + \sum_i \hat{S}_i(t) \hat{\sigma} \hat{S}_i^\dagger(t). \tag{B2}
\]

This equation shows again the interpretation of \( \hat{S}_i(t) \) as being quantum-jump operators that are responsible for spontaneous Raman processes where a photon is emitted with polarization \( \hat{t} \).

Therefore we may simulate quantum trajectories as realizations of single experimental runs by sequential application of the non-unitary evolution operator

\[
\hat{U}_{\text{eff}}(t,t') = \mathcal{T} \exp \left[ -\frac{i}{\hbar} \int_{t'}^t d\tau \hat{H}_{\text{eff}}(\tau) \right], \tag{B3}
\]

where \( \mathcal{T} \) denotes time ordering, and the jump operators \( \hat{S}_i(t) \). That is, starting from the normalized state \( | \psi(t_0) \rangle \) at time \( t_0 \) a quantum trajectory is given by

\[
| \psi(t) \rangle \{(t, i)_n, \ldots, (t, i)_1 \} = \hat{U}_{\text{eff}}(t, t_n) \hat{S}_{i_n}(t_n) \ldots \hat{S}_{i_2}(t_2) \hat{U}_{\text{eff}}(t_2, t_1) \hat{S}_{i_1}(t_1) \hat{U}_{\text{eff}}(t_1, t_0) | \psi(t_0) \rangle, \tag{B4}
\]

where \( (t, i)_k \) denote the time \( t_k \) of a spontaneous Raman transition and the polarization \( i_k \) of the spontaneously emitted photon.

Given the trajectory \( | \psi(t_n) \{ (t, i)_n, \ldots, (t, i)_1 \} \rangle \) right after a spontaneous Raman process at time \( t_n \), the probability for a further spontaneous process to happen at a later time \( t \) is given by

\[
P(t) = 1 - \frac{\langle \psi(t) | \{ (t, i)_n, \ldots, (t, i)_1 \} | \psi(t) | \{ (t, i)_n, \ldots, (t, i)_1 \} \rangle}{\langle \psi(t_n) | \{ (t, i)_n, \ldots, (t, i)_1 \} | \psi(t_n) | \{ (t, i)_n, \ldots, (t, i)_1 \} \rangle} \left[ \frac{1}{\pi \hbar} \int_{t_n}^t d\tau \hat{H}_R(\tau) \right] \langle \psi(t_n) | \{ (t, i)_n, \ldots, (t, i)_1 \} | \psi(t_n) | \{ (t, i)_n, \ldots, (t, i)_1 \} \rangle. \tag{B5}
\]

Drawing a random number \( R \in (0, 1] \) the condition \( P(t) = R \) determines the time \( t = t_{n+1} \) when the next spontaneous process
and $\psi(t_{n+1})\{\langle (t, i)_{n, \ldots, (t, i)_1}\}\rangle$)
$$W_i = \langle \psi(t_{n+1})\{\langle (t, i)_{n, \ldots, (t, i)_1}\}\rangle|\tilde{S}_i(t_{n+1})\tilde{S}_i(t_{n+1})|\psi(t_{n+1})\{\langle (t, i)_{n, \ldots, (t, i)_1}\}\rangle\rangle\rangle$$
(\sum_j\langle \psi(t_{n+1})\{\langle (t, i)_{n, \ldots, (t, i)_1}\}\rangle|\tilde{S}_j(t_{n+1})\tilde{S}_j(t_{n+1})|\psi(t_{n+1})\{\langle (t, i)_{n, \ldots, (t, i)_1}\}\rangle\rangle\rangle)

\begin{equation}
\left\{\begin{array}{c}
x \text{ if } 0 < R' \leq W_x, \\
y \text{ if } W_x < R' \leq W_x + W_y, \\
z \text{ if } W_x + W_y < R' \leq 1.
\end{array}\right.
\end{equation}

According to the chosen polarization $i_{n+1}$ the resulting trajectory is then
$$\langle \psi(t_{n+1})\{\langle (t, i)_{n, \ldots, (t, i)_1}\}\rangle\rangle = \tilde{S}_{i_{n+1}}(t_{n+1})|\psi(t_{n+1})\{\langle (t, i)_{n, \ldots, (t, i)_1}\}\rangle\rangle. \tag{B9}$$

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