Rotational Alignment Decay and Decoherence of Molecular Superrotors

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We present the quantum master equation describing the coherent and incoherent dynamics of a rapidly rotating molecule in the presence of a thermal background gas. The master equation relates the rate of rotational alignment decay and decoherence to the microscopic scattering amplitudes, which we calculate for anisotropic van der Waals scattering. For large rotational energies, we find quantitative agreement of the resulting alignment decay rate with recent superrotor experiments.

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Introduction.—The precise control of molecular rotation dynamics is a challenging task holding the prospect of orientation-resolved metrology, enhancement of chemical reaction rates, and state-selective collision studies [1–3]. Over the past few decades, various techniques have been conceived and established to manipulate the orientation and rotation state of small molecules and nanoparticles [1–5]. Recently, it was demonstrated that optical centrifuge beams [6] can produce rotational wave packets of unprecedentedly high angular momentum [7–13]. The high rotation rates of such *molecular superrotors* [14] were predicted to suppress the rotational-translational energy transfer [15–18], so that their center-of-mass motion can be trapped and buffer-gas cooled without appreciably affecting the rotational population [15,19].

This stability of superrotor rotations with respect to collisions was indeed observed experimentally with nitrogen and oxygen superrotors at ambient conditions [10,12,13,20]. Classical simulations of a gas of superrotors show that, while the high rotation rates are conserved initially, they rapidly relax towards thermal equilibrium once the rotational-translational energy exchange becomes relevant [17,18,21]. With a duration of a few nanoseconds, the initial stage of approximately constant rotation energy is relatively short in state-of-the-art experiments [10], but it is expected to be orders of magnitude longer in high vacuum. Notwithstanding its fundamental relevance and significance for future applications, a microscopic theory that quantitatively describes the initial quantum dynamics of a superrotor in its thermal environment and that predicts the alignment decay and decoherence time is still lacking.

Here we establish the Markovian quantum master equation of a rapidly rotating molecule immersed in a thermal gas. Based on the monitoring approach [22–24], this Lindblad-type equation describes, in terms of the exact scattering amplitudes, how the rotation state of a superrotor loses its alignment and decoheres. The master equation preserves the rotational energy, reflecting the fact that the collisions are approximately elastic due to the high rotation rates of superrotors [15–18]. This is in contrast to orientational decoherence of slowly rotating particles [25–27], which occurs if the molecular orientation barely changes during the scattering process, and to quantum rotational thermalization [28], which describes how the gas induces linear friction and diffusion of the quantized angular momentum vector.

We calculate the rate of initial alignment decay for nitrogen superrotors and find remarkable agreement with experimental data [10]. This demonstrates the predictive power of the theory, which involves no free parameters. The decay rate exhibits a markedly different scaling for large rotational energies than the energy-corrected sudden approximation [10,20,29], a difference that is likely to become observable in future superrotor collision studies. The presented master equation is expected to be instrumental for these experiments, as well as for future sensing and metrology applications with superrotors, whose sensitivity will be ultimately limited by the collisional interaction between the rotor and its thermal environment.

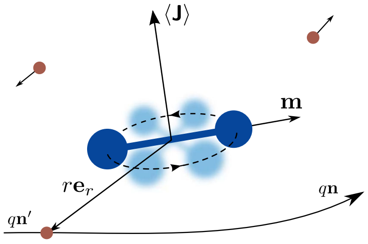

FIG. 1. A rapidly rotating linear molecule (blue) embedded in a homogeneous thermal gas (red) of density n_g and temperature T experiences collisions with environmental gas particles. If the molecule rotates multiple times during the collision, as in the case of superrotors, the interaction with the gas leads to rotational decoherence as well as reorientation of the mean angular momentum $\langle \mathbf{J} \rangle$. The rotor of orientation $\mathbf{m}$ interacts via the attractive van der Waals interaction [Eq. (4)] with a gas particle at distance r, which impinges with relative momentum $q\mathbf{n}'$ and leaves with relative momentum $q\mathbf{n}$.

Master equation.—The dynamics of rotational alignment decay and decoherence can be derived from the monitoring master equation for a massive particle with internal degrees of freedom (d.o.f.) [24]. The latter provides a nonperturbative Markovian quantum master equation for a tracer particle moving and revolving in a thermal environment. The description is based on the microscopic collision rate operator and the scattering matrix of an individual collision between the tracer and a gas particle.

In the present case, we consider a linear rigid rotor of mass M and moment of inertia I revolving in a homogeneous monoatomic gas of density n_g, temperature T, and pressure $p_g = n_g k_B T$, see Fig. 1. For a rapidly rotating molecule, the rotational energy is approximately conserved, since it revolves multiple times during the collision with a gas particle [30], as is also seen in classical simulations [18]. Thus, the scattering rate operator and the scattering matrix are close to diagonal in the total angular momentum quantum number [15,16], an approximation also confirmed in Fig. 2 by the almost unit fraction of j-conserving collisions for large j.

Tracing out the gas and the thermalized center-of-mass motion yields the master equation $\partial_t \rho = -i[\mathsf{H} + \mathsf{H}_g, \rho]/\hbar + \mathcal{D}\rho$ for the rotation state ρ; see Ref. [30]. The free linear-top Hamiltonian is denoted by H. The gas affects the rotor dynamics coherently through the energy shift

$$\mathsf{H}_g = -2\pi\hbar^2 \frac{n_g}{\mu} \int_0^\infty dq q^2 \nu_{\text{th}}(q) \int_{S_2} d^2\mathbf{n} \mathrm{Re}[\mathsf{f}(q\mathbf{n}, q\mathbf{n})] \tag{1a}$$

and incoherently through the Lindblad superoperator

$$\begin{aligned} \mathcal{D}\rho = \frac{n_g}{\mu} \int_0^\infty dq q^3 \nu_{\text{th}}(q) \int_{S_2} d^2\mathbf{n} \int_{S_2} d^2\mathbf{n}' \\ \times \bigg[\mathsf{f}(q\mathbf{n}, q\mathbf{n}')\rho \mathsf{f}^\dagger(q\mathbf{n}, q\mathbf{n}') \\ - \frac{1}{2}\{\mathsf{f}^\dagger(q\mathbf{n}, q\mathbf{n}')\mathsf{f}(q\mathbf{n}, q\mathbf{n}'), \rho\} \bigg]. \end{aligned} \tag{1b}$$

Both contributions (1a) and (1b) are characterized by the thermal distribution of relative momenta $\nu_{\text{th}}(q) = \exp(-q^2/q_{\text{th}}^2)/(\sqrt{\pi} q_{\text{th}})^3$, with the momentum $q_{\text{th}} = \sqrt{2\mu k_B T}$ determined by the reduced mass $\mu = m_g M/(m_g + M)$. The Lindblad operators are given by the operator-valued microscopic scattering amplitudes

$$\mathsf{f}(q\mathbf{n}, q\mathbf{n}') = \sum_{j=0}^{\infty} \sum_{m,m'=-j}^{j} f_{jm,jm'}(q\mathbf{n}, q\mathbf{n}') |jm\rangle\langle jm'| \tag{2}$$

for incoming and outgoing relative momenta $q\mathbf{n}'$ and $q\mathbf{n}$. Here $|jm\rangle$ is the linear rotor eigenstate with energy $E_j = \hbar^2 j(j+1)/2I$ and azimuthal quantum number m. While Eq. (2) conserves the total angular momentum quantum number j of a rapidly rotating molecule, it accounts for elastic scattering to different m. If the gas particles have internal d.o.f., the scattering amplitudes depend on the incoming and outgoing internal gas states. Tracing out the latter under the assumption that the gas is internally thermal yields the generalization of Eq. (1) in a straightforward calculation.

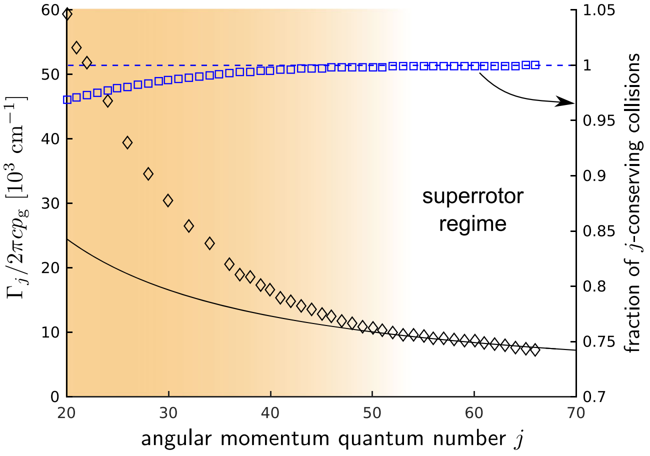

FIG. 2. In the superrotor regime, characterized by the absence of inelastic collisions, the theoretically predicted decay of rotational coherences (black solid line) compares very well with the experimental data (black diamonds) taken from Ref. [10]. The theoretical rate [Eq. (5)] includes no free parameters but is based on the microscopic scattering amplitudes of individual superrotor–gas particle collisions. For the considered nitrogen molecules, the superrotor regime starts at $j \simeq 50$, as can be seen from the fraction of j-conserving collisions (blue squares, right axis) approaching unity. The elastic fraction is obtained by numerically calculating the total scattering cross sections (using MOLSCAT [40]) for atom-linear-rotor scattering with a Lennard-Jones potential exhibiting the orientation dependence of Eq. (4). The molecular polarizabilities are taken from Ref. [41], and the C_6 constant is from the Lennard-Jones parameters listed in Ref. [42].

The incoherent term (1b) describes how a superrotor loses coherence in a thermal monoatomic gas, while the coherent term (1a) renormalizes the rotor energy [31]. We will show next that (1b) describes how the quantum state of a rapidly rotating particle dealigns and decoheres due to collisions with surrounding gas particles.

Rotational decoherence and alignment decay.—An optical centrifuge consists of two superimposed laser beams of opposite circular polarization, which propagate in the same direction along the z axis and whose frequency detuning increases linearly with time [6]. The resulting total electromagnetic field is linearly polarized; the polarization direction rotates with increasing frequency in the x-y plane orthogonal to the beam axis. An initially orientationally trapped linear molecule adiabatically follows the field polarization until the laser is instantaneously switched off, releasing the molecules in a superposition of high-angular-momentum eigenstates $|jj\rangle$. The total state operator ρ of the propelled molecule is thus of the form $\rho = \sum_{j,j'=0}^{\infty} \rho_{jj'} |jj\rangle\langle j'j'|$, where the coefficients $\rho_{jj'}$ depend on the details of the centrifuge beam [32,33].

On a short timescale, the derived master equation describes how the matrix elements of the superrotor state ρ oscillate and decay, i.e., $\partial_t \rho_{jj'} \simeq -(i\Delta_{jj'} + \gamma_{jj'})\rho_{jj'}$, with the decay rate

$$\begin{aligned}\gamma_{jj'} = {} & \frac{n_g}{2\mu}\int_0^\infty dq q^3 \nu_{\text{th}}(q) \int_{S_2} d^2\mathbf{n} \int_{S_2} d^2\mathbf{n}' \\ & \times \Bigg(|f_{jj,jj}(q\mathbf{n}, q\mathbf{n}') - f_{j'j',j'j'}(q\mathbf{n}, q\mathbf{n}')|^2 \\ & + \sum_{m=-j}^{j-1} |f_{jm,jj}(q\mathbf{n}, q\mathbf{n}')|^2 + \sum_{m'=-j'}^{j'-1} |f_{j'm',j'j'}(q\mathbf{n}, q\mathbf{n}')|^2 \Bigg).\end{aligned} \tag{3}$$

The first term describes decoherence between the states $|jj\rangle$ and $|j'j'\rangle$ due to the information acquired by the scatterer during the collision [22]. While this first term vanishes for $j = j'$, the remaining two terms are always nonzero, since they describe how the plane of rotation of the superrotor changes due to collision-induced transitions, $jj \to jm$ with $m = -j, \ldots, j-1$. This reorientation of the molecular angular momentum vector is the dominant contribution to the experimentally observed decay of rotational coherences of nitrogen superrotors [10,20], as will be demonstrated below.

We remark that a generalization of the optical theorem implies that isotropic states, $\sum_{j=0}^{\infty} \rho_j \sum_{m=-j}^{j} |jm\rangle\langle jm|$, are stationary under the superoperator $\mathcal{D}$ irrespective of their distribution ρ_j of rotational energies. An arbitrary initial superrotor state with matrix elements $\rho_{jj'}$ will thus approach the isotropic, mixed state on the timescale $1/\gamma_{jj'}$, provided that scattering to all m is allowed. The master equation therefore predicts the timescale on which ensembles of superrotors can be used for state-selective collision studies. After quantum coherence ceases to play a role and j-changing collisions become relevant, the thermalization of superrotors and their ensuing center-of-mass rotational correlations can be described classically [17,18,34].

Van der Waals scattering.—Comparing the decoherence and alignment decay rate [Eq. (3)] to experiment requires solving the scattering problem of an individual collision between the superrotor and a gas particle. As a generic situation, we consider the scattering of gas atoms off a diatomic molecule interacting via the attractive anisotropic van der Waals potential [35]:

$$V(r\mathbf{e}_r, \mathbf{m}) = -\frac{C_6}{r^6}\left[1 + \frac{2\Delta\alpha}{3\bar{\alpha}} P_2(\mathbf{e}_r \cdot \mathbf{m})\right]. \tag{4}$$

Here, C_6 quantifies the strength of the van der Waals interaction, and $\Delta\alpha = \alpha_\parallel - \alpha_\perp$ is the polarizability anisotropy of the linear rotor with $\alpha_\parallel$ and $\alpha_\perp$ being its polarizabilities along the symmetry axis and orthogonal to it; $\bar{\alpha} = (2\alpha_\perp + \alpha_\parallel)/3$ is the mean polarizability. The relative distance vector from the molecular center of mass to the atom is denoted by $r\mathbf{e}_r$, $\mathbf{m}$ is the direction of the rotor symmetry axis (see Fig. 1), and $P_2(x) = (3x^2 - 1)/2$ is the second-order Legendre polynomial.

Scattering can be described by the purely attractive interaction potential [Eq. (4)] when thermal collisions with large orbital angular momentum dominate, ensuring that the repulsive core can be neglected [36,37]. Indeed, the resulting total cross section for nitrogen-nitrogen collisions at ambient conditions (see the Supplemental Material [30]) agrees well with measurements of the mean free path [38]. If the gas particles are anisotropic, the interaction potential depends also on their orientation. As a first approximation, the strength of this orientation dependence is proportional to the anisotropy of the gas particles [35], so that the resulting rotational coupling between the two collision partners scales with the product of their anisotropies. For instance, for nitrogen-nitrogen collisions, the terms in the interaction potential depending on both orientations are approximately proportional to $\Delta\alpha^2/\bar{\alpha}^2$.

In order to calculate the rotation-state-dependent scattering amplitudes $f_{jm,jm'}(q\mathbf{n}, q\mathbf{n}')$, we use Schiff's approximation [39] in the limit of a rapidly rotating particle and assume that small-angle scattering dominates the amplitude. After a direct but nontrivial calculation (see the Supplemental Material [30]), one obtains the rates

$$\gamma_{jj'} \simeq \Gamma\left(\frac{13}{5}\right)\Gamma^2\left(\frac{3}{5}\right)\frac{\sqrt{\pi} n_g q_{\text{th}}^3}{10\mu\hbar^2}\left(\frac{\Delta\alpha}{30\bar{\alpha}}\right)^2\left(\frac{3\pi\mu C_6}{8\hbar q_{\text{th}}}\right)^{4/5} A_{jj'}, \tag{5a}$$

whose dependence on the rotation state is described by

$$\begin{aligned}A_{jj'} = {} & \left[P_2\left(\frac{2j}{2j+1}\right) - P_2\left(\frac{2j'}{2j'+1}\right)\right]^2 \\ & + \frac{1}{6}\left[P_2^1\left(\frac{2j-1}{2j+1}\right)\right]^2 + \frac{1}{6}\left[P_2^1\left(\frac{2j'-1}{2j'+1}\right)\right]^2 \\ & + \frac{1}{24}\left[P_2^2\left(\frac{2j-2}{2j+1}\right)\right]^2 + \frac{1}{24}\left[P_2^2\left(\frac{2j'-2}{2j'+1}\right)\right]^2.\end{aligned} \tag{5b}$$

Here, $P_2^m(x)$ are associated Legendre polynomials.

The decay rate in Eq. (5) can be directly compared to the decay of rotational coherences observed in Ref. [10] with nitrogen superrotors. In this experiment, their alignment decay was monitored by circularly polarized Raman scattering. The resulting signal is proportional to

$|\langle jj|\rho|j-2j-2\rangle|^2$ so that its decay rate $\Gamma_j = 2\gamma_{jj-2}$ follows directly from Eq. (5).

In Fig. 2, we show a comparison between the theoretically expected signal decay rate and the experimentally observed rates as reported in Ref. [10]. In the superrotor regime $j \gtrsim 50$, where the rotational energy is approximately conserved during the scattering process, the theory agrees with the experiment. We emphasize that the theory involves not a single free parameter but is based on the microscopic scattering amplitudes, underlining the predictive power of the approach. In the Supplemental Material [30], we show that the prediction of Eq. (5) is also in quantitative agreement with the $T = 503$ K superrotor data from Ref. [10]. This agreement supports the picture that the orientational d.o.f. of the gas particle are of minor relevance because they would enter Eq. (4) with the prefactor $4\Delta\alpha^2/9\bar{\alpha}^2 \ll 1$. Note that this might not hold for more complicated superrotor-gas interactions.

For large j, the signal decays as $1/j$ due to the asymptotic behavior of the associated Legendre polynomials, $A_{jj-2} \sim 6/j$ for $j \to \infty$. This is in marked contrast to the prediction $\Gamma_j \sim 1/j^4$ of the energy-corrected sudden approximation [10,29], valid only for weakly nonadiabatic collisions. Unambiguous identification of this asymptotic behavior will require further experiments.

Conclusion.—In summary, we established the quantum master equation of a molecular superrotor revolving in a thermal environment. It is based on the scattering amplitudes of superrotor-gas collisions, following directly from the intermolecular interaction potential. The ensuing alignment decay rates agree well with experimental observations. The theory predicts the timescales for quantum coherent experiments with superrotors. Combined with *ab initio* scattering calculations, it can be applied to any superrotating system, paving the way for future state-resolved collision studies and coherence experiments.

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