Rotational Alignment Decay and Decoherence of Molecular Superrotors — Supplemental Material

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Here we provide some calculational details to our Letter 'Rotational Alignment Decay and Decoherence of Molecular Superrotors'.

I. MASTER EQUATION

To derive the quantum dynamics of rotational alignment decay and decoherence of molecular superrotors we start from the master equation for a linear molecule of mass M and moment of inertia I immersed in a homogeneous gas of density $n_{\rm g}$, mass $m_{\rm g}$ and temperature T. Adapting the theory presented in [A. Smirne and B. Vacchini, Phys. Rev. A **82**, 042111 (2010)], one obtains for the combined rotational-center-of-mass state $\rho_{\rm tot}$ the Markovian master equation

$$\partial_t \rho_{\rm tot} = -\frac{i}{\hbar}\left[\mathsf{H}_{\rm tot} + \mathsf{H}_n, \rho_{\rm tot}\right] + \mathcal{L}\rho_{\rm tot}. \tag{S1}$$

Here the total free Hamiltonian is $\mathsf{H}_{\rm tot} = \mathsf{P}^2/2M + \mathsf{J}^2/2I$ (operators are denoted by sans-serif characters), the gas-induced energy shift

$$\mathsf{H}_n = -2\pi\hbar^2 \frac{n_{\rm g}}{\mu} \sum_{j=0}^{\infty} \sum_{m,m'=-\ell}^{\ell} \int d^3\mathbf{p}\, \mu_{\rm g}(\mathbf{p}) {\rm Re}\left[f_{jm,jm'}({\rm rel}(\mathbf{p},\mathsf{P}),{\rm rel}(\mathbf{p},\mathsf{P}))\right] |jm\rangle\langle jm'|, \tag{S2}$$

and the Lindblad superoperator

$$\mathcal{L}\rho_{\rm tot} = \sum_{\mathcal{E}} \int d^3\mathbf{Q} \int_{\mathbf{p}\perp\mathbf{Q}} d^2\mathbf{p} \left[\mathsf{L}_{\mathbf{Q}\mathbf{p}\mathcal{E}}\rho_{\rm tot}\mathsf{L}^\dagger_{\mathbf{Q}\mathbf{p}\mathcal{E}} - \frac{1}{2}\left\{\mathsf{L}^\dagger_{\mathbf{Q}\mathbf{p}\mathcal{E}}\mathsf{L}_{\mathbf{Q}\mathbf{p}\mathcal{E}}, \rho_{\rm tot}\right\}\right]. \tag{S3}$$

with the Lindblad operators

$$\mathsf{L}_{\mathbf{Q}\mathbf{p}\mathcal{E}} = e^{i\mathbf{Q}\cdot\mathsf{X}/\hbar} \sum_{\substack{jj'=0\\ E_j - E_{j'} = \mathcal{E}}}^{\infty} \sum_{m=-j}^{j} \sum_{m'=-j'}^{j'} L_{jm,j'm'}(\mathbf{p},\mathsf{P};\mathbf{Q}) |jm\rangle\langle j'm'| \tag{S4}$$

where

$$\begin{aligned} L_{jm,j'm'}(\mathbf{p},\mathbf{P};\mathbf{Q}) = {} & \sqrt{\frac{n_{\rm g} m_{\rm g}}{\mu^2 Q}} \sqrt{\mu_{\rm g}\left[\mathbf{p}_\perp + \frac{m_{\rm g}}{M}\mathbf{P}_\parallel + \left(1+\frac{m_{\rm g}}{M}\right)\frac{\mathbf{Q}}{2} + \frac{E_j - E_{j'}}{Q^2/m_{\rm g}}\mathbf{Q}\right]} \\ & \times f_{jm,j'm'}\left[{\rm rel}(\mathbf{p}_\perp,\mathbf{P}_\perp) - \frac{\mathbf{Q}}{2} + \frac{E_j - E_{j'}}{Q^2/\mu}\mathbf{Q}, {\rm rel}(\mathbf{p}_\perp,\mathbf{P}_\perp) + \frac{\mathbf{Q}}{2} + \frac{E_j - E_{j'}}{Q^2/\mu}\mathbf{Q}\right]. \end{aligned} \tag{S5}$$

In addition to the notation of the main manuscript, $\mu_{\rm g}(\mathbf{p})$ denotes the thermal momentum distribution of the gas, P is the center-of-mass momentum operator of the rotor, X its position operator, $E_j = \hbar^2 j(j+1)/2I$ the rotation energy and we defined the relative momentum

$${\rm rel}(\mathbf{p},\mathbf{P}) = \frac{\mu}{m_{\rm g}}\mathbf{p} - \frac{\mu}{M}\mathbf{P}. \tag{S6}$$

For superrotors generated by an optical centrifuge the center-of-mass and rotation state are approximately uncorrelated [A. A. Milner, A. Korobenko, J. W. Hepburn and V. Milner, Phys. Rev. Lett. **113**, 043004 (2014)], $\rho_{\rm tot} = \rho_{\rm cm}\otimes\rho$. In addition, the rotational energy is approximately conserved during a collision if the rotor revolves rapidly enough (see Fig. 2 and App. II), $f_{jm,j'm'}(\mathbf{q},\mathbf{q}') = \delta_{jj'} f_{jm,jm'}(\mathbf{q},\mathbf{q}')$. Tracing out the center-of -mass under these two simplifications yields after a straight-forward but lengthy calculation the master equation for the rotation state ρ,

$$\partial_t \rho = -\frac{i}{\hbar}\left[\mathsf{H} + \widetilde{\mathsf{H}}_n, \rho\right] + \widetilde{\mathcal{L}}\rho, \tag{S7}$$

with

$$\widetilde{\mathsf{H}}_n = -2\pi\hbar^2 \frac{n_\mathrm{g}}{\mu} \int d^3\mathbf{p} d^3\mathbf{P} \langle \mathbf{P} \,|\, \rho_\mathrm{cm} \,|\, \mathbf{P}\rangle \mu_\mathrm{g}(\mathbf{p}) \mathrm{Re}\left[\mathsf{f}\left(\mathrm{rel}(\mathbf{p},\mathbf{P}), \mathrm{rel}(\mathbf{p},\mathbf{P})\right)\right], \tag{S8}$$

and

$$\begin{aligned} \widetilde{\mathcal{L}}\rho = {} & \frac{n_\mathrm{g} m_\mathrm{g}^3}{\mu^4} \int d^3\mathbf{P} \int_0^\infty dq q^3 \int_{S_2} d^2\mathbf{n} d^2\mathbf{n}' \langle \mathbf{P} \,|\, \rho_\mathrm{cm} \,|\, \mathbf{P}\rangle \mu_\mathrm{g}\left(\frac{m_\mathrm{g}}{\mu} q\mathbf{n}' + \frac{m_\mathrm{g}}{M}\mathbf{P}\right) \\ & \times \left[\mathsf{f}(q\mathbf{n}, q\mathbf{n}')\rho \mathsf{f}^\dagger(q\mathbf{n}, q\mathbf{n}') - \frac{1}{2}\left\{\mathsf{f}^\dagger(q\mathbf{n}, q\mathbf{n}')\mathsf{f}(q\mathbf{n}, q\mathbf{n}'), \rho\right\}\right]. \end{aligned} \tag{S9}$$

Finally, using that the center-of-mass momentum $\mathbf{P}$ is thermalized with the gas and integrating it out yields the master equation presented in the main text of the manuscript.

II. SCATTERING AMPLITUDE

In order to calculate the rotation-state dependent scattering amplitude $f_{jm,j'm'}(q\mathbf{n}, q\mathbf{n}')$ as required for our purpose we start with the time-dependent Schrödinger equation in relative coordinates,

$$i\hbar\partial_t \left|\Psi\right\rangle = \left[\frac{\mathsf{q}^2}{2\mu} + \frac{\mathsf{J}^2}{2I} + V(\mathsf{r}, \mathsf{m})\right] \left|\Psi\right\rangle, \tag{S10}$$

where $V(\mathbf{r}, \mathbf{m})$ is the attractive van-der-Waals potential (see main text) and q is the relative momentum operator. (Operators are denoted by sans-serif characters.) Expanding the total state as

$$\left|\Psi\right\rangle = \sum_{j=0}^{\infty} e^{-iE_j t/\hbar} \sum_{m=-j}^{j} \left|\chi_{jm}\right\rangle \left|jm\right\rangle, \tag{S11}$$

yields the coupled Schrödinger equations

$$i\hbar\partial_t \left|\chi_{jm}\right\rangle = \frac{\mathsf{q}^2}{2\mu}\left|\chi_{jm}\right\rangle + \sum_{j'=0}^{\infty} e^{i(E_j - E_{j'})t/\hbar} \sum_{m'=-j'}^{j'} \left\langle jm \,|\, V(\mathsf{r}, \mathsf{m}) \,|\, j'm'\right\rangle \left|\chi_{j'm'}\right\rangle. \tag{S12}$$

If the molecule rotates multiple times during the collision, $E_j t/\hbar \gg 1$, the exponential function in (S12) averages to zero for $j \neq j'$ and the different j values are effectively decoupled. In this limit, one obtains for each j a vectorial Schrödinger equation for the vector $\left(\left|\underline{\chi}_j\right\rangle\right)_m = \left|\chi_{jm}\right\rangle$

$$i\hbar\partial_t \left|\underline{\chi}_j\right\rangle = \left[\frac{\mathsf{q}^2}{2\mu} + \mathrm{V}_j(\mathsf{r})\right] \left|\underline{\chi}_j\right\rangle \tag{S13}$$

involving the coupling matrix $(\mathrm{V}_j)_{mm'}(\mathsf{r}) = \langle jm \,|\, V(\mathsf{r}, \mathbf{m}) \,|\, j'm'\rangle$.

The vectorial scattering problem described by Eq. (S13) can be solved in the eikonal approximation [J. J. Sakurai, *Modern Quantum Mechanics* (Addison Wesley, Reading, Massachusetts, 1993)] (Schiff's approximation [L. I. Schiff, Phys. Rev. **103**, 443 (1956)]) for incoming relative momentum $q\mathbf{n}'$ and outgoing relative momentum $q\mathbf{n}$, yielding the (matrix-valued) scattering amplitude

$$\mathrm{f}_j(q\mathbf{n}, q\mathbf{n}') = -i\frac{q}{2\pi\hbar} \int_{\mathbf{b}\perp\mathbf{n}'} d^2\mathbf{b} e^{-iq\mathbf{b}\cdot\mathbf{n}/\hbar} \left[\exp\left\{-\frac{i\mu}{\hbar q}\int_{-\infty}^{\infty} dz \mathrm{V}_j\left(\mathbf{b} + z\mathbf{n}'\right)\right\} - \mathbb{1}_j\right]. \tag{S14}$$

Here $\mathbb{1}_j$ denotes the $(2j+1)\times(2j+1)$ dimensional unity matrix. The desired state-dependent scattering amplitudes are $f_{jm,jm'}(q\mathbf{n}, q\mathbf{n}') = (\mathrm{f}_j)_{mm'}(q\mathbf{n}, q\mathbf{n}')$. They can be explicitly calculated by carrying out the integrations in (S14).

In particular, we first integrate the coupling matrix along the eikonal trajectory z in the exponent. Since the resulting matrix is hermitian, the spectral theorem can be applied to rewrite the matrix exponential in terms of trigonometric functions, so that the radial integration over the impact parameter b can be carried out. We now exploit that forward scattering gives the strongest contribution to the scattering amplitude in order to limit ourselves to calculating $\mathrm{f}_j(q\mathbf{n}', q\mathbf{n}')$. Making use of the integrals

$$\int_0^\infty db b \sin\left(\frac{a}{b^5}\right) = \frac{1}{2}\mathrm{sign}(a)|a|^{2/5}\Gamma\left(\frac{3}{5}\right)\cos\left(\frac{3\pi}{10}\right) \tag{S15a}$$

and

$$\int_0^\infty db b \sin^2\left(\frac{a}{2b^5}\right) = \frac{1}{4}|a|^{2/5}\Gamma\left(\frac{3}{5}\right)\sin\left(\frac{3\pi}{10}\right) \tag{S15b}$$

yields

$$\mathrm{f}_j(q\mathbf{n}', q\mathbf{n}') = \frac{q^{3/5}}{4\pi\hbar}\Gamma\left(\frac{3}{5}\right)\left(\frac{3\pi\mu C_6}{8\hbar}\right)^{2/5} e^{i3\pi/10}\oint_{\mathbf{e}_b\perp\mathbf{n}'} d\mathbf{e}_b \left[\mathbb{1}_j + \mathrm{B}_j(\mathbf{n}', \mathbf{e}_b)\right]^{2/5}, \tag{S16}$$

where $\mathbf{e}_b = \mathbf{b}/b$ and the only nonzero entries of the tridiagonal matrix B_j are given by

$$(\mathrm{B}_j)_{mm}(\mathbf{n}', \mathbf{e}_b) = -\frac{\Delta\alpha}{3\overline{\alpha}}\sqrt{\frac{j(j+1)}{(2j-1)(2j+3)}}P_2\left(\frac{2m}{2j+1}\right)\left[\frac{5}{2}(\mathbf{e}_b\cdot\mathbf{e}_z)^2 + \frac{1}{2}(\mathbf{n}'\cdot\mathbf{e}_z)^2 - 1\right] \tag{S17a}$$

$$(\mathrm{B}_j)_{mm\pm1}(\mathbf{n}', \mathbf{e}_b) = \frac{\Delta\alpha}{18\overline{\alpha}}\sqrt{\frac{j(j+1)}{(2j-1)(2j+3)}}P_2^1\left(\frac{2m\pm1}{2j+1}\right)\left[5\mathbf{e}_b\cdot\mathbf{e}_z(\mathbf{e}_x\pm i\mathbf{e}_y)\cdot\mathbf{e}_b + \mathbf{n}'\cdot\mathbf{e}_z(\mathbf{e}_x\pm i\mathbf{e}_y)\cdot\mathbf{n}'\right] \tag{S17b}$$

$$(\mathrm{B}_j)_{mm\pm2}(\mathbf{n}', \mathbf{e}_b) = -\frac{\Delta\alpha}{72\overline{\alpha}}\sqrt{\frac{j(j+1)}{(2j-1)(2j+3)}}P_2^2\left(\frac{2m\pm2}{2j+1}\right)\left[5[\mathbf{e}_b\cdot(\mathbf{e}_x\pm i\mathbf{e}_y)]^2 + [\mathbf{n}'\cdot(\mathbf{e}_x\pm i\mathbf{e}_y)]^2\right]. \tag{S17c}$$

In order to carry out the $\mathbf{e}_b$ integration in (S16), we note that

$$\left[\mathbb{1}_j + \mathrm{B}_j(\mathbf{n}', \mathbf{e}_b)\right]^{2/5} \simeq \mathbb{1}_j + \frac{2}{5}\mathrm{B}_j(\mathbf{n}', \mathbf{e}_b), \tag{S18}$$

and use the integrals

$$\frac{1}{2\pi}\oint_{\mathbf{e}_b\perp\mathbf{n}'} d\mathbf{e}_b\ (\mathbf{e}_b\cdot\mathbf{e}_z)^2 = \frac{1}{2}|\mathbf{n}'\times\mathbf{e}_z|^2 \tag{S19a}$$

$$\frac{1}{2\pi}\oint_{\mathbf{e}_b\perp\mathbf{n}'} d\mathbf{e}_b\ [\mathbf{e}_b\cdot\mathbf{e}_z(\mathbf{e}_x\pm i\mathbf{e}_y)\cdot\mathbf{e}_b] = -\frac{1}{2}\mathbf{n}'\cdot\mathbf{e}_z(\mathbf{e}_x\pm i\mathbf{e}_y)\cdot\mathbf{n}' \tag{S19b}$$

$$\frac{1}{2\pi}\oint_{\mathbf{e}_b\perp\mathbf{n}'} d\mathbf{e}_b\ [\mathbf{e}_b\cdot(\mathbf{e}_x\pm i\mathbf{e}_y)]^2 = -\frac{1}{2}[\mathbf{n}'\cdot(\mathbf{e}_x\pm i\mathbf{e}_y)]^2. \tag{S19c}$$

Inserting this into (S16) yields the forward scattering amplitudes. The latter can be inserted into the general form of the decay rate, yielding after integration over $\mathbf{n}'$ and $\mathbf{n}$ (giving a factor of 2π because the amplitude is strongly peaked in the forward direction) the expression in the main text. The total scattering cross section can be calculated from the forward scattering amplitude via the optical theorem, yielding the rotation-state dependent analogue of the scalar van-der-Waals cross section [K. Walter, B. A. Stickler, and K. Hornberger, Phys. Rev. A **93**, 063612 (2016)]. The latter can be used to estimate the mean free path in the gas, yielding 66 nm at standard laboratory conditions, in good agreement with measurements [W. H. Haynes (editor in chief), *Handbook of Chemistry and Physics* (CRC Press - Boca Raton, 2012)].

III. ALIGNMENT DECAY AT $T = 503$ K

In Fig. 1 we show the alignment decay rate (5) as a function of j for the gas temperature $T = 503$ K compared to the data of Ref. [A. A. Milner, A. Korobenko, J. W. Hepburn and V. Milner, Phys. Rev. Lett. **113**, 043004 (2014)]. We also plot the fraction of rotationally elastic collisions in order to identify the superrotor regime. In contrast to Fig. 2 of the main text, the superrotor regime starts at higher j-values due to the higher relative kinetic energy. The agreement in the superrotor regime is good, but further data will help to unambiguously verify Eq. (5).

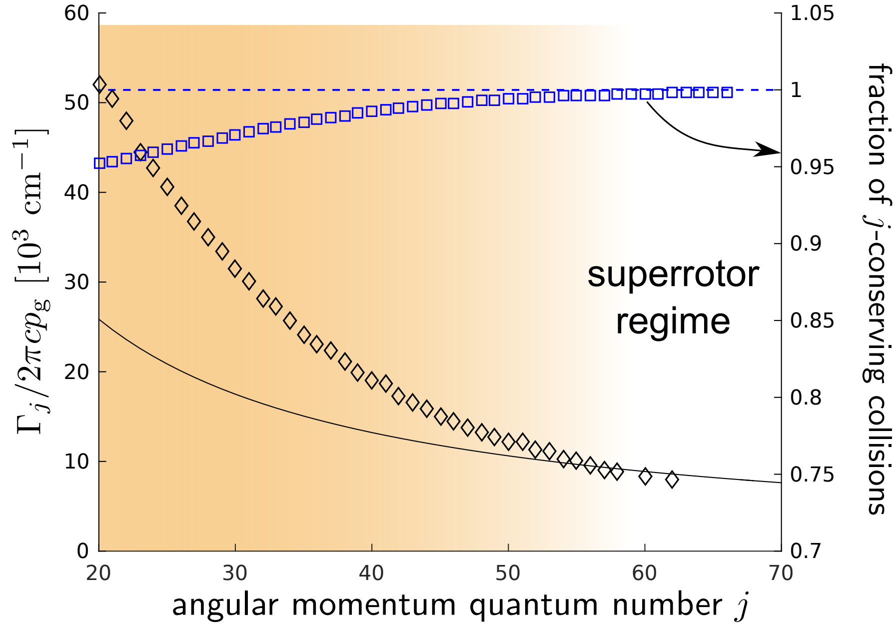

Figure 1. The alignment decay rate (5) (black solid line) at the gas temperature $T = 503$ K compareed to the experiment (black diamonds) from Ref. [A. A. Milner, A. Korobenko, J. W. Hepburn and V. Milner, Phys. Rev. Lett. **113**, 043004 (2014)]. The superrotor regime is identified by full-fledged Molscat calculations of the fraction of rotationally elastic collisions (blue squares). All other parameters are as in Fig. 2 in the main text.