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Characterization of methanol as a magnetic field tracer in star-forming regions

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Magnetic fields play an important role during star formation¹. Direct magnetic field strength observations have proven particularly challenging in the extremely dynamic protostellar phase^{2–4}. Because of their occurrence in the densest parts of star-forming regions, masers, through polarization observations, are the main source of magnetic field strength and morphology measurements around protostars². Of all maser species, methanol is one of the strongest and most abundant tracers of gas around high-mass protostellar disks and in outflows. However, as experimental determination of the magnetic characteristics of methanol has remained largely unsuccessful⁵, a robust magnetic field strength analysis of these regions could hitherto not be performed. Here, we report a quantitative theoretical model of the magnetic properties of methanol, including the complicated hyperfine structure that results from its internal rotation⁶. We show that the large range in values of the Landé *g* factors of the hyperfine components of each maser line lead to conclusions that differ substantially from the current interpretation based on a single effective *g* factor. These conclusions are more consistent with other observations^{7,8} and confirm the presence of dynamically important magnetic fields around protostars. Additionally, our calculations show that (nonlinear) Zeeman effects must be taken into account to further enhance the accuracy of cosmological electron-to-proton mass ratio determinations using methanol^{9–12}.

The presence of a magnetic field within an astrophysical maser produces partially polarized radiation. Linear polarization provides information on the magnetic field direction, while the magnetic field strength can be determined by comparing the field-induced frequency shifts between left- and right-circularly polarized maser emission. Extraction of the relevant information from polarized maser spectra requires knowledge of the Zeeman parameters that describe the response of the maser molecule/atom to a magnetic field. These Zeeman parameters are known for maser molecules such as hydroxide (OH), water and silicon monoxide, but not for methanol (CH₃OH).

Various torsion-rotation transitions of methanol have been observed as astrophysical masers. It has long been known that these transitions have a hyperfine structure, but only recently has an accurate model of this structure been presented⁶. It was shown that the so-called torsional motion of methanol about the carbon-oxygen (C–O) bond drastically complicates the hyperfine interactions and that ‘spin-torsion’ terms occur in addition to the usual ‘spin-rotation’ and spin-spin coupling terms. The magnetic moments that

produce the hyperfine structure also interact with an external magnetic field, that is, a Zeeman effect. Here, we extend the model of methanol’s hyperfine structure with the Zeeman interactions. We quantitatively determine all of the relevant coupling parameters, including effects from the torsional motion, by quantum chemical *ab initio* calculations and an estimate of the torsional Zeeman effect based on experimental results¹³. With this model, we can determine the Zeeman splitting of the hyperfine states within all the known methanol maser transitions. Zeeman interactions are usually described in a first-order approximation by the Landé *g* factor. In methanol, each torsion-rotation transition is actually split into a number of transitions between individual hyperfine levels of the upper and lower torsion-rotation states (Fig. 1). The Landé *g* factors calculated for the different hyperfine transitions differ strongly, and although these transitions cannot be individually resolved in the observed maser spectra, we show that this is important for the interpretation of the measured polarization effects. Furthermore, we find that, in several cases, the energy gaps between hyperfine levels are so small that hyperfine states with different total angular momenta *F* get mixed even by a weak magnetic field. In such cases, the first-order approximation for the Zeeman interactions breaks down, and the Zeeman splittings depend nonlinearly on the magnetic field strength (Fig. 2). Also, the Einstein *A* coefficients of transitions between two hyperfine levels become magnetic-field-dependent quantities in these cases (Supplementary Fig. 2). This behaviour has not previously been seen in Zeeman interactions for non-paramagnetic molecules, and is therefore not accounted for in current maser polarization theory^{14,15}.

To apply our results to maser polarization measurements, we must consider hyperfine-specific effects in the maser action. The individual hyperfine lines are not spectrally resolved, but the maser action can favour specific hyperfine transitions by the following mechanisms: (1) varying radiative rates for stimulated emission (see the Einstein coefficients of the various hyperfine components within a torsion-rotation line (Supplementary Information)); (2) kinematic effects, when there are two maser clouds along the line of sight with different velocities, such that a hyperfine transition in the foreground cloud amplifies emission from a different hyperfine transition in the background cloud¹⁶; (3) population inversion of the levels involved in maser action is preceded by collisional and radiative de-excitation of higher torsion-rotation levels¹⁷, with rate coefficients that are hyperfine-state specific¹⁸. The last effect has been overlooked in current maser excitation models¹⁷, and thus no quantitative information is available. To obtain a qualitative understanding, we consider the relative hyperfine-specific collisional and

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Fig. 1 | Hyperfine structure of the torsion-rotation levels in the 6.7 GHz ($5_{15}A_2 \rightarrow 6_{06}A_1$) transition. The energy of the $6_{06}A_1$ torsion-rotation level is set to zero. Because hyperfine interactions (~ 10 kHz) are much smaller than the torsion-rotation energy difference (~ 10 GHz), we have broken the y axis. Torsion-rotation states of A symmetry have nuclear spin quantum numbers $l=1$ and 2 , so that for rotational states with $J \geq 2$ there are six levels with $F=J, J \pm 1$ and two levels with $F=J \pm 2$, each $2F+1$ -fold degenerate. Hence, the $F=J, J \pm 1$ states contain both $l=1$ and $l=2$ components, which are mixed⁶. The hyperfine structure of the torsion-rotation levels is ~ 30 kHz wide. Arrows indicate the strongest hyperfine transitions with $\Delta F = \Delta J = 1$, with the Einstein A coefficients (in 10^{-9} s^{-1}) indicated above. Landé g factors, g_l , of the transitions in a magnetic field of 10 mG are given at the right-hand side of the upper energy levels. The rightmost numbers are the F quantum numbers of the hyperfine states.

radiative rates within a torsion-rotation transition. We find for de-excitation collisions of methanol with helium atoms (equation (8)) and for radiative emission (equation (12)) that the hyperfine levels with the highest F quantum number have the largest relative de-excitation rate coefficients.

Until now, methanol maser circular-polarization observations have been made for the 6.7 GHz ($5_{15}A_2 \rightarrow 6_{06}A_1$)^{2,19}, 44 GHz ($7_{07}A_2 \rightarrow 6_{16}A_1$)^{4,20} and 36 GHz ($4_{-1}E \rightarrow 3_0E$)³ torsion-rotation transitions. Because the magnetic characteristics of methanol were not known, (hyperfine-unspecific) estimates of the Zeeman parameters were used. In the following, we re-analyse some of the observations, using our calculated Zeeman parameters (Table 1). We take into account that within a torsion-rotation transition the various hyperfine transitions have different Landé g factors (Supplementary Tables 1–18) and that the maser action can be hyperfine-state specific.

We begin with the circular-polarization observations of class II methanol masers at 6.7 GHz, occurring in protostellar disks. We assume that the transition with the largest Einstein coefficient for

Fig. 2 | Splitting of the eight hyperfine levels of the torsion-rotation $4_{-1}E$ state as a function of the magnetic field strength. The quantum number F of each hyperfine level is given in the upper left-hand corner. In a magnetic field, each hyperfine level splits into $2F+1$ magnetic substates. The energy on the vertical axis is defined relative to the energy of the corresponding torsion-rotation state $4_{-1}E$.

stimulated emission, the $F=3 \rightarrow 4$ transition (see Fig. 1 and Supplementary Table 3), will be favoured and that the maser action is limited to this transition. Then, the Zeeman-splitting coefficient α_Z (related to the Landé g factor g_l as $\alpha_Z = \mu_N g_l$, with μ_N being the nuclear magneton) of the maser transition will be $\alpha_Z = -1.135 \text{ Hz mG}^{-1}$, which is ten times larger than the value currently used for magnetic field estimates^{2,5}. In the methanol maser regions probed by these class II masers, with an H_2 number density of $n_{H_2} \approx 10^8 \text{ cm}^{-3}$ (ref. 17), application of our new results to a large sample of maser observations² indicates an average field strength $\langle |B| \rangle \approx 12 \text{ mG}$. If, instead of by the $F=3 \rightarrow 4$ hyperfine transition, the polarization is caused by a combination of hyperfine components or by any of the other components, the derived magnetic field strength would be higher. Including all hyperfine components would result in an average $\alpha_Z \approx 0.17 \text{ Hz mG}^{-1}$ and an average $\langle |B| \rangle \approx 80 \text{ mG}$. This is considerably larger than expected based on OH masers observed at similar densities^{7,8}. The results based on the $F=3 \rightarrow 4$ transition are in good agreement with OH maser polarization observations^{7,8} as well as with the extrapolated magnetic field versus density relation $B \propto n^{1/2}$ (refs 21,22). This indicates, as already suggested by linear polarization studies^{19,23}, that methanol masers probe the large-scale magnetic field around massive protostars. Reversely, extending the magnetic field versus density relation by almost two orders of magnitude in density provides important constraints on the theory of massive star formation, because it implies that the magnetic energy density remains important up to densities of $n_{H_2} \approx 10^9 \text{ cm}^{-3}$. The conclusions are also supported by a more specific study of Cepheus A HW2 (ref. 23 and Fig. 3), where our reinterpretation confirms a slightly supercritical maser region, giving rise to magnetically regulated accretion towards the disk of Cepheus A HW2.

Polarization observations of class I methanol masers in the outflows of massive star-forming regions have been made for the 36 GHz and 44 GHz torsion-rotation transitions. In both lines, the individual hyperfine transitions are clustered in two groups, giving rise to a doublet structure in the spectra⁶. Considering kinematic effects favouring one of the two peaks, and selecting from this peak the transition with the largest coefficient for stimulated emission, we assume that

Fig. 3 | Total intensity and circular-polarization (V) spectra of the 6.7 GHz ($5_{15}A_2 \rightarrow 6_{06}A_1$) methanol masers around the disk of the high-mass protostar Cepheus A HW2²³. Total intensity is flux density in $\text{Jy} = 10^{-26} \text{ W m}^{-2} \text{ Hz}^{-1}$. The velocity is defined with respect to the local standard of rest, V_{LSR} . The spectra (solid) were observed with the Effelsberg 100 m telescope. They originate from methanol masers with different velocities along the same line of sight and can be approximated by ten Gaussian peaks (dashed, total intensity). If we assume that a single hyperfine component is dominant, our calculations (dashed, circular polarization) imply an average line-of-sight magnetic field strength $B_{\parallel} = 7.7 \pm 1.0 \text{ mG}$. The field strengths (in mG) extracted from the individual components, with errors of $\sim 20\%$ s.d., are indicated in the figure for each Gaussian. These correspond to a total magnetic field strength of $|B| = 26 \text{ mG}$. In one of the peaks, the maser radiation is oppositely polarized with respect to the other peaks, which suggests a reverse magnetic field. However, this could be due to pumping of a different hyperfine component with a different Landé g factor. If this argument holds, the magnetic field (denoted by the asterisk) extracted from this component has the same direction and is of similar magnitude as the fields from the other maser components. Using information on the masing gas and the mass of the region where the magnetic field is probed²³, the recalculated ratio between the thermal and magnetic energy, $\beta = 0.2$, shows the dominance of the magnetic field. The recalculated mass to magnetic flux ratio compared with the critical ratio is 1.5.

the $F=3 \rightarrow 2$ (36 GHz) and $F=5 \rightarrow 4$ (44 GHz) hyperfine lines are favoured and that the maser action is limited to these transitions. Then, the Zeeman-splitting coefficients of the maser transitions will be $\alpha_Z = -0.704 \text{ Hz mG}^{-1}$ for the 36 GHz line and $\alpha_Z = -0.920 \text{ Hz mG}^{-1}$ for the 44 GHz line (Supplementary Tables 10 and 4). The observed class I methanol masers are expected to occur in shocked regions of the outflows at densities of an order of magnitude lower than class II masers²⁴. The Zeeman splitting of the 36 GHz and 44 GHz lines was found to be of the order of several tens of hertz^{3,4,20}. Using our analysis, this would indicate magnetic field strengths of 20–75 mG. Because class I masers are shock excited, shock compression is expected to increase the magnetic field strength. For the outflow velocities in the class I maser regions, a preshock magnetic field as observed in the OH maser regions ($\sim 5 \text{ mG}$) will be amplified to $>20 \text{ mG}$, consistent with the observations. We thus suggest that class I methanol maser polarization observations provide important information on the shock conditions of protostellar outflows.

Our results also suggest an explanation for a surprising feature observed in both class II (6.7 GHz) and class I (44 GHz) masers. Observations have shown reversals in the sign of polarization over areas of small angular extent in the sky (fig. 3 (6.7 GHz) and fig. 2 (44 GHz) in ref. ²⁰). Such reversals have usually been interpreted as a change in field direction. However, reversals on AU-scales would be surprising if one considers the agreement between the fields probed by methanol masers and dust emission²⁵. A more plausible explanation favoured by our results is that in the masers with opposite signs of polarization, the masing process itself is due to the dominance of different hyperfine transitions. If we assume for the 6.7 GHz spectrum that for the oppositely polarized maser the $F=7 \rightarrow 8$ hyperfine transition is favoured by kinematic effects, instead of the $F=3 \rightarrow 4$ transition for the other masers, we find a magnetic field comparable to the result from other masers along the line of sight (Fig. 3). For the 44 GHz maser, if we assume the $F=8 \rightarrow 7$ transition to be favoured for the oppositely polarized maser instead of the $F=5 \rightarrow 4$ transition for the other maser, we also get Zeeman-splitting coefficients with opposite signs, and we find similar magnetic fields of $\sim 50 \text{ mG}$ from both masers composing the signal. We thus find that an alternative preferred hyperfine transition in the maser action is able to explain opposite circular polarization along the line of sight, and we obtain magnetic fields comparable to the results from other masers that trace similar areas around the protostar.

Our model is also important for the study of methanol maser absorption in red-shifted cosmological sources. Methanol's high sensitivity to variation of the electron-to-proton mass ratio in the torsion-rotational structure is enhanced by its torsional motion¹¹. Extragalactic absorption measurements of the $3-1E \rightarrow 20E$ (12.2 GHz) transition have been used to provide the strongest constraints on the time variation of the electron-to-proton mass ratio^{9,10}. Recently, measurements with a high spatial resolution have been able to selectively observe methanol absorption in an extragalactic cold core²⁶. Hyperfine effects shift the centre of torsion-rotation lines, which is an effect not accounted for in the current torsion-rotation fitting Hamiltonian²⁷ from which the parameters are used in determination of the sensitivity coefficients^{11,28}. Also, in cold extragalactic regions, temperature broadening effects are smaller than the hyperfine splittings, which could be resolved with a sufficiently high spectral resolution. Furthermore, in regions with strong magnetic fields ($>30 \text{ mG}$), this structure will be affected by Zeeman effects. These effects should be included in the error-accounting of the constraints to the time variation of the electron-to-proton mass ratio¹².

Theoretical modelling of (nonlinear) Zeeman effects for other molecular species such as hydrogen cyanide (HCN) and formaldehyde (H_2CO) can also be done according to the theory presented here. The same care should be taken in the assessment of Zeeman effects in radical species, where the magnetic field can mix fine-structure states, which is analogous to hyperfine mixing. This will be particularly important for thioxoethynylidene (CCS)^{29,30}, for which the Zeeman characteristics are still poorly known, but which will be one of the prime molecules for Zeeman studies with the Square Kilometre Array.

Methods

We theoretically modelled the response of methanol to weak magnetic fields by the addition of magnetic field (Zeeman) interactions to the model for methanol's hyperfine structure from Lankhaar et al.⁶. Here, we briefly revisit methanol's hyperfine structure and describe the relevant Zeeman interactions. Next, we detail the computational methods used to obtain the molecule-specific coupling parameters. Finally, we describe the methods used to compute the magnetic-field-dependent spectrum of methanol.

Hyperfine structure. The elucidation of methanol's hyperfine structure has been a challenge. The CH_3 group in methanol can easily rotate with respect to the OH group, which leads to an extension of the usual rigid-rotor hyperfine Hamiltonian with nuclear spin-torsion interactions³¹. In contrast with the nuclear spin-rotation

Table 1 | Zeeman-splitting parameters α_z for the strongest $\Delta F = \Delta J$ transitions of the investigated maser lines

Transition	α_z (Hz mG ⁻¹)							
	$F = J-2$	$F = J-1$	$F = J$	$F = J+1$	$F = J+2$			
$5_{15}A_2 \rightarrow 6_{06}A_1$ (6.7 GHz)	-1.135	-0.516	-0.467	-0.127	0.002	0.224	0.261	0.472
$7_{07}A_2 \rightarrow 6_{16}A_1$ (44 GHz)	-0.920	-0.436	-0.403	-0.016	-0.108	0.207	0.203	0.413
$4_{-1}E \rightarrow 3_0E$ (36 GHz)		-0.704	-0.075	0.056	0.424			
		-0.729	-0.274	0.174	0.486			

The ranges of the quantum number F for states of A symmetry are explained in the caption of Fig. 1. Torsion-rotation states of the E symmetry state have nuclear spin $I=0$ and 1, so that for $J \geq 1$ there are hyperfine states with $F=J$ and $F=J \pm 1$. Each torsion-rotation function of E symmetry yields two sets of hyperfine states of overall symmetry A_1 and A_2 (ref. 9). The hyperfine lines for each $J \rightarrow J'$ torsion-rotation transition are indicated by their initial F value, relative to the corresponding J value. For A symmetry, a single transition is associated with each $F=J \pm 2$ and two transitions with each $F=J, J \pm 1$. For E symmetry, two transitions $A_1 \rightarrow A_2$ and $A_2 \rightarrow A_1$ are associated with each $F=J \pm 1$ and four transitions with $F=J$.

coupling parameters, for which the ab initio calculated values have recently been experimentally confirmed³², the torsional hyperfine coupling parameters cannot be obtained from quantum chemical ab initio calculations^{6,33}. Experiments probing the hyperfine structure of methanol have proven difficult to interpret, because the hyperfine transitions cannot be individually resolved. Lankhaar et al.⁶ revised the derivation of a Hamiltonian that includes the torsional hyperfine interactions, and obtained the coupling parameters in this Hamiltonian from both ab initio calculations and experimental data^{31,33}. The hyperfine spectra of methanol calculated from this Hamiltonian agree well with the spectra observed for several torsion-rotation states of both A symmetry and E symmetry. In our present calculations of the Zeeman interactions of methanol in external magnetic fields, we start from this hyperfine Hamiltonian. For a detailed description, see Lankhaar et al.⁶.

Zeeman Hamiltonian. Zeeman interactions are governed by the same magnetic moments that determine the hyperfine structure, interacting with an external magnetic field $\mathbf{B}$. For a closed-shell diamagnetic molecule such as methanol, three contributions are important: the overall rotation term, the internal rotation term or torsional term and the nuclear spin term. The most abundant ¹²C and ¹⁶O nuclei have spin zero, so the nuclear spin of methanol (CH₃OH) comes from the three protons in the CH₃ group and the proton in the OH group. As derived in appendix A of Lankhaar et al.⁶ for the corresponding hyperfine Hamiltonian, the rotational Zeeman Hamiltonian

$$\hat{H}_{BR} = -\frac{\mu_N}{\hbar} \mathbf{B} \cdot \mathbf{g}(\gamma) \hat{\mathbf{J}} + \frac{\mu_N}{\hbar} f \mathbf{B} \cdot \mathbf{g}(\gamma) \lambda (\hat{\mathbf{p}}_\gamma - \rho \cdot \hat{\mathbf{J}}) \quad (1)$$

depends not only on the overall rotation angular momentum $\hat{\mathbf{J}}$, but also on the torsional angular momentum $\hat{\mathbf{p}}_\gamma = (\hbar/i)\partial/\partial\gamma$, where $\hbar$ is Planck's constant divided by 2π and i is the imaginary number. The coupling tensor $\mathbf{g}$ has the same form as for rigid molecules, but for molecules with internal rotation, it depends on the torsional angle γ . The unit vector λ describes the direction of the internal rotation axis in the principal-axes frame of the molecule, and $\rho = \mathbf{I}^{-1} \mathbf{I}^{\text{CH}_3} \lambda$, where $\mathbf{I}$ is the total inertia tensor and $\mathbf{I}^{\text{CH}_3}$ is the inertia tensor of the CH₃ group. The dimensionless factor f depends on the ratio of the moments of inertia of the OH frame and the rotating CH₃ top about the torsional axis⁶.

In addition, we must account for torsional Zeeman effects. Similarly to the torsional hyperfine Hamiltonian $\hat{H}_{ST}$ in Lankhaar et al.⁶, the torsional Zeeman Hamiltonian

$$\hat{H}_{BT} = -\frac{\mu_N}{\hbar} f \mathbf{B} \cdot \mathbf{b}(\gamma) (\hat{\mathbf{p}}_\gamma - \rho \cdot \hat{\mathbf{J}}) \quad (2)$$

with the coupling vector $\mathbf{b}(\gamma)$, not only contains the torsional angular momentum operator $\hat{\mathbf{p}}_\gamma$, but also the total angular momentum $\hat{\mathbf{J}}$. By absorbing the second term of equation (1) into equation (2), the remaining rotational Zeeman Hamiltonian obtains the usual form it has for a rigid molecule, and we obtain an effective $\hat{H}_{BT}$, with $\mathbf{b}(\gamma)$ replaced by

$$\mathbf{b}'(\gamma) = \mathbf{b}(\gamma) - \mathbf{g}(\gamma) \lambda \quad (3)$$

Finally, the intrinsic magnetic moments of the protons $K=1, 2, 3$ in the CH₃ group and proton $K=4$ in the OH group interact with the magnetic field as

$$\hat{H}_{BS} = -\frac{\mu_N}{\hbar} g_p \sum_K \mathbf{B} \cdot \hat{\mathbf{I}}_K \quad (4)$$

where g_p is the proton g factor. The total Zeeman Hamiltonian is a sum of the rotational, torsional and nuclear spin Zeeman terms

$$\hat{H}_{\text{Zeeman}} = \hat{H}_{BR} + \hat{H}_{BT} + \hat{H}_{BS} \quad (5)$$

Coupling tensors. The response of methanol to magnetic fields is theoretically modelled by including the coupling of the relevant angular momenta—the rotational angular momentum, the torsional momentum and the nuclear spin angular momentum—to the magnetic field vector. The couplings between these angular momentum operators and the magnetic field involve a rank-2 coupling tensor and a coupling vector. This coupling tensor and vector are specific for methanol. The derivation of the hyperfine coupling tensors is given in Lankhaar et al.⁶, and that of the Zeeman coupling tensors is in the Supplementary Information. In the following, we describe the methods used to evaluate all coupling parameters.

Rotational g tensor. Rotational Zeeman effects are represented by the molecule-specific g tensor, which for rigid non-paramagnetic molecules has been extensively studied experimentally for its valuable information on the electronic structure^{34–37}. Nowadays, quantum chemical calculations^{38,39} are able to reproduce these experiments with high accuracy. The rotational g tensor $\mathbf{g}(\gamma)$ can be obtained from ab initio electronic structure calculations with the program package CFOUR⁴⁰. We carried out calculations with CFOUR at the coupled-cluster level of theory including single and double excitations with perturbative addition of the triples contribution (CCSD(T)), in an augmented triple-zeta correlation-consistent (aug-cc-pVTZ) basis set⁴¹. The geometry of methanol was optimized at this level, which yields OH, CO and CH bond lengths of 0.956 Å, 1.427 Å and 1.096 Å, respectively, COH and OCH bond angles of 108.87° and 109.91°, respectively, and an HOCH torsional angle of 180°. The electronic contributions to $\mathbf{g}(\gamma)$ were calculated at the same level of theory for 13 equidistant values of γ by fixing the HOC fragment and rotating the CH₃ group over these angles about the OC bond axis. The nuclear contribution to $\mathbf{g}(\gamma)$ was also given by CFOUR, but was also calculated directly from the nuclear coordinates. Because of methanol's symmetry, we could fit our ab initio calculated values for the rotational $\mathbf{g}(\gamma)$ -tensor elements to either $\sum_n a_{3n} \cos(3n\gamma)$ or $\sum_n a_{3n} \sin(3n\gamma)$ functions of the internal rotation angle. The expansion coefficients, a_{3n} , are listed in Supplementary Table 1.

Torsional b -vector. Torsional Zeeman interactions are represented by the molecule-specific b -vector (Supplementary equations (16) and (21)). The calculation of the electronic contribution to the b -vector has not been implemented in the available quantum chemical program packages. To estimate the torsional Zeeman effects in methanol, we compare its internally rotating CH₃ group with the CH₃ groups of nitromethane and methyl-boron-difluoride, of which the torsional Zeeman effect has been investigated experimentally^{13,42}.

The torsional Zeeman coupling vectors of nitromethane and methyl-boron-difluoride were determined to be $\mathbf{b} = g_\gamma \lambda$, with $g_\gamma = 0.347$ and 0.3415, respectively. In these molecules, the unit vector λ that defines the direction of the internal rotation axis lies along the main principal axis. The small difference in the g values of these two molecules is explained by the electron drainage from the CH₃ groups by the attached functional group (see Supplementary Information). This electron drainage can be estimated from the partial atomic charges given by a Mulliken population analysis⁴³. We calculated Mulliken populations, P , of the CH₃ groups of nitromethane and methyl-boron-difluoride at the CCSD(T) level in an augmented double-zeta correlation consistent (aug-cc-pVDZ) basis, at their ab initio optimized geometries, and found these to be $P_{\text{CH}_3(-\text{NO}_2)} = 8.714$ and $P_{\text{CH}_3(-\text{BF}_2)} = 9.232$, respectively. We computed the Mulliken population of the CH₃ group in methanol at the same level and found this to be $P_{\text{CH}_3(-\text{OH})} = 8.737$. Then, we obtained the b -vector of methanol by interpolation as $\mathbf{b} = g_\gamma \lambda$, with $g_\gamma = 0.3468$ (see Supplementary Table 1). In this estimate of $\mathbf{b}$, we have assumed that it is independent of the torsional angle γ and is parallel to λ . The latter assumption holds only when λ is directed along one of the principal axes, which is almost the case for methanol^{42,7}.

Matrix elements and spectrum. With the knowledge of the coupling tensors $\mathbf{g}(\gamma)$ and $\mathbf{b}(\gamma)$ in the Zeeman Hamiltonian of equation (5) and the use of the hyperfine Hamiltonian from Lankhaar et al.⁶, we computed the magnetic field dependence of the hyperfine levels. The total Hamiltonian is diagonalized in the basis $\{|(I_{123}, I_4)J, I\rangle FM_F\rangle\}$, obtained by coupling the eigenfunctions of the torsion–rotation Hamiltonian²⁷ with the nuclear spin functions $|(I_{123}, I_4)I\rangle$ of the appropriate symmetry, defined in section IIC of Lankhaar et al.⁶. The hyperfine interactions couple the total nuclear spin I with the torsion–rotation angular momentum J to a total (hyperfine) angular momentum F , with projection M_F on the space-fixed z axis chosen along the magnetic field direction. When the external magnetic field is included, only M_F remains a good quantum number. Hyperfine states with different F may get mixed, which occurs to a substantial extent when there is a small energy gap between the hyperfine levels.

The torsion–rotation wave functions²⁷ have symmetry A or E and quantum numbers ν_r, J and K_a , where ν_r is the torsional quantum number and K_a the projection of J on the principal a -axis. For symmetries A and E , the nuclear spin basis has $I_{123} = 3/2$ and $1/2$, respectively (see section IIC in Lankhaar et al.⁶). The energy gaps between torsion–rotation states are typically of the order of a few gigahertz, whereas the hyperfine and Zeeman interactions in methanol (for fields $B < 10$ G) amount to about 10 kHz. Hence, we may restrict our basis to a single value of ν_r and J and derive an effective Zeeman Hamiltonian of which the matrix elements are more easily evaluated (Supplementary Information).

The matrix of the total Zeeman plus hyperfine Hamiltonian over the hyperfine basis with quantum numbers F and M_F was evaluated and diagonalized. This yielded the splitting of the hyperfine levels into $2F + 1$ sublevels, with M_F as the only good quantum number. Intensities and Einstein A coefficients for transitions between the individual hyperfine levels were obtained with the procedures described in Lankhaar et al.⁶.

Hyperfine-state resolved de-excitation. We emphasize in this letter that the Landé g factors of the different hyperfine components of each torsion–rotation transition vary over a large range of values. It is therefore important to know the populations of the individual hyperfine levels of the torsion–rotation states involved in the methanol maser action. This maser action is preceded by collisional and radiative de-excitation of higher torsion–rotation levels. Here, we derive formulas to estimate relative hyperfine-state-specific collisional and radiational de-excitation rate coefficients.

Hyperfine-state resolved collisional rate coefficients. Hyperfine splittings are negligible with respect to the collision energy, so to an excellent approximation the collision dynamics depends only on the scattering conditions and on the torsion–rotation structure of the molecule, and is not affected by hyperfine effects^{18,44}. As a consequence, obtaining hyperfine-state-specific $F \rightarrow F'$ transition rate coefficients from the usual rate coefficients for rotationally inelastic $J \rightarrow J'$ collisions requires only the use of an appropriate basis in which the angular momentum J is coupled with the total nuclear spin I to total angular momentum F (refs^{18,45}).

Davis⁴⁶ analysed the collision dynamics of a structureless atom (such as helium) and a molecule with one internal rotation (such as methanol), using a simple torsion–rotation model and neglecting the molecule's vibrational modes. The presence of the torsional modes leads to additional inelastic scattering processes, but the angular momentum algebra in the expressions for the scattering amplitudes and cross-sections are similar for collisions with methanol and with diatomic molecules. The methanol symmetric rotor quantum number K_a and torsional quantum numbers ν_r and σ play only a spectator role with regard to the angular momentum (re-)coupling⁴⁶.

Performing coupled-channel calculations for collisions of methanol with helium in a hyperfine basis would exceed the scope of this letter. Rather, we want to get an idea of the general trends of the hyperfine inelastic scattering rates with respect to the corresponding rotational rates. To this end, we use a formalism that relates the torsion–rotation inelastic scattering cross-sections to hyperfine-state-specific cross-sections. This is most conveniently done by representing the cross-sections in terms of tensor opacities^{44,46}

$$\sigma_{(K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J'} = \frac{\pi}{[J]k^2_{(K_a\sigma\nu_r)J}} \sum_L P^{(L)}((K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J') \quad (6)$$

for a transition from initial state $|(K_a\sigma\nu_r)J\rangle$ to a final state $|(K'_a\sigma'\nu'_r)J'\rangle$, where $k_{(K_a\sigma\nu_r)J}$ is the wave vector dependent on the collision energy and the torsion–rotation energy of the initial state, L is the rank of the tensor opacity $P^{(L)}$, and the square bracket notation designates $[J] = 2J + 1$. Recoupling the nuclear-spin-free opacity to the hyperfine-state-specific opacity yields⁴⁴

$$P^{(L)}((K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J') = [F][F'] \begin{Bmatrix} J & J' & L \\ F & F' & I \end{Bmatrix}^2 P^{(L)}((K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J') \quad (7)$$

The expression in curly brackets is a $6j$ -symbol. Substitution of this result into equation (6) yields the hyperfine-state-specific collisional cross-sections

$$\begin{aligned} \sigma_{(K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J'} &= \frac{\pi}{k^2_{(K_a\sigma\nu_r)J}} \times \\ &\sum_L P^{(L)}((K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J') \\ &= \frac{\pi[F']}{k^2_{(K_a\sigma\nu_r)J}} \times \\ &\sum_L \begin{Bmatrix} J & J' & L \\ F & F' & I \end{Bmatrix}^2 P^{(L)}((K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J') \end{aligned}$$

The triangular condition imposes the constraint $|J - J'| \leq L \leq J + J'$. Each of these values of L contributes to the total hyperfine-state-specific collisional rates. Except for very low collision energies where resonances may occur, which are not important under the methanol maser conditions, the largest contribution comes from $L = |\Delta J|$. Considering this contribution only would directly relate the hyperfine-state-specific rate with the rotational rate⁴⁵

$$\sigma_{(K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J'} = [J][F'] \begin{Bmatrix} J' & J & |\Delta J| \\ F' & F & I \end{Bmatrix}^2 \sigma_{(K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J'} \quad (9)$$

To analyse which final hyperfine levels, F' , are mostly populated by (de-) excitation, we must sum equation (9) over all initial hyperfine states F . Then, we find, for example, for the collisional de-excitation $J = 6 \rightarrow J' = 5$ that the $F' = J' + 2$ state has a 14% higher propensity to be populated than the $F' = J' - 2$ state. The other hyperfine states with $F' = J'$ and $J \pm 1$ are linear combinations of two nuclear spin states, and have population propensities lower than the $F' = J' + 2$ state and higher than the $F' = J' - 2$ state.

Actually, one can also analyse the ratio between hyperfine rates including all L channels with equation (8), and find that hyperfine-state-specific collision propensities for the $F' = J' + 2$ state are even higher for the other L channels. We can therefore say that the hyperfine collisional de-excitation propensity is over 14% higher for the $F' = J' + 2$ state than for the $F' = J' - 2$ state. Hyperfine-state-specific collision rate propensities of intermediate F' states are somewhere between the two extremes. More generally, we find consistently that in collisional (de-)excitation, for $\Delta J < 0$ transitions, high F' states have a higher propensity for every L channel. In $\Delta J = 0$ transitions, there is no hyperfine preference, and in $\Delta J > 0$ transitions, low F' hyperfine states have the highest probability to be populated.

Hyperfine-state resolved radiative rates. To investigate which hyperfine transitions are favoured by radiative de-excitation, we recouple the line strength of a torsion–rotation transition to a hyperfine basis. From the line strength, one can easily compute the Einstein coefficient.

The line strength of a transition between torsion–rotation states $(K_a\sigma\nu_r)J$ and $(K'_a\sigma'\nu'_r)J'$ is

$$S_{(K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J'} = \sum_{MM'} | \langle (K_a\sigma\nu_r)JM | \mathbf{d} | (K'_a\sigma'\nu'_r)J'M' \rangle |^2 \quad (10)$$

where $\mathbf{d}$ stands for the total dipole moment vector of all charged particles, electrons and nuclei. In recoupling the rotational line strength to hyperfine-state-specific line strengths, we recognize that the line strength transforms as a rank-1 tensor opacity, and we use equation (7) to obtain

$$S_{(K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J'} = [F][F'] \begin{Bmatrix} J' & J & 1 \\ F' & F & I \end{Bmatrix}^2 S_{(K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J'} \quad (11)$$

The Einstein A coefficient is related to the line strength by

$$A_{(K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J'} = \frac{2\omega^3}{3\epsilon_0 h c^3 [F]} S_{(K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J'} \quad (12)$$

where ϵ_0 , h and c are the vacuum permittivity, Planck's constant and the speed of light, respectively; ω is the transition frequency, which to a very good approximation does not depend on the hyperfine splittings of the rotational states.

To analyse which final hyperfine levels F' are mostly populated by (de-) excitation, we must sum equation (9) over all initial hyperfine states F :

$A_{(K_a\sigma\nu_r)J \rightarrow (K'_a\sigma'\nu'_r)J'}$. Then, we find for a $J = 6 \rightarrow J' = 5$ emission, for example, that the ratio between the Einstein coefficients for de-excitation to the final hyperfine states with $F' = J' + 2$ and $F' = J' - 2$ is

$$\frac{A_{(K_a\sigma\nu_r)6 \rightarrow (K'_a\sigma'\nu'_r)5[7]}}{A_{(K_a\sigma\nu_r)6 \rightarrow (K'_a\sigma'\nu'_r)5[3]}} = 1.14 \quad (13)$$

The intermediate hyperfine states with $F' = J'$ and $J' \pm 1$ are linear combinations of two nuclear spin states, and have population propensities lower than the $F' = J' + 2$ state and higher than the $F' = J' - 2$ state. The ratio calculated in equation (13) increases exponentially for lower J . For rotational states with higher J , it decreases to 1.

Data availability. The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

Received: 8 June 2017; Accepted: 13 November 2017;

Published online: 29 January 2018

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Acknowledgements

Support for this work was provided by the Swedish Research Council (VR), and by the European Research Council under the European Union's Seventh Framework Programme (FP7/2007–2013), through the European Research Council consolidator grant agreement no. 614264.

Author contributions

B.L., A.v.d.A. and W.V. wrote the paper. B.L., A.v.d.A. and G.C.G. modelled the Zeeman effect in methanol. B.L. and W.V. performed the analysis of the astrophysical maser spectra, based on methanol's Zeeman model. W.V., H.J.v.L. and G.S. provided expertise on maser polarization in astrophysics and initiated the project. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing financial interests.

Additional information

Supplementary information is available for this paper at <https://doi.org/10.1038/s41550-017-0341-8>.

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