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Separation and conversion dynamics of nuclear-spin isomers of gaseous methanol

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All symmetrical molecules with non-zero nuclear spin exist in nature as nuclear-spin isomers (NSIs). However, owing to the lack of experimental information, knowledge is rare about interconversions of NSIs of gaseous molecules with torsional symmetry. Here we report our separation and conversion observations on NSI-torsion-specific transition systems of gaseous methanol from a light-induced drift experiment involving partially spatial separation of the ortho and para isomers. We find that vibrationally excited molecules of the methanol spin isomer have a smaller collision cross-section than their ground-state counterparts. Interconversion of the enriched ortho isomer with the para isomer, which is generally considered improbable, has been quantitatively studied by sensitive detections of the spectral intensities. Rather counterintuitively, this reveals that the interconversion is inhibited with increasing pressure. Our results suggest that the spin conversion mechanism in methanol is via a quantum relaxation process with the quantum Zeno effect induced by molecular collisions.

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In quantum mechanics¹, nuclear-spin isomers (NSIs) are different molecular species and each of the NSIs of a molecule can be spectroscopically identified by different classes of quantum numbers in the ground-state levels of transitions of the molecule. However, despite the fact that continuous studies of NSIs of molecules began as early as the first separation and conversion of ortho- and para-H₂ in 1929 (ref. 2), yet very little is known about the interconversion dynamics of NSIs of gaseous molecules with torsional symmetry. Although many symmetrical molecules have distinct NSIs, to date, separation and conversion dynamics have been successfully studied for just a few gaseous molecules, including H₂, CH₃F (ref. 3), ¹³CH₃F (refs 4 – 6), H₂CO (ref. 7), ¹³CCH₄ (ref. 8), C₂H₄ (refs 9,10) and H₂O (refs 11,12). All the NSIs of these molecules are identified by rotational quantum numbers. Among these molecules, only the NSIs of CH₃F, ¹³CH₃F, ¹³CCH₄ and C₂H₄ have been separated at ambient temperature in the gas phase by the method of light-induced drift¹³ (LID) and the nuclear-spin conversion mechanisms of them have been explained by the model of quantum relaxation¹⁴. In astrophysics, measurements of the ortho-to-para ratios of any interstellar molecules can give important molecular formation information^{15–19}. However, despite the fact that methanol (CH₃OH) is one of the most abundant interstellar molecules^{20,21}, so far this has not been achieved for CH₃OH.

CH₃OH is the simplest alcohol, having a C_{3v}(M) symmetry point group and displaying internal rotation or torsion of the CH₃ group with respect to the OH group. It is from the three spin-1/2 hydrogen nuclei of this CH₃ group that the ortho (total nuclear spin quantum number $I = 3/2$) and para ($I = 1/2$) nuclear spin isomers are formed, which are distinguished respectively by the symmetry quantum numbers $\sigma = 0$ and ± 1 . Here, each σ value corresponds to a torsional-symmetry species of the C₃ group A ($\sigma = 0$) and E ($\sigma = \pm 1$), and combines with the A - and E -species in the spin part of the molecular wavefunction. Although CH₃OH is one of the simplest asymmetric-top molecules with one hindered large-amplitude torsion, its spectrum is quite complicated due to strong coupling of torsion with other vibrational modes and has been extensively studied for many years as a prototype nonrigid molecule in molecular physics^{22–24}. To date, however, little experimental information about the specific physical properties of two spin-isomer molecules, such as their stability and how the collision cross-section (CCS) of the ortho- or para-isomer molecules varies on excitation, has been obtained for gaseous CH₃OH. No population transfers between the A - and E -levels have ever been observed and no evidence of weak intramolecular hyperfine interactions producing the ortho-para state mixing in CH₃OH has been found. Thus, to seek the possibility of separation of the ortho and para isomers by the LID method and to provide experimental evidence and explanation of mechanisms to the interconversion between these two spin isomers, we performed separation and conversion observations on CH₃OH in the gas phase.

In this work, we report experimental results on performing nuclear spin enrichment and nuclear spin conversion in gaseous CH₃OH. The enrichment is performed by the LID method and shows an unusual LID effect, which has the opposite direction of the drift of the NSIs to that observed in the LID effect for other molecular NSIs. We demonstrate the observation of the decreasing of nuclear spin conversion rate with increasing pressure and explain this novel and interesting phenomenon in a free molecule by the model of quantum relaxation. The experiment has been performed several times with different pressures for the ortho and para isomers of CH₃OH independently. Importantly, in contrast to the molecular NSIs studied before, the mixing between ortho and para states involves

torsional wavefunctions and the intramolecular torsion is involved in the nuclear spin conversion in CH₃OH. In this work we provide experimental evidence for the existence of the weak nuclear-spin-dependent intramolecular hyperfine interactions in gaseous CH₃OH.

Results

E a b. A schematic of our experimental setup is shown in Fig. 1, which has been described in detail previously⁹. The experimental schemes for CH₃OH are shown in Table 1. The 9P16 CO₂ laser line was selected to create a non-equilibrium isomeric mixture near the front end of the 1-m-long separation cell and in the test cell through the valve- T by using the effect of LID. The centre frequency of the 9P16 CO₂ laser line $f_0(9P16)$, from the reported observations and spectral assignments in high-resolution Fourier-transform spectra of CH₃OH (refs 22,23), was calculated to be ~ 67 MHz below the centre frequency of the $R(\sigma v_t K, J) = R(A 0 0, 10)$ line, where v_t is the torsional quantum number, and J and K are quantum numbers of the rotational angular momentum and its projection along the axis of the CH₃ group, respectively. This laser line was thus tuned into the Doppler-broadened absorption profile of the $R(A 0 0, 10)$ line for separating the ortho isomer from the para isomer in the experiment. Another frequency-stabilized CO₂ laser was used for detection of the ortho (Case 1) or para isomer (Case 2) concentration with shifting its centre frequency of 100 MHz by an infrared acousto-optic modulator. By using an optical chopper, two probe laser beams from the second laser were aligned in anti-phase simultaneously passing through the test cell and the reference cell for sensitive detections of the differential spectral intensities. As such, the output of the detector recombined from these detection cells directly reflects the non-equilibrium concentrations of spin isomers in the test cell. Here, the reference cell is of the same size as the test cell and kept at the equilibrium composition. Accordingly, the LID effects and the decay curves arising from subsequent population transfer between the ortho and para isomers after closing the valve- T were observed by employing a three-period signal recording method (see Methods). Typical recorded differential absorption signals are shown in Fig. 2a for Case 1, with the $R(A 0 5, 13)$ line detected by the probe laser frequency at $f_0(9P12) + 100$ MHz, and in Fig. 2b for Case 2, with the $P(E 0 1, 5)$ line detected by the probe laser frequency at $f_0(9P42) - 100$ MHz.

The first signal period (Stage 1) represents the zero-difference baseline corresponding to the equilibrium level of the ortho isomer or the para isomer in the natural abundance ratio. It was

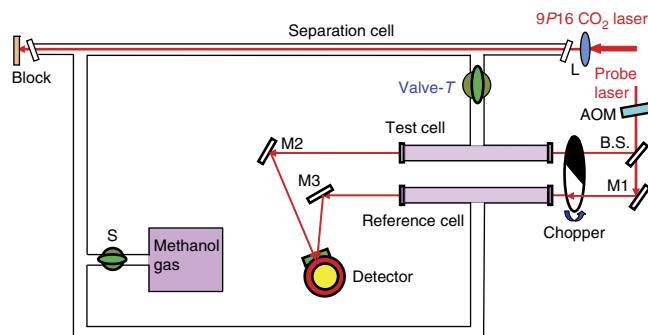


Table 1 | Experimental schemes and the det

Case and number	CH ₃ OH transition
Separation	$R(A\ 0\ 0, 10)$
Probe	
1	$R(A\ 0\ 5, 13)$
2	$P(E\ 0\ 1, 5)$
Average of Cases 1 and 2	

The CH₃OH transition $R/P(\sigma\ v_i\ K, J)$ is from the ground state to the v_i excited state with total angular momentum J and its projection along the

population transfers and transitions between the *A* and *E* two different torsional-symmetry species are generally considered improbable, because they are forbidden by the electric-dipole selection rules of the molecule and their spectral intensities would be extremely weak; therefore, such transfers and transitions have never been directly seen for gaseous CH₃OH. However, we have observed the population variations of the ortho and para isomers, as seen from the third period (Stage 3) of the signals in Fig. 2. The spectral intensity of the ortho isomer decreases (Fig. 2a) and that of the para isomer increases (Fig. 2b) towards their equilibrium levels. This general phenomenon and the offset between the new equilibrium level and the zero-difference baseline can be qualitatively explained as follows. In the initial seconds of Stage 2, as the hot ortho-CH₃OH molecules from the separation cell quickly enter and the para-CH₃OH molecules fast exit the test cell through the valve-*T* due to the unusual LID effect, and also because the inner surface of the test cell (mainly the part opposite to the sidearm of the valve-*T*) gets in their way of such rapid influxes of the hot ortho-CH₃OH molecules, there are head-on collisions and therefore enhanced net adsorptions of the ortho-CH₃OH molecules on the wall of the test cell, leading to the degree of enrichment of the ortho isomer to be smaller than the degree of depletion of the para isomer. However, as the isomeric conversion also takes place simultaneously and competes against the isomeric separation in Stage 2, the enrichment and the enhanced adsorption gradually saturate as the separation proceeds and reach saturations when the test cell is isolated by closing the valve-*T*. Hence, relative to the zero-difference baseline, a reduced equilibrium level of the isomeric conversion exists and remains almost unchanged in the subsequent isomeric decay stage over the time range studied. In the isolated test cell, apart from the surface-molecule collisions, there are also molecule-molecule collisions within the bulk gas, through which the ortho and para molecules can move up and down within their own manifolds of states. There are certain particular pairs of ortho and para states whose energy gaps are so small that they are coupled and strongly mixed by the weak nuclear-spin-dependent intramolecular hyperfine interactions of CH₃OH, allowing molecules arriving in these doorway states to freely move between ortho and para manifolds during the mixing²⁶. However, the time evolution of this state mixing is interrupted by the next collision, following

in Fig. 3 (smooth curves). Here, $b = (\omega/40\pi)^2$, a is a rate constant and c is the constant for a linear pressure term, terms cp and $ap/(b+p^2)$ stand for the rates of the spin conversions contributed from molecular population transfers via the level pairs with $\omega_{\alpha\alpha'}$

about the dynamics of separation and conversion of NSIs of torsion-type molecules in various scientific disciplines. It will also be interesting as a potential application of the conversion rates observed here for CH₃OH in the microscopic world to extend them to the macroscopic universe, notably in interstellar space¹⁹, to explore the formations and evolutions of stars and planets.

Methods

The three-period signal recording method. In our experiment, we use a dual-beam differential absorption method to sensitively probe the spin-isomer compositions by a liquid-N₂-cooled HgCdTe detector. Two 20-cm-long detection cells (test cell and reference cell) are set side-by-side in parallel. The test cell is connected to the front end of the 1-m-long separation cell via a glass valve-*T* and the reference cell is kept at the equilibrium composition. Apparently, the output of the detector should be zero when the separation laser is blocked and not introduced to the separation cell, giving a zero-difference baseline in the recorded absorption signals in Stage 1. The first signal period is usually set at ~ 30 s. After 30 s, the separation laser was suddenly unblocked and thus the high-power laser beam was focused through the separation cell. This is a process involving LID effect, which causes the drift of one isomer species and produces a non-equilibrium isomeric mixture near the front end of the separation cell and in the test cell through the valve-*T*. The optimum time for this period, which corresponds to the second signal period Stage 2, usually takes ~ 60 s before the valve-*T* is closed to get an isolated test cell from the separation cell. At the 90th second, the valve-*T* was closed. The subsequent conversion signals between ortho and para isomers were then observed by the HgCdTe detector from the transmissions of the two detection cells, processed by a lock-in amplifier at a time constant of 0.3 s, and recorded by a computer.

Derivation of equation $\gamma_{\text{op}} \approx ap/(b+p^2) + cp$. From equation (1), we have

$$\begin{aligned} \gamma_{\text{op}} &= \sum_{\substack{\alpha \in o \\ \alpha' \in p}} \frac{2\Gamma_{\alpha\alpha'} |V_{\alpha\alpha'}|^2}{\Gamma_{\alpha\alpha'}^2 + \omega_{\alpha\alpha'}^2} [W_B(\alpha) + W_B(\alpha')] \\ &= \sum_{\alpha\alpha'} \frac{(\Gamma_{\alpha\alpha'}/2\pi) (|V_{\alpha\alpha'}|^2/\pi)}{(\Gamma_{\alpha\alpha'}/2\pi)^2 + (\omega_{\alpha\alpha'}/2\pi)^2} [W_B(\alpha) + W_B(\alpha')]. \end{aligned} \quad (2)$$

Taking the approximation of $\Gamma_{\alpha\alpha'}/2\pi = Cp$ with pressure p and $C=20$ MHz Torr⁻¹ (refs 22,27) for all transition levels, we can rewrite equation (2) as

$$\begin{aligned} \gamma_{\text{op}} &\approx \sum_{\alpha\alpha'} \frac{(Cp) (|V_{\alpha\alpha'}|^2/\pi)}{(Cp)^2 (\omega_{\alpha\alpha'}/2\pi)^2} [W_B(\alpha) + W_B(\alpha')] \\ &= \sum_{\alpha\alpha'} \frac{p (|V_{\alpha\alpha'}|^2/\pi C)}{p^2 + (\omega_{\alpha\alpha'}/2\pi C)^2} [W_B(\alpha) + W_B(\alpha')] \\ &= \sum_{\alpha\alpha'} \frac{a_{\alpha\alpha'} p}{b_{\alpha\alpha'} + p^2}, \end{aligned} \quad (3)$$

where $a_{\alpha\alpha'} = (|V_{\alpha\alpha'}|^2/\pi C) [W_B(\alpha) + W_B(\alpha')]$, $b_{\alpha\alpha'} = (\omega_{\alpha\alpha'}/2\pi C)^2$.

In terms of energy gaps, one can classify all pairs of the *A*- and *E*-levels with the variable $\alpha \in o, \alpha' \in p$ into the variable category $m \in o, m' \in p$ with $b_{mm'} \sim p^2$ and $n \in o, n' \in p$ with $b_{nn'} \gg p^2$. Thus, from equation (3), we have

$$\begin{aligned} \gamma_{\text{op}} &\approx \sum_{\substack{m \in o \\ m' \in p}} \frac{a_{mm'} p}{b_{mm'} + p^2} + \sum_{\substack{n \in o \\ n' \in p}} \frac{a_{nn'} p}{b_{nn'} + p^2} \\ &\approx \sum_{mm'} \frac{a_{mm'} p}{b_{mm'} + p^2} + \sum_{nn'} \frac{a_{nn'} p}{b_{nn'}} \\ &= \sum_{mm'} \frac{a_{mm'} p}{b_{mm'} + p^2} + \sum_{nn'} c_{nn'} p \\ &= \frac{ap}{b+p^2} + \dots + p \sum_{nn'} c_{nn'} p \\ &= \frac{ap}{b+p^2} + \dots + cp. \end{aligned} \quad (4)$$

Suppose parameters a and b are related to the level pair with the closest energy gap, the rate of the conversion contributed from weak nuclear-spin-dependent intramolecular hyperfine interactions can then be approximately expressed as

$$\gamma_{\text{op}} \approx \frac{ap}{b+p^2} + cp. \quad (5)$$

Suppose a pressure-independent term d approximately expresses the induced rate of spin conversion by the interactions of isomer molecules with the wall of the test cell in Stage 3, the observed conversion rate γ in our experiment can be written as

$$\gamma \approx \gamma_{\text{op}} + d \approx \frac{ap}{b+p^2} + cp + d. \quad (6)$$

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Y.Z. carried out results interpretation. All authors discussed the results and the manuscript.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

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