

Dark State Illuminated: Infrared Spectrum and Inverted Torsional Structure of the ν_{11} Out-of-Plane CH_3 -Rocking Mode of Methanol

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The ν_{11} out-of-plane CH_3 -rocking band of methanol, one of the last fundamentals remaining en route to full vibrational description of this prototype internal rotor, has been identified in the Fourier transform spectrum of CH_3OH in the 1150 cm^{-1} region. The ν_{11} torsional energy pattern is found to be inverted, the first such discovery for a bending state and an important pointer to potential generality of this phenomenon for the whole class of threefold internal rotor molecules. Level-crossing resonances giving transfer channels for intramolecular vibrational energy redistribution (IVR) have been found, and new insights are reported for far-infrared laser emission involving ν_{11} levels.

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This Letter reports a breakthrough in the vibrational spectroscopy of methanol with the observation and assignment of 23 subbands of the ν_{11} out-of-plane CH_3 -rocking (ro) fundamental in the high-resolution Fourier transform spectrum of CH_3OH . Detection of this elusive “dark” state is a notable discovery from four perspectives:

(i) Accurate characterization of the ν_{11} mode is of key importance for successful modeling of the dynamics and internal force field of methanol, a primary testbed for theories of internal rotation and torsional coupling with vibration. The fitting of the methanol vibrational fundamentals is still far from experiment, despite normal mode studies extending over many decades [1,2]. A major factor is the impact of torsion on the spectral contours, with shifts in apparent band centers and vibrational frequencies that are only now coming to light with the fully resolved spectra achievable by modern instruments. The ν_{11} band presents a dramatic case in point, showing anomalously wide spreading due to unexpected torsional effects which undoubtedly served to defeat the many determined earlier efforts to locate the band at low resolution [1,2]. With our new results, the ν_{11} band origin can now be determined, and differs significantly from the best previous estimate.

(ii) Remarkably, the ν_{11} torsional energy structure is inverted, with the same breakdown of the conventional torsional Hamiltonian as the ν_2 and ν_9 asymmetric CH stretches [3,4]. This ν_{11} inversion is the first found for a bending state, and represents the crucial second independent observation that points to universality of behavior. The discovery of torsional inversion for two distinctly different types of vibrational motion strongly reinforces Perry’s conjecture [4] that this is a systematic phenomenon characteristic of all torsional molecules for particular classes of vibration. This accelerates the need to change our whole qualitative thinking about simply adding torsion to vibration via an effective Hamiltonian with adjustable barrier height, and instead reformulate the problem from the beginning in terms of a coupled torsion-vibration basis.

(iii) Observations of the perturbing effects of dark states (with small transition moment) on more visible bright states give important information on the coupling channels through which energy may flow in the processes of intramolecular vibrational redistribution (IVR). We have now found and quantified J -localized level-crossing resonances between ν_{11} and ν_8 (CO-stretch) states, explaining anomalies in the strong ν_8 band and providing small doorways for intermode IVR transfer. We emphasize that while a mode may be spectroscopically dark, it can, nevertheless, be active dynamically and play a substantial role in IVR transfer, underscoring the importance of a full understanding of the ν_{11} energy level structure and its interactions with other modes.

(iv) Methanol and its isotopomers are the richest sources of optically pumped far-infrared laser (FIRL) lines. Assignment of the laser transitions has been an ongoing spectroscopic challenge, and new progress is uncovering unexpected energy level schemes giving unique information on vibrational coupling and intermode transitions [5]. Here, our results successfully confirm previous tentative FIRL assignments involving ν_{11} levels [5–8], and the first FIRL transition system with pumping directly into the ν_{11} state has been identified. Infrared pumping is an important excitation mechanism for strong interstellar methanol masers seen in protostellar regions, hence data on new pumping and FIR radiative routes are of astrophysical relevance.

In the present work, we have assigned over 900 lines in 23 subbands of the weak ν_{11} fundamental of CH_3OH [9]. The spectrum was recorded at a resolution of 0.002 cm^{-1} on the modified Bomem DA3.002 Fourier transform instrument in the laboratory of J. W. C. Johns at the National Research Council of Canada in Ottawa. The weaker features were enhanced by employing a pressure of 750 mTorr at a path length of 2.0 m. Under these conditions the strong ν_8 CO-stretching band was heavily saturated.

The key to the ν_{11} discovery was the recognition of Q subbranches with \underline{a} -type character around 1150 cm^{-1} ,

implying upper-state torsion-vibration energies around 1284 cm^{-1} with addition of the torsional zero-point energy of 134 cm^{-1} . Comparison with our predicted energy map [5] then clearly identified this state as the ν_{11} out-of-plane CH_3 rock. Observation of \underline{a} type rather than \underline{c} type character was unexpected, and must reflect borrowing of parallel transition moment via coupling to other modes.

By making educated guesses about the Q -subbranch quantum numbers and predicting the related P and R lines using known ground-state energies [8,10], we were able by much trial and error to pin down the very weak P and R subbranch partners in the dense spectral forest. This established the full $(n, K, J) T_s$ labeling, where n is the torsional state, K is the \underline{a} component of rotational angular momentum J , and T_s is the A or E torsional symmetry [5,8,11]. The Q origins followed a systematic pattern, allowing fur-

ther subbands to be located. We now have assignments and upper-state term values for 17 \underline{a} -type ν_{11} subbands, all of relatively high K as selected by the Q -branch intensity proportional to K^2 . A few $\Delta|K| = 1$ subbands were also seen to the $K = 4, 5, 6,$ and $8 A \nu_{11}$ states, confirming those state assignments.

To examine the ν_{11} energy structure, we fitted the term values to $J(J+1)$ expansions to obtain W^{ro} substate origins, then found K -reduced torsion-vibration energies as $[W^{\text{ro}} - (A - B)^{\text{ro}} K^2]$ where $(A - B)^{\text{ro}}$ is the effective K -rotational constant. In Dennison's model [11], these energies lie on τ curves of period 3 in a variable $(1 - \rho)K$, where $\rho \approx I_{a2}/I_a$, and I_{a2} and I_a are the moments of inertia of the methyl group and the whole molecule, respectively [12]. The $\tau = 2$ and $\tau = 3$ curves are shifted by -1 and $+1$ units relative to the $\tau = 1$ curve, hence the energies can be modeled as a Fourier series:

$$W^{\text{ro}} - (A - B)^{\text{ro}} K^2 = E_v^{\text{ro}} + a_0^{\text{ro}} + a_1^{\text{ro}} \cos\{[(1 - \rho)K - \sigma]2\pi/3\} + a_2^{\text{ro}} \cos\{[(1 - \rho)K - \sigma]4\pi/3\},$$

where E_v^{ro} is purely vibrational energy, a_0^{ro} is the zero-point torsional energy, a_1^{ro} and a_2^{ro} are Fourier coefficients, and σ equals 0, -1 , or $+1$ for $\tau = 1, 2,$ and 3 . In the conventional model, the $\tau = 1 A$ level lies below the degenerate $\tau = 2/3 E$ level for $K = 0$ in the ground torsional state, thus we expect $a_1^{\text{ro}} < 0$ for $n = 0$. The A/E ordering then alternates with n for higher torsional states.

Figure 1 shows our data and the fit to the Fourier model with $(E_v^{\text{ro}} + a_0^{\text{ro}}) = 1287.16\text{ cm}^{-1}$, $a_1^{\text{ro}} = 5.3002\text{ cm}^{-1}$, $a_2^{\text{ro}} = -0.3443\text{ cm}^{-1}$, $\rho = 0.7905$, and $(A - B)^{\text{ro}} = 3.4602\text{ cm}^{-1}$. The two circled points are estimated from FIRL observations [5–8], so were excluded from the fit, as were the three bracketed points perturbed by interactions with $n = 4$ ground-state levels.

The curves in Fig. 1 represent the data well but, with $a_1^{\text{ro}} > 0$, are *inverted* compared to the $n = 0$ ground state. Thus, the out-of-plane rock cannot be modeled by an effective torsional Hamiltonian with modified barrier height, opposite to our earlier finding for the in-plane rock [13]. To evaluate the vibrational frequency E_v^{ro} , we must subtract the appropriate zero-point torsional energy from $(E_v^{\text{ro}} + a_0^{\text{ro}})$. In the absence of a model accounting for the ν_{11} torsional inversion, we assume the ground state value of 134.1 cm^{-1} , giving $E_v^{\text{ro}} = 1153.1\text{ cm}^{-1}$. This is now close to the 1155.1 cm^{-1} from normal mode analyses [1,2], supporting the idea in point (i) above that strong torsional effects on the energy structure have contributed to past difficulties in fitting the vibrational spectrum of methanol.

Our study has also revealed interactions coupling the ν_{11} mode to other vibrational states, exposing new intramolecular pathways for energy relaxation. Initially, small anomalies in certain ν_8 CO-stretching subbands and the three tentative assignments of far-infrared laser lines accessing ν_{11} levels [6–8] gave useful clues for our de-

ductive work. For example, we were able to trace a newly discovered perturbation of the $(n, K)^v = (0, -7)^{\text{co}} E$ state at $J = 12$ to a level-crossing resonance with the unseen $(0, -4)^{\text{ro}} E$ state. When we extrapolated from $J = 12$ back to the K -reduced $(0, -4)^{\text{ro}} E$ origin, we obtained close agreement with the FIRL result circled in Fig. 1, giving convincing support for the $(0, -4)^{\text{ro}} E$ energy.

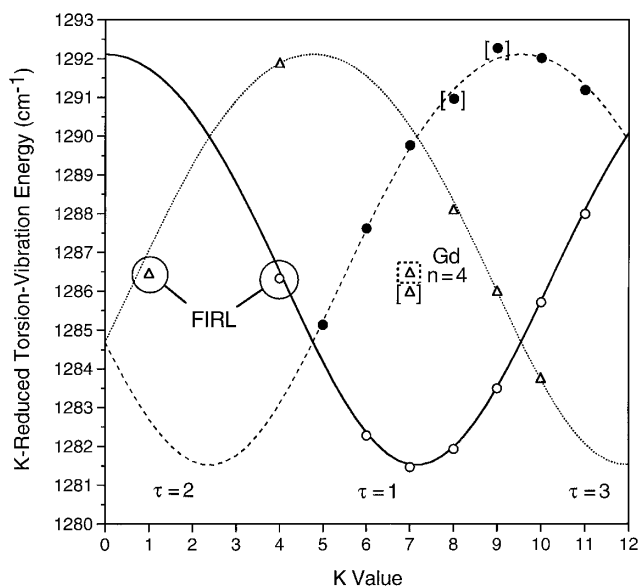


FIG. 1. Observed torsion-vibration energies (plotted points) and fitted τ curves for the $n = 0$ state of the ν_{11} out-of-plane CH_3 -rocking mode of CH_3OH . The two circled points, extrapolated from high- J far-infrared laser observations, were excluded from the fit, as were the three points in brackets which are believed to be perturbed. The point in the dashed square is a calculated $n = 4$ ground state energy. The τ curves are inverted compared to the $n = 0$ picture for the conventional one-dimensional torsional Hamiltonian.

Another striking J -localized resonance couples $(0, 8)^{ro}$ and $(0, 10)^{co}$ A states. The energy ladders cross at $J = 17$, as shown in Fig. 2, and are almost fully mixed at resonance with two lines of similar intensity seen for each transition up to $J = 17$. The interaction matrix element is approximately half the perturbed separation in Fig. 2, giving $W_{int} \approx 0.075 \text{ cm}^{-1}$. A second $\Delta K = 2$ level crossing occurs for the $(0, 8)^{ro}$ and $(0, 10)^{co}$ E states at $J = 25$, with $W_{int} \approx 0.172 \text{ cm}^{-1}$. In torsionally mediated coupling to $n = 1 \nu_8$ states, the $(0, 7)^{ro}$ and $(1, 5)^{co}$ E ladders cross at $J = 10$, with $W_{int} = 0.038 \text{ cm}^{-1}$, and the $(0, -6)^{ro}$ and $(1, -2)^{co}$ E levels at $J = 15$ with $W_{int} = 0.0064 \text{ cm}^{-1}$.

The ν_{11} state displays $\Delta K = 0$ perturbations as well due to level crossings with $n = 4$ ground-state curves [5]. The $(n, \tau, K)^v = (0, 3, 7)^{ro}$ and $(4, 3, 7)^{gr}$ states are particularly close and can interact strongly. Our bracketed $\tau = 3, K = 7$ point at 1286 cm^{-1} in Fig. 1 is just below the calculated $n = 4$ energy, so it is likely a down-shifted mixed state of mainly $(4, 3, 7)^{gr}$ character. A complementary $(0, 3, 7)^{ro}$ mixed state should then lie just above the $\tau = 3$ curve, but has not been seen. The other two $(0, 2, 8)^{ro}$ and $(0, 2, 9)^{ro}$ bracketed points lie about 30 cm^{-1} below and above their $n = 4$ partners [5], so they are perturbed downward and upward as seen in Fig. 1.

Next we consider the application of our results to assignments of methanol FIRL emission. Figure 3 shows part of the extensive system pumped by the $9P(14)$ CO_2 line [5–8], with FIRL lines to both $(0, -4)^{ro}$ and $(0, -6)^{ro}$ E levels. For the latter, our data yield $L_c = 123.7048 \text{ cm}^{-1}$, in agreement with the 123.70 cm^{-1} found from accurate wavelength measurements [7]. We have not seen the

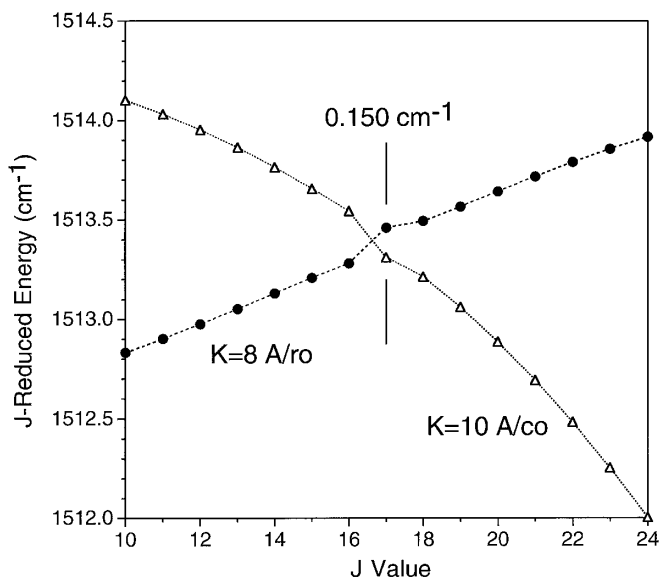


FIG. 2. J -reduced energies for the $(n, K)^v = (0, 8)^{ro}$ and $(0, 10)^{co}$ A substates of CH_3OH , showing the level crossing at $J = 17$ and the resulting J -localized perturbations. The energies are equal to the term values minus $0.8J(J + 1)$, where 0.8 cm^{-1} is the approximate B value.

$(0, -4)^{ro}$ E subband, so cannot confirm line L_b and its partner in the analogous $9P(24)$ system [5,6]. However, the W^{ro} origins extrapolated from the $J = 15$ and $J = 8$ levels in the $9P(14)$ and $9P(24)$ systems agree to within 0.2 cm^{-1} , and are supported independently via the resonance with the $(0, -7)^{co}$ E state discussed above.

For the $(0, 1)^{ro}$ A FIRL system, the circled point in Fig. 1 lies encouragingly close to the $\tau = 3$ curve. That energy was derived from the $9P(22)$ transition scheme shown in Fig. 3 of Ref. [5], with overall uncertainty of about $\pm 0.6 \text{ cm}^{-1}$ in estimating the K doubling and extrapolating from $J = 18$ back to $J = 0$, similar to the deviation in Fig. 1.

We also have a new FIRL assignment with the first known pumping into the ν_{11} state, shown in Fig. 4. Our prediction for the $Q(14)$ line of the $K = 9 \leftarrow 10$ A subband is 1083.479 cm^{-1} , coincident with the $9R(28)$ CO_2 line at $+20 \text{ MHz}$ offset which pumps FIRL lines at 51.47 and 74.07 cm^{-1} [7]. Our data give $L_a = 51.4440 \text{ cm}^{-1}$ and $L_b = 73.9220 \text{ cm}^{-1}$ in good agreement with the observations [7]. The reported L_b parallel polarization is a problem, however, as our scheme has $\Delta J_{FIR} \neq \Delta J_{pump}$ for this line, requiring perpendicular polarization.

In summary, the present assignments for the ν_{11} dark state of CH_3OH represent a significant breakthrough in the vibrational spectroscopy of the lower modes of methanol, answering the open questions about the exact position and

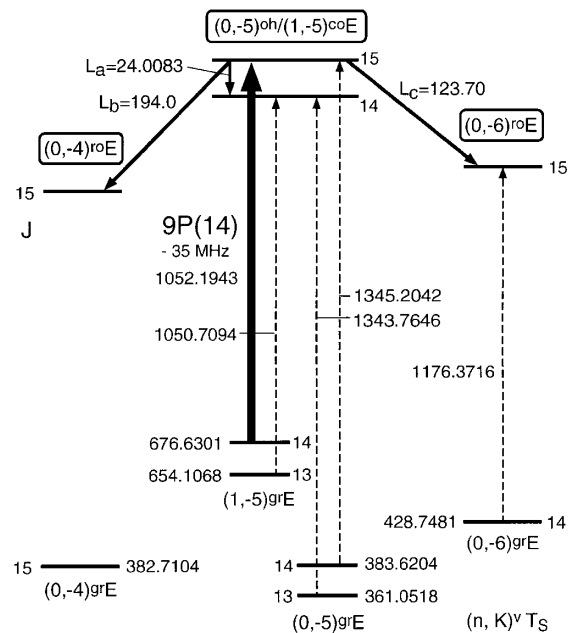


FIG. 3. Part of the transition scheme for far-infrared laser lines of CH_3OH optically pumped by the $9P(14)$ CO_2 laser line at -35 MHz offset [5–8], showing FIRL transitions to ν_{11} out-of-plane rocking levels. The upper pump level is a mixed OH-bending/ CO -stretching state [5]. The ground-state energies are obtained from the model of Ref. [10]. Combination difference loops based on the spectroscopic data yield the wave number $L_c = 123.7048 \text{ cm}^{-1}$.

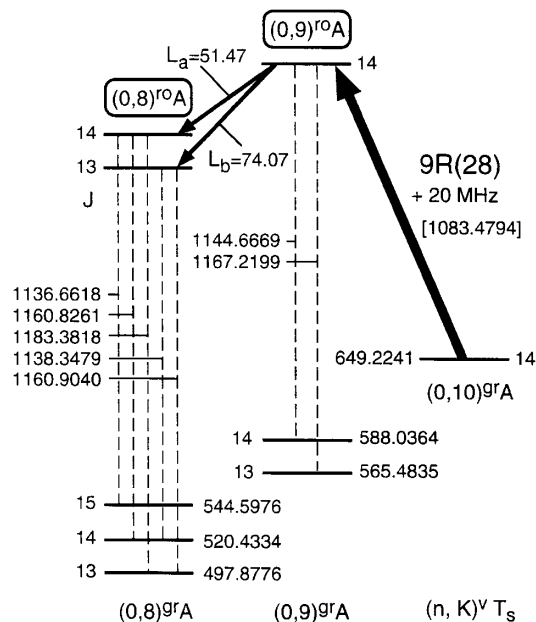


FIG. 4. Proposed transition scheme for FIRL lines of CH_3OH optically pumped by the $9R(28)$ CO_2 laser line at 20 MHz offset [7]. Pump wave number is calculated from the reported offset, and ground-state energies are from the model of Ref. [10]. Combination difference loops based on the spectroscopic data yield FIRL wave numbers of $L_a = 51.4440 \text{ cm}^{-1}$ and $L_b = 73.9220 \text{ cm}^{-1}$.

the torsional structure of the ν_{11} mode. Our ν_{11} energy of 1153.1 cm^{-1} differs markedly from the previous estimate of $1145 \pm 4 \text{ cm}^{-1}$ [1], and is in better agreement with the 1155.1 cm^{-1} from normal mode calculations [1,2]. The observation of inverted torsional curves, the first for bending modes of methanol, is an important pointer towards potential universality of this phenomenon. Its discovery now for the ν_{11} mode as well as ν_2 and ν_9 CH stretches [3,4] will stimulate searches for torsional inversion in other modes and molecules, and drive theoretical work towards a new global torsion-vibration formalism to go beyond the previous one-dimensional effective torsional Hamiltonian.

Observations of J -localized level-crossing resonances coupling the ν_{11} and ν_8 modes have explained perturbations in the CO-stretching spectrum and revealed new channels for intermode mixing and IVR energy transfer. Our results have placed tentative assignments of FIRL emission to ν_{11} levels on a secure footing, and the first FIRL system wholly within the ν_{11} state has been identified, pumped by the $9R(28)$ CO_2 line.

We will seek in the future to extend the ν_{11} assignments to lower K , and to analyze the ν_4 , ν_5 , and ν_{10} CH_3 -bending bands as well to probe the torsional structure. Whether a variant of Wang and Perry's successful internal coordinate model for the CH-stretching modes [4] will apply to the CH_3 rocking and bending cases is an interesting question. How to define "local" modes is less clear for bending than for stretching vibrations, but we envisage an approach treating the angular motions of the three equivalent CH bonds as coupled two-dimensional harmonic oscillators which may lead to a unified picture.

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- [1] A. Serrallach, R. Meyer, and Hs. H. Günthard, *J. Mol. Spectrosc.* **52**, 94 (1974).
- [2] F. C. Cruz *et al.*, *J. Mol. Spectrosc.* **156**, 22 (1992).
- [3] Li-Hong Xu, X. Wang, T. J. Cronin, D. S. Perry, G. T. Fraser, and A. S. Pine, *J. Mol. Spectrosc.* **185**, 158 (1997).
- [4] X. Wang and D. S. Perry, *J. Chem. Phys.* **109**, 10795 (1998).
- [5] R. M. Lees and Li-Hong Xu, *J. Mol. Spectrosc.* **196**, 220 (1999).
- [6] J. O. Henningsen, *Int. J. Infrared Millim. Waves* **4**, 707 (1983).
- [7] J. O. Henningsen, *Int. J. Infrared Millim. Waves* **7**, 1605 (1986).
- [8] G. Moruzzi, B. P. Winnewisser, M. Winnewisser, I. Mukhopadhyay, and F. Strumia, *Microwave, Infrared, and Laser Transitions of Methanol: Atlas of Assigned Lines from 0 to 1258 cm^{-1}* (CRC Press, Boca Raton, Florida, 1995).
- [9] Detailed line assignments will not be given in this paper, but are available from the authors on request.
- [10] Li-Hong Xu and J. T. Hougen, *J. Mol. Spectrosc.* **173**, 540 (1995).
- [11] D. G. Burkhard and D. M. Dennison, *J. Mol. Spectrosc.* **3**, 299 (1959).
- [12] R. M. Lees and J. G. Baker, *J. Chem. Phys.* **48**, 5299 (1968).
- [13] R. M. Lees, Li-Hong Xu, D. Hurtmans, and Z. Lu, in *Proceedings of the 52nd International Symposium on Molecular Spectroscopy*, Columbus, Ohio, 1997 (Report No. WF04, unpublished).