

Giant K Doubling in the Infrared Spectrum of CH_3OH : A Sensitive Probe for CH_3 -Rock/ CO -Stretch/ OH -Bend Vibrational Coupling

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The asymmetry splittings of K -doublet levels in excited vibrational state of methyl alcohol are found to be sensitive indicators of intermode interactions. Fourier transform spectra reveal giant K doubling of the $(n\tau K)^V = (122)^r$ CH_3 -rocking levels due to a near resonance with the CO stretch. Several spectral anomalies are thereby explained, and a significant far-infrared laser transition system is reassigned. The K -doublet splittings will provide a useful tool for the study of torsion-mediated mode coupling and intramolecular energy transfer channels in methanol.

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This Letter reports Fourier transform infrared (FTIR) spectroscopic results for CH_3OH in which coupling among the CH_3 -rocking, CO -stretching, and OH -bending vibrational modes is manifested by dramatic perturbations to the asymmetry splittings of levels of A torsional symmetry. A near-degeneracy between the $K = 0$ CO stretching and $K = 2$ CH_3 rocking $\nu_t = 1$ excited torsional substates, where K is the axial component of rotational angular momentum J , leads to a remarkable enhancement in the $K = 2$ rocking splitting which we term "giant" K doubling. The identification of this resonance resolves several spectroscopic puzzles for CH_3OH and alters the interpretation of an important far-infrared (FIR) laser transition system optically pumped by the $9P(16)$ CO_2 laser line. The recognition of strong torsion-mediated vibrational coupling and interstate mixing sheds new light on the diffuse structure of the bending bands in the low-resolution IR spectrum of CH_3OH and will lead to a more definitive analysis of the normal modes and the vibrational force field.

Methyl alcohol is one of the simplest and most fundamental of the large class of molecules in which a threefold-symmetric CH_3 internal top can execute large-amplitude torsional motion. The axial moments of inertia of the CH_3 top and the OH framework are small and the potential barrier hindering the internal rotation is relatively low. Thus torsional tunneling is rapid compared to the overall rotation and the appropriate molecular symmetry group is isomorphic to C_3 , giving torsion- K -rotation levels of A and E symmetry. However, methanol is a slightly asymmetric top, and the torsion-rotation Hamiltonian has $\Delta K = \pm 2$ asymmetry matrix elements. These represent symmetry-breaking terms for the C_3 representation and act to reestablish the customary asymmetric rotor J_{K_a, K_c} four-group species by removing the $\pm K$ torsion-rotation degeneracy of the A levels for $K > 0$ and by mixing E levels of $+K$ and $-K$ together (often called E_1 for $+K$ and E_2 for $-K$) [1]. The magnitude of the K doubling for A levels with $K > 1$ is sensitive to the separation between asymmetry-coupled levels of differ-

ent K , generally decreases rapidly with K , and is normally much smaller for higher torsional states than for the $\nu_t = 0$ ground state. However, in the complex manifold of excited torsion-vibration states for methanol, $|K\rangle^V$ and $|K \pm 2\rangle^V$ levels of different vibrational states may accidentally lie much closer than those within the same V state. This can significantly perturb the asymmetry splitting from the expected value, so that the K doubling serves as a sensitive probe of interactions among the excited vibrational modes.

The present work is based on new spectroscopic assignments in the FTIR spectrum of CH_3OH from 1000 to 1400 cm^{-1} , recorded at a resolution of 0.002 cm^{-1} on the modified Bomem DA3.002 instrument in the laboratory of J. W. C. Johns at the National Research Council of Canada in Ottawa. This region contains the strong and well-explored CO -stretching R branch, and the OH -bending band seen at low resolution as a broad peak centered at 1360 cm^{-1} . Schematic torsion-vibration energy curves are plotted for the three vibrational modes in Fig. 1, showing the complex pattern in the region of the $\nu_t = 0$ OH -bending state. The $\nu_t = 0$ OH -bending curves are crossed by those of the $\nu_t = 1$ torsionally excited CO -stretching and CH_3 -rocking states, as well as the $\nu_t = 4$ curves rising up from the vibrational ground state, leading to significant intermode level-crossing resonances and mixing. Interactions in the region highlighted by the circle in Fig. 1 are of particular interest in the present work.

The τ index for the curves of Fig. 1 follows Dennison's $(n\tau K^\pm, J)^V$ energy level notation [3], which is common in the literature. The torsional quantum number n is identical to ν_t , τ defines the A , E_1 or E_2 torsional symmetries, and V labels the vibrational state as $V = \text{CO}$, $V = r$, $V = \text{OH}$, or $V = 0$. The \pm superscript on K distinguishes the two members of a K doublet and is particularly important in the present context. The $K = 0$ levels have no splitting and are A^+ levels. The parity of an A^\pm level is given by $\pm(-1)^{J+\nu_t}$; thus the selection rules for transitions are $+\leftrightarrow-$ for $\Delta(J +$

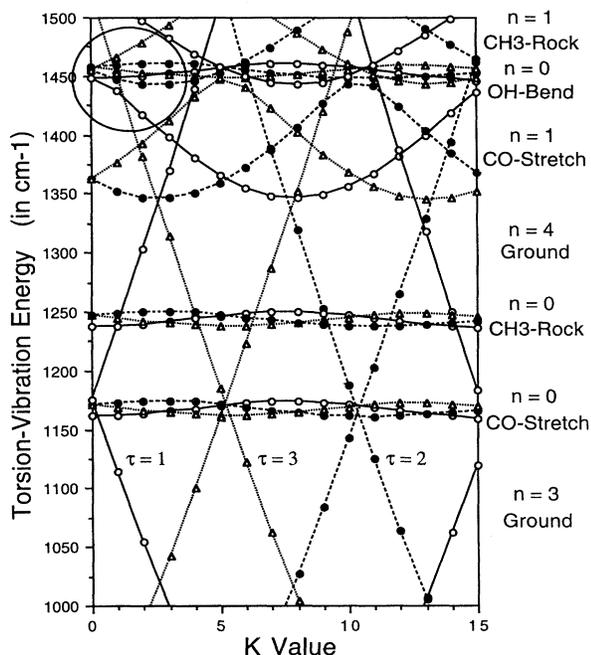


FIG. 1. Schematic torsion-vibration energy curves for different torsional n states of the lower vibrational modes of CH_3OH and high-lying $n = 3$ and $n = 4$ levels of the vibrational ground state. The circle highlights a region of particular relevance for the present work, in which Fermi resonance couples the $n = 0$ OH-bending, $n = 1$ CO-stretching states.

v_t) = even, but $\pm \leftrightarrow \pm$ for $\Delta(J + v_t) = \text{odd}$ [3,4]. However, perturbations occur between states of the same parity, hence an A^+ state interacts with an A^- state for $\Delta v_t = 1$, but only with another A^+ state for $\Delta v_t = 0$.

Recently we have assigned a number of $v_t = 1$ CH_3 -rocking subbands and $v_t = 0$ OH-bending subbands, using insights gained from parallel studies of the ^{18}O and ^{13}C isotopic species in our group [5,6]. As with the other isotopomers, there are striking anomalies in the K doubling for the A levels and evidence of strong torsion-mediated Fermi coupling between the $v_t = 0$ OH-bend and the torsionally excited $v_t = 1$ CH_3 -rocking mode. Figure 2 is a sample transition diagram highlighting special features for the $K = 2A$ substate. The IR and FIR wave numbers given in the caption show that the closure relations are satisfied going around closed combination loops and that the separation between the Fermi-coupled $(022)^{\text{OH}}$ and $(122)^r$ states is about 25 cm^{-1} . One of the noteworthy features in Fig. 2 is the $(022)^{\text{OH}} \leftarrow (122)^0$ and $(122)^r \leftarrow (022)^0$ transitions, which are forbidden because (022) and (122) wave functions are different eigensolutions of the torsional Hamiltonian and so should be orthogonal. The observation of these transitions points to Fermi mixing between the $(022)^{\text{OH}}$ and $(122)^r$ states [5] and consequent intensity borrowing from the allowed $\Delta v_t = 0$ subbands to produce the forbidden lines in the

spectrum. Also, as for the ^{18}O isotopomer [5], the A^\pm ordering is reversed for the $(022)^{\text{OH}}$ doublets compared to the ground state. However, the most striking aspect of Fig. 2 is the giant K doubling of the $(n\tau K, J)^V = (122, 12)^r$ levels, which is almost 2 order of magnitude larger than that of the $(122, 12)^0$ ground state doublet.

The origin of the giant K doubling emerges when the CO-stretching state is brought into the picture. We had assigned $v_t = 1$ subbands of the CO stretch about ten years ago, and an unsettled mystery was the presence of two subbands lying close together in the spectrum and each having a $(110)^0$ lower state on the basis of ground-state combination differences. Now, however, knowing the location of the $(122)^r$ levels from the rocking-band assignments and the ground state energy structure, we can identify the upper state of the second “ $(110)^{\text{CO}}$ ” subband as the $(122^+)^r$ state and explain the anomalies as the result of intermode mixing and perturbation between the near-degenerate $(122^+)^r$ and $(110^+)^{\text{CO}}$ states. The energy scheme is shown in Fig. 3, with term values given by adding the IR subband origins to known ground-state energies. All of the states shown are of A torsional symmetry and are labeled in $(n\tau K^\pm)^V$ notation. The $(110)^r$ subband has not yet been identified; hence the term value was calculated using the barrier height of 557 cm^{-1} from microwave results for the CH_3 -rocking mode [7].

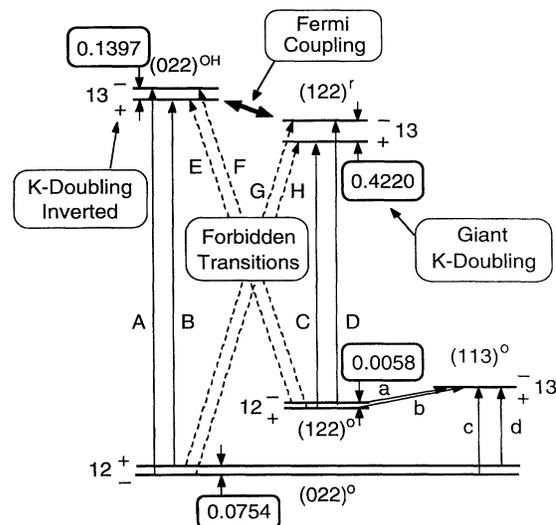


FIG. 2. Sample energy level system involving the $(n\tau K)^V = (122)^r$ rocking levels of CH_3OH showing a wide variety of anomalous features, including Fermi coupling to the $(022)^{\text{OH}}$ levels, large variations in K -doublet splittings, and forbidden $\Delta v_t = 0$, $\Delta K = 0$ transitions. Giant K doubling is seen for the $(122)^r$ levels, and the A^\pm ordering is inverted for the $(022)^{\text{OH}}$ doublets. IR wave numbers (in cm^{-1}) are $A = 1338.2541$, $B = 1338.0390$, $C = 1131.8117$, $D = 1132.2278$, $E = 1157.0469$, $F = 1157.1923$, $G = [1313.221]$ (seen in spectrum plot but missing from FTIR peak list), and $H = 1312.8744$. FIR wave numbers are [13] $a = 88.647$, $b = 88.6536$, $c = 269.7160$, and $d = 269.6407$.

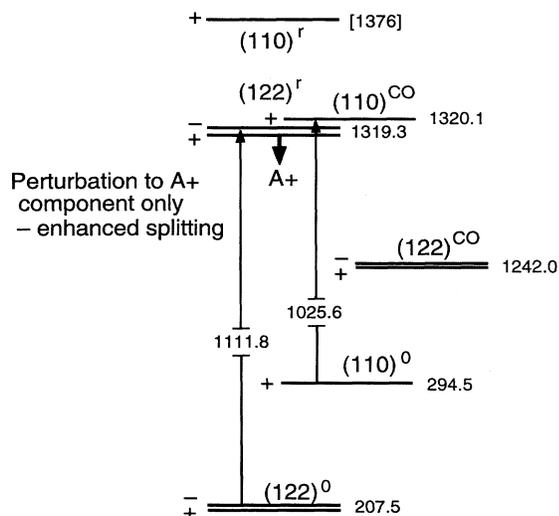


FIG. 3. Torsion- K -rotation energy level structure for CH_3OH showing the near-degeneracy between the $(122)^r$ and $(110)^{\text{CO}}$ states. Term values are obtained by adding IR subband origins to ground state energies. The $(110)^r$ term value is estimated from calculations using a 557 cm^{-1} barrier height for the rocking mode [7].

The giant K doubling arises because the $(110^+)^{\text{CO}}$ state in Fig. 3 interacts only with the A^+ component of the $(122)^r$ doublet lying just underneath it, perturbing it downward strongly but leaving the A^- component untouched. This magnifies the splitting of the $(122)^r$ doublet enormously, justifying the title of giant K doubling. Normally a $K = 2^+$ doublet splitting arises through the interaction of the $K = 2^+$ level with the $K = 0^+$ level in the same ν_t and V states and is given to second-order perturbation theory by [3]

$$\Delta_2(J) = \{(B - C)^2/8\}[J(J + 1) - 2]J(J + 1) \\ \times \langle \nu_t, K = 2 | \nu_t, K = 0 \rangle^2 / |E(\nu_t, K = 2)^V \\ - E(\nu_t, K = 0)^V|,$$

where $(B - C)$ is a molecular asymmetry constant and $\langle | \rangle$ denotes a torsional overlap matrix element. For the excited $\nu_t = 1$ CH_3 -rocking state, the energy denominator for Δ_2 is seen from the term values in Fig. 3 to be 57 cm^{-1} , as compared to the separation between the $(122)^r$ and $(110)^{\text{CO}}$ states of only about 0.8 cm^{-1} . Thus, even though a perturbation matrix element coupling a doublet level to a different vibrational state may be small, this can be compensated by a major reduction in energy denominator in a near-resonance. The sensitivity of the K doublet splittings to the energy denominators in the relations for the $\Delta_K(\nu_t, J)$ is precisely what makes them excellent probes for intermode interactions in the excited state manifold, particularly for the higher ν_t states seen in

Figs. 1 and 3 to have large energy level separations within a given V mode.

The mixing of the $(122^+)^r$ levels with the $(110)^{\text{CO}}$ levels accounts for the second $(110)^{\text{CO}}$ subband as the forbidden $(122^+)^r \leftarrow (110)^0$ subband arising from intensity borrowing. It also explains a third anomaly in the IR spectrum in which the A^+ member of a doublet in the $(122)^r P$ subbranch is distinctly weaker than its A^- partner. This intensity discrepancy is due to the stealing of intensity by forbidden $(110, J - 1)^{\text{CO}} \leftarrow (122^+, J)^0$ transitions, which can be seen in the spectrum lying just above the allowed lines of the $(122)^r$ subbranch.

From our IR spectroscopic data for the $(122)^r$, $(110)^{\text{CO}}$, and $(122^+)^r \leftarrow (110)^0$ subbands plus information on the ground-state energies, the positions of the $(122, J)^r$ doublet levels and the interacting $(110, J)^{\text{CO}}$ levels can all be determined relative to the ground-state $(110, J)^0$ levels as shown in Fig. 4. The $(122)^r$ doublet splitting starts small, as it should, but grows rapidly with J . Since the effective rotational B value is slightly greater for the CH_3 rock than the CO stretch, the $(110, J)^{\text{CO}}$ levels slowly approach the $(122, J)$ levels at first, but then encounter the Fermi avoided crossing and gradually move away while the $(122)^r$ doublet splitting keeps increasing steadily.

The $(122)^r$ mixing is significant to the assignment of the seven FIR laser lines optically pumped by the $9P(16)$ CO_2 laser line at an offset of -56 MHz , one of the first FIR laser systems observed for CH_3OH in 1970 [8]. The IR pump absorption has been reported several times in the literature to be the $R(110, 16)^{\text{CO}}$ transition [9-11], but we have now established that it is actually the Fermi-induced $(122^+, 17)^r \leftarrow (110, 16)^0$ forbidden transition. The energy level and transition scheme is illustrated in Fig. 5, with three of the FIR laser lines shown. Two of the laser frequencies have

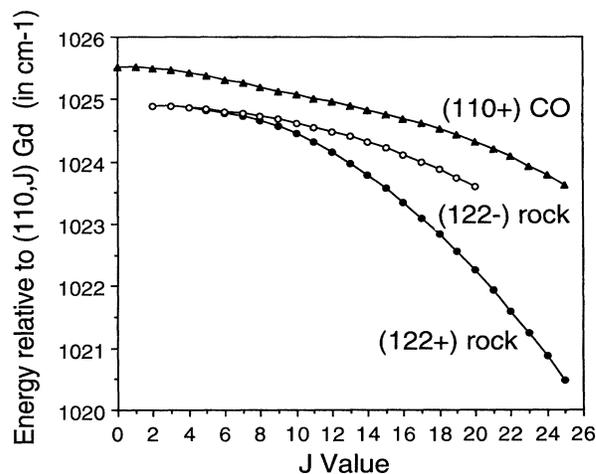


FIG. 4. Energies of the $(110^+, J)^{\text{CO}}$ and $(122^\pm, J)^r$ levels of CH_3OH relative to the $(110, J)^0$ ground-state levels, showing the giant splitting of the $(122)^r$ doublets and the repulsion between the $(110^+)^{\text{CO}}$ and $(122^+)^r$ levels.

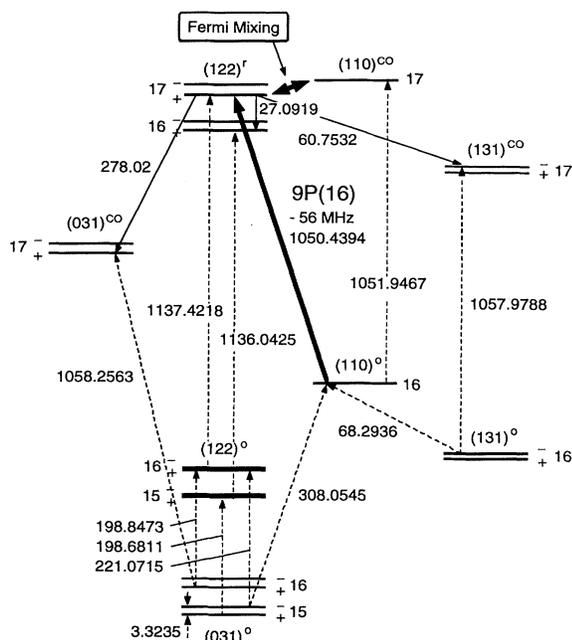


FIG. 5. Energy level scheme for FIR laser lines of CH_3OH optically pumped by the $9P(16)$ CO_2 laser line at -56 MHz offset. The pump absorption was previously identified as the $R(110,16)^{\text{CO}}$ transition in the literature [9–11] but is now reassigned as shown. Transition wave numbers are in cm^{-1} .

been accurately measured [12]; hence the closure relations for combination loops containing those transitions should be satisfied within a net experimental uncertainty of approximately $\pm 0.001 \text{ cm}^{-1}$. Picking a loop containing the pump line and the 60.7532 cm^{-1} FIR laser line as an example, we find

$$\begin{aligned} \delta_{\text{loop}} &= 1050.4393 + 68.2936 - 1057.9788 - 60.7532 \\ &= 0.0010 \text{ cm}^{-1}, \end{aligned}$$

consistent with the measurement tolerance. For the high-frequency laser line, the following combination loop yields an accurate wave number:

$$\begin{aligned} V_L &= 1137.4218 + 198.8473 - 1058.2563 \\ &= 278.0128 \text{ cm}^{-1}. \end{aligned}$$

This checks with the reported wave number of 278.02 [9], confirming the assignment. Other FIR laser lines for this system were assigned to transitions to $(031)^r$ and $(131)^r$ levels; we are still searching for these rocking subbands in the spectrum. We note that our reassignment for this system resolves the problems recognized in previous work [9] that the effective B value required by the 27.0919 cm^{-1} line was too high for the CO stretch, while the term value for the pumped state was lower than expected for the $(110)^{\text{CO}}$ state. The latter discrepancy was suggested as due to Fermi interaction with the $(010)^{\text{OH}}$

state [9], which is at least partially correct as the $(010)^{\text{OH}}$, $(122)^r$ and $(110)^{\text{CO}}$ states are clearly all coupled together in a Fermi polyad.

The three-way nature of the coupling makes quantitative analysis of the perturbations a challenging problem, given our present limited insight into the unperturbed positions of the interacting levels. We expect in the near future to obtain a fuller picture of the excited state manifold from further spectroscopic assignments and to use this to guide a deperturbation analysis to determine the Fermi coupling constants. Our results show that these are of substantial magnitude and provide significant relaxation channels for torsionally mediated intramolecular vibrational energy redistribution (IVR) among the lower modes of CH_3OH . In exploring these IVR mechanisms, the unique structure of the methanol levels of A symmetry with their small K -doublet splittings will offer a sensitive tool for probing the variety of the interaction channels and for unraveling the complex pattern of intermode resonances and vibrational mixing for the various isotopomers of methanol.

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