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Infrared–Infrared Double-Resonance Spectra Involving Fermi Perturbed Levels and CO Stretch Band Transitions of CD_3OH

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Abstract. Infrared–infrared double-resonance spectroscopy has been carried out for CD_3OH. Seven of the observed double resonance signals occur in the congested Q-branch region of the C–O stretch band while one is a transition to an excited torsional state. The signals appear as single signals as opposed to the more regular appearence as pairs. Three of the observed transitions involve excited-state levels which are shifted by Fermi resonance between excited C–O stretch-state levels and levels of high-lying torsional modes of the vibrational ground state. These resonances result in a considerable change in the Stark shift for the excited-state levels compared with unperturbed levels. The a-component μ_a'' of the permanent electric-dipole moment value has been determined for several ground-state levels. The average value in the ground state is calculated to be $\mu_a'' = 0.918$D. The results have allowed the assignment of several previously reported far-infrared laser lines and also confirmed assignments proposed by other workers.

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Several different techniques have over the past decade been used to study the complicated spectra of methanol and its isotopic derivatives in the infrared region of the spectrum. The techniques include Fourier-transform and diode-laser spectrometers for high-resolution absorption spectroscopy. The observation and frequency measurement of optically-pumped far-infrared laser lines from the molecules and the use of double-resonance techniques have been an important aid in the analysis of the congested C–O stretch band. The interest in these molecules is partly due to their great success as efficient laser gases in optically pumped far-infrared (FIR) lasers. The molecules are also some of the simplest species exhibiting internal rotation.

The C–O stretch band of methanol and its isotopes is located in the 10-μm region and coincides with the CO_2 laser emission lines. The 10-μm absorption region of the CD_3OH molecule has previously been studied using diode-laser spectroscopy [1, 2] and Fourier-transform spectroscopy [3, 4]. Similar to the other isotopomers of methanol, CD_3OH is a very rich source of optically pumped FIR laser lines and the total number of reported FIR laser lines is now approximately 340 [5, 6]. There are still very few of these transitions that have been assigned. In CD_3OH the intramultiplet splitting is typically $0.1\,\mathrm{cm}^{-1}$. This is much reduced compared with CH_3OH where it is typically $1\,\mathrm{cm}^{-1}$. We therefore expect fewer coincidences between CO_2 laser lines and torsional ground-state transitions in CD_3OH.

Weber et al. [2] have identified the prescence of a Fermi resonance between pure CO stretch-state levels and torsional-excited levels of the ground state. Fermi resonance is a perturbation occuring for energy levels of nearly the same energy and results from the interactions between different vibrations of the same symmetry and the same rotational quantum numbers. The strongest interaction occurs for $\tau = 1$ levels at $K = 1$, and $\tau = 3$ levels at $K = 8$, however, also neighbouring K-stacks are perturbed resulting in shifts of the energy levels of varying amount for the different K-stacks. This complicates the analysis of the CD_3OH spectrum.

In the present work we have applied the infrared–infrared double-resonance technique (IRIRDR) to the very congested Q-branch region of the C–O stretch band of the CD_3OH molecule. The technique makes use of a single side-band modulation of the CO_2 laser frequency in the presence of a Stark field. Most of the observed spectra consist of a single double-resonance signal rather than pairs of double-resonance signals, as is usually observed in symmetric top or near symmetric top molecules like methanol and its isotopomers. The transitions have been assigned to ${}^QQ$ transitions in the CO stretch band except for one transition which has been assigned to a high-lying torsional state. Three of these transitions involve Fermi perturbed levels. It has not been possible to completely assign all transitions. Following the assignments it was possible to determine dipole-moment components for several levels of the ground state and we have also proposed assignment of several previously observed optically pumped far-infrared (FIR) laser lines.

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1 Experimental

The experimental arrangement has recently been described in detail [7, 8] and is in principle simular to the setup previously used by Bedwell and Duxbury [9]. Briefly, the experiments make use of a semi-sealed low-pressure CO_2 laser, thus allowing the use of different isotopic derivatives of CO_2. This choice of laser does, however, limit the tunability to ±60 MHz around the line center and only absorption transitions within this range can be reached. The power used was generally less than 1 W.

In the IRIRDR experiment we use 50% of the infrared beam directly from the laser, the other beam is obtained from generating an upshifted sideband on part of the other 50% by using an acousto-optic modulator with a center frequency of 49 MHz. The two beams are focused into and sent co-propagating through a multipass Stark cell. On one plate we apply a fixed field of −200.0 V while the other plate is connected to a programmable high voltage supply which is driven by a ramp. We apply a small modulation field in addition to the regular field which could be ramped from 0 to −2000 V. Phase sensitive detection can then be used. This was done at $2f$ detection so that absorption-like (second derivative) signals were observed. A constant amplitude of the electric-field modulation was used, which results in the apparent linewidth being greater for high-field resonances. The plate separation was calibrated against a pair of double resonance signals from CH_3F [10] and $^{13}CH_3F$ [11] for which there is a very accurate determination of the electric-dipole moment. A field of up to 9500 V/cm could be applied between the plates. A HgCdTe detector was used to monitor the change in CO_2 laser power. In the present work we also had the option of using a quarter-wave plate in one of the beams thus changing the polarization from being linear to circular.

2 Results and Analysis

The rovibrational states are described by the notation $(n\tau K, J)$, where J is the total angular momentum quantum number, K is the projection along the molecular a axis, n indicates the torsional level and τ, which can take on values of 1, 2, and 3 is used to characterize the symmetry class. The classification E_1, A, E_2 correspond to $\tau + K = 3N$, $3N+1$, $3N+2$, respectively, where N is an integer. The E states are doubly degenerate while asymmetry removes the $\pm K$ degeneracy of the A states.

Methanol is a near-prolate symmetric top molecule with a threefold-hindered internal rotation potential. The permanent dipole moment can be resolved into two components, μ_a along the prolate top axis almost parallel to the C–O bond, and μ_b lying perpendicular to the principal top axis. The contribution from μ_b is negligible for CH_3OH at the small electric fields used while for the isotopomer CH_3OD the contribution is sizable [8]. For CD_3OH the contribution is expected to be similar to that of CH_3OH since the asymmetry parameter D_{ab} is not very different from that of CH_3OH [12]. The C–O stretch band is a predominantly parallel band, thus the overall selection rule is $\Delta K = 0$. In the present work we have only observed levels of E_1 and E_2 symmetry showing first order Stark effect.

In the presence of a Stark field the degeneracy of each energy level will be lifted and the shift Δ of each M_J component of a level is given by

$$\Delta = \frac{\mu_a E K M_J}{J(J+1)} . \tag{1}$$

The splitting between two M components, $\Delta_1 - \Delta_2$, will therefore be tuned. When the splitting equals the frequency difference between the two laser beams, one from the carrier and one from the sideband, and both are polarized perpendicular to the electric field, the overall selection rule is $|\Delta M| = 2$, thus resulting in the double-resonance condition

$$\Omega_{\mathrm{RF}} = \Delta_1 - \Delta_2 = \frac{2\mu_a E K}{hJ(J+1)} , \tag{2}$$

or

$$\frac{E}{\Omega_{\mathrm{RF}}} = \frac{hJ(J+1)}{2\mu_a K} , \tag{3}$$

where Ω_{RF} is the applied radiofrequency, E the applied electric field, and h is Planck's constant. IRIRDR signals usually comes in pairs where one is associated with a common ground-state level and one with a common excited-state level. Each component of the doublet is composed of a large number of transitions that are exactly degenerate in the case of first-order Stark effect. The relationship between such pairs for a ^{Q}Q transition is

$$E_1/E_2 = \mu_a''/\mu_a' , \tag{4}$$

where $E_1 < E_2$. It has been observed in $^{12}CH_3OH$ and $^{13}CH_3OH$ [7] and in $CH_3{}^{18}OH$ [13] that excited-state dipole-moment values generally are larger than the values for the ground state. If we assume the same is the case for CD_3OH then we notice from (4) that the DR associated

Table 1. Observed infrared–infrared double-resonance signals in CD_3OH

CO_2 laser line	E_1/Ω_{RF}	E_2/Ω_{RF}	Assignment $(n\tau K, J)$	Dipole moments	
	Observed[a] [V/cm MHz]			μ_a'' [D]	μ_a' [D]
$10R(36)$		18.749(5)	$^{Q}Q(039,12)$	0.9182(3)	
$10R(18)$[b]		18.77(10)	$(039,12)^{O}$ → $(439,13)^{O}$	0.917(5)	
$10R(30)$[b]		17.97(10)	$^{Q}Q(0\tau 8,11)$[e]		0.912(5)
$10R(34)$	19.408(21)[c]	19.408(21)[c]	$^{Q}Q(118,8)$	0.9209(8)	0.9209(8)
$10R(34)$	27.501(18)	29.576(18)	$^{Q}Q(0312,17)$	0.9209(6)	
$10R(34)$	32.476(17)	32.476(17)	$^{Q}Q(114,20)$	0.9175(15)	0.9175(15)
$10R(32)$		13.031(22)	$^{Q}Q(011,3)$[d]	0.9145(15)	

[a] Figures in parenthesis indicate the uncertainty attached to the least significant figures

[b] $^{12}C^{18}O_2$-laser line

[c] Observed with the selection rule $|\Delta M| = \pm 1$

[d] The upper state is the Fermi mixed $([(011)^{CO}/(411)^{O}])$ state

[e] τ is either 1 or 2

with a common excited state appears at the lower field. The observed values of E and Ω_{RF} are listed in Table 1 as E/Ω_{RF} for easy comparison with (3). The maximum obtainable value of E/Ω_{RF} is approximately 190 V/cm MHz. By comparison with (3) we find that this will correspond to very high J values unless K is very small. By rearranging (3) it is noticed that the dipole-moment component for the individual rovibrational–torsional state can be calculated once J and K have been determined.

The use of a modulation scheme as described above results in an increasing linewidth of the double-resonance signals with increasing electric field given by the expression (14),

$$\gamma/\Omega_{RF} = \Delta E/E_{res}\,, \tag{5}$$

where γ is the half-width at half maximum for the absorption linewidth, ΔE is the width of the signal in V/cm, and E_{res} is the resonant field. The value of γ/Ω_{RF} is the same for all transitions when Ω_{RF} is kept constant. Thus $\Delta E/E_{res}$ from (3) must also be constant and as E_{res} is increased the linewidth must increase. This is important to notice when analyzing Q-branch transitions, where signals due to a common ground state level can overlap with signals due to a common excited state level since the difference in position is solely due to the difference in the dipole-moment component μ_a, as shown in (4). Since the electric potential difference goes through zero, a zero field level-crossing signal will be observed and this observation is a prerequisite for observing double-resonance signals [15].

The strong Fermi interaction between $n = 0$ levels of the C–O stretch state and the $n = 3$ and $n = 4$ torsionally excited levels of the ground vibrational state result in a shift of the involved energy levels [2, 16]. The largest shift is observed for $\tau = 1$ levels around $K = 1$ and is around $2.14\,\mathrm{cm}^{-1}$, while for $\tau = 3$ levels around $K = 8$ it is approximately $0.3\,\mathrm{cm}^{-1}$. Transitions involving the former levels have been observed. The large shift of the $(011)^{CO}$ levels is due to the almost 50:50 mixing with the $(410)^{O}$ levels [2]. The two almost degenerate levels are therefore shifted considerably in opposite directions and are labelled $[(011)^{CO}/(411)^{O}]^{u}$, and $[(011)^{CO}/(411)^{O}]^{d}$, where the u and d indicates the mixed state which is shifted up and down, respectively.

We have observed double-resonance spectra associated with five different CO_2 -laser lines. These spectra all exhibit first-order Stark effect. That the observed signals are indeed double-resonance signals is confirmed by in turn blocking the through beam and the sideband and observe that the signals disappear. In addition, by changing the radiofrequency by 0.2–2 MHz on either side of the center one should observe the double-resonance signals move while other signals remain stationary. The observed signals are listed in Table 1. We will now discuss the individual signals.

2.1 10R(36)$^{12}C^{16}O_2$*-Laser Line*

One strong double-resonance signal was observed using this pump line and is shown in Fig. 1. This CO_2-laser line is the pump line for 17 previously observed FIR laser lines. However, only four of these can be obtained with the offset attainable with a conventional CO_2 laser similar to the one used in the present work. The pump transition for these four lines was assigned several years ago by Kachi and Kon [16] to the $^{Q}Q(039,12)$ infrared absorption transition in the CO stretch band and later verified by Mukhopadhyay et al. [4] using combination relations from the FT spectrum. The present observation agrees with the previous assignment and allows us to obtain the permanent electric-dipole moment for the ground state. This value is also shown in Table 1. The double-resonance signal associated with the excited state does not seem to be present. It could in principle overlap with the ground-state signal. However, this is not likely, since the linewidth of the observed signal is of the order of 200 kHz and no indication of a second signal is noticed. If they indeed overlap we would find the same dipole moment for both the excited CO stretch state and the ground state. Kachi and Kon [16] showed that the excited state level was shifted by approximately $0.332\,\mathrm{cm}^{-1}$ due to the above mentioned Fermi resonance. This interaction may be the reason that we do not observe a second-double resonance signal possibly due to a considerable change in the effective dipole moment value of the upper level. The Stark behavior of the 253.7 µm FIR laser line, which is one of the four observed laser lines, was observed by Yoshida et al. [17] and by Ioli et al. [18]. Both of these groups reported lower Stark coefficients than expected from theoretical calculations by assuming the present assignment and a dipole-moment value of approximately 0.9 D. A lower Stark coefficient suggests that a double-resonance signal will occur at a larger field, however, none were observed within the tuning range available in the present experiment. The infrared and FIR transitions involved in this scheme are shown in Fig. 2.

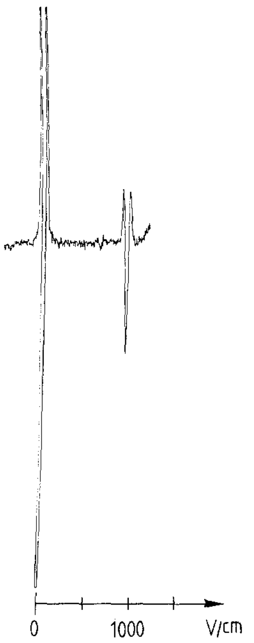

Fig. 1. IRIRDR signal of the $^{Q}Q(039, 12)$ transition of CD_3OH using the $10R(36)^{12}C^{16}O_2$ laser line. Gas pressure: 8 mtorr; modulation amplitude: $1.00\,\mathrm{V\,cm}^{-1}$; time constant; 300 ms

An accurate determination of the Fermi interaction could in principle be obtained by observing the FIR transition $(039,12)^{CO} \rightarrow (439,12)^{O}$. This is an allowed transition

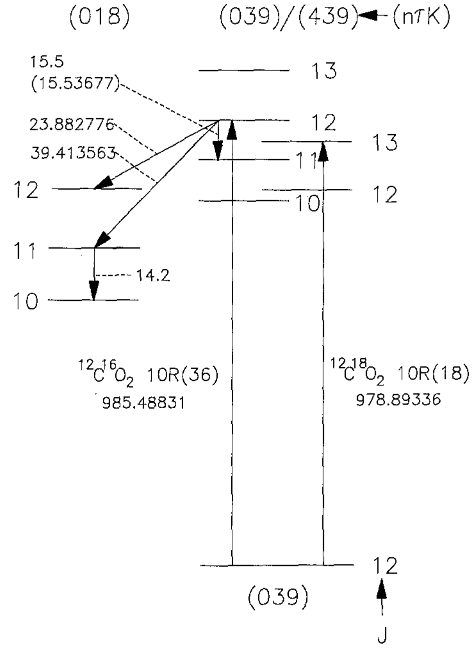

Fig. 2. Energy level diagram showing the Fermi perturbed levels pumped by the $10R(36)^{12}C^{16}O_2$ and $10R(18)^{12}C^{18}O_2$ laser lines. The arrows indicate IR and FIR laser transitions. The transition frequencies are in cm^{-1}. The frequency in parenthesis is obtained from the difference between two infrared transitions

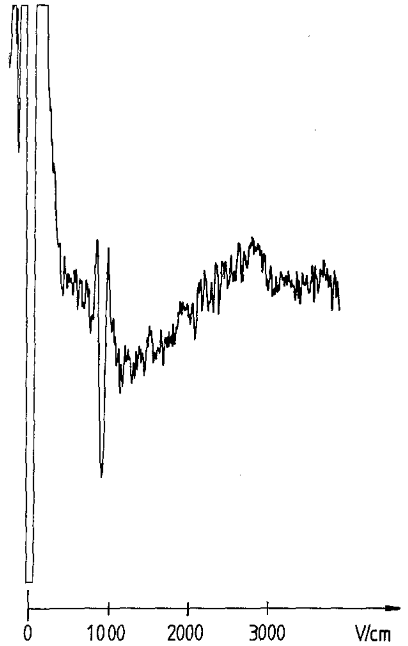

Fig. 3. IRIRDR signal of the $(039,12)^O \rightarrow (439,13)^O$ transition of CD_3OH using the $10R(18)^{12}C^{18}O_2$ laser line. Gas pressure: 40 mtorr; modulation amplitude: $2.00\,V\,cm^{-1}$; time constant: 300 ms

through the Fermi mixing, however, without this mixing it would be a forbidden transition since $\Delta K = 0$ and $\Delta\tau = 0$. The observation of this transition from a wavelength measurement could be difficult since the wavelength will be very close to the already observed $(039,12)^{CO} \rightarrow (018,12)^{CO}$ transition at $23.88\,cm^{-1}$. Using the heterodyne technique to measure the frequency of this line should allow a separation of the two lines.

2.2 $10R(18)^{12}C^{18}O_2$-*Laser Line*

The observed double-resonance signal is shown in Fig. 3. The observation of only one double-resonance signal leads to the expectation that pumping occurs into a perturbed level in the excited state. This laser line coincides with the $n = 0$, $P(5)$ multiplet and most of these transitions have been assigned and are listed in [2]. Those which have not been assigned do not have quantum numbers which together with the observed E/Ω_{RF} fulfill (3). We can conclude that the transition is not a $n = 0$ transition in the C–O stretch band. We note that the obtained E/Ω_{RF} value, within the uncertainty of the experiment, is equal to the value obtained with the $10R(36)^{12}C^{16}O_2$ laser line and we therefore propose that the two laser lines pump the same ground-state level, which is (039,12). The frequency of the $R(039,12)$ transition can be calculated using excisting molecular parameters [2, 12, 19] to be $1002.324\,cm^{-1}$ where the upward shift of $0.332\,cm^{-1}$ [16] has been included. Since levels in the $(039)^{CO}$ stack lie approximately $23\,cm^{-1}$ above the $(439)^O$ levels we find that the transition $(039,12)^O \rightarrow (439,13)^O$ has a frequency close to $979\,cm^{-1}$ which is very close to the laser frequency at $978.89336\,cm^{-1}$. We therefore propose that this laser line is pumping the above-mentioned transition. This infrared transition is a torsional transition, and normally a forbidden transition. However, due to the above-mentioned Fermi mixing it becomes allowed. Again, there is no double resonance associated with a common ground state. There has been no report on FIR laser lines from CD_3OH when pumping with $^{12}C^{18}O_2$-laser lines thus no additional information is available. The energy level scheme associated with the $10R(18)^{12}C^{18}O_2$ pump lines is also shown in Fig. 2. Using existing molecular parameters for calculating the far infrared rotational transitions together with the known infrared transition frequencies of the two laser lines we calculate the differences between the $J = 13$ and the $J = 12$ perturbed levels to be $23.43\,cm^{-1}$ and $23.42\,cm^{-1}$, respectively. These values are expected to be close since the Fermi perturbation is almost J independent. By substracting the calculated FIR transition from the above calculated infrared transition we obtain $978.89\,cm^{-1}$ which is very close to the laser frequency.

2.3 $10R(30)^{12}C^{18}O_2$-*Laser Line*

The observed double resonance signal is shown in Fig. 4. Due to the additional feature just above the double-resonance signal it is not possible to determine if the signal consists of two overlapping signals or an additional double-resonance signal is present on the shoulder of this feature. If the former is the case it will lead to the same calculated dipole moment values for both the ground and excited state levels. Based on (2) there are two possible set of candidates for (J, K). These are (11,8) and (13,11). With the accuracy with which the infrared transition frequencies with $n = 0$ can

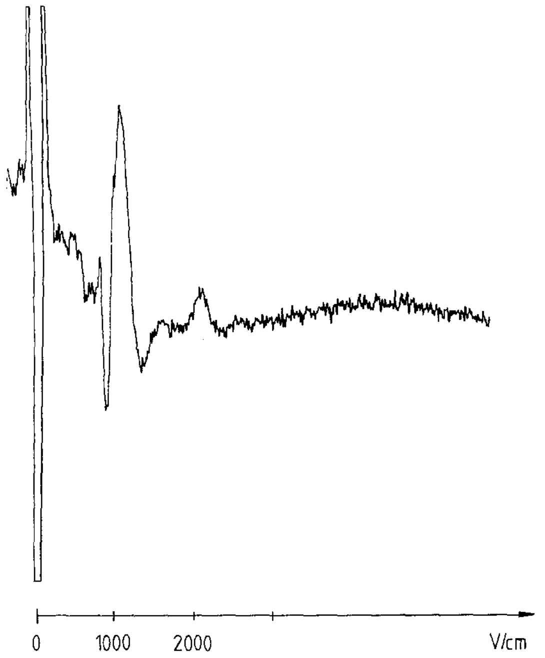

Fig. 4. IRIRDR signal of CD_3OH using the $10R(30)$ $^{12}C^{18}O_2$ laser line. Gas pressure: 11 mtorr; modulation amplitude: $1.85\,V\,cm^{-1}$; time constant: 300 ms

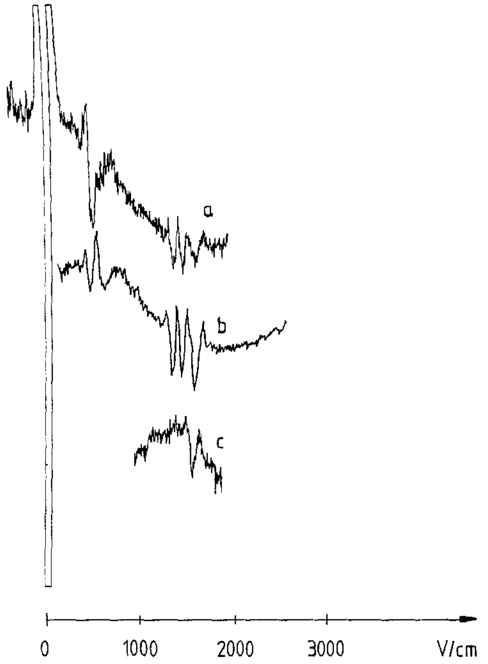

Fig. 5. IRIRDR signals from CD_3OH using the $10R(34)$ $^{12}C^{16}O_2$ laser line. Modulation amplitude: $1.50\,V\,cm^{-1}$; time constant: 300 ms. Spectra were observed with different tuning of the CO_2-laser line. **a** negative offset with respect to the CO_2-laser line center, gas pressure: 15 mtorr; **b** CO_2-laser center, gas pressure; 15 mtorr; **c** large positive offset, gas pressure: 23 mtorr.

be calculated we can only exclude the $Q(038,11)$ transition which is Fermi perturbed downwards by approximately $0.3\,cm^{-1}$ [4]. The best agreement between calculated infrared transition frequency and CO_2-laser frequency is obtained for the transitions $Q(0\tau 8,11)$ with $\tau = 1$ or 2. We therefore propose this assignment. The results are shown in Table 1. Since we have excluded the Fermi perturbed level we find from (4) that it is the dipole-moment value of the excited state level we calculate. Additional information is necessary for an unambiguous assignment. The observation of FIR laser lines using this pump line or a complete analysis of the FT spectrum should allow an unambiguous assignment of τ.

2.4 10R(34)$^{12}C^{16}O_2$-Laser Line

The double-resonance spectra are shown in Fig. 5. We notice that there are four signals, one at very low electric field and three very close together at somewhat higher fields. The one at low field has an unusual shape for a double resonance. Of the three, the first and second signal appear to have the same linewidth while the third is broader. This indicates that the latter indeed consist of two overlapping signals. Although the linewidth is increasing with increasing electric field as discussed above, this cannot account for the increase observed here. In Figs. 5a–c we have varied the offset of the CO_2 laser line. At a large positive offset only the third resonance remaines indicating that it is independent of the two. The doublet always appear together with almost the same intensity of the two signals indicating that they belong to the same infrared transition. While the three close lines disappear when either the through beam or the sideband is blocked, the signal at low field does not disappear. However, it does change shape. In order to find out if there is a double-resonance signal overlapping with another feature we inserted a quarter-wave plate in one of the beams thereby changing the polarization from being linear to circular. In addition to the overall selection rule $|\Delta M| = \pm 2$, we then also have the selection rule $|\Delta M| = \pm 1$ and double-resonance signals should then appear at a field of double the magnitude as can be seen from (3). This is indeed the case as is seen in Fig. 6. We have at present no explanation for why the one at low field becomes so strong while the three at high fields become very weak at double the fields.

The only possible assignment of (J, K) for the signal at low field is (8,8). However, a calculation of the infrared transition frequencies corresponding to the three values of τ and $n = 0$ indicate that the transition is not a $n = 0$ transition even taking into account the Fermi shift of the (038) level. It is necessary to obtain information from other studies for a complete assignment. The $10R(34)$ laser line is the most prolific pump line for generating FIR laser lines in CD_3OH. Approximately 33 optically pumped FIR laser lines have been reported [5, 6]. Several of these have to be pumped with a large offset, however, there are still 24 lines that can be generated by a conventional CO_2 laser. Since $K' = 8$ we do not have a $\Delta K = 0$, $\Delta J = -1$ FIR transition. For a hypothetical $J' = 8 \to 7$ transition we would expect a FIR laser line with a frequency of $2 \times 8 \times 0.648\,cm^{-1} = 10.368\,cm^{-1}$ ($\perp$). The parenthesis indicate the expected polarization relative to the polarization of the CO_2 laser line. The only FIR laser line corresponding to a calculated transition frequency for a $\Delta K = -1$,

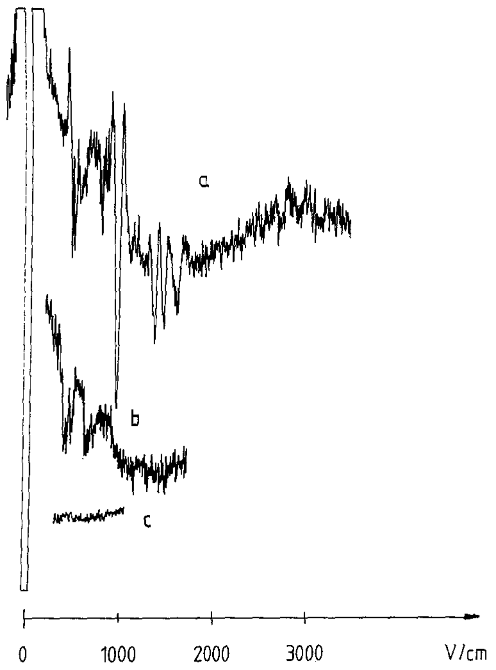

Fig. 6. **a** IRIRDR signals from CD_3OH using the $10R(34)$ $^{12}C^{16}O_2$ laser line with a $\lambda/4$ plate in one of the beams. Gas pressure: 23 mtorr; modulation amplitude: $1.50\,V\,cm^{-1}$; time constant: 300 ms, **b** sideband blocked; **c** sideband only

$\Delta J = 0$ for any of the τ's and $n = 1$ is a line at $45.001136\,cm^{-1}$ [20]. However, this line is reported to have a relative perpendicular polarization which is opposite of what is expected for a $\Delta K = -1$, $\Delta J = 0$ transition in the Q-branch. A transition with $\Delta K = -1$, $\Delta J = -1$ should then have a frequency of approximately $55.37\,cm^{-1}$ ($\perp$). A transition at $55.327940\,cm^{-1}$ ($\perp$) has been reported [20]. We therefore propose the assignment $^{Q}Q(118,8)$ for the infrared transition. It should be mentioned that the two lines are reported to have the same offset [20]. A calculation of both FIR and IR transition frequencies are attached with some uncertainty since only the molecular parameters corresponding to $n = 0$ have been reported in the literature (2). In Table 2 we have included the $45.00\,cm^{-1}$ line, however, it then remains to be shown that the relative polarization is parallel. Five FIR transitions with the same offset have all been reported to have a relative perpendicular polarization which is an unusual situation.

We have at present only a speculative assignment of the two signals which appear as a pair. Due to the separation of the two signals one could expect that they belong to either a R- or P-transition, however, agreement with (3) cannot be obtained for either of these. Using (4) we notice that in the case where they belong to the same ^{Q}Q transition the dipole moment value in the excited state must have changed condiserably. We know from the above discussion that this is possible when a perturbation is present. The possible assignments of (J, K) for the ground state are then (17,12) or (19,15). From a calculation of the infrared transition frequencies and the expected Fermi shift the former of the two seems the most likely. The tentative assignment is therfore $^{Q}Q(0312,17)$.

The signal at high field is found to have several possible assignments of (J, K) when applying (2). Again we make use of the reported FIR laser lines together with the calculated infrared transition frequencies. Then we are left with only one possible assignment which is $(J, K) = (20,14)$ for both the ground state and the excited state. A FIR laser line with a measured transition frequency of $25.90423\,cm^{-1}$ ($\perp$) can be assigned to the $J' = 20 \to 19$. Together with two other lines at $52.258581\,cm^{-1}$ ($\|$) and $78.104332\,cm^{-1}$ ($\perp$) the three lines form a triad if they have the same offset. In [20] the first line is reported to have an offset different from that of the latter two although the offsets have not been specified. Judging from the sum in the triad it seems unlikely that they should have different offsets. We therefore propose the assignment $^{Q}Q(0114,20)$ for the IRIRDR transition and also for the transition giving rise to the three FIR laser lines discussed above. The assignments are shown in Table 2 and in Fig. 7.

2.5 10R(32)$^{12}C^{16}O_2$-Laser Line

The observed double-resonance signal is shown in Fig. 8. Since only one double-resonance signal is observed we again expect the excited-state level to be perturbed. Based on (3) we find that there are several possible assignments of (J, K). These are (3,1), (8,6), and (11,11). A calculation of all nine infrared frequencies shows that all transitions with $n = 0$ have too large a frequency. However, it is necessary to take possible Fermi interactions into consideration. We can expect the excited state levels (011,3), (036,8), and (0311,11) to be shifted. A shift of more than $2\,cm^{-1}$ towards lower energy is necessary for all three levels in order for the calculated transition frequency to be in coincidence with the laser frequency. Such a large shift is not possible for the (036,8) and (0311,11) levels due to the large energy difference between these levels and the perturbing levels, which are $(436.8)^{0}$ and $(4311,11)^{0}$, respectively. The (011) stack in the excited state is strongly perturbed due to the above mentioned alsmost 50:50 mixing with the (411) levels of the ground state [2]. The two mixed levels are shifted in op-

Table 2. Proposed assignment of FIR laser lines in CD_3OH

Pump line	Pump assignment	Far-infrared emission $[cm^{-1}]$	Emission assignment	Calculated[a] frequency $[cm^{-1}]$
$10R(34)$	$^{Q}Q(118,8)$	45.001136	$(118,8) \to (127,8)$	45.47
		55.327940	$\to (127,7)$	55,86
$10R(34)$	$^{Q}Q(0114,20)$	25.90423	$(0114,20) \to (0114,19)$	25.83
		52.258581	$\to (0213,20)$	52.22
		78.104332	$\to (0213,19)$	78.06

[a] Calculated using published molecular parameters [2]

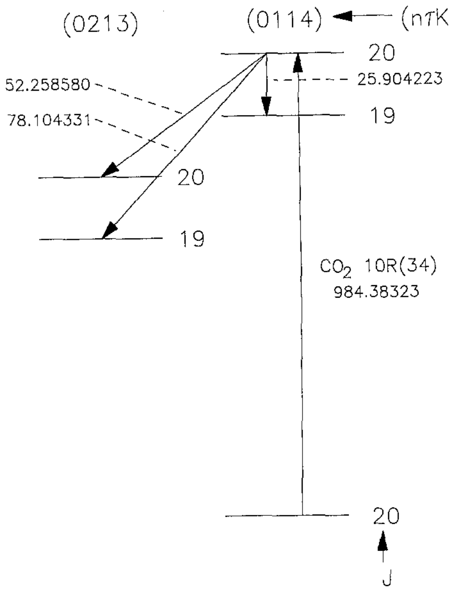

Fig. 7. Energy level diagram showing the level pumped by the $10R(34)$ $^{12}C^{16}O_2$ laser line. Single arrows indicate IR and FIR laser transitions. The transition frequencies are in cm^{-1}

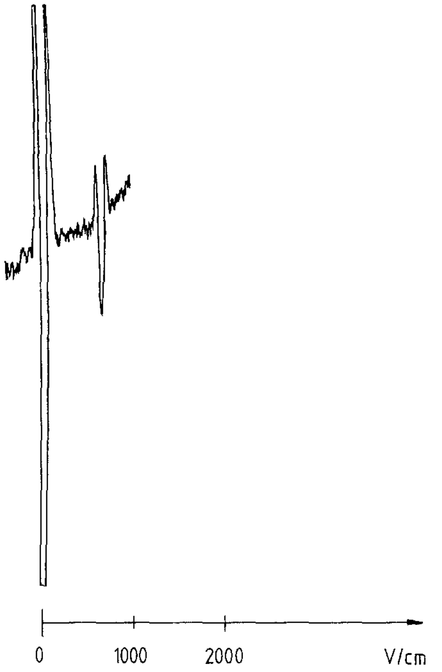

Fig. 8. IRIRDR signals from CD_3OH using the $10R(32)$ $^{12}C^{16}O_2$ laser line. Gas pressure: 13 mtorr; modulation amplitude: $1.90\,V\,cm^{-1}$; time constant: 300 ms

posite directions each by approximately $2.14\,cm^{-1}$ [2]. We propose the assignment $(011,3) \rightarrow ([(011^{CO}/(411)^{O}]^{d},3)$ for the infrared transition, where the notation has been explained above. The calculated transition frequency for the unperturbed $(011,2)^{O} \rightarrow (011,3)^{CO}$ transition is $985.4860\,cm^{-1}$ which is $2.23\,cm^{-1}$ higher than the laser frequency. The latter value is very close to the shift of $2.14\,cm^{-1}$. Additional indication that this is the correct assignment is that none of the 24 FIR laser lines reported pumped by this CO_2 laser line can be associated with any of the above mentioned values of (J, K). For the proposed assignment, the expected FIR wavelengths are too long to be observed in most FIR lasers, while for the larger values of J and K, FIR lines should have been observed if the corresponding levels were pumped.

3 Conclusion

We have observed and assigned several IRIRDR transitions in CD_3OH. Three of these are transitions involving Fermi perturbed levels, two in the excited C–O stretch state and one in a torsional-excited state. These levels were characterized by spectra consisting of only one double-resonance signal presumably due to a considerable change in the dipole moment value for the upper-state level. Regular spectra observed in several previous studies of methanol and its isotopomers consist of pairs of spectra. The analysis has allowed the determination of the μ_a dipole-moment component for several levels of the ground state. We have confirmed previously reported assignments of FIR laser lines from this molecule as well as proposed new assignments.

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