

Far-infrared laser magnetic resonance of vibrationally excited CD₂

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We report the detection of 13 rotational transitions in the first excited bending state (010) of CD₂ using the technique of far-infrared laser magnetic resonance spectroscopy. Molecular parameters for this state are determined from these new data together with existing infrared observations of the ν_2 band. Additional information on the ground vibrational state (000) is also provided by the observation of a new rotational transition, and this is combined with existing data to provide a refined set of molecular parameters for the CD₂ ground state. One spectrum has been observed that we assign as a rotational transition within the first excited symmetric stretching state (100) of CD₂. These data will be of use in refining the structure and the potential function of the methylene radical.

1. INTRODUCTION

The methylene radical CH₂ occupies an important place in chemistry as the model for all carbene compounds. Experimentally, an understanding of the structure of methylene began in 1959 when Herzberg and Shoosmith¹ reported the observation of electronic spectra in the visible and ultraviolet that was later analyzed in more detail by Herzberg² and by Herzberg and Johns.³ From this work, it was inferred that the ground state of the molecule was a triplet (\tilde{X}^3B_1), and this was later confirmed by ESR studies^{4,5} of methylene isolated in low-temperature matrices. However, little structural information on the ground electronic state was available until the recent observation of infrared^{6,7} and far-infrared⁸ spectra using the laser magnetic resonance (LMR) technique. Subsequent studies of the ν_2 band of ¹³CH₂¹⁰ and the rotational spectrum of CH₂¹¹ by means of LMR spectroscopy and of the ν_2 band of CH₂ by means of tunable diode laser spectroscopy¹² have allowed a more-precise potential surface for the \tilde{X}^3B_1 state to be determined.¹³ A detailed listing of CH₂ transition frequencies and intensities in the far-infrared and 10- μ m regions has been compiled to aid in astronomical searches for methylene.¹⁴ In addition, the detection of LMR transitions between perturbed levels in the excited \tilde{d}^1A_1 state of CH₂ has resulted in an accurate experimental determination of the singlet-triplet energy splitting.^{15,16}

In the present work, we report the observation of pure rotational transitions in excited vibrational states of CD₂ using far-infrared LMR. Specifically, we have identified and analyzed components of 13 rotational transitions in the first excited bending state (010) and one in the first excited symmetric stretching state (100). These results will permit a further refinement of the structure and potential function of methylene. In particular, they lead to the experimental determination of the A rotational constant in the (010) state, which was not determined in the earlier¹² diode laser study of the ν_2 band since the transitions observed in that work in-

cluded only those with $K_a = 0$ in the (010) state. Because of the large-amplitude nature of the bending modes in methylene, large changes occur in A on excitation of the bending mode. In addition to the 17 transitions reported for the ground vibrational state (000) of CD₂ in Ref. 11, we report here the observation of a further transition, 5₂₃-5₁₄. The present data are fitted to the standard effective Hamiltonian to determine refined rotational, centrifugal distortion, spin-spin, and spin-rotation parameters for the (000) and (010) vibrational states of CD₂. The values obtained are compared with those of CH₂ (Refs. 7 and 8) and ¹³CH₂.¹⁰

2. EXPERIMENTAL DETAILS AND RESULTS

All the spectra were recorded at the National Bureau of Standards Boulder laboratory using the far-infrared LMR spectrometer described previously.⁸ The CD₂ radicals were produced in the laser cavity by a continuous reaction between fully deuterated methane and fluorine atoms that were produced by flowing a mixture of F₂ and He through a microwave discharge. Typical partial pressures of the reactants were 0.7 Pa CD₄, 2 Pa F₂, and 19 Pa He, where 1 Pa = 7.5 mTorr. The LMR signals assigned to vibrationally excited CD₂ and those assigned to the ground state appeared to maximize at approximately the same chemical conditions, although the variations of signal strength with pressures around this maximum differed for the different vibrational states.

The first spectra of rotational transitions within the (010) state of CD₂ were observed accidentally using a laser line of CH₃OH at 70.5 μ m while searching for $K_a = 3-2$ transitions¹⁷ in the (000) ground state. Part of this LMR spectrum is illustrated in Fig. 1. We assigned the resonances observed at 70.5 μ m to three different (010) state transitions: 2₂₀-2₁₁, 2₂₁-2₁₂, and 3₂₁-3₁₂. Their measured positions (with spin splittings removed) were about 0.7 cm⁻¹ below the predicted values from the nonrigid benjer fit made by Bunker and Jensen¹³ to previously observed methylene spectra.^{7,8,10-12} It

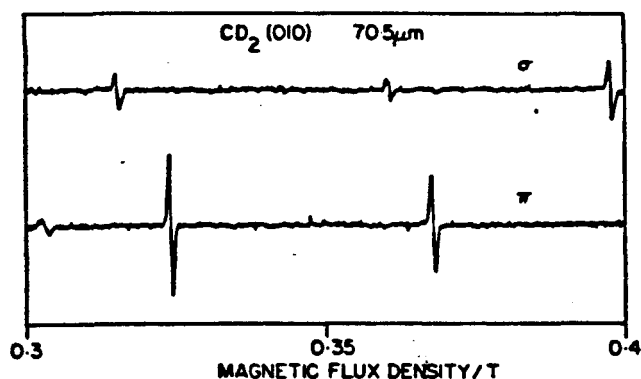


Fig. 1. LMR spectrum of CD_2 obtained with the 70.5- μm laser line of CH_3OH . With the exception of the weak line at 0.304 T, the resonances are assigned to Zeeman components of the $2_{20}-2_{11}$ rotational transition within the (010) first excited bending state. In the upper trace the laser radiation is perpendicular (σ) to the applied Zeeman field, and in the lower trace it is parallel (π).

was then possible to apply a small correction to the results of Ref. 13 and to estimate the frequencies of further (010) state transitions. The observation and the assignment of these transitions were relatively straightforward, and ultimately 13 such transitions were analyzed. The laser frequencies used for the observations are given in Table 1, and a complete list of measured resonances is given in Table 2. The field measurements are generally accurate to about 0.0003 tesla (T) below 1 T and to 0.001 T above 1 T [1 T = 10^4 gauss (G)].

During the search for CD_2 (010) state spectra, we found a prominent series of resonances on each of two laser lines (110.4 and 85.3 μm) that could not be assigned to (010) transitions. The first of these series, at 110.4 μm (90.553 cm^{-1}), was assigned to the $5_{23}-5_{14}$ transition in the (000) ground vibrational state of CD_2 . The central portion of this spectrum is illustrated in Fig. 2, and the measured resonant fields and quantum-number assignments are listed in Table 3. Since this transition contains new information on the ground state, we have added the new measurements to the existing data¹¹ and performed a new fit to obtain a refined set of molecular parameters. The results of this fit are listed in Table 4, and a comparison with the results of Ref. 11 shows only relatively minor changes in the parameter values. We use the parameters of Table 4 subsequently in this paper to represent the ground state of CD_2 .

The second spectrum, which could not be assigned to the (010) state at 85.3 μm (117.2095 cm^{-1}), is illustrated in Fig. 3. Some resonances observed at this frequency had been assigned to the (000) state $3_{22}-2_{11}$ transition¹¹ and to the (010) state $2_{21}-3_{12}$ transition (Table 2), but the characteristic series between 0.01 and 0.05 T in both polarizations (Fig. 3) belongs neither to (000) nor to (010). It may, however, be convincingly assigned as a different $3_{22}-2_{11}$ rotational transition of CD_2 . On the basis of the predictions of Bunker and Jensen¹³ we assign this transition to the first excited symmetric stretching state (100) of CD_2 . Since we have not been able to identify any further transitions within (100) and since the nuclear hyperfine structure of the lines was not resolved, the assignment is not quite so certain as those of the analogous (100) state transitions in CH_2 .^{8,11} The observed resonant fields and assignments for the (100) state $3_{22}-2_{11}$ transition are listed in Table 5.

The signal strengths of the vibrationally excited CD_2 spectra were lower than those observed for ground-state

transitions, but the difference was not so great as expected for a near-room-temperature Boltzmann vibrational population distribution. As was mentioned above, the relative strengths depended strongly on chemical conditions (even though the optimum conditions were fairly similar for the various states), and so it is difficult to specify unique values for them. However, we estimate that the (010) state spectra were of the order of four times weaker than those of (000), implying an effective temperature of about 800 K for the bending mode. As with CH_2 , the effective temperature of the ν_1 mode must be considerably greater (well over 1000 K) in order for (100) state transitions to be observed. These results strongly suggest that methylene radicals are formed directly in excited vibrational states during the chemical reaction used in our experiments. It should also be possible to observe rotational transitions within the (010) state of CH_2 . Such transitions have not yet been observed because they occur at high frequencies [which are due to the large A rotational constant of CH_2 in (010)], where there are relatively few laser lines available for LMR spectroscopy. At any rate, the energy levels of this state are already quite well known from the ν_2 -band LMR spectrum.⁷

3. ANALYSIS AND DISCUSSION

The data given in Table 2 were fitted together with the ν_2 -band diode-laser measurements of McKellar et al.¹² to determine a set of molecular parameters for the (010) state of CD_2 . The two sets of data were accorded equal weights in the fit, except in the case of a few blended or weak LMR lines that were given reduced weights (see Table 2). We used the effective Hamiltonian given by Sears et al.⁸ and a computer program that set up the calculation in a fully coupled parity-conserving basis set of prolate symmetric top functions. The basis was cut off to include all states with $\Delta N \leq \pm 2$ and $\Delta K \leq \pm 2$, a practical limit that was empirically found to introduce

Table 1. Far-Infrared Laser Lines Used to Observe LMR Spectra of CD_2

Lasing Gas	Laser Wavelength (μm)	Laser Wave Number* (cm^{-1})	CD_2 Transition ^b
CD_2F_2	218.3	45.815473	$1_{11}-2_{02}$
CH_2DOH	159.2	62.806994	$2_{11}-2_{02}$
$^{13}\text{CH}_3\text{OH}$	157.9	63.319802	$2_{11}-2_{02}$ $3_{12}-3_{03}$
CH_3OD	144.1	69.387647 ^c	$1_{11}-0_{00}$
CH_3OH	129.5	77.190467	$2_{12}-1_{01}$
CH_3OH	118.8	84.150936	$3_{13}-2_{02}$
$^{13}\text{CH}_3\text{OH}$	110.4	90.553151	$4_{14}-3_{03}$ $5_{23}-5_{14}(\text{000})$
$^{13}\text{CH}_3\text{OH}$	85.3	117.209532 ^c	$2_{21}-3_{12}$ $3_{21}-2_{12}(\text{100})$
CH_3OH	70.5	141.820579	$2_{20}-2_{11}$ $2_{21}-2_{12}$ $3_{21}-3_{12}$
$^{13}\text{CH}_3\text{OH}$	63.1	153.487690	$2_{20}-1_{11}$ $2_{21}-1_{10}$

* Sources for the laser wave-number references may be found in Ref. 20.

^b Transitions are within the (010) excited vibrational state except where otherwise indicated.

^c Transitions in the ground vibrational state of CD_2 have previously been observed with these laser lines (see Ref. 11).

Table 2. Observed Resonant Fields and Assignments of LMR Transitions in the (010) Excited Vibrational State of CD_2

Laser Line (cm ⁻¹) ^a	Resonant Field (T) ^b	Assignment ^c			Observed-Calculated		TR ^d
		N _{KK}	J	M _J	(MHz)	Γ (G) ^b	
45.8155	0.05920	111-202	1-3	0-0	3.1	3.7	-0.85
45.8155	0.20200	111-202	1-1	-1-1	9.8	7.6	-1.29
45.8155	0.01820	111-202	1-3	-1-0	-5.8	-4.0	-1.46
45.8155	0.02350	111-202	1-3	0-1	0.0	0.0	-1.33
62.8070	0.09198	211-202	3-3	-1-2	-5.3	2.1	2.58
62.8070	0.10706	211-202	1-1	0-1	10.7	4.4	-2.41
62.8070	0.13768	211-202	1-1	1-0	11.9	8.2	-1.45
62.8070	0.14770	211-202	3-3	0-1	-2.3	2.9	0.79
63.3198	0.25420 ^e	211-202	2-1	0-0	16.5	-3.9	4.23
63.3198	0.32360 ^e	211-202	2-1	-1-1	6.7	-1.4	4.86
63.3198	0.02950	312-303	4-3	3-3	-0.5	0.4	1.19
63.3198	0.02950	312-303	4-3	3-3	-0.5	0.4	1.19
63.3198	0.28760	312-303	4-3	3-3	-20.3	-17.6	-1.15
63.3198	0.01810	312-303	4-3	4-3	6.7	-3.3	-2.05
63.3198	0.02580	312-303	4-3	3-2	1.7	-1.3	1.32
63.3198	0.23920	312-303	4-3	3-2	-16.6	-14.5	-1.14
69.3876	0.09099	111-000	2-1	0-1	-25.0	-12.0	-2.09
69.3876	0.11828	111-000	1-1	0-1	-11.2	11.8	0.94
77.1905	0.13560	212-101	1-0	0-0	16.1	16.3	-0.99
77.1905	0.20310 ^e	212-101	2-2	-2-2	0.9	-0.4	2.53
77.1905	0.36380	212-101	2-2	1-1	-1.4	0.6	2.26
77.1905	0.50500	212-101	3-2	-1-1	-4.7	1.8	2.64
77.1905	0.56020	212-101	2-1	-1-1	-4.6	1.6	2.88
77.1905	0.04450	212-101	1-0	1-0	6.3	4.1	-1.52
77.1905	0.13440 ^e	212-101	2-2	-1-2	14.3	-3.3	4.32
77.1905	0.15400 ^e	212-101	2-2	0-1	18.5	-4.5	4.09
77.1905	0.21240	212-101	2-2	1-0	3.5	-1.1	3.11
77.1905	0.21540	212-101	1-0	-1-0	12.3	8.3	-1.48
77.1905	0.26140	212-101	2-2	-1-0	10.1	-3.4	2.97
77.1905	0.38190	212-101	2-2	0-1	2.7	-1.2	2.27
84.1509	0.24865	313-202	3-3	3-3	-4.6	-4.7	-0.97
84.1509	0.39010	313-202	3-3	-2-2	3.7	-1.5	2.49
90.5532	0.08870	414-303	5-3	-3-3	0.3	-0.1	2.27
90.5532	0.12280	414-303	5-3	-3-2	-1.5	1.3	1.08
90.5532	0.13770	414-303	5-3	-2-3	-1.3	1.1	1.17
117.2095	0.00430	221-312	3-4	-3-3	-4.7	-6.9	-0.68
117.2095	0.00680	221-312	3-4	-2-2	-5.1	-12.7	-0.40
117.2095	0.00680	221-312	3-4	-2-2	-5.1	-12.7	-0.40
117.2095	0.05670	221-312	3-2	-2-2	0.7	0.9	-0.75
117.2095	0.07870	221-312	3-2	-2-2	-6.2	20.7	0.30
117.2095	0.13210	221-312	3-4	-1-1	2.7	5.7	-0.47
117.2095	0.07210	221-312	3-4	1-2	-7.3	20.3	0.36
117.2095	0.10710	221-312	3-4	0-1	-6.3	13.4	0.47
117.2095	0.38860	221-312	3-4	1-2	-7.4	-17.5	-0.42
141.8206	0.26560	220-211	3-1	-1-1	5.2	-2.0	2.62
141.8206	0.32440	220-211	3-3	2-2	9.7	-4.2	2.32
141.8206	0.36780	220-211	3-3	-2-2	12.6	-5.9	2.13
141.8206	0.16500 ^e	220-211	1-2	-1-2	-7.0	3.1	2.23
141.8206	0.19720	220-211	3-1	0-1	-5.7	1.8	3.10
141.8206	0.24220	220-211	3-3	-1-2	-2.0	0.8	2.60
141.8206	0.24220	220-211	3-3	2-1	-12.0	4.9	2.45
141.8206	0.24740	220-211	3-1	-1-0	1.8	-0.7	2.50
141.8206	0.25620	220-211	3-3	3-2	-2.8	1.0	2.51
141.8206	0.31490	220-211	3-1	-2-3	-0.9	0.4	2.09
141.8206	0.36010	220-211	1-3	1-2	7.5	-3.5	2.17
141.8206	0.39730	220-211	3-1	-2-1	10.8	-4.8	2.20
141.8206	0.66100	221-212	2-2	-1-1	-6.2	-1.2	-5.36
141.8206	0.63230	221-212	2-2	-1-0	12.4	2.3	-5.38
141.8206	0.63940	221-212	2-2	0-1	6.4	1.2	-5.36
141.8206	0.67720	221-212	2-2	0-1	12.9	2.4	-5.34
141.8206	0.69610	221-212	2-2	1-0	-4.0	-0.9	-5.26
141.8206	0.69970	221-212	2-2	1-2	15.0	2.9	-5.25

(continued on next page)

Table 2. continued

Laser Line (cm ⁻¹) ^a	Resonant Field (T) ^b	Assignment ^c			Observed-Calculated		TRD
		$N_K K_c$	J	M_J	(MHz)	(G) ^d	
141.8206	0.49460	3 2 1 ← 3 1 2	2 ← 2	-2 ← -2	7.9	-1.4	5.48
141.8206	0.50570	3 2 1 ← 3 1 2	2 ← 2	-1 ← -1	18.5	-3.4	5.49
141.8206	0.97120	3 2 1 ← 3 1 2	3 ← 4	-3 ← -3	-14.3	5.2	2.77
141.8206	0.97540	3 2 1 ← 3 1 2	2 ← 4	-2 ← -2	-6.4	2.3	2.78
141.8206	0.50020	3 2 1 ← 3 1 2	2 ← 2	-1 ← 0	-4.7	0.9	5.47
141.8206	0.50310	3 2 1 ← 3 1 2	2 ← 2	1 ← 0	2.1	-0.4	5.47
141.8206	0.50440	3 2 1 ← 3 1 2	2 ← 2	-2 ← -1	-4.2	0.8	5.49
141.8206	0.50760	3 2 1 ← 3 1 2	2 ← 2	0 ← -1	0.8	-0.1	5.49
141.8206	0.97900 ^e	3 2 1 ← 3 1 2	3 ← 2	0 ← 1	-8.3	3.0	2.76
141.8206	0.97900 ^e	3 2 1 ← 3 1 2	2 ← 4	-1 ← -2	-12.7	4.6	2.78
141.8206	0.97900 ^e	3 2 1 ← 3 1 2	3 ← 2	2 ← 1	22.3	-8.1	2.76
158.4877	0.07260	2 2 0 ← 1 1 1	3 ← 2	-2 ← -2	-0.5	0.4	1.20
158.4877	0.17480	2 2 0 ← 1 1 1	1 ← 2	1 ← 1	-17.4	-7.7	-2.26
158.4877	0.37420	2 2 0 ← 1 1 1	3 ← 2	-1 ← -1	-0.7	4.7	0.16
158.4877	0.11350	2 2 0 ← 1 1 1	3 ← 2	1 ← 0	-4.0	6.7	0.60
158.4877	0.12220	2 2 0 ← 1 1 1	1 ← 0	-1 ← 0	3.4	-5.1	0.68
158.4877	0.28310	2 2 0 ← 1 1 1	3 ← 2	1 ← 0	-13.4	-22.6	-0.59
158.4877	0.45030 ^e	2 2 0 ← 1 1 1	1 ← 2	0 ← 1	-9.1	-19.9	-0.46
158.4877	0.16360	2 2 0 ← 1 1 0	1 ← 1	-1 ← -1	-8.1	1.9	4.27
158.4877	0.44955	2 2 0 ← 1 1 0	1 ← 2	-1 ← -1	-8.0	3.1	2.57
158.4877	0.81480	2 2 0 ← 1 1 0	3 ← 2	-2 ← -2	24.9	-9.4	2.66
158.4877	0.19560 ^e	2 2 0 ← 1 1 0	1 ← 1	-1 ← 0	-13.5	3.3	4.11

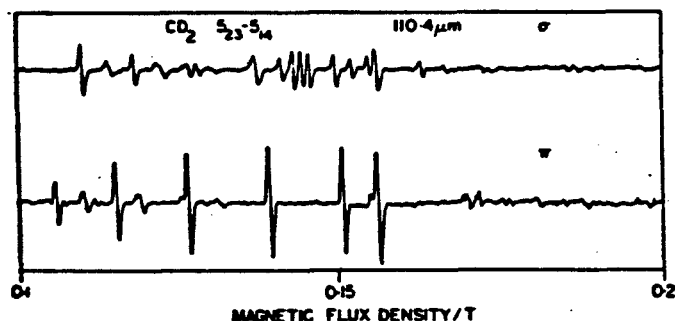
^a See Table 1.^b 1 T = 10⁴ G.^c The assignment given for J is that with which the given M_J level correlates at zero field.^d Calculated tuning rate in megahertz/gauss.^e These transitions were given a reduced weight in the least-squares fit (0.1) because of weakness and/or blending.

Fig. 2. Part of the LMR spectrum of the $5_{23}-5_{14}$ rotational transition of CD_2 in the (000) ground vibrational state, observed using the 110.4- μm laser line of $^{13}CH_3OH$. Some of the weaker lines in σ polarization are assigned to the $4_{14}-3_{03}$ transition in the (010) state (see Tables 2 and 3).

negligible errors. The hyperfine interaction was ignored, since hyperfine splittings were observed for only a few LMR resonances. The parameters resulting from the analysis are listed in the right-hand column of Table 4, and the quality of the fit may be inferred from the Observed-Calculated column of Table 2. The standard deviation of the fit was 11 MHz, which is not so good as the value of 5.2 MHz obtained for the ground state of CD_2 ¹¹ but is still satisfactory in view of the lower signal-to-noise ratio of the (010) state data and the inclusion of the ν_2 diode-laser results.

The major parameters in the effective Hamiltonian are well determined for the (010) state. The only off-diagonal elements of the correlation matrix greater than 0.9 were those between $\frac{1}{2}(B-C)$ and Δ_N , $\frac{1}{2}(B+C)$ and δ_K , and Δ_N and δ_K .

For quasi-linear molecules such as methylene, the standard expansion of the rotational and centrifugal distortion Hamiltonian does not converge rapidly. The large change in the moment of inertia about the a -rotational axis on excitation of the bending mode in CD_2 and the large values obtained for the K_a -dependent centrifugal distortion constants (see Table 4) are reflections of this poor convergence and arise because of the large-amplitude anharmonic nature of the bending motion in this molecule. For this reason we chose to fix the

Table 3. Observed Resonant Fields for the $5_{23}-5_{14}$ Transition in the (000) Ground Vibrational State of CD_2 Observed with a $^{13}CH_3OH$ Laser Line at 90.55315 cm⁻¹

Observed Field	Assignment		Obs. - Calc. ^a	
	$J' \leftarrow J''$	$M_{J'}' \leftarrow M_{J''}$	(MHz)	(G)
0.1105	4 ← 5	4 ← 5	+2.4	+0.8
0.1186	4 ← 5	3 ← 4	-0.6	-0.2
0.1273	4 ← 5	2 ← 1	+0.2	+0
0.1417	4 ← 5	1 ← 0	-0.6	-0.2
0.1499	4 ← 5	-2 ← -1	-4.5	-1.2
0.6194	5 ← 5	-5 ← -4	+3.9	+1.5
0.6561	6 ← 6	5 ← 6	+0.6	+0.2
0.1062	4 ← 5	4 ← 4	-0.3	-0.1
0.1157	4 ← 5	3 ← 3	0	0
0.1271	4 ← 5	2 ← 2	+0.3	+0.1
0.1397	4 ← 5	1 ← 2	-4.5	-1.2
0.1511	4 ← 5	0 ← 0	-3.3	-0.8

^a From a combined fit to these data and those of Ref. 11, resulting in the parameters of Table 4, 1 T = 10⁴ G.

Table 4. Molecular Parameters for the (000) and (010) Vibrational Levels of CD₂ in its \tilde{X}^3B_1 Ground Electronic State (in inverse centimeters)

Parameter	(000) State ^a	(010) State ^a
ν_0		752.3785(4)
A	37.786829(60)	70.45524(38)
$\frac{1}{2}(B+C)$	3.962159(12)	3.930017(27)
$\frac{1}{2}(B-C)$	0.26757(10)	0.3029(46)
ΔK	0.560228(16)	4.991843(60)
Δ_{NK}	$-0.49753(79) \times 10^{-3}$	$-0.019590(62)$
Δ_N	$0.09242(63) \times 10^{-3}$	$0.1062(52) \times 10^{-3}$
δ_K	$0.2783(50) \times 10^{-3}$	$1.71(23) \times 10^{-3}$
δ_N	$0.2231(23) \times 10^{-4}$	$0.232(18) \times 10^{-4}$
Φ_K	0.0196 ^c	0.278 ^c
Φ_{KN}	$-0.2433(19) \times 10^{-3}$	$-2.3749(66) \times 10^{-3}$
Φ_{NK}	$-0.189(18) \times 10^{-3}$	-0.189×10^{-3} ^d
Φ_N	0 ^e	0 ^e
D	0.776466(93)	0.78835(24)
E	0.040580(65)	0.03727(24)
ϵ_{ss}	$0.282(36) \times 10^{-3}$	$0.565(90) \times 10^{-3}$
$\frac{1}{2}(\epsilon_{bb} + \epsilon_{cc})$	$-0.2342(19) \times 10^{-3}$	$-0.2420(48) \times 10^{-3}$
$\frac{1}{2}(\epsilon_{bb} - \epsilon_{cc})$	$-0.262(18) \times 10^{-3}$	$-0.25(8) \times 10^{-3}$

^a From a fit to the previous¹¹ far-infrared LMR data with the addition of the measurements of the $5_{22} - 5_{11}$ transition given in Table 2.

^b From a fit to ν_2 -band diode-laser measurements¹² and the data of Table 2. For both states, magnetic g values were fixed at theoretical values,^{2,20} and the numbers in parentheses are one standard deviation from the least-squares fit expressed in units of the last quoted digit.

^c Fixed at a value determined from the energy levels given by Bunker and Jensen.¹³

^d Fixed at the ground-state value.

^e This parameter and all others not listed were fixed at zero.

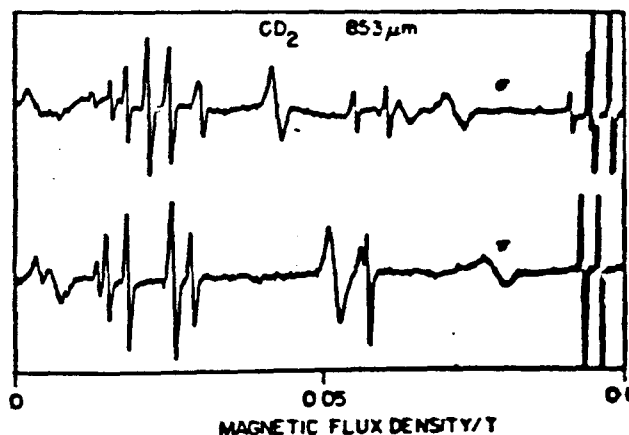


Fig. 3. LMR spectrum of CD₂ obtained by using the 85.3- μ m laser line of ¹³CH₃OH. Resonances arising from the vibrational states (000), (010), and (100) are all visible in these traces (see Table 2 and 5, and Table II of Ref. 11).

sextic centrifugal distortion constant Φ_K at a calculated value determined from the nonrigid bender energy levels of Bunker and Jensen.¹³ This parameter could not be determined from our data since we did not observe levels with $K_a > 2$, but it has a significant effect on the observed levels. Because of the poor convergence of the Hamiltonian, the parameters given in Table 4 should be used with caution when extrapolating to rotational levels beyond those observed in the present work and Refs. 11 and 12.

An important result of the present (010) state fit is that the A -rotational constant is found to be 0.14 cm^{-1} larger and the Δ_K constant is found to be 0.07 cm^{-1} larger than those ob-

tained from the calculated energy levels of Bunker and Jensen.¹³ This result implies that the new data presented here should improve our determination of the structure and potential function. It should be noted that only $K_a = 0, 1$ levels have been observed for the (010) state of CH₂,^{7,10} so that the (010) $K_a = 2$ levels observed here in CD₂ do indeed probe a new region of the methylene intramolecular potential surface. Ultimately, an improved potential function should improve the determination of the singlet-triplet splitting in CH₂, since the best estimate¹³ relies on the potential and the nonrigid bender Hamiltonian to estimate the energies of more highly excited bending levels [(020) and (030)] of the \tilde{X}^3B_1 state in near resonance with levels of the \tilde{d}^1A_1 state.

The convergence problems encountered in fitting the rotational structure do not extend to the fine-structure splittings. As was noted for CH₂,^{7,8} there appears to be no need to include centrifugal distortion terms in the spin-spin and spin-rotation interactions in order to fit the data to within experimental accuracy. The major contribution to the fine structure arises from the electron spin-spin dipolar term that involves two parameters: D representing the isotropic effect and E , which takes into account the departure from cylindrical symmetry caused by the molecule's nonlinearity. In Table 6, we summarize the experimental determinations of these parameters for the three isotopic forms of methylene studied in the gas phase. The general trend is for an increase in D of about 2% and a decrease of E of about 10% on excitation of the fundamental bending mode. The latter is expected, since E will be zero at linearity. The change in D is of the same sign as, but considerably larger than, the value calculated *ab initio* by Langhoff and Kern.¹⁸

The spin-rotation parameters determined to date for methylene isotopes are also given in Table 6. For the ground state of CH₂ and CD₂, the ratios of the spin-rotation parameters are roughly the same as the ratios of the corresponding

Table 5. Observed Resonant Fields for the $3_{22} - 2_{11}$ Transition in the (100) Excited Vibrational State of CD₂ Observed with a ¹³CH₃OH Laser Line at $117.209532 \text{ cm}^{-1}$

Observed Field (T)	Assignment	
	$J' - J''$	$M_J' - M_J''$
0.0135	4-3	2-2
0.0151	4-3	1-1
0.0183	4-3	0-0
0.0256	4-3	-1--1
0.0286	3-3	2-2
0.0519	4-3	-2--2
0.0575	4-1	-1--1
0.1219	4-1	0-0
0.0129	4-3	0-1
0.0156	4-3	-1-0
0.0181	4-3	2-1
0.0216	4-3	1-0
	4-3	-2--1
0.0249	4-3	3-2
0.0299	4-3	0--1
0.0423	4-3	-3--2
0.0534	4-1	-2--1
0.0607	4-1	0--1
0.0635	4-3	-1--2
0.1222	4-1	1-0

Table 6. Comparison of Experimental Fine-Structure Parameters for Isotopic Forms of Methylene (in inverse centimeters)

Parameter	CH_2		$^{13}\text{CH}_2$		CD_2	
	(000) ^a	(010) ^b	(000) ^c	(010) ^c	(000) ^d	(010) ^d
D	0.7784	0.7956	0.7801	0.7977	0.7765	0.7894
E	0.0399	0.0354	0.0418	0.0384	0.0406	0.0373
ϵ_{aa}	0.00045	0.00352			0.00028	0.00059
ϵ_{bb}	-0.00515	-0.00470			-0.00260	-0.00270
ϵ_{cc}	-0.00411	-0.00458			-0.00208	-0.00214

^a Ref. 8.^b Ref. 7.^c Ref. 10. Note that spin-rotation parameters for $^{13}\text{CH}_2$ were fixed at $^{12}\text{CH}_2$ values and not independently determined.^d Present work.

rotational constants, as expected from simple theoretical arguments. For CD_2 in the (010) excited state, the changes in ϵ_{aa} , ϵ_{bb} , and ϵ_{cc} appear to be consistent. However, for CH_2 the increase in ϵ_{aa} is somewhat larger than expected on the basis of the increase in A . This slight anomaly may be due to our neglect of centrifugal distortion¹⁹ in the spin-rotation interaction, which is expected to be largest for ϵ_{aa} in the (010) state. However, ϵ_{aa} makes only a small contribution to the observed fine-structure splittings, and for this reason a detailed investigation of centrifugal distortion effects will require more-accurate measurements of levels with higher values of K_a .

We turn now to the analysis of the spectrum shown in Fig. 3, which we assigned in Section 2 to the $3_{22}-2_{11}$ transition in the (100) excited vibrational state of CD_2 . The position of this transition, with zero spin splitting, was experimentally determined to be 117.187 cm^{-1} . This may be compared with values of $3_{22}-2_{11}$ predicted by Bunker and Jensen¹³ to be 115.98 and 111.82 cm^{-1} in the (100) and (001) states, respectively. The other component of the asymmetry doublet, $3_{21}-2_{12}$, has a predicted¹³ position of 117.56 cm^{-1} in the (100) state, but we can exclude this assignment on the basis of the observed Zeeman pattern. Since only a portion of one transition has been identified for the (100) state, there is little point in attempting to determine a set of molecular parameters. An analysis of the observed resonances (Table 5) indicates that the Zeeman pattern can be well fitted by using ground-state spin-spin and spin-rotation parameters (Table 4) with a slight increase in the parameter D to 0.784 cm^{-1} . Such an increase in D is entirely consistent with that found for the (100) state in CH_2 ,¹¹ lending support to the present assignment.

4. CONCLUSIONS

Thirteen rotational transitions within the (010) first excited bending state of CD_2 have been observed and assigned, as well as one transition in the (100) stretching state and one new transition in the (000) ground vibrational state. The (010) measurements, together with previous ν_2 -band tunable-diode-laser data, are analyzed to determine all the major molecular parameters for the molecule in this state. In particular, the A -rotational constant and the Δ_K centrifugal distortion constant are found to differ somewhat from the best¹⁵ previous (theoretical) estimates.

The new data will permit the further refinement of the methylene structure and intramolecular potential energy

Table 7. Observed Rotational Transitions in CD_2 with Spin Splittings Removed

<u>Transition</u>	<u>Wave Number</u>
<u>$(\nu_1\nu_2\nu_3)$</u>	<u>(cm^{-1})</u>
$(010)^a$	$1_{11} \leftarrow 2_{02}$ 45.8637
(010)	$2_{11} \leftarrow 3_{02}$ 62.7231
(010)	$3_{12} \leftarrow 3_{03}$ 63.6418
(010)	$1_{11} \leftarrow 0_{00}$ 69.4368
(010)	$2_{12} \leftarrow 1_{01}$ 76.8260
(010)	$3_{13} \leftarrow 2_{02}$ 83.9800
(010)	$4_{14} \leftarrow 3_{03}$ 90.9033
(010)	$2_{21} \leftarrow 3_{12}$ 117.0708
(010)	$3_{21} \leftarrow 3_{12}$ 140.8969
(010)	$2_{20} \leftarrow 2_{11}$ 141.5486
(010)	$2_{21} \leftarrow 2_{12}$ 143.1560
(010)	$2_{21} \leftarrow 1_{10}$ 157.8676
$(010) \quad -$	$2_{20} \leftarrow 1_{11}$ 158.4080
$(000)^b \quad -$	$5_{23} \leftarrow 5_{14}$ 90.9683
(100)	$3_{22} \leftarrow 2_{11}$ 117.1872

^a Five ν_2 -band rotation-vibration transitions [(010) \rightarrow (000)] were reported in Ref. 12.^b Seventeen additional transitions were reported in Ref. 11.

surface^{9,13} and will therefore help to reduce the uncertainty in the determination of the singlet-triplet splitting.¹⁵ For this purpose we list in Table 7 the experimentally derived zero-field positions, with spin splittings removed, of the 15 transitions assigned in the present study. Our results provide further information on the dependence of the electron spin-spin and spin-rotation parameters on molecular geometry and should encourage more-detailed calculations of these important electronic properties by *ab initio* methods.

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REFERENCES

1. G. Herzberg and J. Shoosmith, "Spectrum and structure of the free methylene radical," *Nature (London)* **183**, 1801-1802 (1959).

2. G. Herzberg, "The spectra and structures of free methyl and free methylene," *Proc. R. Soc. Lond. Ser. A* 262, 291-317 (1961).
3. G. Herzberg and J. W. C. Johns, "The spectrum and structure of singlet CH_2 ," *Proc. R. Soc. Lond. Ser. A* 295, 107-128 (1966).
4. R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, "Electron paramagnetic resonance of triplet CH_2 ," *J. Chem. Phys.* 53, 1280-1281 (1970).
5. R. Wasserman, W. A. Yager, and V. J. Kuck, "EPR of CH_2 : a substantially bent and partially rotating ground state triplet," *Chem. Phys. Lett.* 7, 409-413 (1970); E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, "Electron paramagnetic resonance of CD_2 and CHD . Isotope effects, motion, and geometry of methylene," *J. Am. Chem. Soc.* 92, 7491-7493 (1970).
6. T. J. Sears, P. R. Bunker, and A. R. W. McKellar, "Observation of the ν_2 band of CH_2 by laser magnetic resonance," *J. Chem. Phys.* 75, 4731-4732 (1981).
7. T. J. Sears, P. R. Bunker, and A. R. W. McKellar, "The laser magnetic resonance spectrum of the ν_2 band of the methylene radical CH_2 ," *J. Chem. Phys.* 77, 5363-5369 (1982).
8. T. J. Sears, P. R. Bunker, A. R. W. McKellar, K. M. Evenson, D. A. Jennings, and J. M. Brown, "The rotational spectrum and hyperfine structure of the methylene radical CH_2 studied by far infrared laser magnetic resonance spectroscopy," *J. Chem. Phys.* 77, 5348-5362 (1982).
9. P. Jensen, P. R. Bunker, and A. R. Hoy, "The equilibrium geometry, potential function, and rotation-vibration energies of CH_2 in the \tilde{X}^3B_1 ground state," *J. Chem. Phys.* 77, 5370-5374 (1982).
10. A. R. W. McKellar and T. J. Sears, "Laser magnetic resonance spectrum of $^{13}\text{CH}_2$ around 11 μm : determination of ^{13}C hyperfine interactions and ν_2 isotope shift for methylene," *Can. J. Phys.* 61, 480-488 (1983).
11. P. R. Bunker, T. J. Sears, A. R. W. McKellar, K. M. Evenson, and F. J. Lovas, "The rotational spectrum of the CD_2 radical studied by far infrared laser magnetic resonance spectroscopy," *J. Chem. Phys.* 79, 1211-1219 (1983).
12. A. R. W. McKellar, C. Yamada, and E. Hirota, "Detection of the ν_2 bands of CD_2 and CH_2 by infrared diode laser spectroscopy," *J. Chem. Phys.* 79, 1220-1223 (1983).
13. P. R. Bunker and P. Jensen, "A refined potential surface for the \tilde{X}^3B_1 electronic state of methylene CH_2 ," *J. Chem. Phys.* 79, 1224-1228 (1983).
14. T. J. Sears, A. R. W. McKellar, P. R. Bunker, K. M. Evenson, and J. M. Brown, "Infrared and far-infrared transition frequencies for the CH_2 radical," *Astrophys. J.* 276 (to be published, 1984).
15. A. R. W. McKellar, P. R. Bunker, T. J. Sears, K. M. Evenson, R. J. Saykally, and S. R. Langhoff, "Far infrared laser magnetic resonance of singlet methylene: singlet-triplet perturbations, singlet-triplet transitions, and the singlet-triplet splitting," *J. Chem. Phys.* 79, 5251-5264 (1983).
16. T. J. Sears and P. R. Bunker, "A reinterpretation of the CH_2 photoelectron spectrum," *J. Chem. Phys.* 79, 5265-5271 (1983).
17. Such transitions (with $K_a = 3-2$) have not yet been observed for CD_2 or CH_2 .
18. S. R. Langhoff and C. W. Kern, "Molecular fine structure," in *Modern Theoretical Chemistry*, H. F. Schaefer, ed. (Plenum, New York, 1977), Vol. IX, pp. 381-437.
19. J. M. Brown and T. J. Sears, "A reduced form of the spin rotation Hamiltonian for asymmetric top molecules, with applications to HO_2 and NH_2 ," *J. Mol. Spectrosc.* 75, 111-133 (1979).
20. D. J. E. Knight, "Ordered list of far-infrared laser lines," NPL Rep. Qu 45 (Rev. 1) (National Physical Laboratory, United Kingdom, 1981). For CD_2F_2 , see E. C. C. Vasconcellos, F. R. Peterson, and K. M. Evenson, "Frequencies and wavelengths from a new, efficient FIR lasing gas: CD_2F_2 ," *Int. J. Infrared Millimeter Waves* 2, 533-535 (1981).
21. R. F. Curl, "The relationship between electron spin rotation coupling constants and g -tensor components," *Mol. Phys.* 9, 585-597 (1965).
22. C. E. Barnes, J. M. Brown, A. Carrington, J. Pinkstone, T. J. Sears, and P. J. Thistethaite, "The EPR spectrum of the HO_2 radical and determination of ground state parameters," *J. Mol. Spectrosc.* 72, 86-101 (1978).