Abstract

The frequencies of 28 lines of the ^{12}CF4 (ν_2+ν_4) → ν_2 laser have been measured with an accuracy of +0.2 cm^{-1} for ^{12}C^{16}0$_2$ pump lines from *P*(14) to *R*(24). The CF_4 pump and laser transitions have been identified and the band origin and rotational constant of the ν_2 level determined to be ν_2 = 435.27 + 0.06 cm^{-1} , B_2 = 0.19143 + 0.00007 cm^{-1}. From these constants the laser frequencies expected from any given pumping frequency can be predicted to within +0.2 cm^{-1}.

Spectroscopy of the CF_4 laser

Robin S. McDowell, Chris W. Patterson, C. R. Jones, Melvin I. Buchwald, and John M. Telle

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87545

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The frequencies of 28 lines of the $^{12}CF_4$ $(\nu_2 + \nu_4) \rightarrow \nu_2$ laser have been measured with an accuracy of ± 0.2 cm^{-1} for $^{12}C^{16}O_2$ pump lines from $P(14)$ to $R(24)$. The CF_4 pump and laser transitions have been identified and the band origin and rotational constant of the ν_2 level determined to be $\nu_2 = 435.27 \pm 0.06$ cm^{-1}, $B_2 = 0.19143 \pm 0.00007$ cm^{-1}. From these constants the laser frequencies expected from any given pumping frequency can be predicted to within ± 0.2 cm^{-1}.

Since Tiee and Wittig[1] first reported stimulated 16-μm emission on the $(\nu_2 + \nu_4) \rightarrow \nu_2$ transition in CO_2-pumped CF_4, this system has been the subject of numerous investigations.[2–8] The CF_4 laser provides an abundance of emission frequencies in the region 605–655 cm^{-1}. Energies of approximately 0.1 J (Refs. 5 and 8) and energy-conversion efficiences of >10% (Ref. 8) have been reported at 615 cm^{-1}. It thus offers considerable promise as a practical source for photodissociation and laser-induced chemistry experiments.

The first high-resolution spectroscopy of the CF_4 pump transitions was reported by Radziemski *et al.*,[9] who measured the absorption coefficients and frequency detunings in $^{12}CF_4$ near the $R(10)$, $R(12)$, and $R(18)$ lines of the 9.4-μm CO_2 band. However, prospects for improving the CF_4 laser, and especially for obtaining output at a specific desired frequency, depend largely on a detailed understanding of the rovibrational energy levels involved. Recently, an analysis[10] of the $\nu_2 + \nu_4$ pump band has enabled us to make specific quantum-level assignments for the pump and laser transitions, and concurrently we have systematically investigated the CF_4 laser frequencies as a function of pump frequency.

Experiment

The CF_4 cavity was about 4 m long; the 3-m gain cell consisted of a 3-cm-diameter copper tube cooled to ~140 K with boil-off from liquid nitrogen. One end of the cell was formed by an internal metal mirror ($R = 10$ m) with a 2-mm coupling hole sealed by a KBr window. The other end of the cell was sealed by a ZnSe Brewster window. The cavity was completed by an external metal mirror ($R = 10$ m).

The CO_2 pump laser was a free-running Lumonics Model 103-2 spark-preionized TEA laser with an output energy of ~4 J per pulse on the strong lines. The multilongitudinal-mode output was constrained with an intracavity iris to, at most, a few transverse modes. This output was roughly collimated by an external mirror ($R = 10$ m) to a diameter of 12 mm and then was introduced into the CF_4 cavity through a NaCl window on a side arm attached to the copper tube. The CO_2 pump radiation was polarized perpendicularly to the plane of incidence of the Brewster window to maximize its reflectivity (~50% per surface), and after reflecting from this window it propagated collinearly with the CF_4 laser axis. The pump laser had an estimated emission linewidth of ~0.6 GHz FWHM, based on measurements using a similar CO_2 laser. As each longitudinal mode drifted in frequency because of thermal drifting of the cavity length, it interacted with various CF_4 absorption features; the resulting emission lines are listed in Table 1. All CF_4 laser lines were erratic when pumped by the unstabilized CO_2 laser.

Laser frequencies were measured using a 1-m Spex monochromator equipped with a 60 line/mm grating blazed at 16 μm. Just before the exit slit of the monochromator, a small mirror directed the laser beam onto the face of a pyroelectric vidicon. The vidicon system was used to expedite the detection and measurement of the lines because of the erratic nature of the laser output; it displayed a 7-cm^{-1} range in laser frequency for a given dial setting and required a pulse fluence of ~10 μJ/cm^2 for positive identification. He–Ne and various CO_2 laser lines were used to calibrate the vidicon. The frequencies of some of the stronger lines in Table 1 were also measured by ordinary methods, and the quoted experimental accuracy of ± 0.2 cm^{-1} was always sustained.

More recently a stabilized, tunable CO_2 laser system, consisting of a stable TEA CO_2 oscillator and a Lumonics Model 103-2 laser used as an amplifier, has been used to pump CF_4.[8] This source can be tuned ± 1.5 GHz from line center and drifts less than 5 MHz/h. Several of the transitions listed in Table 1 have been investigated with this pumping system [e.g., $R(12)$-pumped $R^+(28)$ and $R^+(29)$], and the emission frequencies measured with a 0.25-m spectrometer agreed with the reported values.

Identification of Laser Lines

An energy-level diagram for the CF_4 laser is shown in Fig. 1. From the spectroscopy of the $\nu_2 + \nu_4$ combination,[10] it is known that the Coriolis splitting in this band is much larger than the anharmonic splitting between the F_1 and F_2 vibrational substates. As a result of the strong mixing between these substates, all nine branches

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Table 1. CF_4 Laser Transitions: Identification and Predicted and Observed Frequencies (cm^{-1})

CO_2 Pump			CF_4 Pump Transition			Laser Transition		Observed Laser Lines		
Isotope[a]	Line	Freq.	Identification	Offset (GHz)[b]	Rel. Int.[c]	Ident.	Calc. Freq.	This Work[d]	Tiee & Wittig[e]	Alimpiev et al.[f]
626	P(14)	1052.196	$P^+(27)$	[g]		P(27)	617.1	617.0		
			$P^0(36)$	[g]		Q(35)	631.1	630.8		
626	P(12)	1053.924	$P^0(32)$	[g]		Q(31)	631.2		631.12 M,Q	
626	P(10)	1055.625	$P^-(43)$	[g]		R(41)	653.4	652.2	653.32 MS	
			$P^+(21)\ F_2^1+F_1^2$	[g]	15	P(21)	620.5	620.0		620.6
626	P(8)	1057.300	$P^-(35)$	[g]		R(33)	648.8	648.2	649.3±1 M	649.3
			$P^+(18)\ A_2^0+F_2^0+E^0$	[g]	56	P(18)	622.1			622.4
626	P(6)	1058.949	$P^-(29)\ A_2^3+F_2^{12}+E^8$	+0.20	72	R(27)	645.7	645.1	646.1±1 MS	646.0
			$P^+(14)\ E^4+F_1^6+A_1^2$	[g]	1	P(14)	623.7			624.4
828	P(32)	1059.158	$P^-(28)\ E^8+F_2^{12}+A_2^4$	-0.60	84	R(26)	645.1			645.5
626	P(4)	1060.571	$P^-(23)\ F_2^8+E^5$	+0.07	40	R(21)	642.7	642.4	642.4±1 MS	642.0
						R(22)[h]	643.2	643.0		
			$P^0(15)\ E^3$	+0.07	18	Q(14)	631.1	631.3		
						?		630.8[i]		
			$Q^+(41)$	[g]		P(42)	609.7	609.6		
828	P(30)	1060.836	$P^-(22)\ F_2^7$	+0.11	24	R(20)	642.2			
			$P^-(22)\ F_1^7$	-0.05	25	R(20)	642.2			
						?R(21)[h]	642.7			643.2
828	P(28)	1062.495	$P^0(10)\ A_1^1$	+0.09	43	Q(9)	631.1			
			$P^-(16)\ F_2^3$	-0.01	20	R(14)	639.2			
			$Q^+(28)\ A_2^1+F_2^6+F_1^6+A_1^2$	-0.01	67	P(29)	616.3			
						?P(30)[h]	615.8			615.4
			$P^+(8)\ E^0+F_1^0+A_1^0$	-0.59	50	P(8)	627.2			627.3
828	P(26)	1064.135	$Q^+(16)\ F_1^4+E^2+F_2^4$	+0.24	85	P(17)	622.4			
			$P^-(9)\ F_1^3$	-0.24	21	R(7)	635.4			635.2
828	P(24)	1065.756	$Q^+(4)\ F_2^1$	-0.16	19	P(5)	628.6			
828	P(22)	1067.359	$Q^-(5)\ F_2^0$	+0.33	5	R(4)	634.0			
			$Q^-(6)\ A_1^0$	-0.31	7	R(5)	634.4			
626	R(4)	1067.539	$Q^-(6)\ F_1^0$	-0.87	5	R(5)	634.5			
828	P(20)	1068.942	$Q^-(17)\ E^2+F_2^3$	-0.04	29	R(16)	640.3			
			$R^+(10)\ A_1^1$	+0.22	70	P(12)	624.9			624.9
			$R^+(10)\ F_1^5$	-0.26	41	P(12)	624.9			
626	R(6)	1069.014	$R^0(6)\ E^1$	+0.2[g,j]	3	?Q(7)	631.1	631.8		
			$Q^-(19)\ A_1^2+F_1^7+E^5$	0.0[g,j]	13	R(18)	641.1	640.9		
			$Q^-(17)\ E^0+F_2^0+A_2^0$	-0.21	18	R(16)	640.3			
626	R(8)	1070.462	$Q^-(30)$	[g]		?P(32)[k]	614.6	614.7		
828	P(18)	1070.507	$R^+(17)\ F_2^9+F_1^9$	+0.73	96	P(19)	621.2			621.4
			$R^0(10)\ F_2^5+E^2$	+0.07	9	Q(11)	631.1			
626	R(10)	1071.884	$R^+(23)\ F_2^{12}+F_1^{12}$	+0.44	80	P(25)	618.0	618.2	618.11 MS	618.3
			$R^-(9)\ F_1^0+F_2^0$	-0.17	11	R(9)	636.6	636.7		636.8
			$R^0(13)\ F_2^3$	-0.58	16	Q(14)	631.3			
828	P(16)	1072.053	$R^+(23)\ E^5$	-0.03	22	P(25)	618.2			
			$R^0(14)\ F_2^6$	-0.03	9	Q(15)	631.1			
626	R(12)	1073.278	$R^+(29)\ A_1^4+E^9+F_1^{14}$	+0.019[l]	88	P(31)	614.9	615.1	615.06 S	615.3
			$R^+(28)\ F_2^8+E^6+F_1^8$	-0.41	53	P(30)	615.6	615.7		
828	P(14)	1073.579	$R^+(30)\ F_1^{13}+F_2^{13}$	-0.03	45	P(32)	614.4			
			$R^0(18)\ F_2^6+E^3$	-0.54	18	Q(19)	631.1			
626	R(14)	1074.646	$R^+(34)$	+0.73		P(36)	612.5			
						?P(35)[h]	613.0	613.7		
			$R^0(21)$[m]	+0.38	103[m]	Q(22)	631.1			
			$R^+(35)$	-0.34		P(37)	611.7	612.2	611.99 MS	612
626	R(16)	1075.988	$R^-(17)$[n]	[g,n]	15[n]	R(17)	640.8	640.9	640.73 M	641.4
626	R(18)	1077.303	$R^-(20)\ E^5+F_2^8+A_2^3$	+0.3[g,j]	3	R(20)	642.1	641.9		
			$R^0(27)\ E^0+F_1^0+A_1^0$	[g]	2	Q(28)	631.5	631.5		
			$R^0(28)$	-0.10		Q(29)	631.1	630.8	631.05 MS,Q	
626	R(20)	1078.591	$R^-(22)$[p]	[g,p]	28[p]	R(22)	643.5	643.1	643.23 MS	643.9
626	R(22)	1079.852	$R^0(35)$	[g]		Q(36)	631.1	631.4	631.15 M,Q	
			$R^0(36)$	[g]		Q(37)	630.8	630.8		
626	R(24)	1081.087	$R^-(27)$	[g]		R(27)	646.0	645.5		646.2

[a] 626 and 828 are abbreviations for $^{12}C^{16}O_2$ and $^{12}C^{18}O_2$, respectively.

[b] Offset = (CF_4 absorption line frequency) - (CO_2 laser line frequency).

[c] Relative intensities calculated for T = 150 K. [d] Estimated accuracy ±0.2 cm^{-1}.

[e] Reference 2. Accuracy ±0.1 cm^{-1} unless stated otherwise; relative intensities are in the ratio S:MS:M ≈ 9:3:1. Q-branch lines, so identified by their preferred polarization, are indicated by Q.

[f] S. S. Alimpiev, G. S. Baranov, N. V. Karlov, A. I. Karchevskii, V. L. Martsykian, Sh. Sh. Nabiev, B. G. Sartakov, E. M. Khokhlev, and V. G. Averin, paper presented at the IXth National Conf. on Coherent and Nonlinear Optics (Leningrad, 13-16 June 1978).

[g] Line not explicitly identified in the CF_4 $\nu_2+\nu_4$ absorption spectrum, but calculations indicate that it lies very near the specified pump line.

[h] Upper level presumably reached by relaxation from an adjacent J level.

[i] Unidentified laser line. [j] Calculated value.

[k] This assumes that the $J=30^-$ upper state relaxes to $J=31^+$; there seems to be no other way to account for the observed laser frequency. Only a few very weak, unassigned absorption features fall within ±1 GHz of the CO_2 pump line. [l] Reference 9.

[m] 14 transitions of $R^0(21)$ with a total intensity of 103 form a broad, unresolved absorption feature at +0.38 GHz from CO_2 R(14).

[n] 8 transitions of $R^-(17)$, total intensity 15, are calculated to fall within ±0.6 GHz of CO_2 R(16).

[p] 9 transitions of $R^-(22)$, total intensity 28, are calculated to fall within ±0.6 GHz of CO_2 R(20).

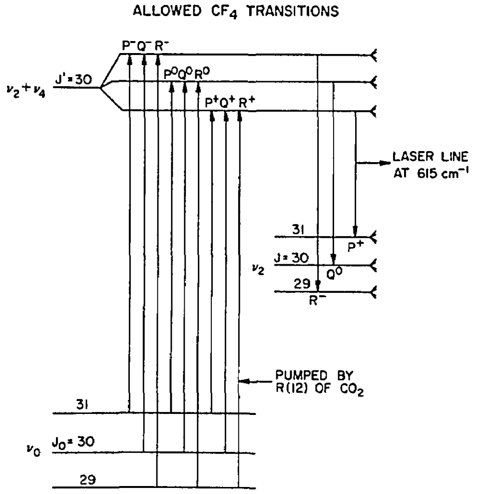

Fig. 1. Typical energy-level diagram for the CF$_4$ laser, with the total angular momentum quantum numbers in the vibrational ground state and in $\nu_2+\nu_4$ and ν_2 denoted by J_0, J', and J, respectively. The arrows indicate allowed transitions to the three Coriolis sublevels of $J' = 30$ of $\nu_2+\nu_4$ and allowed laser transition down to ν_2. $R(12)$ of $^{12}C^{16}O_2$ pumps the transition $R^+(29)$, populating the + level of $J' = 30$; stimulated emission occurs from this level to $J = 31$ of ν_2, producing the strong laser line $P(31)$ at 615 cm^{-1}.

of $\nu_2+\nu_4$ are allowed in absorption (i.e., P, Q, and R transitions to each of the +, 0, − Coriolis sublevels), as Fig. 1 illustrates. Since ν_2 and ν_4 are weakly coupled, the selection rule for the laser transition $(\nu_2+\nu_4) \rightarrow \nu_2$ will to a good approximation be simply that for ν_4, which carries the dipole moment. Thus only P^+, Q^0, and R^- laser lines are allowed, and we have the following relation between the nine types of pump transitions and the corresponding laser transitions (dropping the Coriolis-level identification on the latter as redundant):

$$\begin{array}{lll} P^+(J){:}P(J) & Q^+(J){:}P(J+1) & R^+(J){:}P(J+2) \\ P^0(J){:}Q(J-1) & Q^0(J){:}Q(J) & R^0(J){:}Q(J+1) \\ P^-(J){:}R(J-2) & Q^-(J){:}R(J-1) & R^-(J){:}R(J) \end{array}$$

Identifications of the pump transitions follow from Ref. 10 and are listed in Table 1 for pumping frequencies between 1052 and 1082 cm^{-1}. [Detailed spectra and assignments in the vicinity of $P(4)$, $R(10)$, and $R(12)$ of $^{12}C^{16}O_2$ and $P(14)$ of $^{12}C^{18}O_2$ are illustrated in Ref. 10.] From Fig. 1 it follows that the frequency of laser emission expected from pumping a transition at frequency ν_P is

$$\nu_L = \nu_P + B_0J_0(J_0+1) - \nu_2 - B_2J(J+1), \quad (1)$$

where $B_0 = 0.191688$ cm^{-1}.[10] (We have ignored the tetrahedral splitting in ν_2, which we estimate to be <0.1 cm^{-1} for $J < 30$.) From a least-squares fit of Eq. (1) to 26 well-determined laser frequencies, we obtained the following values of the spectroscopic constants for the ν_2 fundamental:

$$\nu_2 = 435.27 \pm 0.06 \text{ cm}^{-1},$$

$$B_2 = 0.19143 \pm 0.00007 \text{ cm}^{-1}.$$

The limits given are 1σ errors, and the standard deviation of the residuals is 0.18 cm^{-1}. (The accuracy of these constants could be considerably improved if more-precise measurements of the laser frequencies were available.) Table 1 gives the laser frequencies calculated from Eq. (1) using these constants, and the agreement between observed and calculated values is seen to be excellent. A few of the observed laser lines can be accounted for only by assuming that a relaxation of J value and/or Coriolis sublevel takes place in $\nu_2+\nu_4$.

Discussion

The density of transitions in $\nu_2+\nu_4$ of CF$_4$ is such that, with a free-running CO$_2$ laser, resonances are almost guaranteed. In fact, in most cases more than one transition is pumped and consequently several different lines are observed to lase. The strength of the well-known 615-cm^{-1} emission when pumped by a normal multimode TEA CO$_2$ laser is due to the fact that $^{12}C^{16}O_2$ is very nearly resonant with a strong, narrow $\nu_2+\nu_4$ transition.

To produce single-frequency CF$_4$ laser output that is steady in amplitude, it is necessary to constrain the pump laser to operate on a single longitudinal and transverse mode; the frequency of this mode must be tuned to the appropriate CF$_4$ absorption and stabilized to within about 5 MHz. Conversion efficiencies will then be much greater than those obtained with a multimode unstabilized pump laser.

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