THE ASTROPHYSICAL JOURNAL, **318**:873–875, 1987 July 15 © 1987. The American Astronomical Society. All rights reserved. Printed in U.S.A.

C-TYPE TRANSITIONS IN METHYL FORMATE

GRANT M. PLUMMER I. Physikalisches Institut, Universität zu Kœln

AND

ERIC HERBST AND FRANK C. DE LUCIA Department of Physics, Duke University Received 1986 November 19; accepted 1986 December 24

ABSTRACT

In a previous laboratory analysis of the millimeter-wave spectrum of the asymmetric top methyl formate in its ground $(v_t = 0)$ torsional E (degenerate) substate, we predicted the transition frequencies and intensities of a large number of rotational transitions below 300 GHz in frequency, with angular momentum quantum number $J \leq 30$, and with upper state rotational energy $E_u \leq 350 \text{ cm}^{-1}$. These transitions are mainly of two types: *a*-type spectra, in which the K_{-1} (prolate) quantum number doesn't change and the K_1 (oblate) quantum number changes by one unit, and *b*-type spectra, in which both K_{-1} and K_1 change by one unit. We have recently come to the realization that there are some additional moderately strong spectral lines called *c*-type transitions—which would be forbidden in methyl formate, since it does not possess a dipole moment along the *c*-principal axis, except for the perturbative influence of internal rotation (torsional motion). Based on our previously determined spectral constants for methyl formate in its ground torsional ($v_t = 0$) degenerate (*E*) substate, we have calculated the frequencies and intensities of these *c*-type transitions, as well as other "forbidden" transitions labeled as *x*-type. The stronger *c*-type transitions below 300 GHz in frequency, with angular momentum quantum number $J \leq 30$, and with upper state rotational energy $E_u \leq 350 \text{ cm}^{-1}$ have been included in a list of spectral frequencies presented in this paper. Because the *c*-type transitions borrow intensity from the *b*-type transitions, we have recalculated the intensities of strongly affected *b*-type spectra and present these recalculated intensities as well.

Subject headings: interstellar: molecules — line identifications — molecular processes

I. INTRODUCTION

The millimeter spectrum of OMC-1 contains a large number of rotational lines of methyl formate (HCOOCH₃), a molecule with internal rotation (torsional motion) which possesses a dense, complex spectrum due to the interaction of the rigid body rotation of the molecule and its torsional motion. Indeed, in their survey of Orion in the 215-247 GHz frequency range, Sutton et al. (1985) found 130 lines of methyl formate, most of which were assigned based on work from this laboratory. Our previous laboratory work on the millimeter- and submillimeter-wave spectrum of methyl formate has consisted of two papers. In the first paper (Plummer et al. 1984), we analyzed the spectrum of methyl formate in its ground $(v_r = 0)$ torsional A (symmetric) substate. In this state, the effects of torsional motion are unimportant, and the molecule can be analyzed as a semirigid asymmetric top. In the second paper (Plummer et al. 1986), we analyzed the more complex spectrum of the ground $(v_t = 0)$ torsional E (degenerate) substate of methyl formate, in which torsional effects are quite pronounced. Our method of analysis was based on a classical treatment of internal rotation labeled the principal axis method (PAM; see Herschbach 1959) in which internal rotation is treated by van Vleck perturbation theory to high order. This approach does not require large amounts of computer time and has allowed us to assign spectra up to quite high values of the rotational angular momentum quantum number J.

For molecules in which the effects of internal rotation are even stronger than in methyl formate, a perturbative treatment is inappropriate. Consequently, we have developed another approach for such molecules (CH₃OH, CH₃SH, CH₃CHO) in which perturbation theory is not utilized. This approach, an extension of another classical method called the internal axis method (IAM; Herbst *et al.* 1984 and references therein, especially Lees and Baker 1968), requires the use of large matrices and consequently cannot be utilized for high J values unless supercomputer technology is employed. However, one advantage of the IAM approach is that it can be used to fit spectral lines from different torsional (v_i) states and substates (A, E)simultaneously.

In a study in progress of millimeter-wave spectra from the first excited ($v_t = 1$) torsional states (A, E) of methyl formate, we utilized the IAM approach because of its ability to analyze data from several torsional states in one global fit. During this study, we found a discrepancy between selected IAM predictions and previous PAM predictions for spectral line intensities in the ground torsional E substate of this species. In particular, the IAM approach predicted fairly intense unusual transitions that were not predicted in the PAM calculations to be anywhere near as intense. Our IAM predictions were in agreement with a previous IAM analysis of the ground torsional substates of methyl formate (Bauder 1979). Upon analysis, we realized that the IAM predictions were indeed correct and have modified our PAM analysis to handle the unusual transitions correctly. How these transitions arise is discussed in § II.

II. FORBIDDEN TRANSITIONS AND PREDICTED FREQUENCIES

The appearance of "forbidden" transitions in the rotational spectrum of methyl formate in its E substates results from the fact that the internal rotation can lead to a mixing of the

 TABLE 1

 B-Type Transitions with Corrected Intensities

TABLE 2

C-TYPE TRANSITIONS

ASSIGNMENT a	FREQUENCY	s	F
I'(K' - K' -) I''(K'' - K'' -)	(MHz)	5	(cm^{-1})
<u> </u>	(10112)		(em)
12(5,7) - 12(4,8)	119175.71 (0.05)	5.5	44
11(5, 6) - 11(4, 7) 10(5, 5) - 10(4, 6)	121161.70 (0.06)	4.1	39
12(5, 8) - 12(4, 9)	122610.20 (0.05)	5.4	44
11(5,7) - 11(4,8) 10(5,6) - 10(4,7)	122862.91 (0.05)	4.0	39 34
15(6,9) - 15(5,10)	146747.95 (0.08)	6.1	66
14(6,8) - 14(5,9)	148418.91 (0.07)	5.0	60
13(6,10) - 13(5,11) 14(6,9) - 14(5,10)	148655.95 (0.08)	5.0	60
13(6,7) - 13(5,8)	149611.33 (0.06)	4.8	54
13(6, 8) - 13(5, 9) 12(6, 6) - 12(5, 7)	149924.42 (0.06)	4.8 4.9	54 49
12(6,7) - 12(5,8)	150504.48 (0.05)	4.9	49
19(7,12) - 19(6,13) 18(711) - 18(612)	172103.89 (0.11)	8.5 6.9	101
19(7,13) - 19(6,14)	174061.67 (0.11)	8.4	101
18(7,12) - 18(6,13) 17(7,10) 17(6,11)	174996.08 (0.11)	6.9 6.4	93 85
17 (7,11) - 17(6,12)	175882.61 (0.09)	6.4	85
16(7,9) - 16(6,10)	176585.23 (0.06)	6.6	78
5(5, 1) - 4(4, 0)	185629.08 (0.12)	0.0	18
5(5,0) - 4(4,1)	186239.16 (0.12)	0.0	18
23(8,15) - 23(7,16) 6(5,2) - 5(4,1)	197293.92 (0.13)	0.0	20
6(5,1) - 5(4,2)	198492.31 (0.11)	0.0	20
23(8,16) - 23(7,17) 22(8,14) - 22(7,15)	199206.73 (0.13) 199404 66 (0.14)	11.2 9 1	143
22(8,14) - 22(7,16) 22(8,15) - 22(7,16)	200412.38 (0.14)	9.1	134
21(8,13) - 21(7,14) 21(8,14) - 21(7,15)	201078.86 (0.12)	8.0	125
20(8,12) - 20(7,13)	201339.10 (0.12)	8.2	116
20(8,13) - 20(7,14)	202571.58 (0.09)	8.2	116
7(5, 3) - 6(4, 2) 7(5, 2) - 6(4, 3)	210725.80 (0.11)	0.0	23
8(5,4) - 7(4,3)	222345.09 (0.10)	0.1	26
8(5,3) - 7(4,4) 26(917) - 26(818)	222925.73 (0.10) 224619.52 (0.18)	12.2	182
6(6,1) - 5(5,0)	225523.06 (0.14)	0.0	25
26(9,18) - 26(8,19) 6(6,0) - 5(5,1)	225624.59 (0.18) 226232 89 (0.14)	12.1	182
25(9,16) - 25(8,17)	226468.63 (0.18)	9.9	171
25(9,17) - 25(8,18) 24(9,15) - 24(8,16)	226973.14 (0.18)	9.9 9.4	171
24(9,15) - 24(8,10) 24(9,16) - 24(8,17)	228204.81 (0.14)	9.4	161
23(9,14) - 23(8,15)	229260.20 (0.08)	10.2	151
23(9,15) - 25(8,16) 9(5,5) - 8(4,4)	234479.63 (0.08)	0.4	30
9(5,4) - 8(4,5)	235087.58 (0.09)	0.4	30
7(6, 2) - 6(5, 1) 7(6, 1) - 6(5, 2)	237/91.44 (0.13)	0.0	28 28
10(5,6) - 9(4,5)	246456.53 (0.08)	1.5	34
10(5,5) - 9(4,6) 8(6,3) - 7(5,2)	247242.03 (0.08)	1.5	34
8(6,2) - 7(5,3)	250730.69 (0.12)	0.0	31
28(10,18) - 28(9,19) 28(10,19) - 28(9,20)	253395.22 (0.26)	11.0	213
27(10,17) - 27(9,18)	254838.61 (0.20)	10.6	202
27(10,18) - 27(9,19)	254938.77 (0.20)	10.6	202
26(10,16) - 26(9,17) 26(10,17) - 26(9,18)	256094.47 (0.11)	11.9	190
11(5,7)-10(4,6)	258152.89 (0.07)	2.7	39
11(5, 6) - 10(4, 7) 9(6, 4) - 8(5, 3)	262287.63 (0.07)	2.7	39 35
9(6,3) - 8(5,4)	262951.59 (0.12)	0.0	35
7(7, 1) - 6(6, 0) 7(7, 0) - 6(6, 1)	265418.91 (0.18) 266208 97 (0.18)	0.0	34 34
12(5,8) - 11(4,7)	269404.72 (0.06)	3.9	44
12(5,7) - 11(4,8) 10(5,5) - 0(5,4)	271779.72 (0.06)	3.8	44
10(0, 3) - 9(5, 4) 10(6, 4) - 9(5, 5)	275139.38 (0.11)	0.0	39
8(7,2) - 7(6,1)	277691.38 (0.17)	0.0	37
8(7, 1) - 7(6, 2) 30(11, 19) - 30(10.20)	278404.30 (0.17) 281645.91 (0.40)	10.5	247
30(11,20) - 30(10,21)	281710.88 (0.40)	10.5	247
29(11,18) - 29(10,19) 29(11,19) - 29(10,20)	282871.44 (0.25) 282882.09 (0.25)	12.3 12.3	235
11(6,6) - 10(5,5)	286655.63 (0.11)	0.0	44
11(6,5) - 10(5,6) 9(7,3) - 8(6,2)	287281.13 (0.11) 289957 (09 (0.16)	0.0	44 41
9(7,2) - 8(6,3)	290711.19 (0.16)	0.0	41
12(6,7) - 11(5,6) 12(6,6) - 11(5,7)	298747.50 (0.12)	0.2	49 40
12(0,0)-11(3,7)	277300.00 (0.12)	0.2	-+2

$ \begin{array}{c} r(m^{-1}) \\ \hline r(r, r(k_+1) - J^{*}(K^{*}_{-1}K^{*}_{+1}) & (MHz) \\ \hline r(m^{-1}) \\ r(m^{-1}) \\ \hline r(m^{-1}) \\ r(m^{-1}) \\ \hline r(m^{-1}) \\ \hline r(m^{-1}) \\ \hline r(m^{-1}) \\ r(m^{-1}) \\ \hline r(m^{-1}) \\ r(m^{$	$\begin{array}{c} J(K_{-1}K_{+1}) - J^{*}(K_{-1}K_{+1}) & (MHz) & (cm^{-1}) \\ \hline \\ 12(5,8) - 12(4,8) & 118803.90 (0.05) & 0.9 & 44 \\ 11(5,7) - 11(4,7) & 120859.64 (0.06) & 1.5 & 39 \\ 10(5,6) - 10(4,6) & 122298.20 (0.05) & 0.9 & 44 \\ 11(5,6) - 11(4,8) & 123164.96 (0.06) & 1.5 & 39 \\ 10(5,5) - 10(4,7) & 122398.07 (0.07) & 1.5 & 34 \\ 15(6,10) - 15(5,10) & 146440.73 (0.09) & 1.7 & 66 \\ 14(6,9) - 14(5,9) & 148124.75 (0.09) & 2.1 & 60 \\ 15(6,9) - 15(5,11) & 148961.17 (0.09) & 1.7 & 66 \\ 14(6,9) - 14(5,5) & 148920.63 (0.09) & 2.1 & 60 \\ 13(6,8) - 13(5,8) & 149307.86 (0.10) & 1.6 & 54 \\ 14(6,6) - 12(5,7) & 150132.72 (0.11) & 0.7 & 49 \\ 13(6,7) - 13(5,9) & 150227.89 (0.10) & 1.6 & 54 \\ 12(6,6) - 12(5,8) & 150227.89 (0.10) & 1.6 & 54 \\ 12(6,6) - 12(5,8) & 150227.89 (0.10) & 1.6 & 54 \\ 12(6,6) - 12(5,8) & 150227.89 (0.10) & 1.6 & 54 \\ 12(6,6) - 12(5,6) & 150227.09.78 (0.16) & 2.3 & 85 \\ 19(7,12) - 19(6,13) & 171821.05 (0.13) & 1.8 & 101 \\ 17(7,11) - 17(6,11) & 175298.78 (0.16) & 2.3 & 85 \\ 18(7,11) - 18(6,13) & 175228.14 (0.14) & 2.5 & 93 \\ 17(7,10) - 17(6,12) & 176155.00 (0.16) & 2.3 & 85 \\ 16(7,10) - 16(6,10) & 176295.95 (0.17) & 1.3 & 78 \\ 5(5,1) - 4(4,1) & 185906.91 (0.06) & 4.5 & 18 \\ 5(5,0) - 4(4,0) & 185961.34 (0.06) & 4.5 & 18 \\ 5(5,1) - 4(4,1) & 185906.91 (0.06) & 4.5 & 18 \\ 5(5,1) - 5(4,2) & 198165.77 (0.06) & 4.5 & 20 \\ 6(5,1) - 5(4,2) & 198128.56 (0.06) & 4.5 & 20 \\ 6(5,1) - 5(4,2) & 198128.56 (0.06) & 4.5 & 18 \\ 5(5,1) - 5(4,2) & 198128.56 (0.06) & 4.5 & 20 \\ 6(5,1) - 5(4,2) & 10456.66 (0.05) & 4.5 & 20 \\ 6(5,1) - 5(4,2) & 10456.66 (0.05) & 4.5 & 20 \\ 6(5,1) - 5(4,2) & 10456.66 (0.05) & 4.5 & 20 \\ 2(8,13) - 20(7,14) & 202804.55 (0.23) & 2.1 & 116 \\ 20(8,12) - 20(7,14) & 202804.55 (0.23) & 2.1 & 116 \\ 20(8,12) - 20(7,14) & 202804.55 (0.23) & 2.1 & 116 \\ 20(8,12) - 20(7,14) & 202804.55 (0.23) & 2.1 & 116 \\ 20(8,12) - 20(7,14) & 202804.55 (0.23) & 2.1 & 116 \\ 20(8,12) - 20(7,14) & 202804.55 (0.23) & 2.1 & 116 \\ 20(8,12) - 20(7,14) & 202804.55 (0.23) & 2.1 & 116 \\ 20(8,12) - 20(7,14) & 202804.55 (0.23) & 2.1 & 116 \\ 20(8,12)$
12(5, 8) - 12(4, 8)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
12(6,7) - 11(5,7) 299049.53 (0.05) 5.5 49	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

^a Upper level is indicated by primes, lower level by double primes.

^a Upper level is indicated by primes, lower level by double primes.



FIG. 1.-Some allowed (heavy lines) and "forbidden" transitions for methyl formate in its ground torsional E substate are depicted among levels involving angular momentum quantum number J = 6, 7. Transitions in which J changes by one and zero units are labeled R and Q, respectively.

so-called K doublet states. These states, which in a prolate asymmetric rotor such as methyl formate share the same J and the same K_{-1} quantum number, are coupled by the perturbation operator in the PAM treatment. The resultant mixing of the states allows transitions which do not occur in the absence of internal rotation (Gordy and Cook 1984). In Figure 1, we show a variety of allowed and "forbidden" transitions in which the quantum number K_{-1} changes by 0 or 1 units among some energy levels in methyl formate for which J = 6and 7. The "forbidden" transitions are of several varieties, labeled x-type and c-type (Woods 1966). The x-type transitions $(\Delta K_{-1} = 0, \Delta K_1 = 0, 2)$ are "forbidden" partners of normal *a*-type transitions $(\Delta K_{-1} = 0, \Delta K_1 = 1)$ whereas the *c*-type transitions $(\Delta K_{-1} = \pm 1, \Delta K_1 = 0, \pm 2)$ are partners of normal *b*-type transitions ($\Delta K_{-1} = \pm 1$, $\Delta K_1 = \pm 1$, 3). Note that *c*-type transitions are perfectly allowed if the molecule possesses a component of its permanent dipole moment along the *c*-axis. Here, however, there is no such component. Both the x-type and c-type transitions in methyl formate E torsional substates can be thought of as borrowing intensity from their more normal counterparts.

Utilizing our previously determined spectral constants for methyl formate in its ground torsional degenerate state, we have predicted the frequencies and intensities of a large number of x-type and c-type transitions below 300 GHz in frequency involving the rotational angular momentum quantum number $J \leq 30$ and upper state rotational energy $E_{\mu} \leq 350 \text{ cm}^{-1}$. Most of these transitions are considerably below the lower intensity limit set in our previous paper (Plummer et al. 1986) and are not included here. Our previous paper did include a significant number of b-type transitions in

Bauder, A. 1979, J. Phys. Chem. Ref. Data, 8, 583. Curl, R. F. 1959, J. Chem. Phys., 30, 1529.

- Gordy, W., and Cook, R. L. 1984, Microwave Molecular Spectra (New York: Wilev).
- Herbst, E., Messer, J. K., De Lucia, F. C., and Helminger, P. 1984, J. Molec. Spectrosc., 108, 42.

Herschbach, D. R. 1959, J. Chem. Phys., 31, 91.

Lees, R. M., and Baker, J. G. 1968, J. Chem. Phys., 48, 5299.

Plummer, G. M., Blake, G. A., Herbst, E., and De Lucia, F. C. 1984, Ap. J. Suppl., 55, 633.

which the calculated intensities are too large because "borrowing" of these intensities via the forbidden transitions was not treated correctly. These b-type transitions, in which the previously calculated intensities are too large by 10% or more, are contained in Table 1 with the correct intensities. The corresponding *c*-type transition frequencies and intensities are listed in Table 2. Some of these *c*-type transitions should be observable in interstellar sources such as Orion, especially those involving a change in the J quantum number. The intensities in both tables are expressed in terms of the line strength S (Townes and Schawlow 1955); to obtain a total intensity one must multiply by μ_b^2 , the square of the dipole moment in the b direction ($\mu_b = 0.68$ Debye; Curl 1959). The uncertainties in the predicted frequencies of Tables 1 and 2 are 1 σ values and should be viewed with caution considering that our fit to the data (Plummer et al. 1986) does not reproduce experimental accuracy. Limited experimental checks of the predicted frequencies have been undertaken and show the predictions to be reliable to better than 1 MHz. Only two x-type transitions have been found to be of sufficient intensity to be listed here according to our previous criteria (Pummer et al. 1986) but the large uncertainties in the predicted frequencies of these transitions (23_{20,4}-22_{20,2} and 23_{20,3}-22_{20,3}) preclude our listing them.

E. H. and F. C. D. acknowledge the support of NASA via grant NAGW-189 for our program in laboratory astrophysics and of the NSF via grant CHE-8515331 for our program in spectroscopy. G. M. P. wishes to thank the Alexander von Humboldt Foundation for a research fellowship.

REFERENCES

Plummer, G. M., Herbst, E., De Lucia, F. C., and Blake, G. A. 1986, Ap. J. Suppl., 60, 949

Sutton, E. C., Blake, G. A., Masson, C. R., and Phillips, T. G. 1985, Ap. J. Suppl., 58, 341.

Townes, C. H., and Schawlow, A. L. 1955, Microwave Spectroscopy (New York : McGraw Hill) Woods, R. C. 1966, J. Molec. Spectrosc., 21, 4.

FRANK C. DE LUCIA and ERIC HERBST: Department of Physics, Duke University, Durham, NC 27706

GRANT M. PLUMMER: I. Physikalisches Institut, Zülpicher Strasse 77, Universität zu Kœln, Cologne, Federal Republic of Germany