Millimeter-Wave Spectrum of Ethyl Formate

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The rotational spectrum of ethyl formate has been investigated up to 240 GHz. High J transitions of both a-type and b-type have been measured for the two isomers and fitted to a centrifugally distorted Hamiltonian including some sextic coefficients. The results of the analysis are sufficiently accurate for the prediction of all strong transitions throughout the millimeterwave range. No splitting due to the internal rotation of the methyl group was observed, which indicates that the barrier to internal rotation is of the order of 3 kcal/mole or greater.

Introduction

Ethyl formate ($HCOOC_2H_5$) was previously studied in the centimeter-wave range by Riveros and Wilson [1] who showed that at least two isomeric forms exist and that the trans form is lower in energy than the gauche form by $E_G^0 - E_T^0 = 186\ (60)$ cal/mole. They determined the rotational constants (for the ground and several excited torsional states) and the dipole moment components of these two forms. Later Meyer [2] analyzed from a theoretical point of view the variation of the rotational constants with the skeletal torsion about the CH_2-O bond. Kaushik [3] determined the centrifugal distortion constants of the gauche form in its ground state and in the $v = 1$ torsional state using the measurements of Riveros [1].

Formic acid (HCOOH) [4], ethanol (C_2H_5OH) [5], and methyl formate ($HCOOCH_3$) [6, 7] have already been found in the interstellar space, so ethyl formate could be a possible candidate for interstellar detection, and more probably its trans form, because it is more stable, its rotational constants are larger (see Table 3) and it has the largest component of the dipole moment: $\mu_a = 185$ D compared with $\mu_a = 1.45$ D for the gauche form.

For this reason we have measured the millimeter-wave spectrum of ethyl formate and carried out a complete centrifugal distortion analysis so that accurate measurements and predictions would be available for the radioastronomers.

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Experimental Details

The sample of ethyl formate was purchased commercially from Fluka AG (Buchs, Switzerland) and was used without further purification. The measurements were carried out in a waveguide-type millimeter-wave spectrometer with or without source modulation. Phase-stabilized klystrons (varian 60–80 GHz) supply a harmonic generator (Custom microwave) with fundamental power. To obtain good sensitivity and to be sure to work with only one harmonic frequency, superheterodyne detection is used: the local oscillator is kept at a constant frequency difference of 600 MHz from the source oscillator. After the detection the signal is digitally averaged and is then processed by a microcomputer (ITT 2020) which allows digital filtering (baseline subtraction and if necessary line smoothing) and which calculates the line frequencies [8]. All spectra were measured at room temperature and at pressures below 5 mTorr. The accuracy of the measurements depends on the S/N ratio, it is about 30 kHz for the strongest lines and can be as poor as 100 kHz for some weak lines.

Analysis of the Spectrum

The largest component of the dipole moment is μ_a for both forms, so the a-type R – branch spectra were searched first. Their assignment was easy because the spectra are intense and because the constants of Riveros [1] and Kaushik [3] could be used for a prediction. In each case the assignment was started by observing the splitting of the K-doublet transitions. These $^aR_{01}$ transitions, were

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Table 1. Measured ground state transitions of the trans isomer of ethyl formate.

$J'_{K'_a K'_c} \leftarrow J_{K_a K_c}$ [a]		ν_{exp} [MHZ]	$\nu_{calc} - \nu_{exp}$ [MHz]	$J'_{K'_a K'_c} \leftarrow J_{K_a K_c}$ [a]		ν_{exp} [MHZ]	$\nu_{calc} - \nu_{exp}$ [MHz]
2_{02}	1_{01}	10962.44	− 0.01	$29_{0,29}$	$28_{0,28}$	151804.93	0.01
2_{12}	1_{11}	10642.26	− 0.10	$29_{1,29}$	$28_{1,28}$	151755.54	0.00
2_{11}	1_{10}	11293.29	0.04	$29_{1,28}$	$28_{1,27}$	156768.59	− 0.08
2_{11}	2_{02}	15498.26	0.15	$29_{2,28}$	$28_{2,27}$	155921.54	− 0.03
3_{13}	2_{12}	15959.95	− 0.02	$29_{4,26}$	$28_{4,25}$	159935.96	− 0.08
3_{03}	2_{02}	16430.40	− 0.03	$29_{6,24}$	$28_{6,23}$	159621.00	0.02
3_{22}	2_{21}	16451.67	− 0.03	$29_{8,22}$	$28_{8,21}$	159351.13	0.07
3_{21}	2_{20}	16472.82	0.01	29_{10}	28_{10}	159233.51	0.07
3_{12}	2_{11}	16936.62	− 0.01	29_{12}	28_{12}	159175.01	0.13
3_{13}	2_{02}	30481.52	0.07	29_{14}	18_{14}	159144.71	0.02
3_{12}	3_{03}	16004.65	− 0.01	29_{15}	28_{15}	159135.70	− 0.00
4_{14}	3_{13}	21273.80	− 0.01	29_{16}	28_{16}	159129.55	− 0.04
4_{04}	3_{03}	21882.48	− 0.04	29_{17}	28_{17}	159125.63	− 0.07
4_{23}	3_{22}	21931.41	− 0.08	29_{21}	28_{21}	159124.33	− 0.19
4_{22}	3_{21}	21984.09	0.14	29_{22}	28_{22}	159126.27	− 0.15
4_{13}	3_{12}	22575.74	0.01	29_{23}	28_{23}	159128.58	0.13
4_{14}	3_{03}	35324.96	0.04	29_{24}	28_{24}	159131.44	0.31
4_{13}	4_{04}	16697.93	0.02	$30_{0,30}$	$29_{0,29}$	156952.56	− 0.03
5_{14}	4_{13}	28209.29	− 0.03	$30_{1,30}$	$29_{1,29}$	156913.32	− 0.03
5_{05}	4_{04}	27313.56	− 0.03	$30_{1,30}$	$29_{0,29}$	157097.12	− 0.02
5_{24}	4_{23}	27407.45	− 0.02	$33_{6,27}$	$33_{5,28}$	160505.90	0.00
5_{15}	4_{14}	26582.59	− 0.03	$39_{1,39}$	$39_{0,39}$	157931.05	0.02
5_{23}	4_{22}	27512.91	0.05	$44_{1,43}$	$43_{1,42}$	233537.93	0.04
5_{14}	5_{05}	17593.71	− 0.03	$44_{1,43}$	$43_{2,42}$	233310.87	− 0.03
8_{17}	8_{08}	21692.04	− 0.07	$44_{2,43}$	$43_{2,42}$	233491.53	0.05
9_{18}	9_{09}	23601.58	− 0.02	$44_{2,43}$	$43_{1,42}$	233718.67	0.04
$11_{1,10}$	$11_{0,11}$	28358.31	− 0.14	$44_{4,41}$	$43_{4,40}$	241377.07	− 0.21
$27_{2,25}$	$26_{2,24}$	151203.62	− 0.15	$44_{7,38}$	$43_{7,37}$	242713.24	0.06
$27_{3,24}$	$26_{3,23}$	151655.44	− 0.08	$44_{9,36}$	$43_{9,35}$	242082.08	0.08
$28_{1,27}$	$27_{1,26}$	151682.43	− 0.06	44_{11}	43_{11}	241775.42	0.21
$28_{2,27}$	$27_{2,26}$	150704.02	− 0.05	44_{13}	43_{13}	241609.71	0.13
$28_{2,27}$	$27_{1,26}$	156805.59	− 0.04	44_{15}	43_{15}	241513.69	− 0.02
$28_{3,26}$	$27_{3,25}$	153498.12	− 0.10	44_{17}	43_{17}	241456.50	− 0.16
$28_{3,25}$	$27_{3,24}$	157421.25	− 0.10	44_{19}	43_{19}	241422.74	− 0.26
$28_{4,25}$	$27_{4,24}$	154410.68	− 0.07	44_{21}	43_{21}	241403.64	− 0.03
$28_{4,24}$	$27_{4,23}$	155376.95	0.01	$45_{0,45}$	$44_{0,44}$	234188.63	0.01
$28_{5,24}$	$27_{5,23}$	154303.75	− 0.03	$45_{1,45}$	$44_{1,44}$	234187.68	− 0.02
$28_{5,23}$	$27_{5,22}$	154393.06	− 0.02	$45_{1,45}$	$44_{0,44}$	234191.98	− 0.01
$28_{6,23}$	$27_{6,22}$	154080.46	− 0.02	$45_{0,45}$	$44_{1,44}$	234184.34	0.00
$28_{6,22}$	$27_{6,21}$	154085.00	0.03	$45_{1,44}$	$44_{1,43}$	238677.65	0.03
28_{8}	27_{8}	153837.87	0.06	$45_{2,44}$	$44_{2,43}$	238640.50	0.02
28_{9}	27_{9}	153775.47	0.09	$45_{1,44}$	$44_{2,43}$	238496.97	− 0.03
28_{10}	27_{10}	153732.50	0.11	$45_{2,44}$	$44_{1,43}$	238821.24	0.01
28_{11}	27_{11}	153702.19	0.10	$45_{2,43}$	$44_{3,42}$	240503.70	0.06
28_{12}	27_{12}	153680.48	0.10	$46_{1,46}$	$45_{0,45}$	239338.36	0.03
28_{13}	27_{13}	153664.90	0.06	$46_{3,43}$	$45_{4,42}$	233929.90	− 0.01
28_{14}	27_{14}	153653.79	0.03				
28_{15}	27_{15}	153645.99	0.05				
28_{16}	27_{16}	153640.87	− 0.04				

[a] Where only one subscript is given for a transition the K-type asymmetry doubling was unresolved.

measured up to $J = 46$ and $K = 24$ for the trans form and up to $J = 37$ and $K = 24$ for the gauche form.

These transitions together with the low J measurements of Riveros gave preliminary rotational and centrifugal distortion constants which were then used to predict the weaker b-type transitions. The [b] R transitions of high J and low K were found first. The energy levels for the two symmetry types E_K^+, O_{K+1}^- and O_K^+, E_{K+1}^-, respectively, merge with increasing J (EO splitting) [9]. For instance, the two b-type transition $45_{1,45} \leftarrow 44_{0,44}$ and $45_{0,45} \leftarrow 44_{1,44}$ together with the two a-type transitions $45_{0,45} \leftarrow 44_{0,44}$ and $45_{1,45} \leftarrow 44_{1,44}$ appear as a symmetric quartet

Table 2. Measured ground state transitions of the gauche isomer of ethyl formate.

$J'_{K'_a K'_c} \leftarrow J_{K_a K_c}$ [a]		ν_{exp} [MHZ]	$\nu_{calc} - \nu_{exp}$ [MHZ]	$J'_{K'_a K'_c} \leftarrow J_{K_a K_c}$ [a]		ν_{exp} [MHZ]	$\nu_{calc} - \nu_{exp}$ [MHZ]
2_{02}	1_{01}	14059.24	0.02	22_{21}	21_{21}	155847.24	− 0.13
2_{11}	1_{10}	14731.48	0.06	$23_{1,22}$	$22_{1,21}$	153881.08	0.05
2_{12}	1_{11}	13478.27	− 0.01	$23_{1,22}$	$22_{2,21}$	153842.11	0.06
2_{20}	1_{11}	33841.22	0.07	$23_{2,22}$	$22_{2,21}$	153865.89	− 0.00
2_{12}	1_{01}	19624.22	0.09	$23_{2,22}$	$22_{1,21}$	153904.80	0.05
2_{21}	1_{10}	33168.90	0.19	$23_{2,21}$	$22_{2,20}$	158235.36	0.04
3_{03}	2_{02}	20976.34	0.03	$23_{3,21}$	$22_{3,20}$	157973.93	0.04
3_{12}	2_{11}	22067.24	0.05	$24_{1,23}$	$23_{1,22}$	160284.40	0.04
3_{13}	2_{12}	20189.65	0.04	$24_{1,23}$	$23_{2,22}$	160260.71	0.01
3_{22}	2_{21}	21157.56	0.02	$24_{2,23}$	$23_{2,22}$	160275.06	0.03
3_{22}	3_{13}	21285.30	0.11	$24_{2,23}$	$23_{1,22}$	160298.80	0.01
4_{22}	3_{21}	28614.94	0.12	$26_{6,21}$	$25_{5,20}$	229817.08	0.23
4_{04}	3_{03}	27767.25	0.04	$27_{5,22}$	$26_{6,21}$	159286.24	0.15
4_{13}	3_{12}	29364.08	0.03	$27_{6,22}$	$26_{5,21}$	231845.59	− 0.01
4_{14}	3_{13}	26870.67	0.03	$33_{5,29}$	$32_{5,28}$	230328.35	− 0.06
4_{23}	3_{22}	28174.02	0.01	$33_{6,28}$	$32_{6,27}$	233949.35	− 0.10
4_{04}	3_{13}	22988.95	− 0.03	$33_{7,27}$	$32_{7,26}$	236011.03	0.03
5_{24}	4_{23}	35159.78	− 0.01	$33_{8,26}$	$32_{8,25}$	236274.50	0.16
5_{05}	4_{14}	30532.69	0.01	$33_{9,25}$	$32_{9,24}$	235683.20	0.10
5_{05}	4_{04}	34414.44	0.04	$33_{10,24}$	$32_{10,23}$	235059.40	0.05
5_{23}	5_{14}	16404.61	0.09	$33_{11,23}$	$32_{11,22}$	234599.82	− 0.05
6_{24}	6_{15}	16123.98	0.10	$33_{11,22}$	$32_{11,21}$	234601.09	− 0.07
7_{25}	7_{16}	16311.56	− 0.04	33_{12}	32_{12}	234275.96	− 0.11
8_{17}	8_{08}	22658.60	− 0.08	33_{13}	32_{13}	234045.90	− 0.16
8_{26}	8_{17}	17085.64	0.01	33_{14}	32_{14}	233881.92	− 0.15
9_{18}	9_{09}	27100.97	− 0.12	33_{15}	32_{15}	233766.54	− 0.15
6_{33}	6_{24}	30364.46	− 0.09	33_{16}	32_{16}	233688.01	− 0.08
8_{35}	8_{26}	27909.59	0.02	33_{17}	32_{17}	233638.34	0.01
12_{39}	$12_{2,10}$	24506.40	− 0.03	33_{18}	32_{18}	233611.88	0.01
$20_{4,17}$	$19_{3,16}$	156882.04	− 0.18	33_{19}	32_{19}	233604.24	0.09
$21_{4,18}$	$20_{3,17}$	160458.43	− 0.15	33_{20}	32_{20}	233612.26	0.21
$22_{7,16}$	$21_{7,15}$	156812.05	− 0.17	33_{21}	32_{21}	233633.65	0.19
$22_{8,14}$	$21_{8,13}$	156442.04	− 0.16	33_{22}	32_{22}	233666.40	0.14
$22_{8,15}$	$21_{8,14}$	156437.01	− 0.17	33_{23}	32_{23}	233709.02	0.02
22_{11}	21_{11}	155900.50	− 0.07	33_{24}	32_{24}	233760.36	− 0.29
22_{12}	21_{12}	155825.13	− 0.08	$34_{3,31}$	$33_{3,30}$	232578.66	0.03
22_{13}	21_{13}	155776.58	− 0.01	$34_{4,31}$	$33_{4,30}$	232545.34	0.00
22_{14}	21_{14}	155748.05	0.01	$34_{5,30}$	$33_{5,29}$	236736.23	− 0.06
22_{15}	21_{15}	155734.84	0.03	$34_{6,29}$	$33_{6,28}$	240538.39	0.00
22_{16}	21_{16}	155733.67	0.10	$35_{2,33}$	$34_{3,32}$	234769.04	0.07
22_{17}	21_{17}	155742.40	0.07	$35_{2,33}$	$34_{2,32}$	234771.86	0.07
22_{18}	21_{18}	155759.19	0.10	$35_{3,32}$	$34_{3,31}$	238944.05	0.08
22_{19}	21_{19}	155782.90	0.05	$36_{0,36}$	$35_{0,35}$	232995.95	− 0.09
22_{20}	21_{20}	155812.47	0.01	$37_{0,37}$	$36_{0,36}$	239388.61	0.00

[a] Where only one subscript in given for a transition the K-type asymmetry doubling was unresolved.

which is easy to identify. Their assignment was confined using the "bootstrap" method as described by Kirchhoff [10], and his calculation of the standardized residuals $t(\Delta\nu_i)$ was systematically used to check the assignment of each individual line.

The measured frequencies are listed in Table 1 for the trans form and in Table 2 for the gauche form. To derive the molecular parameters the spectrum was fitted to the Hamiltonian of Watson [11] using the I^r representation. Both the A- and S-reductions were tried. But although both forms are near-symmetric the S-reduction did not give significantly better results. So for the final fit the A-reduction was adopted because the computer programs using it are more currently available.

The rotational and centrifugal distortion constants are given in Table 3 together with their standard deviation and their correlation matrix. For the trans form only the sextic constant H_{KJ} could be determined and only two correlation coefficients are

Table 3. Molecular constants of ethyl formate and correlation matrix[a].

Trans form[b]													
A/MHZ	17746.733 (28)	1.000											
B/MHZ	2904.72853 (72)	− 0.303	1.000										
C/MHZ	2579.14641 (56)	0.145	0.087	1.000									
Δ_J/kHZ	0.62326 (19)	− 0.608	0.717	0.357	1.000								
Δ_{JK}/kHZ	− 3.5435 (33)	0.224	0.063	0.377	− 0.024	1.000							
Δ_K/kHZ	81.80 (48)	0.972	− 0.357	0.115	− 0.610	0.100	1.000						
δ_J/kHZ	0.10127 (11)	− 0.495	0.730	− 0.518	0.506	− 0.229	− 0.499	1.000					
δ_K/kHZ	− 0.881 (17)	− 0.697	− 0.018	0.145	0.563	− 0.000	− 0.655	0.119	1.000				
H_{KJ}/HZ	− 1.1343 (74)	0.066	0.042	0.281	0.071	0.926	− 0.039	− 0.134	− 0.170	1.000			
σ/kHZ[c]	87												
Number of lines	96												
Gauche form[d]													
A/MHZ	9985.6518 (99)	1.000											
B/MHZ	3839.6071 (35)	0.225	1.000										
C/MHZ	3212.8738 (32)	0.100	0.811	1.000									
Δ_J/kHZ	5.9493 (44)	0.188	0.915	0.917	1.000								
Δ_{JK}/kHZ	− 32.3791 (75)	0.010	0.245	0.199	0.051	1.000							
Δ_K/kHZ	85.81 (29)	0.562	− 0.223	− 0.181	− 0.079	− 0.488	1.000						
δ_J/kHZ	2.0004 (15)	0.083	0.311	− 0.091	0.168	0.075	0.177	1.000					
δ_K/kHZ	7.431 (28)	0.076	− 0.052	0.054	0.054	− 0.373	0.257	− 0.572	1.000				
H_J/HZ	− 0.055 (19)	0.196	0.858	0.839	0.956	0.053	− 0.039	0.350	− 0.180	1.000			
H_{JK}/HZ	0.769 (40)	0.003	0.168	0.197	0.075	0.375	− 0.172	− 0.362	0.392	− 0.141	1.000		
H_{KJ}/HZ	− 3.664 (126)	− 0.020	0.070	0.050	0.022	0.490	− 0.292	0.119	− 0.255	0.116	− 0.465	1.000	
h_J/HZ	− 0.02616 (87)	0.091	0.310	0.011	0.234	0.084	0.187	0.967	− 0.648	0.449	− 0.471	0.197	1.000
σ/kHZ[c]	102												
Number of lines	88												

[a] The uncertainties shown in parentheses are in units of the last digit and are standard errors.
[b] $H_J = H_{JK} = H_K = h_J = h_{JK} = H_K = 0$ assumed.
[c] Standard deviation of the fit.
[d] $H_K = h_{JK} = h_K = 0$ assumed.

greater the 0.9: $\varrho(A, \Delta_K) = 0.97$ and $\varrho(\Delta_{JK}, H_{KJ}) = 0.93$. For the gauche form four sextic coefficients H_J, H_{JK}, H_{KJ} and h_J had to be included to reproduce the observed frequencies within experimental error.

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