Millimeter-Wave Spectrum of Ethyl Acetylene Centrifugal Distortion, Coriolis Interaction and Internal Rotation

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The rotational spectrum of ethyl acetylene has been investigated between 70 and 320 GHz. A Coriolis interaction has been found between the first excited state of the methyl torsion and the $C-C\equiv C$ in plane deformation. Splittings of transitions in the first excited torsional state show that the barrier hindering internal rotation of the methyl group amounts to 3271 cal/mole.

Introduction

The microwave spectrum of ethyl acetylene (butyne-1: $H-C\equiv C-CH_2CH_3$) was measured in the centimeter range by Job and coll. [1] who determined the rotational constants for the ground state and two excited vibrational states (CH_3-torsion and $C-C\equiv C$ bending). But although they could observe the splittings of the rotational lines in the first excited state of internal rotation, they did not analyze them. As the barrier hindering internal rotation of the methyl group has been determined for many ethyl derivatives [2], it would be interesting to determine this barrier potential for ethyl acetylene too. The presence of ethyl acetylene in space is probable, but the frequencies in the millimeter region, which are of great potential interest to radioastronomers could not be predicted reliably with the constants of Job. For these reasons we have measured the millimeter-wave spectrum of ethyl acetylene.

Experimental

The sample of ethyl acetylene was obtained commercially from Matheson (Oevel, Belgium) and was used without further purification. The measurements were performed between 70 and 320 GHz with a 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 [3]. All spectra were measured at room temperature and at pressures below 5 mTorr. The accuracy is about 30 kHz.

Ground State Spectrum

The dipole moment of ethyl acetylene points approximately in the direction of the *a*-axis, so the most intense transitions are the ${}^aR_{01}$. The assignment of the transitions of lowest J was easy because the spectrum is rather sparse and strong and because an approximate spectrum could be predicted with the constants of Job [1]. Then higher J transitions were assigned using the "bootstrap" method as described by Kirchhoff [4]. The measured frequencies are listed in Table 1. The program VT 30 of TYPKE was used, which is based on the following Hamiltonian:

$$\begin{aligned} H = {} & A' P_a^2 + B' P_b^2 + C' P_c^2 - D'_J P^4 \\ & - D'_{JK} P^2 P_a^2 - D'_K P_a^4 - 2\,\delta'_J P^2 (P_b^2 - P_c^2) \\ & - 2 R'_6 [3 (P_b^2 P_c^2 + P_c^2 P_b^2) - P_b^4 - P_c^4] \\ & + H'_J P^6 + H'_{JK} P^4 P_a^2 + H'_{KJ} P^2 P_a^4 + H'_K P_a^6 \\ & + H'_5 P^4 (P_b^2 - P_c^2) \\ & + \tfrac{1}{2} H'_6 P^2 [P_b^4 + P_c^4 - 3 (P_b^2 P_c^2 + P_c^2 P_b^2)] \\ & + H'_{10} (P_b^2 - P_c^2)^3 . \end{aligned} \qquad (1)$$

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Table 1. Measured ground state transitions of ethyl acetylene.

$J'_{K'_-K'_+} \leftarrow J_{K_-K_+}$[a]		ν_{exp} [MHz]	$\nu_{\text{calc}} - \nu_{\text{exp}}$ [kHz]
$17_{1.16}$	$16_{1.15}$	148848.347	26
$17_{2.15}$	$16_{2.14}$	149875.734	10
$17_{3.15}$	$16_{3.14}$	147122.558	20
$17_{4.13}$	$16_{4.12}$	147158.755	34
$17_{4.14}$	$16_{4.13}$	147120.281	32
$17_{5.12}$	$16_{5.11}$	147010.193	54
$17_{5.13}$	$16_{5.12}$	147009.169	35
17_{6}	16_{6}	146952.248	22
17_{7}	16_{7}	146928.455	3
17_{8}	16_{8}	146923.496	−10
17_{9}	16_{9}	146930.570	−13
17_{10}	16_{10}	146946.235	−53
17_{11}	16_{11}	146968.434	−25
17_{12}	16_{12}	146996.121	−50
$18_{0.18}$	$17_{0.17}$	150748.243	−13
$18_{1.18}$	$17_{1.17}$	149998.449	46
$18_{1.17}$	$17_{1.16}$	157324.525	14
$18_{2.17}$	$17_{2.16}$	154283.853	14
$18_{2.16}$	$17_{2.15}$	158816.208	32
$18_{3.16}$	$17_{3.15}$	155777.656	10
$18_{3.15}$	$17_{3.14}$	156693.385	14
$18_{4.15}$	$17_{4.14}$	155808.730	18
$18_{4.14}$	$17_{4.13}$	155866.079	− 9
$18_{5.14}$	$17_{5.13}$	155679.954	7
$18_{5.13}$	$17_{5.12}$	155681.729	−10
18_{6}	17_{6}	155610.315	69
18_{7}	17_{7}	155579.536	4
18_{8}	17_{8}	155570.723	−40
18_{9}	17_{9}	155575.754	−23
18_{10}	17_{10}	155590.560	−20
18_{11}	17_{11}	155612.770	24
18_{12}	17_{12}	155641.151	−40
18_{13}	17_{13}	155674.641	−21
18_{14}	17_{14}	155712.785	−37
18_{15}	17_{15}	155755.123	−21
18_{16}	17_{16}	155801.449	−46
18_{17}	17_{17}	155851.507	−61
$19_{0.19}$	$18_{0.18}$	158867.902	−20
$19_{1.19}$	$18_{1.18}$	158224.720	38
$27_{0.27}$	$26_{0.26}$	223916.235	−37
$27_{1.27}$	$26_{1.26}$	223773.601	73
$27_{1.26}$	$26_{1.25}$	231415.881	6
$27_{2.26}$	$26_{2.25}$	229564.277	−53
$27_{2.25}$	$26_{2.24}$	237655.972	30
$27_{3.25}$	$26_{3.24}$	233148.469	16
$27_{4.24}$	$26_{4.23}$	234097.584	27
$27_{4.23}$	$26_{4.22}$	234974.328	15
$27_{5.23}$	$26_{5.22}$	233902.235	− 1
$27_{5.22}$	$26_{5.21}$	233968.988	46
$27_{6.22}$	$26_{6.21}$	233654.905	−32
$27_{6.21}$	$26_{6.20}$	233657.794	−15
27_{7}	26_{7}	233511.303	−44
27_{8}	26_{8}	233435.560	2
27_{9}	26_{9}	233400.855	54
27_{10}	26_{10}	233393.175	−20
27_{11}	26_{11}	233404.369	92
27_{12}	26_{12}	233430.205	−26
27_{13}	26_{13}	233467.477	−73
27_{14}	26_{14}	233514.305	−69
27_{15}	26_{15}	233569.398	−15
27_{16}	26_{16}	233631.992	−51
27_{17}	26_{17}	233701.367	111
27_{18}	26_{18}	233776.852	− 8
27_{19}	26_{19}	233858.377	−41
27_{20}	26_{20}	233945.507	−62
27_{21}	26_{21}	234037.962	−21
27_{22}	26_{22}	234135.698	−60
27_{23}	26_{23}	234238.360	21
27_{24}	26_{24}	234345.937	101
27_{25}	26_{25}	234458.414	82
27_{26}	26_{26}	234575.510	143
$28_{0.28}$	$27_{0.27}$	232060.337	2
$28_{1.28}$	$27_{1.27}$	231944.949	−18
$28_{1.27}$	$27_{1.26}$	239488.394	18
$36_{1.35}$	$35_{1.34}$	304069.833	31
$36_{2.34}$	$35_{2.33}$	312226.217	2
$36_{3.34}$	$35_{3.33}$	308996.439	85
$36_{3.33}$	$35_{3.32}$	317687.681	−44
$36_{4.33}$	$35_{4.32}$	311910.203	−68
$36_{4.32}$	$35_{4.31}$	316266.804	−27
$36_{5.31}$	$35_{5.30}$	313142.560	1
$36_{5.32}$	$35_{5.31}$	312372.976	−57
$36_{6.31}$	$35_{6.30}$	311971.139	14
$36_{6.30}$	$35_{6.29}$	312035.945	33
$36_{7.30}$	$35_{7.29}$	311611.879	33
$36_{7.29}$	$35_{7.28}$	311615.304	43
36_{9}	35_{9}	311268.036	− 2
36_{13}	35_{13}	311205.304	54
36_{15}	35_{15}	311306.870	43
36_{17}	35_{17}	311459.616	−52
36_{19}	35_{19}	311652.431	66
36_{21}	35_{21}	311879.554	97
36_{23}	35_{23}	312137.370	−48
36_{25}	35_{25}	312423.035	27
36_{27}	35_{27}	312735.206	−73
36_{29}	35_{29}	313072.181	37
36_{31}	35_{31}	313433.174	90
36_{32}	35_{32}	313622.520	−28
36_{33}	35_{33}	313817.501	112
$37_{0.37}$	$36_{0.36}$	305387.097	68
$37_{1.37}$	$36_{1.36}$	305371.868	−90
$37_{1.36}$	$36_{1.35}$	312167.085	−41
$37_{2.36}$	$36_{2.35}$	311769.796	−60
$37_{3.35}$	$36_{3.34}$	317318.688	− 6
$38_{0.38}$	$37_{0.37}$	313532.888	22
$38_{1.38}$	$37_{1.37}$	313520.719	1

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

The representation I^r has been chosen. This Hamiltonian has non-vanishing matrix elements $\langle K \mid K \rangle$, $\langle K \mid K \pm 2 \rangle$, $\langle K \mid K \pm 4 \rangle$, $\langle K \mid K \pm 6 \rangle$, its diagonalization has been discussed in [5].

The rotational and centrifugal distortion constants are given in Table 2. They were fitted to the 106 measured lines with $16 \leqq J \leqq 38$ and $0 \leqq K_- \leqq 33$. The highest contribution due to P^6-terms is about 140 MHz for the transition $36_{33,4} \leftarrow 35_{33,3}$. The

Table 2. Molecular constants of ethyl acetylene[a].

	Ground state	Methyl torsion	C≡C−C bend
A'/MHz	27 147.285 (195)	28 021.4 (33)	26 402.9 (18)
B'/MHz	4 546.5208 (22)	4 544.744 (22)	4 559.107 (20)
C'/MHz	4 086.9146 (21)	4 086.408 (21)	4 092.7256 (86)
D'_J/kHz	2.67807 (88)	2.220 (28)	2.997 (15)
D'_{Jk}/kHz	−45.4081 (25)	−64.31 (109)	−28.64 (58)
D'_K/kHz	524.0 (128)	3 569 (1010)	−1 540 (431)
δ_J/kHz	0.63156 (141)	0.592 (17)	0.6600 (84)
R'_6/kHz	−0.03273 (89)	−0.167 (18)	0.161 (10)
H'_J/Hz	0.00798 (33)		0^b
H'_{JK}/Hz	0.0727 (119)		−4.34 (80)
H'_{KJ}/Hz	−2.029 (39)		
H'_K/kHz	−1.560 (97)		
H'_5/Hz	0.00384 (54)		
1/2 H'_6/Hz	0.00374 (160)		
H'_{10}	0^b		
σ/kHz[c]	51	229	253
Number of lines	106	13	36

[a] The uncertainties shown in parenthesis are in units of the last digit and are standard errors.
[b] Fixed value.
[c] Standard deviation of the fit.

Table 3. Rotational lines of ethyl acetylene for the $v_\tau = 1$ torsional state.

$J'_{K'_-K'_+}$	← $J_{K_-K_+}$	ν_{exp}, $\bar{\nu}_{exp}$[a] [MHz]	$\nu_{calc}-\nu_{exp}$[b] [MHz]	ν_A[c] [MHz]	ν_E[d] [MHz]	$\Delta\nu_{exp}$[e] [MHz]	$\Delta\nu_{calc}$[f] [MHz]
9_{09}	8_{08}	76902.74	−0.06	76902.600	76902.872	0.272	0.249
9_{19}	8_{18}	75436.09	−0.19				
9_{18}	8_{17}	79530.13	−0.25	79529.900	79530.365	0.465	0.470
9_{28}	8_{27}	77559.38	−0.02	77559.224	77559.529	0.305	0.286
9_{27}	8_{26}	78329.45	−0.18	78329.277	78329.625	0.348	0.370
9_{37}	8_{36}	77781.08	0.33				
9_{36}	8_{35}	77808.64	0.34				
$16_{1,15}$	$15_{1,14}$	140353.14	0.08	140352.810	140353.470	0.660	0.686
$16_{2,14}$	$15_{2,13}$	140825.98	−0.03	140825.594	140826.375	0.780	0.776
$17_{2,15}$	$16_{2,14}$	149786.65	0.03	149786.230	149787.060	0.840	0.826
$17_{3,14}$	$16_{3,13}$	147740.07	−0.03	147739.790	147740.350	0.560	0.573
$18_{0,18}$	$17_{0,17}$	150818.28	0.04				
$18_{1,18}$	$17_{1,17}$	150014.56	0.03				
$18_{1,17}$	$17_{1,16}$	157388.22	−0.08	157387.870	157388.560	0.700	0.701
$18_{2,17}$	$17_{2,16}$	154299.55	0.25	154299.320	154299.790	0.470	0.479
$18_{2,16}$	$17_{2,15}$	158731.83	0.02	158731.400	158732.260	0.860	0.872
$18_{3,16}$	$17_{3,15}$	155748.75	−0.37	155748.470	155749.020	0.550	0.519
$18_{3,15}$	$17_{3,14}$	156595.83	−0.08	156595.530	156596.120	0.590	0.624
$19_{0,19}$	$18_{0,18}$	158938.68	−0.08				
$19_{1,19}$	$18_{1,18}$	158244.13	0.04				
$25_{1,24}$	$24_{1,23}$	215440.87	−17.56[g]	215440.590	215441.150	0.560	0.590
$25_{2,24}$	$24_{2,23}$	213039.98	−0.67[g]	213039.730	213040.220	0.490	0.528
$25_{2,23}$	$24_{2,22}$	220481.96	2.04[g]	220481.429	220482.490	1.060	1.032
$26_{0,26}$	$25_{0,25}$	215842.04	−3.87[g]				
$26_{1,26}$	$25_{1,25}$	215641.41	−1.82[g]				
$27_{0,27}$	$26_{0,26}$	223985.04	−5.43[g]				
$27_{1,26}$	$26_{1,25}$	231647.45	9.75[g]				
$27_{2,25}$	$26_{2,24}$	237735.83	2.91[g]	237735.300	237736.360	1.060	1.019
$27_{3,24}$	$26_{3,23}$	237563.53	1.20[g]	237562.970	237564.080	1.110	1.102

[a] $\bar{\nu}_{exp} = (\nu_A + \nu_E)/2$.
[b] ν_{calc} calculated with constants of Table 2.
[c] ν_A A-component of split line.
[d] ν_E E-component of split line.
[e] $\Delta\nu_{exp} = \nu_E - \nu_A$, measured internal rotation splitting.
[f] $\Delta\nu_{calc}$, calculated internal rotation splitting with constants of Table 5.
[g] No included in the fit.

largest deviation is 143 kHz, the mean square deviation $\sigma = 51\,\text{kHz}$ by using 14 parameters. H'_{10} was assumed to be zero because it could not be significantly determined.

Excited States

The ${}^{a}R_{01}$ transitions of two excited states of nearly equal intensity were readily identified. Most of the lines of one excited state show a doublet splitting while the other state has sharp lines. The split lines very likely belong to the first excited torsional state and the other state is probably the C−C≡C bend. The measured lines are given in Tables 3 and 4.

For the split lines the mean value $\bar{\nu}_{\text{exp}} = (\nu_A + \nu_E)/2$ was used for the centrifugal distortion analysis. This is the frequency that would have been measured if the splitting had not been resolved [6]. So the correction of the unsplit lines for the internal rotation contribution is avoided and the centrifugal distortion analysis may be performed independently of the internal rotation analysis.

Table 4. Rotational lines of ethyl acetylene in the first excited state of the C−C≡C bending vibration.

$J'_{K'_-K'_+} \leftarrow J_{K_-K_+}$		ν_{exp} [MHz]	$\nu_{\text{exp}} - \nu_{\text{calc}}$ [MHz]
$17_{0,17}$	$16_{0,16}$	142767.54	−0.03
$17_{1,16}$	$16_{1,15}$	149080.15	−0.17
$17_{2,16}$	$16_{2,15}$	146071.04	−0.01
$17_{2,15}$	$16_{2,14}$	150286.44	0.19
$17_{3,15}$	$16_{3,14}$	147433.72	−0.02
$17_{3,14}$	$16_{3,13}$	148214.02	0.18
$17_{4,14}$	$16_{4,13}$	147440.05	−0.05
$17_{4,13}$	$16_{4,12}$	147485.40	−0.02
$17_{5,13}$	$16_{5,12}$	147316.53	0.09
$17_{5,12}$	$16_{5,11}$	147318.28	−0.36
$17_{6,12}$	$16_{6,11}$	147247.37	0.27
$18_{0,18}$	$17_{0,17}$	150898.79	−0.01
$18_{1,18}$	$17_{1,17}$	150203.21	0.21
$18_{1,17}$	$17_{1,16}$	157548.81	−0.24
$18_{2,17}$	$17_{2,16}$	154535.79	−0.01
$18_{2,16}$	$17_{2,15}$	159239.76	0.13
$18_{3,16}$	$17_{3,15}$	156103.50	−0.07
$18_{3,15}$	$17_{3,14}$	157120.00	0.15
$18_{4,15}$	$17_{4,14}$	156148.34	−0.04
$18_{4,14}$	$17_{4,13}$	156215.92	−0.04
$18_{5,14}$	$17_{5,13}$	156006.17	0.27
$18_{5,13}$	$17_{5,12}$	156009.04	−0.41
$19_{0,19}$	$18_{0,18}$	159028.96	−0.00
$19_{1,19}$	$18_{1,18}$	158437.52	0.16
$25_{1,24}$	$24_{1,23}$	215354.31	−0.02
$25_{3,23}$	$24_{3,22}$	216453.87	−0.67
$25_{4,22}$	$24_{4,21}$	217170.64	0.57
$25_{4,21}$	$24_{4,20}$	217795.51	−0.09
$25_{5,20}$	$24_{5,19}$	216995.44	−0.14
$26_{0,26}$	$25_{0,25}$	216023.72	−0.11
$26_{1,26}$	$25_{1,25}$	215871.36	0.01
$27_{0,27}$	$26_{0,26}$	224178.44	−0.10
$27_{1,27}$	$26_{1,26}$	224055.57	0.02
$27_{1,26}$	$26_{1,25}$	231539.29	0.42
$28_{0,28}$	$27_{0,27}$	232334.99	−0.03
$28_{1,28}$	$27_{1,27}$	232236.29	0.04

The relative intensities indicate that the energy difference between these two vibrational levels is small. Hence, the rotational spectra of these two states may be perturbed by a Coriolis interaction. Indeed the fit of these spectra to the centrifugal distorted Hamiltonian (Eq. (1)) gives a poor fit. The transitions $J \geqq 24$ were excluded from the fit because they seem to be most affected by the perturbation. However the standard deviation of the fit remains much greater than the experimental uncertainty.

The derived rotational and centrifugal constants are reported in Table 2. The two A-rotational constants (and also the two D'_K centrifugal distortion constants) deviate considerably from the ground state A-constant in opposite direction. This indicates the existence of an a-type Coriolis interaction between the two states. The state with negative deviation of A is the lower frequency, it is the C−C≡C bend. The torsion lies a few cm^{-1} above this state.

It is possible to carry the analysis of this Coriolis interaction further if we assume that the variations of the rotational constant A and the centrifugal distortion constant τ'_{aaaa} are due only to this interaction [7]:

$$\Delta A = A(v=1) - A(v=0) = \pm 4\,\frac{A^2(\zeta^{a}_{\delta t})^2}{\omega_\delta - \omega_t}, \quad (2)$$

$$\begin{aligned}\Delta\tau &= \tau'_{aaaa}(v=1) - \tau'_{aaaa}(v=0)\\ &= \pm\frac{4A^4(\zeta^{a}_{\delta t})^4(\omega_\delta + \omega_t)^4}{(\omega_t - \omega_\delta)^3\,\omega_t^2\,\omega_\delta^2}, \end{aligned} \quad (3)$$

where ω_δ represents the frequency of the C−C≡C bend and ω_t that of the methyl torsion. In these equations only the effects of the Coriolis interaction has been taken into account. The other contributions (harmonic and anharmonic) are very likely much smaller (probably some %). These Eqs. (2) and (3) may be further simplified by assuming that ω_δ and ω_t are nearby

$$\Delta A \simeq \pm\frac{4A^2(\zeta^{a}_{\delta t})^2}{\Delta E}, \quad (4)$$

$$\Delta\tau \simeq \pm\frac{64A^4(\zeta^{a}_{\delta t})^4}{\Delta E^3}. \quad (5)$$

Table 5. Internal rotation parameters of ethyl acetylene[a].

s	86.57 (26)
$\sphericalangle$ (a, i)	48.454 (13) °
I_α [amu Å^2]	3.1635[b]
s [kHz]	23
Derived parameters	
V_3 [cal/mol]	3271 (1)
F[GHz]	176.162

[a] The uncertainties shown in parentheses are in units of the last digit and are standard errors.
[b] Assumed value.

The solution of this system of equations gives

$$\Delta E = \omega_t - \omega_\delta \simeq 260 \text{ GHz} = 8.7 \text{ cm}^{-1} \quad \zeta^{a}_{\delta t} \simeq 0.26 \, .$$

These values are not expected to be highly accurate due to te drastic approximations made.

Internal Rotation Analysis

The *A*, *E* doublet splitting of the excited torsional state can be affected by the Coriolis interaction. A treatment of this perturbation has been given by Dreizler et al. [8−10]. But for the case of a high barrier and small asymmetry, it was shown by Laurie [11] that the contribution from Coriolis coupling to the *A*-*E* splittings is small. This conclusion is furthermore strenghtened by the fact that only the torsional excited state shows a splitting due to internal rotation. So the barrier to internal rotation of the methyl group was calculated from the splittings with the conventional principal axis method [12], the calculation used second and fourth order perturbation. The input data for this computation includes, in addition to the observed splittings, the rotational constants and the moment of inertia of the methyl top. This latter quantity was taken equal to that of ethyl fluoride [6]. The results are shown in Table 5. The correlation coefficient between the reduced barrier s and the angle $\sphericalangle$ (a, i) is -0.917. The mean square deviation of the fit is 23 kHz for a mean splitting $\overline{\Delta\nu}$ of 0.649 MHz.

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