



The rotational spectrum of methyl ethyl ketone in its ground vibrational state



Jay A. Kroll^a, Steven T. Shipman^b, Susanna L. Widicus Weaver^{a,*}

^a Department of Chemistry, Emory University, 1515 Dickey Drive Atlanta, GA 30322, USA

^b Division of Natural Sciences, New College of Florida, 5800 Bay Shore Road, Sarasota, FL 34243, USA

ARTICLE INFO

Article history:

Received 11 September 2013

In revised form 16 October 2013

Available online 30 October 2013

Keywords:

2-Butanone

Rotational spectroscopy

Chirped-pulse spectroscopy

Broadband spectroscopy

Microwave spectroscopy

ABSTRACT

The molecule 2-butanone, or methyl ethyl ketone (MEK), $\text{CH}_3\text{COCH}_2\text{CH}_3$, has been studied from 8 GHz to 1 THz using a combination of chirped-pulse Fourier transform microwave spectroscopy and direct absorption millimeter/submillimeter spectroscopy. This molecule is of interest for the field of astrochemistry because it has functional groups in common with several known interstellar molecules, and therefore could serve as a tracer of grain surface formation pathways for complex organics in interstellar clouds. The results of the spectral studies and the analysis of the ground vibrational state of methyl ethyl ketone up to 1 THz are presented here. The challenges of spectral analysis for an organic molecule with spectral complexity arising both from internal rotation and many low-lying vibrational states are discussed. The performances of several standard fitting packages are compared in terms of handling this challenging spectral analysis problem.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

The molecule 2-butanone, or methyl ethyl ketone (MEK), $\text{CH}_3\text{COCH}_2\text{CH}_3$, is a common industrial solvent. MEK is of interest for interstellar chemistry because it contains the methyl, ethyl and carbonyl functional groups, which are found in a variety of complex organic molecules (COMs) observed in star-forming regions. COMs are thought to form through a combination of condensed-phase radical–radical reactions on interstellar grains in cold regions, and gas-phase ion–molecule reactions in warm regions [1]. Examination of the spatial distributions of a set of molecules containing the same functional groups could reveal important information pertaining to the chemical mechanisms at play in interstellar regions, as molecules with similar formation and destruction pathways would be expected to be cospatial in a given interstellar source [2]. MEK therefore could serve as a probe of radical–radical addition reactions involving methyl and ethyl groups with carbonyl-containing molecules. Other previously detected COMs that have functional groups in common with MEK include methanol (CH_3OH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), dimethyl ether (CH_3OCH_3), acetone (CH_3COCH_3), methyl formate (HCOOCH_3), acetaldehyde (CH_3CHO), and propanal ($\text{CH}_3\text{CH}_2\text{COH}$). The chemistry involving these and other molecules that are commonly found in interstellar environments is reviewed by Herbst and van

Dishoeck [3], and further information can be found in that review and references therein.

MEK is a stable molecule that is a liquid at room temperature. The high MEK vapor pressure combined with dipole moment components of $\mu_a = 0.079 \text{ D}$ and $\mu_b = 2.778 \text{ D}$ [4] make collection of its spectrum straightforward. MEK has two terminal methyl groups that can undergo internal rotation. The methyl group closest to the carbonyl has a V_3 barrier to internal rotation of 183 cm^{-1} [4], while the group furthest from the carbonyl has a V_3 barrier to internal rotation of 795 cm^{-1} [5]. Previous laboratory studies have been performed in both the microwave [4,5] and the infrared regions [6], with the microwave work including the range of 9–33 GHz. The work of Pierce et al. [4] focused on the rotational spectrum of the ground vibrational state, and included treatment of effects that arose due to the rotation of the methyl group nearest to the carbonyl bond. The work of Pozdeev et al. [5] involved analysis of the rotation of the methyl group furthest from the carbonyl bond, and the first excited state of the torsional vibration about the central C–C bond. Neither of these previous studies report spectral evidence of the high energy conformer (*cis*-MEK). The barrier to rotation about the central C–C bond was found to be 5500 cm^{-1} [5]. Therefore, the strongest lines in the rotational spectrum of MEK at room temperature can reasonably be attributed to the *trans*-MEK conformer. These previous studies resulted in a total of 22 *A* state and 14 *E* state rotational transitions assigned in the ground vibrational state with a maximum *J* value of 21 [4,5]. MEK has not been studied in the millimeter/submillimeter range, where the Boltzmann peak for a molecule of this size is expected

* Corresponding author. Fax: +1 404 727 6586.

E-mail address: susanna.widicus.weaver@emory.edu (S.L. Widicus Weaver).

to occur under the typical conditions found in regions of star-formation. MEK could exhibit complicated spectral splitting arising from the internal motion of both methyl groups at these higher frequencies, though the level of contribution from the higher-barrier methyl rotation is expected to be minimal. Nonetheless, whether spectral splitting is observed from one or both rotors, the previous lower-frequency laboratory studies do not provide sufficient information to yield a reliable spectral prediction to guide mm/submm observations.

We present here the spectra of MEK in selected frequency ranges from 8 GHz to 1 THz. The microwave spectrum of MEK was acquired using the chirped-pulse waveguide Fourier Transform Microwave (CP-FTMW) spectrometer at New College of Florida, and the millimeter and submillimeter spectra were acquired using the direct absorption flow cell spectrometer at Emory University. Below we detail the laboratory characterization and assignment of the MEK spectrum and discuss the feasibility for interstellar searches.

2. Experimental

The MEK spectrum was acquired using two different methods for spectral collection. The centimeter-wave spectrum from 8.7 to 18.3 GHz was collected at New College of Florida using a chirped-pulse microwave (CP-FTMW) waveguide spectrometer. The millimeter and submillimeter spectra of MEK were collected at Emory University using a direct absorption flow cell spectrometer operating in the frequency range of 73 GHz to 1 THz. The methyl ethyl ketone sample used for all experiments had a purity of 99.0% (Mallinckrodt Chemicals).

The CP-FTMW spectrometer has previously been described in detail [7], and will only be briefly described here. The CP-FTMW waveguide spectrometer uses an arbitrary waveform generator (AWG) to produce a chirped pulse from 0.1 to 4.9 GHz. This pulse is filtered, and the output from a phase-locked oscillator (PLDRO) is subsequently mixed with the filtered signal. The resultant signal is filtered again, and a pre-amplifier and a solid state amplifier are used to amplify the pulse power. The pulse is then coupled into the waveguide that contains the molecular sample. After the molecules interact with the pulse, the signal arising from molecular free induction decay (FID) is collected at the other end of the waveguide. This signal passes through a protective diode limiter and a single-pole, single-throw (SPST) switch and is then amplified with a low-noise amplifier. The signal is mixed with a phase-locked oscillator to downconvert the pulse in frequency, amplified using an intermediate frequency (IF) amplifier, and then filtered again. The FID is detected by a high speed oscilloscope which digitizes the signal and takes a Fourier transform to produce a frequency domain absorption spectrum. An external 10 MHz reference is used to lock the oscilloscope, PLDRO, and AWG. A sample pressure of approximately 10 mTorr was maintained throughout the experiment, and the sample was held at a temperature of 273 K by packing the spectrometer waveguide with water ice.

In addition to the CP-FTMW spectroscopy, the millimeter and submillimeter spectra of MEK were collected from 73 GHz to 1 THz using a direct absorption spectrometer at Emory University, which has also been previously described [8]. Briefly, the light source for the spectrometer is a Schottky diode frequency multiplier chain (Virginia Diodes, Inc.) driven by the output of an Agilent E8257D microwave frequency synthesizer (1–50 GHz). Each multiplier component has a frequency output corresponding to a certain band in the mm/submm window, and full spectral coverage is achieved by combining various frequency doublers and triplers and appropriate power amplifiers to reach the desired frequency range. The signal between 73 and 300 GHz was detected using

solid state, room temperature, zero-biased detectors (Virginia Diodes, Inc.). The spectra from 300 GHz to 1 THz were collected using a QMC Instruments QFI/2BI InSb hot electron bolometer (HEB) cooled with liquid helium. The spectral resolution is 100 kHz for all spectra collected; this value is independent of frequency range because it is dictated by the frequency step size used in scanning the output of the Agilent synthesizer. The signal from the Agilent synthesizer was modulated at 15 kHz using the synthesizer internal reference. The detected signal was rectified via 2f detection using a Stanford Research SR830 lock-in amplifier, resulting in a second-derivative lineshape. The millimeter/submillimeter MEK spectra were collected at room temperature with a sample pressure of approximately 30 mTorr. The sample cell is 2.1 m in length.

Spectral complexity is a difficulty with a molecule like MEK. Millimeter range spectra at lower rotational temperatures were therefore collected at specific frequencies targeting the strongest ^bR-type transitions using a pulsed supersonic expansion source (1 mm nozzle diameter, General Valve Series 9). In this experiment, argon was bubbled through a MEK sample, and the resultant mixture was fed into the valve at a backing pressure of ~1 atm. A chamber pressure of ~30 mTorr was maintained. The frequency sources and detectors used for the flow cell studies were also used for these experiments. Typical rotational temperatures achieved with this setup are <20 K [9].

3. Results and analysis

Sample MEK spectra obtained in the microwave, millimeter, and submillimeter ranges are shown in Figs. 1–4.

A spectral resolution of 100 kHz was assumed for all transitions, equal to the size of the frequency step. This dominates the uncertainties in the line centers at low frequencies. The Doppler broadening dominates the linewidths, and hence the uncertainties in the line centers, at higher frequencies. Therefore, all lines were assigned a conservative estimated frequency uncertainty of 150 kHz.

Thousands of spectral lines were measured for MEK with a complicated spectral pattern arising from internal rotation and multiple low-energy vibrational states. The room temperature and cold millimeter spectra for MEK obtained in the flow cell and pulsed-jet spectrometers, respectively, were compared in an attempt to disentangle the line confusion in the room temperature spectrum and enable unambiguous assignments for the ^bR-type transitions. Given the complexity of this spectrum, four different fitting programs were used for analysis, building up from a standard asymmetric top Hamiltonian with no internal rotation terms, to a full treatment of the internal rotation of the methyl group. Because no splittings originating from the high-barrier methyl group rotation were observed, the ground vibrational state was analyzed as a single-rotor case, focusing on the methyl rotor with the lower barrier to internal rotation.

The spectra were initially analyzed using the SPFIT/SPCAT programs in the CALPGM suite [10,11]. The first set of line assignments treated the internal rotor A state as a standard asymmetric top, and a spectral fit using a Watson A reduction of the Hamiltonian in the I_r representation was obtained. The initial spectral prediction was based on the line assignments of Pierce et al. [4], and these previous assignments were included in all subsequent analyses. Terms for the A, B, and C rotational constants and quartic, sextic, octic, decic, and dodecic centrifugal distortion constants were included in the Hamiltonian used in the CALPGM fit. The resultant parameters are shown in Table 1. A total of 5307 *b*-type transitions (3175 distinct frequencies due to line blending) were assigned to the A state in its ground vibrational state. The microwave RMS of the fit was 350 kHz, which is over twice as large

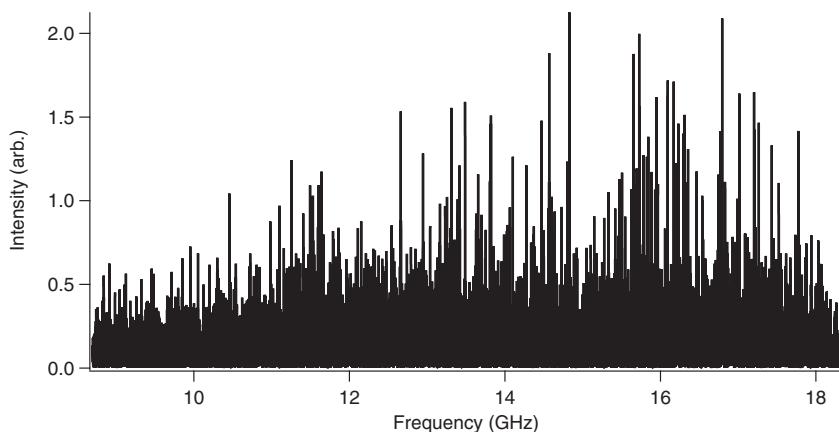


Fig. 1. The cm-wave spectrum of MEK collected using the CP-FTMW spectrometer at New College of Florida. The spectrum is collected in two segments that use slightly different filter configurations. The lower frequency segment has been scaled by a factor of two to match the noise level near the intersection of the two segments at 13.5 GHz. The noise level in the spectrum (after one million averages) is roughly 0.18 units.

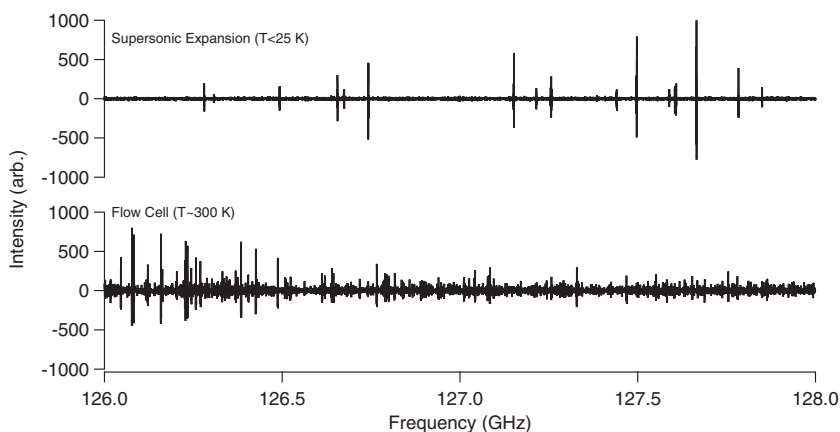


Fig. 2. Sample of the mm-wave spectrum of MEK. The top spectrum is the cold spectrum collected using the supersonic expansion source, while the bottom spectrum is the room temperature spectrum collected using the direct absorption flow cell spectrometer at Emory University.

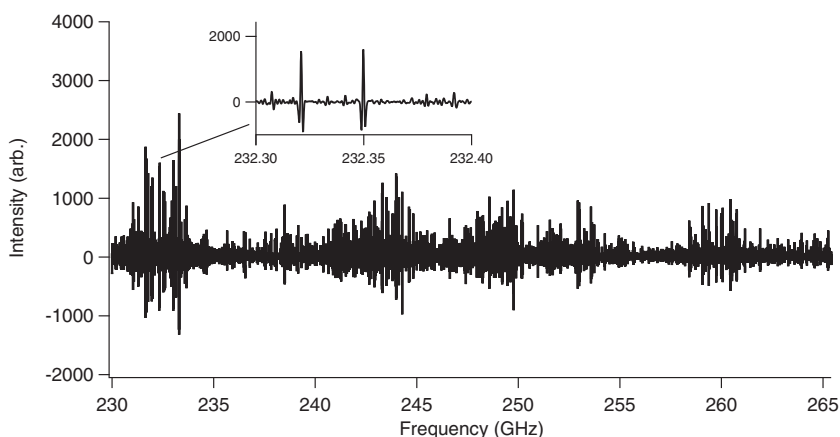


Fig. 3. Sample of the submm-wave spectrum of MEK collected using the direct absorption flow cell spectrometer at Emory University. The inset shows spectral detail for the 41_3-40_4 A/E doublet observed for MEK.

as the 150 kHz frequency uncertainties. The assigned lines with the highest residuals are those with the highest values of J and K_a , and it is those lines that necessitate the use of the higher-order centrifugal distortion constants. It is likely that these higher-order corrections are compensating for the effects of the internal rotation that are not treated by this Hamiltonian. Therefore, while interpolation

within the range of J and K_a values included in this analysis would be quite reliable, extrapolation to higher values should be done with caution. Also, while this A state fit provides the means for first approximation at line assignments for this complicated spectrum, it could only be used to assign a small fraction of the observed spectral lines because the effects of the internal rotor were not in-

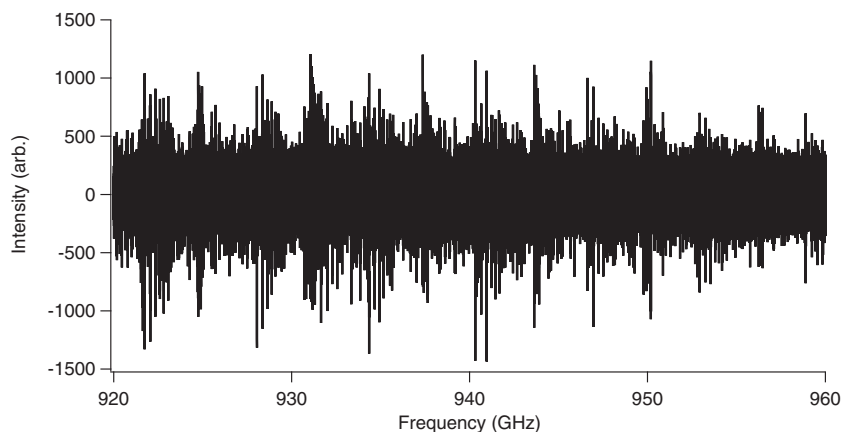


Fig. 4. High frequency sample of the submm-wave spectrum of MEK collected using the direct absorption flow cell spectrometer at Emory University.

cluded. The CALPGM suite of programs can be used for analysis of molecules with internal rotors such as MEK. However, this treatment leads to hundreds of terms in the Hamiltonian, making initial

Table 1

Molecular parameters determined for $\text{CH}_3\text{COCH}_2\text{CH}_3$ using SPFIT in the CALPGM program suite. Uncertainties are standard errors from the PIFORM program [12].

Parameter		
A	9579.2655(27)	MHz
B	3598.19132(84)	MHz
C	2746.61180(91)	MHz
Δ_J	0.67353(55)	kHz
Δ_{JK}	5.9007(38)	kHz
Δ_K	39.7514(77)	kHz
δ_J	0.163592(42)	kHz
δ_K	2.5672(47)	kHz
Φ_J	-0.70(15)	mHz
Φ_{JK}	0.0955(28)	Hz
Φ_K	2.6391(84)	Hz
ϕ_J	0.013644(10)	kHz
ϕ_{JK}	0.0404(25)	Hz
ϕ_K	2.158(18)	Hz
L_J	0.078(22)	μHz
L_{JK}	-4.91(68)	μHz
L_{JKJ}	-0.0823(70)	mHz
L_{KKJ}	-0.469(19)	mHz
L_K	-2.909(13)	mHz
I_J	-7.07(63)	nHz
I_K	-1.044(44)	mHz
I_{JK}	-1.99(55)	μHz
I_{KJ}	-0.0299(29)	mHz
P_J	-5.7(15)	pHz
P_{JK}	-0.516(91)	nHz
P_{JK}	7.06(69)	nHz
P_{KJ}	-0.1273(33)	μHz
P_{KKJ}	0.2531(84)	μHz
P_K	0.2127(53)	μHz
P_{JK}	-0.264(60)	nHz
P_{KKJ}	-0.0224(38)	μHz
P_K	-0.237(14)	μHz
S_J	0.129(36)	fHz
S_{JK}	0.0334(48)	pHz
S_{JK}	6.69(14)	pHz
S_{KKJ}	-7.00(47)	pHz
S_K	-0.01045(38)	nHz
S_{JK}	0.0153(27)	pHz
S_{JK}	0.252(17)	pHz
S_{KKJ}	0.04470(82)	nHz
# Lines	3175 ^a	
Microwave RMS	0.350	MHz

^a This is the number of distinct frequencies included in the fit; a total 5307 transitions with distinct quantum numbers are included.

analysis of a complicated spectrum using a limited line list challenging.

The XIAM program [13] was used for the next step of the analysis. This program uses a simplified internal rotor Hamiltonian compared to that used in CALPGM, yielding a reasonable first approximation for the full internal rotor treatment for MEK with a substantially reduced number of constants. The parameters determined in the semi-rigid rotor analysis using SPFIT were transferred to this program. The Hamiltonian implemented in XIAM included the A, B, and C rotational constants, the quartic and sextic centrifugal distortion constants, the barrier to internal rotation of the methyl group (V_3), and the rotor axis angles. The previously assigned transitions from the A state analysis were transferred to XIAM, and 147 E state assignments were added. These E state assignments could be easily identified in the spectrum with relative certainty due to the small splitting (<50 MHz), which leads to obvious A/E doublets. The lines imported into the XIAM fit were limited to a maximum K_a value of 10 and a maximum J value of 99 due to lack of certainty in assignment of weak transitions with high J or K_a . Additionally, XIAM does not properly weight blended transitions, and so only one transition per blended line was included in the XIAM fit. The final fit in XIAM contained 624 A state transitions and 147 E state transitions for a total of 771 assigned lines with a microwave RMS of 1.8 MHz.

XIAM has some limitations in its applicability to complicated internal rotor problems such as that of MEK, especially for higher J and K states where centrifugal distortion becomes a significant factor and internal rotor centrifugal distortion constants are required. Because of this, the assignments included in the XIAM fit were transferred to another program, ERHAM [14], which is known to be a powerful tool for the analysis of molecules with methyl and ethyl rotors. The ERHAM analysis included the rotational constants, quartic and sextic centrifugal distortion constants, and internal rotation parameters. The initial fit using the lines assigned in the XIAM analysis gave a microwave RMS of ~ 175 kHz, depending somewhat on the choice of starting parameters. This is a substantial improvement over the XIAM fit. This refined fit was then used to generate a new spectral prediction, and analysis continued iteratively until the spectrum from 8 GHz to 1 THz was analyzed for the ground vibrational state of MEK. Due to the extensive spectral coverage in the present data set, combination loops involving ^bR-type and ^bQ-type transitions were used both to verify assignments and to assist in making new assignments. The final list of assigned transitions includes 6772 lines and gives a microwave RMS of 343 kHz.

Addition of higher-order internal rotation terms and higher-order centrifugal distortion constants did not improve the results

achieved using ERHAM. Trials were conducted, but none of these additional terms were well-determined, and their inclusion did not improve the RMS for the fit. This confirms that the higher-order centrifugal distortion terms included in the SPFIT analysis were compensating for the lack of inclusion of internal rotation parameters, and that those centrifugal distortion terms are not needed in a combined analysis of the *A* and *E* states. Nonetheless, residuals from ERHAM resulting from this vibrational ground state fit are larger than might be expected, given the experimental resolution of ~ 100 kHz. This is because the model used by ERHAM is not able to predict the position of transitions at relatively high K_a and J values to experimental accuracy. The exact onset of this behavior depends on the energy of the lower state relative to the internal rotation barrier; in a previous study of 2-methylfuran [15], this behavior was not observed in the analysis of the ground-state spectrum, but it may have been responsible for limiting the maximum K_a value of the fit of the first vibrationally-excited state. MEK has a substantially lower V_3 value than 2-methylfuran (183 cm^{-1} compared to 410 cm^{-1}), and so it is not surprising that issues affecting the 2-methylfuran excited-state fit are important in the MEK ground state fit.

As with 2-methylfuran [15], level mixing can occur in MEK, potentially leading to c R-type *E*-state transitions at high values of J and K_a , even though $\mu_c = 0$ D for this molecule [16–18]. ERHAM predicts that these transitions should have appreciable line-strengths, but due to the fitting difficulties described above, the predicted transitions are not obviously assignable to any features in the experimental spectrum. Strong unassigned transitions at approximately the correct frequencies for these transitions are present in the experimental spectrum, but attempts to assign these to the predicted c R-type *E*-state transitions drastically reduce the overall fit quality because the separation between predicted and experimental frequencies is simply too large. As such, a prediction based on the parameters listed in Table 2 should be regarded as quite reliable for *A*-state transitions or for *E*-state transitions at modest values of K_a , but it does not accurately predict *E*-state transitions in which K_a approaches J for relatively high values of J .

Due to the fitting difficulties with ERHAM, we also fit the MEK data set with RAM36 [19], an internal rotor fitting program based on BELGI which should excel at handling low-barrier cases. As described in a review article by Kleiner [20], the primary difference between ERHAM and RAM36 is that ERHAM uses “local” or “effective” methods for fitting individual torsional states, while BELGI (and by extension, RAM36) uses a “global” method that fits multiple torsional states simultaneously. This “global” method should be able to handle perturbations arising from the interactions of levels from multiple torsional states in a way that the “local” methods cannot. Given the low value of V_3 , it is reasonable to expect that such perturbations may be responsible for the difficulty in fitting the spectrum to experimental resolution.

The results of the RAM36 analysis are shown in Table 3. The RAM36 analysis does give an improvement over the ERHAM analysis, with the microwave RMS dropping to 211 kHz using 2476 distinct frequencies (3716 transitions). The initial parameter set used for the RAM36 analysis included Watson *A*-reduction Hamiltonian parameters from ERHAM and estimates for the F , V_3 , and ρ parameters from XIAM. The initial linelist only included transitions up to $J = 20$. After convergence was achieved, the maximum value of J was increased, and the process was iterated until all assigned values of J were included, at which point a typical fit took roughly 1 h to reach convergence. The maximum value of J included in the fit is 109; including lines with $J > 100$ required recompiling RAM36 from source, as the pre-compiled executable only supports a maximum value of $J = 100$. Throughout the fitting process, the number of *A* and *E* state lines were held to similar values by capping the maximum value of K_a included. Several factors limited our ability

Table 2
Molecular parameters determined for $\text{CH}_3\text{COCH}_2\text{CH}_3$ using ERHAM.

Parameter		
A	9544.7499(38)	MHz
B	3597.07444(61)	MHz
C	2746.66566(36)	MHz
Δ_J	0.66072(14)	kHz
Δ_{JK}	2.6450(22)	kHz
Δ_K	5.0927(37)	kHz
δ_J	0.155781(77)	kHz
δ_K	0.5821(14)	kHz
Φ_J	-1.244(16)	mHz
Φ_{JK}	0.01352(35)	Hz
Φ_{KJ}	-0.0828(22)	Hz
Φ_K	[0]	
ϕ_J	-0.6570(85)	mHz
ϕ_{JK}	2.47(32)	mHz
ϕ_K	-0.0661(30)	Hz
L_{JK}	-0.01119(19)	mHz
L_{KJ}	0.02209(33)	mHz
l_{JK}	0.130(16)	μHz
l_{KJ}	-9.03(26)	μHz
ρ	0.0552320(64)	
β	169.2167(60)	degrees
ϵ_1	-2672.22(48)	MHz
ϵ_2	6.818(77)	MHz
B020 ₁	0.1681(12)	MHz
B200 ₁	-0.03857(40)	MHz
B220 ₁	0.02079(39)	kHz
B240 ₁	-8.79(17)	mHz
B400 ₁	4.383(60)	Hz
B600 ₁	0.3679(53)	mHz
B002 ₁	-0.01030(19)	MHz
B042 ₁	0.02423(37)	Hz
B202 ₁	2.054(35)	Hz
B222 ₁	-2.090(23)	mHz
B402 ₁	0.2056(31)	mHz
# Lines	4091 ^a	
Microwave RMS	0.343	MHz

^a This is the number of distinct frequencies included in the fit; a total 6772 transitions with distinct quantum numbers are included.

to assign additional *E* state lines at higher K_a values. First, as would be expected, these lines are predicted at much lower intensity than those at lower values of K_a . These lower line intensities combined with the extremely high line density observed in the MEK spectrum led to line confusion and precluded higher K_a assignments. Additionally, at higher values of K_a , the *A/E* splitting observed for the lower K_a lines is not readily apparent, and pattern recognition could not be used to guide further assignments. This limitation in higher K_a assignments for the *E* state combined with the required balance between the *A* and *E* state assignments in RAM36 resulted in a much smaller set of *A* state assignments being included in the RAM36 analysis than were included in the ERHAM or CALPGM analyses. Nonetheless, the RAM36 analysis more reliably treats the effects of the internal rotation and provides the means for reliable interpolation of the *E*-state dataset at modest values of K_a .

Comparison between the RAM36 results and those obtained from ERHAM and CALPGM reveal differences between these methods. The rotational constants and the centrifugal distortion constants are similar between the CALPGM and ERHAM analyses, but these values differ from those found in the RAM36 analysis. This is to be expected, as RAM36 uses the rho axis system, rather than the principle axis system used by the other two programs. Also, the higher-order centrifugal distortion terms included in the CALPGM analysis and the higher-order tunneling parameters included in the ERHAM analysis somewhat compensate for the expected perturbations at higher J and K_a that RAM36 directly and more effectively treats. However, the RAM36 analysis has not entirely dealt with such effects, as the value of D_{ab} is very large,

Table 3
Molecular parameters determined for CH₃COCH₂CH₃ using RAM36.

Parameter		
V ₃	175.073(30)	cm ⁻¹
F	5.3718(12)	cm ⁻¹
ρ	0.056039(47)	
A	9318.22(93)	MHz
B	3789.71(26)	MHz
C	2744.93(26)	MHz
D _{ab}	-2070.1(28)	MHz
Δ _J	0.6802(31)	kHz
Δ _{JK}	-1.86(17)	kHz
Δ _K	28.0(10)	kHz
δ _J	0.1659(15)	kHz
δ _K	-0.704(60)	kHz
Φ _J	2.69(13)	mHz
Φ _{JK}	-0.1338(60)	Hz
Φ _{KJ}	1.004(51)	Hz
Φ _K	-1.80(13)	Hz
φ _J	2.70(13)	mHz
φ _{JK}	-0.0889(42)	Hz
φ _K	0.468(26)	Hz
V _{3ab}	-64.8(17)	MHz
V _{3J}	-0.90(12)	MHz
V _{3bc}	-3.56(12)	MHz
V _{3K}	65.6(21)	MHz
F _J	0.2177(18)	MHz
F _K	4.61(24)	MHz
F _{ab}	-4.30(16)	MHz
# Lines	2476 ^a	
Microwave RMS	211	kHz

^a This is the number of distinct frequencies included in the fit; a total 3716 transitions with distinct quantum numbers are included.

indicating that this term might be compensating for other missing higher-order tunneling terms. Further analysis of *E* state lines at higher *K_a* might enable addition of higher-order terms, but such assignments cannot easily be discerned because of the limitations due to spectral line confusion.

Only transitions from the ground torsional state were assigned and included in the analysis presented here. It is likely that perturbations from higher torsional states affect ground state transitions with higher values of *J* and *K_a* than those included in the RAM36 analysis; the most likely states to interact with the ground state are the first excited states of the CO-CH₃ torsion and the skeletal CH₃CH₂ – COCH₃ torsion. These perturbations may be contributing factors in the limited number of *E* state lines that could be assigned. In the absence of information to constrain the properties of the higher torsional levels, it is unlikely that RAM36 will be able to properly handle inter-torsional perturbations and significantly improve on the fit obtained here. Future work on the thousands of unidentified lines remaining in the spectrum should focus on assigning transitions from excited torsional states to address this issue.

The spectral analysis presented here is sufficient for guiding observational searches for MEK, which would focus on the lines involving the lowest *K_a* values for both the *A* and *E* states. However, the internal rotation splitting leads to weak line intensities, hence making interstellar detection a challenge unless the abundance of this molecule is unusually high for a species at this level of molecular complexity. MEK is an expected “next step” from the currently identified interstellar organic molecules, and therefore is expected to be far less abundant than the simpler related species listed in the introduction. This combination of weak line intensities and expected low abundance make it a difficult target for interstellar observation. Nonetheless, as the sensitivity of observational facilities continues to increase, it may become possible to detect the strongest lines from a complex molecule like MEK toward some sources.

4. Conclusion

The rotational spectrum of methyl ethyl ketone was collected from 8 GHz to 1 THz using a combination of chirped-pulse Fourier transform microwave spectroscopy, millimeter spectroscopy in a pulsed supersonic expansion, and room temperature millimeter and submillimeter direct absorption spectroscopy. An *A* state fit of the the ground vibrational state was achieved using the CALPGM program. This CALPGM fit can be used to reliably predict all *A* state transitions with *J* < 120 and *K_a* < 55 at frequencies below 1 THz. Additionally, a combined *A/E* fit to a limited set of transitions was achieved in the RAM36 program, with the *E* state assignments limiting the fit to values of *K_a* < 13. Spectral predictions based on this RAM36 fit are reliable for both *A* state and *E* state transitions at modest values of *K_a*. Future work should focus on assignment of *E* state lines with higher *K_a* values. Such studies might require the use of double resonance techniques so that particular sets of transitions can be distinguished. Additional future work should focus on assignment of higher torsional states, which may enable an improved combined *A/E* fit. Nonetheless, the information provided by the analysis presented here is suitable for guiding astronomical searches. However, the weak line intensities for this molecule limit the likelihood of its detection.

Acknowledgments

S.T.S. acknowledges support from the National Science Foundation Division of Chemistry under Grant No. 1111101 (co-funded by MPS/CHE and the Division of Astronomical Sciences), and also acknowledges New College of Florida for start-up funding. S.L.W.W. acknowledges support for spectrometer development from NASA award number NNX11AI07G, and start-up support from Emory University. J.A.K. acknowledges support from the Emory SURE program, which received funding from Howard Hughes Medical Institute Grant No. 52005873.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jms.2013.10.005>.

References

- [1] R.T. Garrod, S.L. Widicus Weaver, E. Herbst, *Astrophys. J.* 682 (2008) 283–302.
- [2] J.L. Neill, A.L. Steber, M.T. Muckle, D.T. Zaleski, B.H. Pate, V. Lattanzi, S. Spezzano, M.C. McCarthy, A.J. Remijan, D.N. Friedel, S.L. Widicus Weaver, *J. Phys. Chem. A* 115 (2011) 6472–6480.
- [3] E. Herbst, E.F. van Dishoeck, *Ann. Rev. Astron. Astrophys.* 47 (2009) 427–480.
- [4] L.C. Pierce, M. Hayashi, R. Nelson, *J. Molec. Spectrosc.* 32 (1969) 449–457.
- [5] N.M. Pozdeev, A.Kh. Mamleev, L.N. Gunderova, R.V. Galeev, *J. Struct. Chem.* 29 (1988) 52–58.
- [6] J.R. Durig, F.S. Feng, A. Wang, H.V. Phan, *Can. J. Chem.* 69 (1991) 1827–1844.
- [7] B. Reinhold, I.A. Finneran, S.T. Shipman, *J. Molec. Spectrosc.* 270 (2011) 89–97.
- [8] P.B. Carroll, B.J. Drouin, S.L. Widicus Weaver, *Astrophys. J.* 723 (2010) 845–849.
- [9] J.C. Lass, B.M. Hays, S.L. Widicus Weaver, *J. Phys. Chem.* 117 (2013) 9548–9554.
- [10] H.M. Pickett, *J. Molec. Spectrosc.* 148 (1991) 371–377.
- [11] H.M. Pickett, SPFIT/SPCAT package. <<http://spec.jpl.nasa.gov>>.
- [12] Z. Kisiel, PIFORM. <<http://www.ifpan.edu.pl/kisiel/asym/asym.htm#piform>>.
- [13] H. Hartwig, H. Dreizler, *Z. Naturforsch. A* 51 (1996) 923–932.
- [14] P. Groner, *J. Chem. Phys.* 107 (1997) 4483–4498.
- [15] I.A. Finneran, S.T. Shipman, S.L. Widicus Weaver, *J. Molec. Spectrosc.* 280 (2012) 27–33.
- [16] R.C. Woods, *J. Molec. Spectrosc.* 21 (1966) 4.
- [17] G.M. Plummer, E. Herbst, F.C. De Lucia, *Astrophys. J.* 318 (1987) 873.
- [18] D.R. Herschbach, J.D. Swalen, *J. Chem. Phys.* 29 (1958) 761.
- [19] V.V. Ilyushin, Z. Kisiel, L. Pszczółkowski, H. Mäder, J.T. Hougen, *J. Molec. Spectrosc.* 259 (2010) 26–38.
- [20] I. Kleiner, *J. Molec. Spectrosc.* 260 (2010) 1–18.