

The Millimeter-Wave Spectrum of Acetaldehyde in Its Two Lowest Torsional States

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A large number of new millimeter-wave spectral lines of gaseous acetaldehyde have been measured at frequencies up to 250 GHz. These lines arise from rotational transitions of acetaldehyde in its two lowest ($v_t = 0, 1$) torsional states and involve angular momentum quantum numbers $J \leq 12$ and $K \leq 10$. A global data set consisting of 562 lines has been obtained by combining the millimeter-wave lines with previously measured lower frequency data involving the two lowest torsional states. This data set has been analyzed via an internal axis method previously used to study the spectra of CH_3OH and CH_3SH . The root-mean-square deviation of the fit is only 685 kHz. An analogous least-squares fit to $335v_t = 0$ lines yields a root-mean-square deviation of 269 kHz. © 1986 Academic Press, Inc.

I. INTRODUCTION

The study of the rotational spectra of molecules with internal rotation occupies an important niche in the history of microwave molecular spectroscopy (1). Hindered internal rotation, often referred to as torsional motion, complicates the normal rotational spectrum of a semirigid asymmetric top by interacting with the end-over-end rigid body rotation of the molecule. In addition, the torsional motion results in closely spaced vibrational levels which themselves can be studied by far-infrared spectroscopy. In the Duke laboratory, we have recently measured and analyzed the millimeter- and submillimeter-wave rotational spectra of the internal rotors methanol (2), methyl formate (3, 4), and methyl mercaptan (5). Our analyses of the spectra of methanol and methyl mercaptan were based on an extended internal axis method (IAM) which is a generalization of the approach used by Lees and Baker (6) in their classic early study of methanol. This approach, in which the interaction between internal and rigid body rotation is essentially removed from the Hamiltonian, was pioneered by Nielsen (7) and Burkhard and Dennison (8) and subsequently extended by Kirtman (9). Our IAM treatment has yielded fits to large amounts of spectral data from several torsional states of both methanol and methyl mercaptan with root-mean-square deviations on the order of 1 MHz.

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Acetaldehyde (CH_3CHO) is another classic internal rotor. Initially studied in detail in the microwave by Kilb *et al.* in 1957 at frequencies up to 40 GHz (10), it has been studied subsequently by a variety of authors. In 1970, Souter and Wood (11) measured the far-infrared spectrum of acetaldehyde and combined their data with previous rotational spectra to analyze the torsional potential. In 1976, the rotational spectrum was extended in two ways by Bauder and colleagues. Bauder *et al.* (12) measured spectra for the $v_t = 0$ state up to 120 GHz in frequency and modified a program of Woods (13) to analyze the spectra and predict the frequencies of unmeasured transitions through 250 GHz. In addition, Bauder and Günthard (14) measured and analyzed low-frequency data involving the lowest five torsional states. From their data, they were able to obtain significant information about both the torsional potential and structural changes taking place during the torsional motion. To first order in perturbation theory, their analysis is akin to the Kirtman analysis (9) incorporated into our present approach. In 1978, Hollenstein and Winther (15) studied the far-infrared spectrum of acetaldehyde with higher resolution than had been obtained in the past. Most recently, Petty *et al.* (16) have utilized their double resonance spectrometer together with the discovery of numerous combination relations between measured frequencies (6) to assign a large number of rotational lines of acetaldehyde at frequencies below 72 GHz in the lowest three torsional states. In addition to being studied in the laboratory, acetaldehyde has been observed in interstellar space in the well-known Sgr B2 cloud near the center of our galaxy (17, 18) and in the nearby cold dark clouds TMC-1 and L134N (19).

The purposes of this paper are two-fold. We have measured a large number of new rotational spectral lines of acetaldehyde in its first two torsional states at frequencies up to 250 GHz. These lines are needed by radioastronomers working in the millimeter region, because previous predictions based on lower frequency measurements are not always sufficiently accurate for identification and detailed analysis. In addition, it is of interest to determine whether our IAM analysis, previously utilized only for near symmetric tops such as CH_3OH and CH_3SH , can fit the spectrum of a somewhat larger internal rotor such as acetaldehyde to an accuracy approaching the experimental measurement uncertainty (± 50 – 100 kHz). Unlike the cases of methanol and methyl mercaptan, the internal rotation in acetaldehyde is not as dominant an effect because the oxygen atom off the symmetry axis of the methyl subunit is far heavier than the off-axis H atoms of the earlier species studied. Previous treatments of the rotational spectrum of acetaldehyde [see, e.g., Refs. (12, 14, 16)] have not been able to fit the data to anything near the experimental uncertainty.

The remainder of this paper is organized as follows. The experimental details of our measurements are discussed briefly in Section II. In Section III, we present the theory used in our analysis of the data and how the spectral assignments have been made. In Section IV, the results of our analysis are discussed and compared with previous approaches in terms of goodness of fit and determination of the torsional potential.

II. EXPERIMENTAL DETAILS

Most of the spectral line measurements of acetaldehyde reported in this paper have been measured with a broadband millimeter-wave spectrometer briefly discussed pre-

viously (5). In this spectrometer, radiation is produced by a YIG oscillator which is used to drive a 26- to 40-GHz traveling-wave-tube amplifier. This amplifier in turn drives a high-order harmonic generator. This method of generating millimeter waves allows us to produce continuous frequency scans over large spectral regions and to record the spectra automatically. A detailed description of this spectrometer is being written as a section of a paper on new HNO₃ measurements (20).

III. THEORY AND SPECTRAL ASSIGNMENTS

The internal axis method used to analyze the data has been discussed in detail in our previous papers on methanol (2) and methyl mercaptan (5). The Hamiltonian \mathbf{H} , which is an extended version of that used by Lees and Baker (6), is divided into three terms:

$$\mathbf{H} = \mathbf{H}_{\text{rot}} + \mathbf{H}_{\text{tor}} + \mathbf{H}_{\text{d-i}} \quad (1)$$

which describe, respectively, the overall rotation of the molecule, the torsional motion of the methyl group vis-a-vis the CHO end of the molecule, and the distortion and interaction terms among various angular momenta. The separation between overall rotation and torsional motion is not complete in that \mathbf{H}_{tor} does depend on \mathbf{P}_a , the rigid body angular momentum component along the a axis, which in the IAM method is not a principal axis of the molecule but rather is the symmetry axis of the methyl subunit. Use of a nonprincipal axis system results in additional rotation constants; in this case, a fourth constant D_{ab} is added to the normal three constants A , B , and C .

The Hamiltonian is diagonalized seriatim. First, \mathbf{H}_{tor} is diagonalized via use of basis functions consisting of products of free rotor torsional eigenfunctions and eigenfunctions $|K\rangle$ of \mathbf{P}_a . The operator \mathbf{H}_{tor} connects different free rotor functions but does not connect basis functions of differing $|K\rangle$, nor does it connect different symmetry combinations of the torsional basis functions designated by a quantum number $\sigma = 0, +1, \text{ and } -1$. The functions obtained from the initial diagonalization can be characterized by the three quantum numbers K , v_t , and σ , where $v_t = 0, 1, 2, \dots$ is the torsional quantum number. States with $\sigma = 0$ are labeled A while states with $\sigma = 1$ and -1 are labeled E . In general, energy differences between states of different v_t exceed differences between states of differing σ so that A and E designations are said to refer to "substates." Torsional A substates retain a $\pm K$ degeneracy whereas for E substates there is a degeneracy between $\sigma = 1, K$ levels and $\sigma = -1, -K$ levels. One can thus refer to the torsional levels in E states with either $\sigma = 1$ or $\sigma = -1$ and the use of both positive and negative K values, noting that there is a two-fold degeneracy. In this work, we choose $\sigma = 1$. The destruction of the $\pm K$ degeneracy in the E states means that these torsional substates are quite different from states in normal asymmetric tops where the $\pm K$ degeneracy is broken only by off-diagonal terms of the rotational Hamiltonian.

The torsional eigenfunctions $|Kv_t\sigma\rangle$ are themselves utilized in a product basis set $|JKv_t\sigma\rangle$ defined by

$$|JKv_t\sigma\rangle = |JK\rangle|Kv_t\sigma\rangle \quad (2)$$

to diagonalize the remaining two terms of the Hamiltonian for each value of J and σ desired. Here J is the overall angular momentum quantum number and $|JK\rangle$ represents

the remainder of the rigid body symmetric top rotational eigenfunction not utilized in the torsional basis. Selected matrix elements off-diagonal in v_t by up to two units ($\Delta v_t = 0, \pm 1, \pm 2$) have been included (2, 5), although it is a strength of the IAM approach that elements with $|\Delta v_t| > 0$ are not very large. For a given value of J , the dimension of the matrix involving rotation and distortion interaction matrix elements is $[(2J + 1) \times (v_{t,\max} + 3)] \times [(2J + 1) \times (v_{t,\max} + 3)]$ where $v_{t,\max}$ is the highest torsional quantum number needed in the analysis. The resulting large matrices seriously limit the maximum J analyzable via this approach. Matrix elements of H_{rot} and $H_{\text{d-i}}$ are listed in Refs. (2, 5).

The final eigenvectors and energies are characterized exactly by quantum numbers J and σ , and to a high degree of approximation by the quantum number v_t . The quantum number K is only an approximate one for a variety of reasons having to do with the rotational motion. In a normal asymmetric top, $\Delta K = \pm 2$ matrix elements of the rotational Hamiltonian destroy K as a "good" quantum number. The rotational levels can be characterized by a K_{-1}, K_{+1} designation, where K_{-1} and K_{+1} represent the appropriate K eigenvalue in the prolate and oblate symmetric top limits, respectively. Alternately, one can characterize the levels by an approximate $|K|$ quantum number and a parity quantum number (6). In internal rotors, use of the IAM approach results as well in $\Delta K = \pm 1$ terms resulting from the D_{ab} rotation constant because of the fact that the a axis utilized is not a principal axis. In acetaldehyde, these latter terms are substantial because the a axis is approximately 25° from the normal principal axis (12). A parity quantum number can still be used for states with A symmetry but for states with E symmetry the fact that there is no longer a $\pm K$ degeneracy due to the torsional Hamiltonian means that parity is no longer a useful quantum number.

What is the best method of characterizing the torsional-rotational energy levels of an internal rotor with regard to the quantum number K ? The standard K_{-1}, K_{+1} designation can still be used effectively in the presence of internal rotation even with an IAM approach in the sense that the order of the energy levels for a given J, σ block can be defined to follow the normal rigid asymmetric top ordering (1). An alternative approach is to inspect the calculated eigenvectors and to label them via their most appropriate K value, or, in the case of A states where rotation is needed to break the $\pm K$ degeneracy, via their $|K|$ level and parity. In the past, the former approach has been utilized for asymmetric tops with significant but not dominant internal rotation effects such as acetaldehyde (12, 14, 16) and methyl formate (3, 4) whereas the latter approach has been used for near symmetric tops such as methanol (2, 6) and methyl mercaptan (5) with spectra that are dominated by torsional effects.

In this work, we have utilized a composite approach to state designation. For E substates, in which torsional effects are more pronounced, our program examines the final eigenvectors and characterizes them by the K value ($-J \leq K \leq J$) of the most significant basis function. For A substates, we have utilized a fixed ordering procedure relevant to species without internal rotation because we have found such a procedure suitable for the torsional quantum states ($v_t = 0, 1$) involved in our data analysis and because we have experienced some difficulty in devising an algorithm for examining and labeling 100% of the states via the most significant basis function. (Part of the difficulty is due to our use of the symmetry axis of the methyl group for the K quantization). Because we have characterized the E levels via K and not via K_{-1}, K_{+1} , we

also use such a characterization for the A levels. Here, however, the characterization involves the absolute value of K and a parity quantum number of + or - where these designations refer, respectively, to the linear combinations $|J, K, v_t, \sigma = 0\rangle \pm (-1)^K |J, -K, v_t, \sigma = 0\rangle$. The normal ordering of A levels for a given v_t and J in terms of ascending energy is taken to be $K = 0, 1+, 1-, 2-, 2+, 3+, 3-,$ etc., based on our previous studies and the great majority of the CH_3CHO levels for which we can determine a label. Note that the parity designations do not include contributions from J and v_t and therefore are not overall parities (6). The energy of E states of a given v_t and J increases with increasing $|K|$ for the studied torsional states of CH_3CHO although the relative energies of $+K$ and $-K$ states depend on v_t . Significant energy differences between $\pm K$ states exist even for high- K values where the + and - A levels are degenerate.

With the above system of designating eigenvectors and energy levels, the strongly allowed transitions for rotational quanta are

A			E	
$\pm \leftrightarrow \mp$;	$\Delta J = 0$;	$\Delta K = 0, 1$	$\Delta J = 0$;	$\Delta K = \pm 1$
$\pm \leftrightarrow \pm$;	$\Delta J = 1$;	$\Delta K = 0, \pm 1$	$\Delta J = 1$;	$\Delta K = 0, \pm 1$

Since these designations are not exact, other transitions are allowed, such as K doubling ($\Delta J = 0; K \leftrightarrow -K$) transitions in the E sublevels. In the analysis discussed here, the transitions included all follow the above selection rules. Inclusion of other transitions, some of which have already been measured and assigned, will necessitate an alteration of the internal rotor program.

Assignments of spectral transitions have been facilitated by the earlier assignments of numerous workers at lower frequencies. Originally, it had been hoped to study millimeter-wave transitions involving more than just the two lowest torsional states. However, transitions in torsional states with $v_t \geq 2$ appear to be significantly less regular and more difficult to treat via our IAM technique; despite the inclusion of more parameters such as a V_9 term in the torsional potential [see Eq. (3) below], we have experienced difficulties in extending the earlier work of Bauder and Günthard (14) and Petty (16) for $v_t \geq 2$ to significantly higher frequencies and rotational quantum numbers. (Least-squares fits involving our millimeter data and earlier data through $v_t = 3$ result in root-mean-square deviations on the order of 4 MHz, far worse than our fit to the $v_t = 0.1$ data.) The data set analyzed here thus consists of transitions in the A and E sublevels of the $v_t = 0$ and 1 torsional states only. We have included 562 lines with $J \leq 12$ and $K \leq 10$, 335 of which derive from $v_t = 0$ and 227 of which derive from $v_t = 1$. All lines with frequencies above 96 GHz were measured at Duke; lines below this frequency were measured mainly at Manchester (16), while some lines were taken from earlier data (12, 14). Microwave lines involving higher J have recently been reported by Liang *et al.* (23) but are excluded from our fit due to the size of the matrices needed to analyze them. Assignments have been confirmed by combination relations wherever possible and by error curve techniques; misassignments have been checked for exhaustively and, given the excellent fit to the data discussed below, probably eliminated. Some tentatively assigned higher K , a -type, $v_t = 1$ transitions have been rejected based on these techniques.

TABLE II
Acetaldehyde E Transitions

Table with columns: VTOR, SIGMA, J', K', P', J'', K'', P'', FREQUENCY(MHZ), RESIDUAL(MHZ), VTOR, SIGMA, J', K', P', J'', K'', P'', FREQUENCY(MHZ), RESIDUAL(MHZ). Contains multiple rows of spectral transition data.

TABLE III

Rotation, Torsion, Distortion, and Interaction Constants for Acetaldehyde

Constant (MHz unless noted)	Value for fit to $v_t = 0,1^a$	Value for fit to $v_t = 0$ only ^a
A	56518.0708(1874)	56316.9553(2430)
B	10444.5425(600)	10463.4434(2418)
C	9089.53951(1065)	9092.52115(515)
D _{ab}	-3615.6115(4236)	-3685.8926(1.5059)
F(cm ⁻¹)	7.53724364(249723)	7.53724364(fixed)
ρ (unitless)	0.328347410(17973)	0.328805197(11987)
V ₃ (cm ⁻¹)	405.583681(176543)	397.34084(515)
V ₆ (cm ⁻¹)	-12.41659(1891)	
F _v	23.87216(15392)	
G _v x 10 ²	6.9927(7878)	
L _v	0.17257(1576)	
D _J x 10 ³	7.77239(3099)	7.70845(1917)
D _{JK} x 10 ²	-4.965727(11886)	-5.023536(18320)
D _K	0.7202353(42904)	0.72184346(185342)
k ₁	3.312718(440466)	
k ₂	-18.897786(294764)	
k ₃	-6.81227(71991)	
k ₅	-501.89683(573973)	
δ_J x 10 ³	1.30961(2277)	1.27080(1082)
δ_K x 10 ³	5.175(2013)	5.876(963)
c ₁ x 10 ²	2.08001(32402)	
c ₂	11.02272(12848)	
l _v x 10 ²	1.15792(5848)	
H _{JK} x 10 ⁶		-2.4844(7002)

^a Uncertainties in parentheses represent 1 σ deviations. Number of listed significant figures for each constant is necessary to reproduce calculated frequencies to 1-10 kHz. The variance of the fit to the combined $v_t = 0,1$ data is 685 kHz whereas the variance of the fit to the $v_t = 0$ data is 269 kHz.

value of 405.58(18) cm⁻¹ is within experimental uncertainty of the value of 406(10) cm⁻¹ obtained by Kilb *et al.* (10) and the value of 408(10) cm⁻¹ derived by Herschbach (21) using the same data. We differ somewhat from the values of 400.5(2.4) cm⁻¹ obtained by Bauder and Günthard (14) and 401.44(7) cm⁻¹ obtained by Petty (16). The values of 431(7) and 389 obtained by Iijima and Tsuchiya (22) and Souter and Wood (11), respectively, appear to be less accurate.

The three listed values of V₆, ours and those of Bauder and Günthard (14) and Petty (16), are in reasonable agreement with one another although our value differs by more than the combined standard deviations from each of the earlier determinations.

TABLE V
Further Assigned Transitions of CH₃CHO below 72 GHz^a

VTOR	SIGMA	J'	K'	P'	J''	K''	P''	FREQUENCY (MHZ)	RESIDUAL (MHZ)	
1	0	3	1	-	<--	3	0	+	41567.120	-0.264
1	0	3	1	-	<--	2	2	-	-58926.640	-1.340
1	0	4	1	-	<--	3	2	-	-37892.200*	-0.784
1	0	5	1	-	<--	5	0	+	46511.260	-0.419
1	0	5	1	+	<--	4	2	+	-31268.860	-0.216
1	0	8	1	+	<--	7	2	+	13118.600	0.939
1	0	8	2	-	<--	7	3	-	-57696.520*	-0.170
1	0	9	1	+	<--	8	2	+	25935.430	0.576
1	0	9	2	-	<--	8	3	-	-39300.440	0.277
1	0	10	1	+	<--	9	2	+	37570.400	0.456
1	0	11	2	+	<--	11	2	-	12338.300*	-0.409
1	0	11	1	+	<--	10	2	+	47912.960	1.092
1	0	12	2	+	<--	11	3	+	31382.880	-1.164
1	0	12	2	-	<--	11	3	-	13904.900	-0.771
1	1	4	0	--	<--	3	1	--	44666.010*	-0.168
1	1	5	0	--	<--	4	-1	--	25543.000*	-1.289
1	1	5	1	--	<--	4	2	--	-44525.720	-0.678
0	1	6	1	--	<--	6	0	--	58976.050	-0.472
1	1	6	-1	--	<--	5	-2	--	-41555.240*	-0.847
1	1	9	1	--	<--	9	0	--	25935.430	0.933
1	1	9	2	--	<--	8	3	--	-70621.920*	0.118
0	1	11	-2	--	<--	10	-3	--	-24859.100*	-0.425
1	1	11	-2	--	<--	10	-3	--	-26280.940*	0.761
1	1	11	1	--	<--	10	2	--	45032.770	-1.192

^a Measured by Petty (16) unless an asterisk follows the frequency, in which case measured by Liang.

while the others increase. Structural information suggests that this corresponds to changes in the CHO rather than the CH₃ group (16, 23); a more detailed analysis of this and of higher torsional states is in progress.

Our least-squares fit to the 562 transition frequencies of acetaldehyde has enabled us to predict the frequencies of a much larger number of transitions in the lowest two torsional states involving the quantum number $J \leq 12$. These predictions have enabled us to assign some *b*-type ($\Delta K = \pm 1$) transitions, measured at Manchester at frequencies below 72 GHz; the assignments and frequencies are listed in Table V. Many if not most of our frequencies are predicted to an accuracy of better than 1 MHz and should be of interest to radioastronomers. Indeed, the availability and assignment of many transitions of acetaldehyde in its first torsionally excited state might permit astronomers to search for this species in its $v_t = 1$ state and help elucidate regions of active star formation.

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