Ground State Centrifugal Distortion Constants of Trans-Acrolein, $CH_2=CH-CHO$ from the Microwave and Millimeter Wave Rotational Spectra [1,2]

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The pure rotational spectrum of trans-acrolein in the ground vibrational state has been assigned in the frequency region from 8 GHz to 180 GHz. The measured absorption lines encompass *a*-type transitions from the ^qR_K, $^qQ_1$, $^qQ_2$ branches and *b*-type transitions from the $^rP_0$, $^rP_1$, $^rP_2$, $^rR_0$ branches for values of J up to 23. The rotational constants have been refined and all quartic and sextic centrifugal distortion constants have been determined using Watson's reduced Hamiltonian. This information has been used to predict line positions of astrophysical interest to warrant the interstellar line search for trans-acrolein.

I. Introduction

The present paper on trans-acrolein is a continuation of a series of investigations of the microwave and millimeter wave spectra of slightly asymmetric rotor molecules of astrophysical interest [1–5]. The primary objectives are to provide accurate predictions of radio-astronomically interesting transition frequencies and to derive reliable centrifugal distortion parameters, which in turn yield information concerning the molecular force field.

Measurements in the microwave [6,7], infrared [8] and near ultraviolet region [9,10] have demonstrated that the trans-form is the most stable and abundant rotamer form of acrolein. The only evidence so far available of the existence of the cis-form of acrolein came recently from studies of the near ultraviolet spectrum [11]. This identification of the cis-rotamer has been confirmed by two further studies of the magnetic rotation spectra of acrolein [12], and the absorption spectra of acrolein-d_1 ($H_2C=CHCDO$) [13] in the near ultraviolet spectral region. The ground state of the cis-rotamer was found to lie about 700 cm^{-1} above the ground vibrational state of the trans-rotamer, which explains why its rotational spectrum has not been found among the overlapping spectra of excited vibrational states from the trans-acrolein molecule.

In the first microwave study of trans-acrolein the $J=3\leftarrow 2$ *a*-type R branch transitions of the normal species and the *a*-components of the dipole moment were reported [6]. In addition to the $J=2\leftarrow 1$ and $J=3\leftarrow 2$ *a*-type R branch transitions Cherniak and Costain [7] reported for the normal species four *b*-type transitions of the $K_a=1\leftarrow 0$ rotational subband and the *b*-component of the dipole moment. From these transitions improved rotational constants and two quartic distortion constants were derived. A complete r_s-structure was obtained from the analysis of eleven isotopic species. However, these microwave studies did not included high J transitions or measurements of millimeter wave transitions, and a complete set of quartic distortion constants could not be obtained.

II. Comments on Interstellar Importance of Acrolein and Related Molecules

The detection of large interstellar molecules provides presently the most powerful tool to probe deep into the dense interior of the molecular dust clouds

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in the Galaxy and yields information on their physical and chemical state.

Recently interstellar vinyl cyanide ($H_2C=CHCN$) has been detected in the direction of the galactic center source SGR B2 by Gardner and Winnewisser [14]. It is the first interstellar molecule observed which contains a carbon-carbon double bond and is closely related to acrolein ($H_2C=CHCHO$). Both molecules are derivatives of ethylene, in which one of the hydrogen atoms of the ethylene molecule has been replaced by a different functional group, $-CN$ or $-CHO$. The spectroscopic properties of acrolein, such as the energy level scheme, magnitude and direction of the electric dipole moment and transition probabilities are rather similar to those of vinyl cyanide. One could therefore expect on these grounds that acrolein and vinyl isocyanide [5] should be detectable in interstellar space, unless the interstellar production mechanisms of these two molecules are very different from that of vinyl cyanide. A thorough search for interstellar acrolein seems to be warranted, particularly using its low J, $K_a=1$ Q-branch transitions. Since these transitions for molecules with C_s symmetry seem to arise from energy levels with inverted populations under interstellar conditions, they amplify the continuum background radiation and thus become more easily detectable than other transitions [14, 15].

III. Experimental Procedures

The microwave measurements in the frequency region 8 to 40 GHz were carried out with spectrometers located at the Justus Liebig-Universität, Giessen, and at Kyushu University, Hakozaki. The Giessen spectrometer is a Hewlett-Packard Model 8460 A Microwave Rotational Resonance (MRR) spectrometer, presently equipped with two microwave sources to cover the frequency ranges from 8 to 12.8 GHz and 12.4 to 18 GHz. The spectrometer is operated with a two meter X-band Stark absorption cell and 33.333 kHz square wave modulation of the electric field employing the molecular Stark effect. The accuracy of the frequency measurements using this spectrometer is estimated to be about ± 20 kHz. The spectrometer employed at Kyushu University is of Hughes-Wilson type with a 120 kHz square wave Stark modulator, and covers the frequency region 8 to 35 GHz. The absorption cell is a 3 meter long X-band waveguide.

Some measurements in the frequency range 8 to 18 GHz were made independently at both laboratories and were found to be in agreement within ± 80 kHz.

In the frequency region from 80 to 200 GHz the measurements were made with the millimeter wave spectrometer at the Justus Liebig-Universität. The millimeter wave radiation was generated by harmonic multiplication of the fundamental frequencies of different reflex klystrons. The absorption lines were detected with a video-spectrometer employing a dedicated PDP 8/I computer for rapid data acquisition which allows Doppler resolution, high sensitivity and accurate frequency measurements. The spectrometer and its mode of operation have been described previously [16, 17]. The accuracy of the millimeter wave data is estimated to be about ± 15 kHz for strong lines and somewhat less for weak or overlapping lines.

All acrolein data were taken at room temperature with sample pressures smaller than 10^{-2} Torr.

IV. Assignment of the Spectrum

The microwave and millimeter wave spectra of planar slightly asymmetric top molecules as large as trans-acrolein are extremely rich. This feature is caused by the small rotational constants A, B, C, and by the lack of any symmetry axis which allows the occurrence of a-type ($\mu_a=3.06\pm0.04$ Debye) [6] and b-type ($\mu_b=0.54\pm0.14$ Debye) [7] rotational spectra. The superposition of both types of spectra for the vibrational ground state with spectra arising from molecules in excited states leads to a dense spectrum throughout the investigated spectral region, complicating the assignment of the considerably weaker b-type spectrum.

1) The a-type Rotational Spectrum

The a-type spectrum of trans-acrolein exhibits all the typical features of slightly asymmetric rotors, with their characteristic R- and Q-branch transitions. An overview of the a-type spectrum is shown in the Fortrat diagram of Figure 1. The strong R-branch transitions occur at intervals of $(B+C)$ throughout the centimeter and millimeter wave regions. Figure 2 shows a scan of the spectrum near 8.9 GHz with the $J=1\leftarrow0$ R-branch transitions of the ground state and rotational lines arising from molecules in various vibrationally excited states. For each of the higher $J+1\leftarrow J$ transitions of this R-branch the different K_a components form two band heads. One band head occurs at $K_a=2$ and is determined by

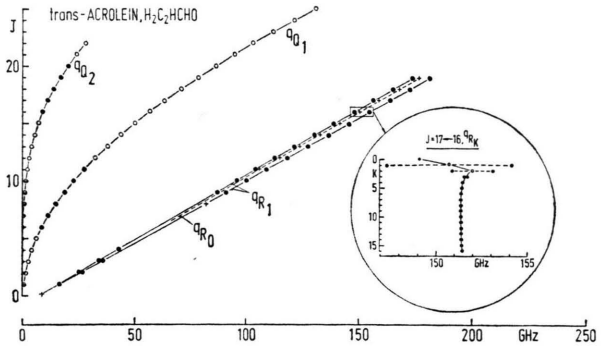

Fig. 1. Fortrat-diagram for *a*-type transitions of *trans*-acrolein. The solid and open circles indicate measured and predicted line positions, respectively. For the *a*-type R branch only the $K_a=0$ and $K_a=1$ transitions are indicated. The inset shows the full K_a-pattern for the transition $J=17 \leftarrow 16$.

the inertial asymmetry of the molecule, whereas the one at values of $K_a \cong 9$ is caused by centrifugal distortion contributions which depend mainly on the term with the coefficient D_{JK}. Figure 3 illustrates a typical K_a-pattern for the $J=15 \leftarrow 14$ transition. The top part shows a recorder tracing of the reversal of the $K_a=8$, 9 and 10 components, while the center presents an overview of the entire transition, plotted and compared in the lower part of Fig. 3 with the calculated spectrum. The rotational spectra of molecules in vibrationally excited states show a similar band-head structure as may be seen

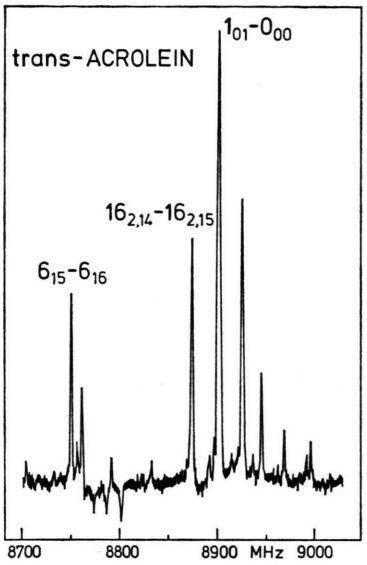

Fig. 2. Fast scan of the *trans*-acrolein spectrum near the $1_{01}-0_{00}$ R-branch ground state line position showing the spectrum from molecules in excited vibrational states and two *a*-type Q-branch transitions.

for the $v_{18}=1$, $J=15 \leftarrow 14$ rotational transition in Figure 3. The formation of such band-heads has been observed previously in the spectra of propynal[1] vinyl cyanide[2] and vinyl isocyanide[5], and is characteristic for heavy, slightly asymmetric top molecules. A comparison of the $J=19 \leftarrow 18$

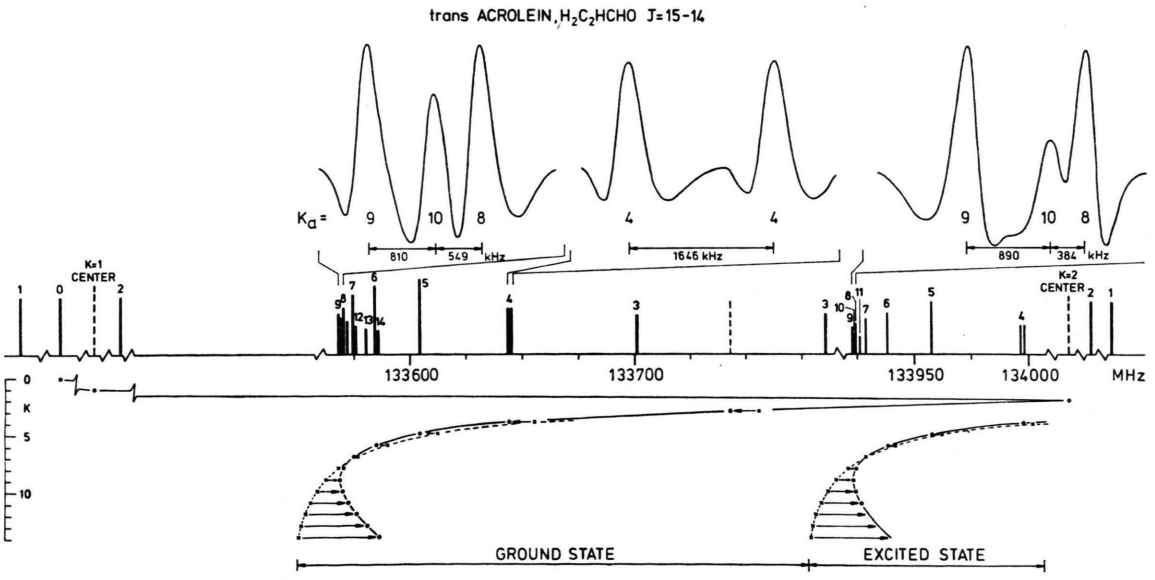

Fig. 3. Recorder tracings of the *a*-type $J=15 \leftarrow 14$ transition of *trans*-acrolein showing the band-head structure. Deviation from rigid rotor frequencies due to centrifugal distortion is indicated by arrows. The weaker lines on the right hand side are believed to arise from molecules in the excited vibrational state $V_{18}=1$.

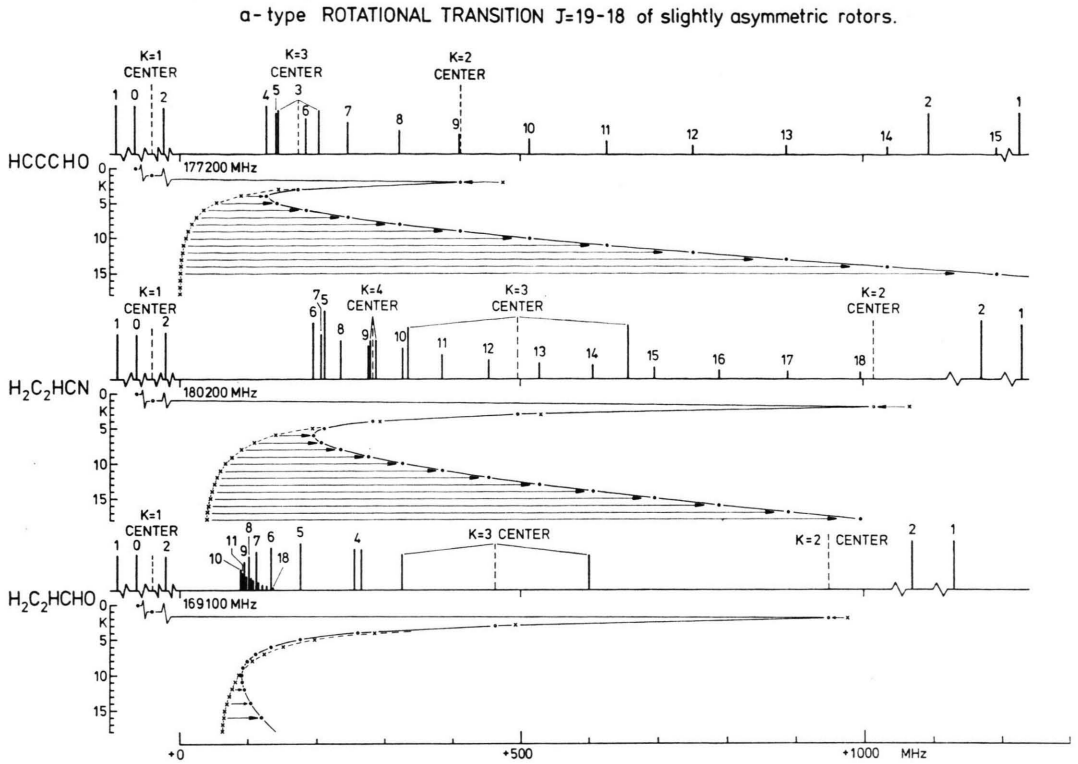

Fig. 4. The band-head structures in the spectrum of propynal, vinyl cyanide and *trans*-acrolein are illustrated for the *a*-type $J=19 \leftarrow 18$ transition. Deviation from the rigid rotor pattern due to centrifugal distortion is indicated by arrows, and demonstrates the rigidity of the *trans*-acrolein molecule.

transition of the molecules propynal, vinyl cyanide and acrolein is shown in Fig. 4, which clearly demonstrates that trans-acrolein is a rather rigid molecule with comparatively little centrifugal distortion. Although rotational transitions have been observed in many different vibrational states we have not attempted to assign and analyse these spectra. However, if a microwave identification of the cis-rotamer is to be attempted, all vibrational satellites of trans-acrolein arising from vibrational energy levels as high as 700 cm^{-1} have to be assigned.

In addition to the R-branch transitions, *a*-type Q-branch transitions were observed. They arise from the *K*-doubling of the $K_a>1$ levels, and therefore their frequency decreases rapidly with increasing *K*.

2) *The b-type Rotational Spectrum*

The measurements of the *a*-type transitions discussed above are not sufficient to obtain a reliable set of spectroscopic constants. $\Delta K_a \cong 2$, *a*-type transitions are extremely weak and therefore difficult to locate. The rotational constants A, D_K and H_K can thus, with few exceptions, only be determined in cases where *b*-type transitions can be observed for $K_a=2 \leftarrow 1$ or higher. A Fortrat diagram of the *b*-type rotational sub-bands in the spectral region up to 250 GHz is shown in Figure 5. For $K_a>1$ each transition is split by *K*-doubling. The intensity of the branches in each sub-band decreases in the

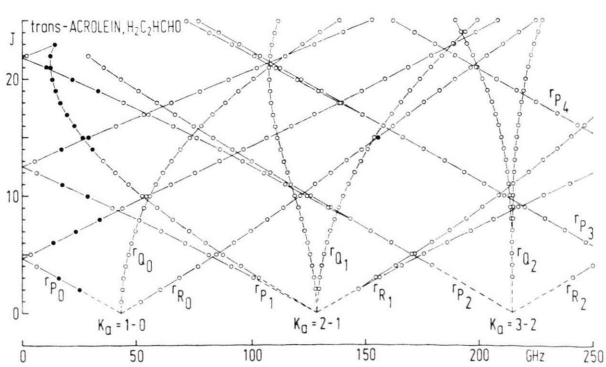

Fig. 5. Fortrat-diagram for the *b*-type transitions of *trans*-acrolein. The solid and open circles indicate measured and predicted line positions, respectively.

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-ACROLEIN in MHz.

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
** A TYPE R BRANCH **							
1(0, 1) -	0(0, 0)	8902.1920(1.0)	8902.1847(0.0004)	0.0073	0.297	0.000	
2(0, 2) -	1(0, 1)	17801.2800(1.0)	17801.3080(0.0007)	-0.0280	0.891	0.297	a
2(1, 1) -	1(1, 0)	18221.1200(1.0)	18221.1621(0.0007)	-0.0421	2.343	1.735	a
2(1, 2) -	1(1, 1)	17387.8200(0.0)	17387.5970(0.0007)	0.2230	2.301	1.721	a, b
3(0, 3) -	2(0, 2)	26694.3500(1.0)	26694.3099(0.0010)	0.0401	1.781	0.891	a
3(1, 2) -	2(1, 1)	27329.7300(1.0)	27329.7694(0.0011)	-0.0394	3.254	2.343	a
3(1, 3) -	2(1, 2)	26079.5000(1.0)	26079.4499(0.0010)	0.0501	3.171	2.301	a
3(2, 1) -	2(2, 0)	26718.7000(0.0)	26718.8091(0.0010)	-0.1091	7.506	6.615	a, b
3(2, 2) -	2(2, 1)	26706.7600(0.0)	26706.6649(0.0010)	0.0951	7.506	6.615	a, b
4(0, 4) -	3(0, 3)		35578.1361(0.0013)		2.968	1.781	
4(1, 3) -	3(1, 2)		36435.9888(0.0014)		4.470	3.254	
4(1, 4) -	3(1, 3)	34768.9670(1.0)	34768.9875(0.0013)	-0.0205	4.331	3.171	
4(2, 2) -	3(2, 1)		35636.7627(0.0013)		8.695	7.506	
4(2, 3) -	3(2, 2)		35606.4101(0.0013)		8.693	7.506	
4(3, 1) -	3(3, 0)		35615.2333(0.0013)		15.848	14.660	
4(3, 2) -	3(3, 1)		35615.1504(0.0013)		15.848	14.660	
5(0, 5) -	4(0, 4)		44449.7496(0.0016)		4.451	2.968	
5(1, 4) -	4(1, 3)		45538.9923(0.0016)		5.989	4.470	
5(1, 5) -	4(1, 4)		43455.4704(0.0016)		5.780	4.331	
6(0, 6) -	5(0, 5)		53306.1503(0.0019)		6.229	4.451	
6(1, 5) -	5(1, 4)		54637.9240(0.0019)		7.811	5.989	
6(1, 6) -	5(1, 5)		52138.1865(0.0019)		7.519	5.780	
7(0, 7) -	6(0, 6)		62144.4119(0.0021)		8.302	6.229	
7(1, 6) -	6(1, 5)		63731.8931(0.0021)		9.937	7.811	
7(1, 7) -	6(1, 6)		60816.4578(0.0021)		9.548	7.519	
8(0, 8) -	7(0, 7)		70961.7241(0.0022)		10.669	8.302	
8(1, 7) -	7(1, 6)		72819.9666(0.0022)		12.366	9.937	
8(1, 8) -	7(1, 7)		69489.6462(0.0023)		11.866	9.548	
9(0, 9) -	8(0, 8)		79755.4620(0.0023)		13.329	10.669	
9(1, 8) -	8(1, 7)	81901.1785(1.0)	81901.1621(0.0023)	0.0164	15.098	12.366	
9(1, 9) -	8(1, 8)		78157.1599(0.0024)		14.473	11.866	
9(2, 7) -	8(2, 6)	80423.8804(1.0)	80423.8724(0.0023)	0.0080	19.115	16.432	
9(2, 8) -	8(2, 7)		80062.7130(0.0022)		19.082	16.411	
10(0,10) -	9(0, 9)	88523.2655(1.0)	88523.2633(0.0024)	0.0022	16.282	13.329	
10(1, 9) -	9(1, 8)	90974.4447(1.0)	90974.4404(0.0023)	0.0043	18.133	15.098	
10(1,10) -	9(1, 9)	86818.4508(1.0)	86818.4580(0.0024)	-0.0072	17.369	14.473	
10(2, 8) -	9(2, 7)	89436.1910(1.0)	89436.1630(0.0023)	0.0280	22.098	19.115	
10(2, 9) -	9(2, 8)	88941.7948(1.0)	88941.7932(0.0023)	0.0016	22.049	19.082	
10(3, 7) -	9(3, 6)	89093.1742(1.0)	89093.1669(0.0022)	0.0073	29.218	26.246	
10(3, 8) -	9(3, 7)	89082.2406(1.0)	89082.2444(0.0022)	-0.0038	29.217	26.246	
10(4, 6) -	9(4, 5)	89059.3515(1.0)	89059.3937(0.0021)	-0.0422	39.230	36.260	
10(4, 7) -	9(4, 6)	89059.3515(1.0)	89059.3042(0.0021)	0.0473	39.230	36.260	
10(5, 5) -	9(5, 4)		89048.2596(0.0020)		52.105	49.134	

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-ACROLEIN in MHz. (CONTINUED)

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
10(5, 6) -	9(5, 5)	89048.2737(1.0)	89048.2592(0.0020)	0.0145	52.105	49.134	
10(6, 4) -	9(6, 3)		89043.5428(0.0020)		67.838	64.868	
10(6, 5) -	9(6, 4)	89043.5470(1.0)	89043.5428(0.0020)	0.0042	57.838	64.868	
10(7, 3) -	9(7, 2)		89041.8815(0.0020)		86.428	83.458	
10(7, 4) -	9(7, 3)	89041.9164(1.0)	89041.8815(0.0020)	0.0349	86.428	83.458	
10(8, 2) -	9(8, 1)		89041.9685(0.0023)		107.874	104.904	
10(8, 3) -	9(8, 2)	89041.9166(1.0)	89041.9685(0.0023)	-0.0519	107.874	104.904	
10(9, 1) -	9(9, 0)		89043.1997(0.0027)		132.173	129.203	
10(9, 2) -	9(9, 1)	89043.1769(1.0)	89043.1997(0.0027)	-0.0229	132.173	129.203	
11(0,11) -	10(0,10)	97263.1342(1.0)	97263.1201(0.0024)	0.0141	19.526	16.282	
11(1,10) -	10(1, 9)	100038.6989(1.0)	100038.6984(0.0023)	0.0005	21.470	18.133	
11(1,11) -	10(1,10)	95473.0534(1.0)	95473.0561(0.0024)	-0.0027	20.554	17.369	
11(2, 9) -	10(2, 8)	98470.8301(1.0)	98470.8234(0.0023)	0.0067	25.383	22.098	
11(2,10) -	10(2, 9)	97815.5921(1.0)	97815.5899(0.0023)	0.0022	25.311	22.049	
11(3, 8) -	10(3, 7)	98019.0443(1.0)	98019.0511(0.0022)	-0.0068	32.488	29.218	
11(3, 9) -	10(3, 8)	98001.3206(1.0)	98001.3199(0.0022)	0.0007	32.486	29.217	
11(4, 7) -	10(4, 6)		97972.2150(0.0021)		42.498	39.230	
11(4, 8) -	10(4, 7)		97972.0362(0.0021)		42.498	39.230	
11(5, 6) -	10(5, 5)		97957.0021(0.0020)		55.372	52.105	
11(5, 7) -	10(5, 6)	97957.0029(1.0)	97957.0012(0.0020)	0.0017	55.372	52.105	
11(6, 5) -	10(6, 4)		97950.2827(0.0020)		71.105	67.838	
11(6, 6) -	10(6, 5)	97950.2859(1.0)	97950.2827(0.0020)	0.0032	71.105	67.838	
11(7, 4) -	10(7, 3)		97947.5510(0.0020)		89.696	86.428	
11(7, 5) -	10(7, 4)	97947.5495(1.0)	97947.5510(0.0020)	-0.0015	89.696	86.428	
11(8, 3) -	10(8, 2)		97947.0670(0.0023)		111.141	107.874	
11(8, 4) -	10(8, 3)	97947.0545(1.0)	97947.0670(0.0023)	-0.0125	111.141	107.874	
11(9, 2) -	10(9, 1)		97948.0270(0.0027)		135.440	132.173	
11(9, 3) -	10(9, 2)		97948.0270(0.0027)		135.440	132.173	
11(10, 1) -	10(10, 0)		97950.0160(0.0033)		162.590	159.323	
11(10, 2) -	10(10, 1)		97950.0160(0.0033)		162.590	159.323	
12(0,12) -	11(0,11)	105973.4634(1.0)	105973.4774(0.0024)	-0.0140	23.061	19.526	
12(1,11) -	11(1,10)	103092.7973(1.0)	103092.7623(0.0023)	0.0350	25.109	21.470	
12(1,12) -	11(1,11)	104120.5353(1.0)	104120.5302(0.0024)	0.0051	24.027	20.554	
12(2,10) -	11(2, 9)		107528.8401(0.0022)		28.970	25.383	
12(2,11) -	11(2,10)		106683.5853(0.0022)		28.870	25.311	
12(3, 9) -	11(3, 8)	106950.3384(1.0)	106950.3832(0.0021)	0.0152	36.055	32.488	
12(3,10) -	11(3, 9)	106922.8513(1.0)	106922.8372(0.0021)	0.0141	36.053	32.486	
12(4, 8) -	11(4, 7)	106887.0254(1.0)	106887.0265(0.0020)	-0.0011	46.064	42.498	
12(4, 9) -	11(4, 8)	106886.6818(1.0)	106886.6912(0.0020)	-0.0094	46.064	42.498	
12(5, 7) -	11(5, 6)	106866.3626(1.0)	106866.3637(0.0019)	-0.0011	58.937	55.372	
12(5, 8) -	11(5, 7)	106866.8626(1.0)	106866.8617(0.0019)	0.0009	58.937	55.372	
12(6, 6) -	11(6, 5)		106857.7038(0.0019)		74.670	71.105	
12(6, 7) -	11(6, 6)	106857.6955(1.0)	106857.7037(0.0019)	-0.0082	74.670	71.105	
12(7, 5) -	11(7, 4)		106853.6433(0.0020)		93.260	89.696	
12(7, 6) -	11(7, 5)	106853.6420(1.0)	106853.6433(0.0020)	-0.0013	93.260	89.696	
12(8, 4) -	11(8, 3)		106852.4227(0.0022)		114.706	111.141	
12(8, 5) -	11(8, 4)		106852.4227(0.0022)		114.706	111.141	
12(9, 3) -	11(9, 2)		106852.9991(0.0026)		139.005	135.440	
12(9, 4) -	11(9, 3)		106852.9991(0.0026)		139.005	135.440	
12(10, 2) -	11(10, 1)		106854.8338(0.0032)		166.154	162.590	
12(10, 3) -	11(10, 2)	106854.8323(1.0)	106854.8338(0.0032)	-0.0015	166.154	162.590	
12(11, 1) -	11(11, 0)		106857.6247(0.0040)		196.152	192.587	
12(11, 2) -	11(11, 1)		106857.6247(0.0040)		196.152	192.587	

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-ACROLEIN in MHz (CONTINUED)

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
13(0,13)	12(0,12)	114653.3256(1.0)	114653.3284(0.0023)	-0.0028	26.885	23.061	
13(1,12)	12(1,11)	118135.3766(1.0)	118135.3813(0.0022)	-0.0047	29.049	25.109	
13(1,13)	12(1,12)	112760.5190(1.0)	112760.5195(0.0023)	-0.0006	27.788	24.027	
13(2,11)	12(2,10)	116610.6359(1.0)	116610.6450(0.0021)	-0.0091	32.859	28.970	
13(2,12)	12(2,11)	115545.2687(1.0)	115545.2665(0.0021)	0.0021	32.724	28.870	
13(3,10)	12(3, 9)	115887.9710(1.0)	115887.9828(0.0020)	-0.0118	39.921	35.055	
13(3,11)	12(3,10)	115846.6983(1.0)	115846.7320(0.0020)	-0.0337	39.917	36.053	
13(4, 9)	12(4, 8)	115804.0183(1.0)	115804.0260(0.0019)	-0.0077	49.927	46.064	
13(4,10)	12(4, 9)	115803.4103(1.0)	115803.4304(0.0019)	-0.0201	49.926	46.064	
13(5, 8)	12(5, 7)	115777.9429(1.0)	115777.9462(0.0018)	-0.0033	62.799	58.937	
13(5, 9)	12(5, 8)	115777.9429(1.0)	115777.9419(0.0018)	0.0010	62.799	58.937	
13(6, 7)	12(6, 6)		115765.8677(0.0018)		78.531	74.670	
13(6, 8)	12(6, 7)	115765.8974(1.0)	115765.8677(0.0018)	0.0297	78.531	74.670	
13(7, 6)	12(7, 5)		115760.1966(0.0019)		97.121	93.260	
13(7, 7)	12(7, 6)	115760.2041(1.0)	115760.1966(0.0019)	0.0075	97.121	93.260	
13(8, 5)	12(8, 4)		115758.0590(0.0021)		118.567	114.706	
13(8, 6)	12(8, 5)	115758.0849(1.0)	115758.0590(0.0021)	0.0259	118.567	114.706	
13(9, 4)	12(9, 3)		115758.1288(0.0025)		142.866	139.005	
13(9, 5)	12(9, 4)	115758.0959(1.0)	115758.1288(0.0025)	-0.0329	142.866	139.005	
13(10, 3)	12(10, 2)		115759.7220(0.0031)		170.015	166.154	
13(10, 4)	12(10, 3)	115759.7054(1.0)	115759.7220(0.0031)	-0.0166	170.015	166.154	
13(11, 2)	12(11, 1)		115762.4546(0.0038)		200.013	196.152	
13(11, 3)	12(11, 2)	115762.4664(1.0)	115762.4546(0.0038)	0.0118	200.013	196.152	
13(12, 1)	12(12, 0)		115766.0971(0.0048)		232.855	228.994	
13(12, 2)	12(12, 1)		115766.0971(0.0048)		232.855	228.994	
14(0,14)	13(0,13)	123302.2920(1.0)	123302.2965(0.0022)	-0.0045	30.998	26.885	
14(1,13)	13(1,12)		127165.2228(0.0022)		33.291	29.049	
14(1,14)	13(1,13)	121392.7360(1.0)	121392.7302(0.0022)	0.0058	31.837	27.788	
14(2,12)	13(2,11)	125716.0380(1.0)	125716.0319(0.0021)	0.0061	37.053	32.859	
14(2,13)	13(2,12)	124400.1337(1.0)	124400.1278(0.0021)	0.0059	36.874	32.724	
14(3,11)	13(3,10)	124832.7602(1.0)	124832.7518(0.0019)	0.0084	44.085	39.921	
14(3,12)	13(3,11)	124772.8729(1.0)	124772.8743(0.0019)	-0.0014	44.079	39.917	
14(4,10)	13(4, 9)	124723.4197(1.0)	124723.4202(0.0018)	-0.0005	54.087	49.927	
14(4,11)	13(4,10)	124722.4159(1.0)	124722.4084(0.0018)	0.0075	54.087	49.926	
14(5, 9)	13(5, 8)	124690.3481(1.0)	124690.3521(0.0017)	-0.0040	66.958	62.799	
14(5,10)	13(5, 9)	124690.3481(1.0)	124690.3434(0.0017)	0.0047	66.958	62.799	
14(6, 8)	13(6, 7)	124674.8354(1.0)	124674.8363(0.0017)	-0.0009	82.690	78.531	
14(6, 9)	13(6, 8)		124674.8363(0.0017)		82.690	78.531	
14(7, 7)	13(7, 6)		124667.2493(0.0018)		101.280	97.121	
14(7, 8)	13(7, 7)	124667.2534(1.0)	124667.2493(0.0018)	0.0041	101.280	97.121	
14(8, 6)	13(8, 5)		124663.9989(0.0020)		122.725	118.567	
14(8, 7)	13(8, 6)	124663.9955(1.0)	124663.9989(0.0020)	-0.0034	122.725	118.567	
14(9, 5)	13(9, 4)		124663.4293(0.0024)		147.024	142.866	
14(9, 6)	13(9, 5)	124663.4082(1.0)	124663.4293(0.0024)	-0.0211	147.024	142.866	
14(10, 4)	13(10, 3)		124664.6862(0.0029)		174.174	170.015	
14(10, 5)	13(10, 4)	124664.6914(1.0)	124664.6862(0.0029)	0.0052	174.174	170.015	
14(11, 3)	13(11, 2)		124667.2910(0.0035)		204.171	200.013	
14(11, 4)	13(11, 3)		124667.2910(0.0035)		204.171	200.013	
14(12, 2)	13(12, 1)		124670.9571(0.0044)		237.014	232.855	
14(12, 3)	13(12, 2)	124670.9521(1.0)	124670.9571(0.0044)	-0.0050	237.014	232.855	
14(13, 1)	13(13, 0)		124675.5038(0.0055)		272.698	268.539	
14(13, 2)	13(13, 1)	124675.5256(1.0)	124675.5038(0.0055)	0.0218	272.698	268.539	

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-ACROLEIN in MHz (CONTINUED)

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
15(0,15) -	14(0,14)	131920.6725(1.0)	131920.6898(0.0022)	-0.0173	35.399	30.998	
15(1,14) -	14(1,13)	136180.8715(1.0)	136180.8679(0.0022)	0.0036	37.833	33.291	
15(1,15) -	14(1,14)	130016.9483(1.0)	130016.9350(0.0022)	0.0133	36.174	31.837	
15(2,13) -	14(2,12)	134844.0802(1.0)	134844.0992(0.0021)	-0.0190	41.551	37.053	
15(2,14) -	14(2,13)	133247.6642(1.0)	133247.6708(0.0021)	-0.0066	41.318	36.874	
15(3,12) -	14(3,11)	133785.6641(1.0)	133785.6776(0.0019)	-0.0135	48.547	44.085	
15(3,13) -	14(3,12)	133701.0640(1.0)	133701.0665(0.0019)	-0.0026	48.539	44.079	
15(4,11) -	14(4,10)	133645.4122(1.0)	133645.4260(0.0017)	-0.0138	58.545	54.087	
15(4,12) -	14(4,11)	133643.7665(1.0)	133643.7719(0.0017)	-0.0054	58.545	54.087	
15(5,10) -	14(5, 9)	133604.1836(1.0)	133604.1840(0.0016)	-0.0004	71.414	66.958	
15(5,11) -	14(5,10)	133604.1836(1.0)	133604.1676(0.0016)	0.0160	71.414	66.958	
15(6, 9) -	14(6, 8)		133584.6714(0.0016)		87.146	82.690	
15(6,10) -	14(6, 9)	133584.6612(1.0)	133584.6713(0.0016)	-0.0101	87.146	82.690	
15(7, 8) -	14(7, 7)		133574.8396(0.0017)		105.735	101.280	
15(7, 9) -	14(7, 8)	133574.8395(1.0)	133574.8395(0.0017)	-0.0001	105.735	101.280	
15(8, 7) -	14(8, 6)		133570.2658(0.0019)		127.181	122.725	
15(8, 8) -	14(8, 7)	133570.2680(1.0)	133570.2658(0.0019)	0.0022	127.181	122.725	
15(9, 6) -	14(9, 5)		133568.9134(0.0023)		151.480	147.024	
15(9, 7) -	14(9, 6)	133568.9147(1.0)	133568.9134(0.0023)	0.0013	151.480	147.024	
15(10, 5) -	14(10, 4)		133569.7323(0.0027)		178.629	174.174	
15(10, 6) -	14(10, 5)	133569.7253(1.0)	133569.7323(0.0027)	-0.0070	178.629	174.174	
15(11, 4) -	14(11, 3)		133572.1341(0.0032)		208.627	204.171	
15(11, 5) -	14(11, 4)	133572.1343(1.0)	133572.1340(0.0032)	0.0003	208.627	204.171	
15(12, 3) -	14(12, 2)		133575.7569(0.0039)		241.469	237.014	
15(12, 4) -	14(12, 3)	133575.7736(1.0)	133575.7669(0.0039)	0.0067	241.469	237.014	
15(13, 2) -	14(13, 1)		133580.4091(0.0048)		277.154	272.698	
15(13, 3) -	14(13, 2)	133580.4046(1.0)	133580.4091(0.0048)	-0.0045	277.154	272.698	
15(14, 1) -	14(14, 0)		133585.9141(0.0063)		315.676	311.220	
15(14, 2) -	14(14, 1)	133585.9042(1.0)	133585.9141(0.0063)	-0.0099	315.676	311.220	
16(0,16) -	15(0,15)		140509.5178(0.0023)		40.086	35.399	
16(1,15) -	15(1,14)	145180.8185(1.0)	145180.8103(0.0025)	0.0082	42.676	37.833	
16(1,16) -	15(1,15)		138632.9754(0.0022)		40.798	36.174	
16(2,14) -	15(2,13)	143993.2241(1.0)	143993.2311(0.0022)	-0.0070	46.354	41.551	
16(2,15) -	15(2,14)	142087.4021(1.0)	142087.4079(0.0022)	-0.0057	46.058	41.318	
16(3,13) -	15(3,12)	142747.8326(1.0)	142747.8348(0.0020)	-0.0022	53.309	48.547	
16(3,14) -	15(3,13)	142631.0494(1.0)	142631.0441(0.0020)	0.0053	53.297	48.539	
16(4,12) -	15(4,11)	142570.2481(1.0)	142570.2738(0.0018)	-0.0257	63.300	58.545	
16(4,13) -	15(4,12)	142567.6413(1.0)	142567.6575(0.0018)	-0.0162	63.300	58.545	
16(5,11) -	15(5,10)	142519.5124(1.0)	142519.5454(0.0016)	-0.0330	76.168	71.414	
16(5,12) -	15(5,11)	142519.5124(1.0)	142519.5156(0.0016)	-0.0032	76.168	71.414	
16(6,10) -	15(6, 9)		142495.4345(0.0016)		91.899	87.146	
16(6,11) -	15(6,10)	142495.4439(1.0)	142495.4344(0.0016)	0.0095	91.899	87.146	
16(7, 9) -	15(7, 8)		142483.0055(0.0017)		110.488	105.735	
16(7,10) -	15(7, 9)	142483.0108(1.0)	142483.0055(0.0017)	0.0053	110.488	105.735	
16(8, 8) -	15(8, 7)		142476.8827(0.0019)		131.933	127.181	
16(8, 9) -	15(8, 8)	142476.9060(1.0)	142476.8827(0.0019)	0.0233	131.933	127.181	
16(9, 7) -	15(9, 6)		142474.5942(0.0022)		156.232	151.480	
16(9, 8) -	15(9, 7)	142474.5804(1.0)	142474.5942(0.0022)	-0.0138	156.232	151.480	
16(10, 6) -	15(10, 5)		142474.8659(0.0025)		183.382	178.629	
16(10, 7) -	15(10, 6)	142474.8719(1.0)	142474.8659(0.0025)	0.0060	183.382	178.629	
16(11, 5) -	15(11, 4)		142476.9842(0.0029)		213.379	208.627	
16(11, 6) -	15(11, 5)		142476.9842(0.0029)		213.379	208.627	
16(12, 4) -	15(12, 3)		142480.5228(0.0034)		246.222	241.469	
16(12, 5) -	15(12, 4)	142480.5188(1.0)	142480.5228(0.0034)	-0.0040	246.222	241.469	

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-ACROLEIN in MHz (CONTINUED)

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
16(13, 3)	15(13, 2)		142485.2130(0.0041)		281.906	277.154	
16(13, 4)	15(13, 3)	142485.2149(1.0)	142485.2130(0.0041)	0.0019	281.906	277.154	
16(14, 2)	15(14, 1)		142490.8779(0.0053)		320.429	315.676	
16(14, 3)	15(14, 2)	142490.8897(1.0)	142490.8779(0.0053)	0.0118	320.429	315.676	
16(15, 1)	15(15, 0)		142497.3961(0.0071)		361.785	357.032	
16(15, 2)	15(15, 1)		142497.3961(0.0071)		361.785	357.032	
17(0,17)	16(0,16)	149070.4679(1.0)	149070.4612(0.0026)	0.0067	45.058	40.086	
17(1,16)	16(1,15)		154153.4570(0.0030)		47.818	42.676	
17(1,17)	16(1,16)		147240.7600(0.0025)		45.710	40.798	
17(2,15)	16(2,14)	153161.1508(1.0)	153161.1244(0.0027)	0.0264	51.463	46.354	
17(2,16)	16(2,15)	150918.8439(1.0)	150918.8631(0.0026)	-0.0192	51.092	46.058	
17(3,14)	16(3,13)	151720.3644(1.0)	151720.3838(0.0023)	-0.0194	58.370	53.309	
17(3,15)	16(3,14)	151562.4663(1.0)	151562.4746(0.0024)	-0.0083	58.352	53.297	
17(4,13)	16(4,12)	151498.1790(1.0)	151498.2099(0.0021)	-0.0309	68.354	63.300	
17(4,14)	16(4,13)	151494.1665(1.0)	151494.1901(0.0021)	-0.0236	68.354	63.300	
17(5,12)	16(5,11)	151436.5082(1.0)	151436.5405(0.0019)	-0.0323	81.220	76.168	
17(5,13)	16(5,12)	151436.5082(1.0)	151436.4884(0.0019)	0.0198	81.220	76.168	
17(6,11)	16(6,10)		151407.1880(0.0018)		96.949	91.899	
17(6,12)	16(6,11)	151407.1669(1.0)	151407.1876(0.0018)	-0.0207	96.949	91.899	
17(7,10)	16(7, 9)		151391.7853(0.0019)		115.538	110.488	
17(7,11)	16(7,10)	151391.7784(1.0)	151391.7853(0.0019)	-0.0069	115.538	110.488	
17(8, 9)	16(8, 8)		151383.8727(0.0021)		136.983	131.933	
17(8,10)	16(8, 9)	151383.8634(1.0)	151383.8727(0.0021)	-0.0093	136.983	131.933	
17(9, 8)	16(9, 7)		151380.4845(0.0024)		161.282	156.232	
17(9, 9)	16(9, 8)	151380.4848(1.0)	151380.4845(0.0024)	0.0003	161.282	156.232	
17(10, 7)	16(10, 6)		151380.0927(0.0026)		188.431	183.382	
17(10, 8)	16(10, 7)	151380.0770(1.0)	151380.0927(0.0026)	-0.0157	188.431	183.382	
17(11, 6)	16(11, 5)		151381.8418(0.0029)		218.429	213.379	
17(11, 7)	16(11, 6)	151381.8471(1.0)	151381.8418(0.0029)	0.0053	218.429	213.379	
17(12, 5)	16(12, 4)		151385.2211(0.0031)		251.272	246.222	
17(12, 6)	16(12, 5)	151385.2240(1.0)	151385.2211(0.0031)	0.0029	251.272	246.222	
17(13, 4)	16(13, 3)		151389.9088(0.0034)		286.956	281.906	
17(13, 5)	16(13, 4)	151389.9289(1.0)	151389.9088(0.0034)	0.0201	286.956	281.906	
17(14, 3)	16(14, 2)		151395.6935(0.0043)		325.479	320.429	
17(14, 4)	16(14, 3)	151395.6928(1.0)	151395.6935(0.0043)	-0.0007	325.479	320.429	
18(0,18)	17(0,17)		157605.7931(0.0031)		50.315	45.058	
18(1,17)	17(1,16)		163127.1338(0.0037)		53.260	47.818	
18(1,18)	17(1,17)	155840.2941(1.0)	155840.2630(0.0031)	0.0311	50.908	45.710	
18(2,16)	17(2,15)		162344.8641(0.0034)		56.878	51.463	
18(2,17)	17(2,16)		159741.5757(0.0033)		56.420	51.092	
18(3,15)	17(3,14)		160704.5659(0.0029)		63.730	58.370	
18(3,16)	17(3,15)	160494.9688(1.0)	160494.9612(0.0030)	0.0076	63.706	58.352	
18(4,14)	17(4,13)	160429.5240(1.0)	160429.5006(0.0026)	0.0234	73.705	68.354	
18(4,15)	17(4,14)	160423.5180(1.0)	160423.4799(0.0026)	0.0381	73.705	68.354	
18(5,13)	17(5,12)		160355.2749(0.0024)		86.569	81.220	
18(5,14)	17(5,13)		160355.1867(0.0024)		86.569	81.220	
18(6,12)	17(6,11)		160319.9933(0.0022)		102.297	96.949	
18(6,13)	17(6,12)	160320.0089(1.0)	160319.9925(0.0022)	0.0164	102.297	96.949	
18(7,11)	17(7,10)		160301.2172(0.0023)		120.885	115.538	
18(7,12)	17(7,11)	160301.2243(1.0)	160301.2172(0.0023)	0.0071	120.885	115.538	
18(8,10)	17(8, 9)		160291.2589(0.0025)		142.330	136.983	
18(8,11)	17(8,10)	160291.2686(1.0)	160291.2589(0.0025)	0.0097	142.330	136.983	
18(9, 9)	17(9, 8)		160286.5972(0.0028)		166.628	161.282	

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-ACROLEIN in MHz (CONTINUED)

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
18(9,10)	17(9, 9)	160286.6496(1.0)	160286.5972(0.0028)	0.0524	166.628	161.282	
18(10, 8)	17(10, 7)		160285.4183(0.0031)		193.778	188.431	
18(10, 9)	17(10, 8)	160285.4210(1.0)	160285.4183(0.0031)	0.0027	193.778	188.431	
18(11, 7)	17(11, 6)		160286.7072(0.0033)		223.776	218.429	
18(12, 7)	17(12, 6)	160289.8618(1.0)	160289.8580(0.0034)	0.0038	256.618	251.272	
19(0,19)	18(0,18)	166118.2658(1.0)	166118.2574(0.0038)	0.0084	55.856	50.315	
19(1,18)	18(1,17)	172070.0816(1.0)	172070.0946(0.0047)	-0.0130	58.999	53.260	
19(1,19)	18(1,18)	164431.5294(1.0)	164431.5214(0.0038)	0.0080	56.393	50.908	
19(2,17)	18(2,16)	171541.0514(1.0)	171541.0410(0.0043)	0.0104	62.600	56.878	
19(2,18)	18(2,17)	168555.1158(1.0)	168555.1016(0.0041)	0.0142	62.043	56.420	
19(3,16)	18(3,15)		169701.6922(0.0037)		69.391	63.730	
19(3,17)	18(3,16)		169428.0448(0.0038)		69.357	63.706	
19(4,15)	18(4,14)	169364.4262(1.0)	169364.4353(0.0034)	-0.0091	79.355	73.705	
19(4,16)	18(4,15)	169355.6264(1.0)	169355.6204(0.0034)	0.0060	79.354	73.705	
19(5,14)	18(5,13)		169275.8554(0.0031)		92.215	86.569	
19(5,15)	18(5,14)		169275.7107(0.0031)		92.215	86.569	
19(6,13)	18(6,12)		169233.9126(0.0029)		107.942	102.297	
19(6,14)	18(6,13)	169233.9128(1.0)	169233.9112(0.0029)	0.0016	107.942	102.297	
19(7,12)	18(7,11)		169211.3392(0.0029)		126.529	120.885	
19(7,13)	18(7,12)	169211.3287(1.0)	169211.3392(0.0029)	-0.0105	126.529	120.885	
19(8,11)	18(8,10)		169199.0644(0.0031)		147.973	142.330	
19(8,12)	18(8,11)	169199.0567(1.0)	169199.0644(0.0031)	-0.0077	147.973	142.330	
19(9,10)	18(9, 9)		169192.9452(0.0035)		172.272	166.628	
19(9,11)	18(9,10)	169192.9566(1.0)	169192.9452(0.0035)	0.0114	172.272	166.628	
19(10, 9)	18(10, 8)		169190.8483(0.0039)		199.421	193.778	
19(10,10)	18(10, 9)	169190.8510(1.0)	169190.8483(0.0039)	0.0027	199.421	193.778	
19(11, 8)	18(11, 7)		169191.5806(0.0042)		229.419	223.776	
19(11, 9)	18(11, 8)	169191.5902(1.0)	169191.5805(0.0042)	0.0096	229.419	223.776	
19(12, 7)	18(12, 6)		169194.4299(0.0044)		262.262	256.618	
19(12, 8)	18(12, 7)	169194.4299(1.0)	169194.4299(0.0044)	0.0000	262.262	256.618	
19(13, 6)	18(13, 5)		169198.9485(0.0044)		297.947	292.303	
19(13, 7)	18(13, 6)		169198.9485(0.0044)		297.947	292.303	
19(14, 5)	18(14, 4)		169204.8425(0.0044)		336.470	330.826	
19(14, 6)	18(14, 5)	169204.8577(1.0)	169204.8425(0.0044)	0.0152	336.470	330.826	
19(15, 4)	18(15, 3)		169211.9111(0.0048)		377.827	372.183	
19(15, 5)	18(15, 4)		169211.9111(0.0048)		377.827	372.183	
19(16, 3)	18(16, 2)		169220.0127(0.0062)		422.014	416.369	
19(16, 4)	18(16, 3)	169220.0034(1.0)	169220.0127(0.0062)	-0.0093	422.014	416.369	
19(17, 2)	18(17, 1)		169229.0440(0.0089)		469.026	463.381	
19(17, 3)	18(17, 2)		169229.0440(0.0089)		469.026	463.381	
19(18, 1)	18(18, 0)		169238.9276(0.0129)		518.860	513.214	
19(18, 2)	18(18, 1)		169238.9275(0.0129)		518.860	513.214	
20(0,20)	19(0,19)		174610.9154(0.0048)		61.681	55.856	
20(1,19)	19(1,18)		180990.5377(0.0058)		65.037	58.999	
20(1,20)	19(1,19)		173014.6312(0.0048)		62.164	56.393	
20(2,18)	19(2,17)		180745.9012(0.0055)		68.629	62.600	
20(2,19)	19(2,18)		177359.0164(0.0052)		67.959	62.043	
20(3,17)	19(3,16)		178713.1281(0.0048)		75.352	69.391	
20(3,18)	19(3,17)		178361.2081(0.0049)		75.307	69.357	
20(4,16)	19(4,15)	178303.3146(1.0)	178303.3311(0.0043)	-0.0165	85.302	79.355	
20(4,17)	19(4,16)	178290.6905(1.0)	178290.6854(0.0043)	0.0051	85.301	79.354	
20(5,15)	19(5,14)		178198.3912(0.0039)		98.159	92.215	
20(5,16)	19(5,15)		178198.1599(0.0039)		98.159	92.215	

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-ACROLEIN in MHz (CONTINUED)

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
20(6,15) -	19(6,13)	178149.0114(1.0)	178149.0026(0.0037)	0.0088	113.884	107.942	
20(7,13) -	19(7,12) }		178122.1895(0.0037)		132.471	126.529	
20(7,14) -	19(7,13) }	178122.1740(1.0)	178122.1895(0.0037)	-0.0155	132.471	126.529	
20(8,13) -	19(8,12)	178107.3127(1.0)	178107.3122(0.0040)	0.0005	153.914	147.973	
20(9,12) -	19(9,11)	178099.5501(1.0)	178099.5412(0.0045)	0.0089	178.213	172.272	
20(10,11) -	19(10,10)	178096.3789(1.0)	178096.3883(0.0051)	-0.0094	205.362	199.421	
20(11, 9) -	19(11, 8)		178096.4622(0.0056)		235.360	229.419	
20(12, 9) -	19(12, 8)	178098.9124(1.0)	178098.9328(0.0060)	-0.0204	268.203	262.262	
20(13, 8) -	19(13, 7)		178103.2786(0.0062)		303.888	297.947	
20(14, 7) -	19(14, 6)	178109.1526(1.0)	178109.1572(0.0063)	-0.0046	342.411	336.470	
20(15, 6) -	19(15, 5)	178116.3249(1.0)	178116.3353(0.0065)	-0.0104	383.768	377.827	
20(16, 5) -	19(16, 4)		178124.6484(0.0073)		427.955	422.014	
20(17, 4) -	19(17, 3)	178133.9635(1.0)	178133.9768(0.0092)	-0.0133	474.968	469.026	
20(18, 3) -	19(18, 2)	178144.2420(1.0)	178144.2311(0.0126)	0.0109	524.802	518.860	
20(19, 1) -	19(19, 0)		178155.3426(0.0175)		577.451	571.508	
** A TYPE Q BRANCH **							
1(1, 0) -	1(1, 1)		416.7855(0.0001)		1.735	1.721	
2(1, 1) -	2(1, 2)		1250.3506(0.0004)		2.343	2.301	
3(1, 2) -	3(1, 3)		2500.6701(0.0007)		3.254	3.171	
4(1, 3) -	4(1, 4)		4167.6715(0.0012)		4.470	4.331	
5(1, 4) -	5(1, 5)		6251.1934(0.0017)		5.989	5.780	
6(1, 5) -	6(1, 6)	8750.9420(1.0)	8750.9309(0.0023)	0.0111	7.811	7.519	
7(1, 6) -	7(1, 7)	11666.3750(1.0)	11666.3663(0.0029)	0.0087	9.937	9.548	
8(1, 7) -	8(1, 8)	14996.7025(1.0)	14996.6867(0.0036)	0.0158	12.366	11.866	
9(1, 8) -	9(1, 9)	18740.6600(1.0)	18740.6890(0.0043)	-0.0290	15.098	14.473	
10(1, 9) -	10(1,10)	22896.7200(1.0)	22896.6714(0.0049)	0.0486	18.133	17.369	
11(1,10) -	11(1,11)	27462.3400(1.0)	27462.3137(0.0055)	0.0263	21.470	20.554	
12(1,11) -	12(1,12)	32434.5360(1.0)	32434.5458(0.0060)	-0.0098	25.109	24.027	
9(2, 7) -	9(2, 8)		996.5586(0.0007)		19.115	19.082	
10(2, 8) -	10(2, 9)		1490.9284(0.0010)		22.098	22.049	
11(2, 9) -	11(2,10)		2146.1620(0.0014)		25.383	25.311	
12(2,10) -	12(2,11)		2991.4168(0.0018)		28.970	28.870	
13(2,11) -	13(2,12)		4056.7952(0.0023)		32.859	32.724	
14(2,12) -	14(2,13)		5372.6993(0.0028)		37.053	36.874	
15(2,13) -	15(2,14)		6969.1277(0.0034)		41.551	41.318	
16(2,14) -	16(2,15)	8874.9710(1.0)	8874.9510(0.0040)	0.0200	46.354	46.058	
17(2,15) -	17(2,16)	11117.2310(1.0)	11117.2122(0.0045)	0.0188	51.463	51.092	
18(2,16) -	18(2,17)	13720.5085(1.0)	13720.5005(0.0051)	0.0080	56.878	56.420	
19(2,17) -	19(2,18)	16706.4525(1.0)	16706.4399(0.0056)	0.0126	62.600	62.043	
20(2,18) -	20(2,19)	20093.2750(1.0)	20093.3247(0.0062)	-0.0497	68.629	67.959	
28(3,25) -	28(3,26)	9348.4450(1.0)	9348.4369(0.0103)	0.0081	133.935	133.623	
29(3,26) -	29(3,27)	11356.9120(1.0)	11356.9105(0.0126)	0.0014	142.630	142.251	
** B TYPE P BRANCH **							
1(1, 1) -	2(0, 2)	24892.5800(1.0)	24892.5730(0.0038)	0.0070	1.721	0.891	a
2(1, 2) -	3(0, 3)	15585.8620(1.0)	15585.8601(0.0038)	0.0019	2.301	1.781	a
3(1, 3) -	4(0, 4)		6087.1738(0.0038)		3.171	2.968	
5(0, 5) -	4(1, 4)		3593.5883(0.0038)		4.451	4.331	
6(0, 6) -	5(1, 5)	13444.2685(1.0)	13444.2688(0.0039)	-0.0003	6.229	5.780	a
7(0, 7) -	6(1, 6)	23450.4600(1.0)	23450.4943(0.0040)	-0.0343	8.302	7.519	a

TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF TRANS-ACROLEIN in MHz (CONTINUED)

TRANSITION UPPER STATE	TRANSITION LOWER STATE	OBSERVED FREQUENCY (WEIGHT)	CALCULATED FREQUENCY (STANDARD DEVIATION)	OBS.-CALC.	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE	REMARKS
8(0, 8) -	7(1, 7)	33595.6840(0.0)	33595.7606(0.0041)	-0.0766	10.669	9.548	b
9(2, 8) -	10(1, 9)	28455.8320(1.0)	28455.7832(0.0076)	0.0488	19.082	18.133	
10(2, 9) -	11(1,10)	17358.8660(1.0)	17358.8779(0.0077)	-0.0119	22.049	21.470	
11(2,10) -	12(1,11)		6081.7056(0.0078)		25.311	25.109	
13(1,12) -	12(2,11)		5370.0905(0.0080)		29.049	28.870	
14(1,13) -	13(2,12)	16990.3600(1.0)	16990.0467(0.0081)	0.0133	33.291	32.724	
15(1,14) -	14(2,13)	28770.6940(0.0)	28770.7868(0.0083)	-0.0928	37.833	36.874	b
13(2,11) -	14(1,14)	30648.6100(1.0)	30648.6486(0.0079)	-0.0386	32.859	31.837	
14(2,12) -	15(1,15)	26347.6980(1.0)	26347.7455(0.0077)	-0.0475	37.053	36.174	
15(2,13) -	16(1,16)	22558.7170(0.0)	22558.8692(0.0075)	-0.1522	41.551	40.798	b
16(2,14) -	17(1,17)	19311.2360(0.0)	19311.3403(0.0071)	-0.1043	46.354	45.710	b
17(2,15) -	18(1,18)	16632.2180(1.0)	16632.2017(0.0067)	0.0163	51.463	50.908	
18(2,16) -	19(1,19)	14545.5470(1.0)	14545.5444(0.0066)	0.0026	56.878	55.393	
19(2,17) -	20(1,20)	13071.9760(1.0)	13071.9542(0.0073)	0.0218	62.600	62.164	
20(2,18) -	21(1,21)	12228.1140(1.0)	12228.1129(0.0093)	0.0011	68.629	68.221	
21(2,19) -	22(1,22)	12026.5630(1.0)	12026.5673(0.0127)	-0.0043	74.965	74.564	
18(3,16) -	19(2,17)	33144.9150(1.0)	33144.9201(0.0099)	-0.0051	63.706	62.600	
19(3,17) -	20(2,18)	21827.0650(1.0)	21827.0637(0.0093)	0.0013	69.357	68.629	
20(3,18) -	21(2,19)	10232.7650(1.0)	10232.7630(0.0090)	0.0020	75.307	74.965	
22(2,20) -	21(3,19)		1639.2593(0.0096)		81.609	81.554	
23(2,21) -	22(3,20)	13787.0510(1.0)	13787.0580(0.0109)	-0.0070	88.559	88.099	
** B TYPE R BRANCH **							
15(1,15) -	14(0,14)	155162.3301(1.0)	155162.3269(0.0056)	0.0032	36.174	30.998	

a) Reported in Ref. (7)

b) Not used in the fit poor measurement

order: Q, R and P, where the Q branch shows roughly the combined intensity of the R and P branch transitions. With the exception of the $^rP_1$ and $^rQ_1$ branch this particular *b*-type spectrum shows very little band head formation. For some high-J $^rP_1$-branch transitions the formation of the band head, structure is shown in Fig. 6 arranged such that only the appropriate high-J *b*-type transitions are entered in the figure. The combined effects of inertial asymmetry and centrifugal distortion, predominantly the former, produce this band head. The Fortrat diagram shows that all but one of the *b*-type transitions assigned in this work lie in the centimeter wave spectral region as do the *a*-type Q-branch transitions. The weak *b*-type lines were assigned by a bootstrap procedure, using successively more accurate frequency predictions.

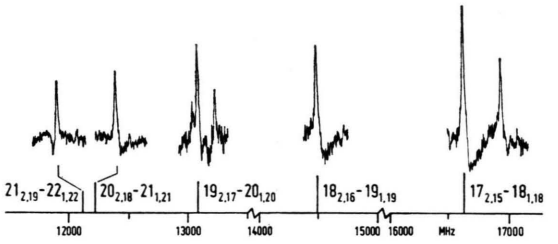

Fig. 6. Line pattern of the *b*-type transitions forming the band-head structure of the high-J $^rP_1$-brank shown in Figure 5.

V. Centrifugal Distortion Analysis

The observed rotational *a*-type and *b*-type transitions have been analysed by the use of the reduced Hamiltonian reported by Watson [18] in which $R_6 = 0$,

$$\begin{aligned}\mathcal{H} = {} & \tfrac{1}{2}(X+Y)J^2 + \{Z - \tfrac{1}{2}(X+Y)\}J_z^2 - \Delta_J (J^2)^2 - \Delta_{JK} J^2 J_z^2 - \Delta_K J_z^4 \\ & + H_J (J^2)^3 + H_{JK}(J^2)^2 J_z^2 + H_{KJ} J^2 J_z^4 + H_K J_z^6 \\ & + (J_x^2 - J_y^2)\{\tfrac{1}{4}(X-Y) - \delta_J J^2 - \delta_K J_z^2 + h_J (J^2)^2 + h_{JK} J^2 J_z^2 + k_K J_z^4\} \\ & + \{\tfrac{1}{4}(X-Y) - \delta_J J^2 - \delta_K J_z^2 + h_J (J^2)^2 + h_{JK} J^2 J_z^2 + h_K J_z^4\}(J_x^2 - J_y^2)\end{aligned}$$

where J, J_x, J_y and J_z are the operators for the total angular momentum and its components. The constants, X, Y, and Z are the Watson's reduced rotational constants $\tilde{B}$, $\tilde{C}$, and $\tilde{A}$, respectively, in the I^r axis representation.

The observed and calculated line frequencies together with astrophysically important line position predictions are listed in Table I.

Several lines were rejected from the fit (zero weighting factor), indicating an error in measurement, and several high K_a lines were omitted from the fit because higher order centrifugal distortion effects appear to contribute to those line frequencies. Accidentally overlapped or partially blended *K*-type doublets are also omitted. Thus 206 lines out of 213 measured transitions have been used for the least-squares analysis and the standard deviation of the fit was obtained to be 18.1 kHz.

The constants obtained from the fit and used for calculation of the predicted frequencies are expressed in the I^r axis representation, and listed in Table II. The Watson determinable parameters which are invariant to a unitary transformation of the Hamiltonian, $\mathfrak{A}$, $\mathfrak{B}$, $\mathfrak{C}$, τ'_{aaaa}, τ'_{bbbb}, τ'_{cccc}, τ_1 and τ_2 are listed in Table III.

Table II. Spectral parameters of acrolein for Watson's reduced Hamiltonian in I^r axis representation [a].

$\tilde{A}$	47353.7106 (44)	MHz
$\tilde{B}$	4659.49924 (19)	MHz
$\tilde{C}$	4242.68964 (19)	MHz
Δ_J	1.04153 (33)	kHz
Δ_{JK}	−8.78252 (28)	kHz
Δ_K	359.91 (46)	kHz
δ_J	0.119849 (84)	kHz
δ_K	5.7986 (22)	kHz
H_{JK}	−0.0123 (53)	Hz
H_{KJ}	−0.4756 (93)	Hz

$\varkappa = -0{,}980663$, $\quad b_p = -4.85762 \times 10^{-3}$.

[a] The standard deviation of the fit is 18.1 kHz for 206 equally weighted lines. Numbers in parentheses are standard errors.

Introducing the planarity conditions among the τ's as indicated in Ref. [18] we can determine the four constants, τ_{aabb}, τ_{bbcc}, τ_{ccaa} and τ_{abab}, which are non-vanishing for a planar molecule. The determined centrifugal distortion constants are listed in Table IV together with the calculated values of these constants using the molecular force constants of trans-acrolein as reported by Fukuyama, Kuchitsu, and Morino [19]. The τ-constants were obtained using the formula [20].

Table III. Watson's determinable rotational constants and quatric centrifugal distortion constants [a] for *trans*-acrolein.

$\mathfrak{A}$	47 353.7127 (50)	MHz
$\mathfrak{B}$	4 659.48071 (20)	MHz
$\mathfrak{C}$	4 242.69477 (20)	MHz
$\tau'_{aaaa}=\hbar^4\tau_{aaaa}$	−1.4087 (20)	MHz
$\tau'_{bbbb}=\hbar^4\tau_{bbbb}$	−5.1249 (25)×10^{-3}	MHz
$\tau'_{cccc}=\hbar^4\tau_{cccc}$	−3.2073 (25)×10^{-3}	MHz
τ_1	0.022632 (30)	MHz
$\tau_2/(\mathfrak{A}+\mathfrak{B}+\mathfrak{C})$	−1.2112 (35)×10^{-3}	MHz
$\Delta\tau'_{cccc}$ [b]	−0.0513 (15)×10^{-3}	MHz

[a] Numbers in parentheses are estimated errors on the basis of the standard error of spectral constants in Table II.
[b] τ-defect: $\Delta\tau'_{cccc}=\tau'_{cccc}-(\tau_2-\mathfrak{C}\cdot\tau_1)/(\mathfrak{A}+\mathfrak{B})$ with $\tau_2=-68.1357\,(30)$ MHz.

$$\tau_{aa\beta\beta}=-\frac{1}{(I_a^e)^2\,(I_\beta^e)^2}\sum_s\frac{a_s^{(aa)}\,a_s^{(\beta\beta)}}{8\pi^2c^2\tilde{\nu}_s^2}$$

where

$$a_s^{(\alpha\alpha)}=2\sum_i\sqrt{m_i}\,[\beta_i^0\,l_{is}^{(\beta)}+\gamma_i^0\,l_{is}^{(\gamma)}]$$

and the l-matrix was kindly supplied by Dr. Fukuyama to the authors. Kyazimova et al.[21] also calculated the centrifugal distortion constants, but their values differ considerably from the observed ones, as shown in Table IV, indicating that their force fields should be revised.

The discrepancy between the calculated and the observed τ_{aaaa} seems to be too large, probably due to the neglect of higher-order contributions in the calculations. For example, the observed vibrational frequencies, on which the force constants are based, are by no means harmonic. This sort of criticism may also hold for the observed τ constants, since we do not correct the constants for vibrational contributions. The reported constants are effective constants for the ground vibrational state, since the τ's are changed considerably by the excitation of the vibrations.

Table IV. Comparison of experimentally determined and calculated centrifugal distortion constants (MHz).

	Observed	Calculated [b]	Calculated [c]
τ'_{aaaa}	−1.4087	−1.21404	−2.169
τ'_{bbbb}	−0.0051249	−0.005536	−0.0081
τ'_{cccc}	−0.0032073	−0.003458	—
τ_{aabb}	0.030528 [a]	0.030615	0.08
τ_{bbcc}	−0.004004 [a]	−0.004331	—
τ_{ccaa}	0.014003 [a]	0.015427	—
τ_{abab}	−0.008948 [a]	−0.013463	−0.0123
Δ_J	0.00104153	0.001114	0.0016
Δ_{JK}	−0.00878252	−0.007006	−0.0293
Δ_K	0.35991	0.3094	0.5701
R_5	−0.00289932	−0.000669	0.00054
R_6	0.0	0.0000052	0.0000093
δ_J	0.000119849	0.0001299	0.00021

[a] Calculated assuming the planarity conditions used in Ref. [5] case 1. [b] This work. [c] Ref. [21].

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