Recording High Resolution Molecular gas phase Spectra at Temperatures between 50 and 296 Kelvin

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Diode Laser Collaborators

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Outline for this talk

Motivation Description of absorption cells and cooling systems TDL systems description Most significant TDL results will be described Frequency comb laser results, if time permits Bruker 125 HR system, cells and some results for methane, ethane and propane

Motivation

• Temperature dependence of spectroscopic line parameters (γ , β , ζ , δ) are required for precise atmospheric sounding of the Earth and outer planets.

• CH₄: important minor constituent for planetary atmospheres (Earth, Jupiter, Saturn, Titan,...).

• CO – He used as a model system for theoretical studies (validation of Potential Energy Surfaces).

• CO₂ O₂ A band C₂H₂ C₂H₆ C₃H₈ of great importance for astrophysics and earth atmosphere calculations \Rightarrow data at low temperature are needed.



Different cooling systems

Cryogenic fluids: - alcohol (T = 200 K) - nitrogen (T = 77 K) - helium (T = 7 K or lower).





Closed-cycle helium refrigeration system \Rightarrow T = 12 K



Cold Herriott cell*

4th generation cold cell (important progress in the temperature stabilization technique). Material: ultra-pure copper (OFHC) for good thermal conductivity Absorption pathlength: 537 and 1280 cm with 14 cm between the mirrors and 19 round trips (relatively small volume of about 1 L)

Herriott cell

Resistor Heater (2×25 Ω)

2nd stage cooler



^{*} J. Mol.Spectrosc. 241 (2007) 18-25 and Appl. Phys. B 100 (2010) 2481-2504)

Interferometer Stabilized Diode Laser setup



Cold Herriott cell coupled with an interferometrically stabilized diode laser spectrometer -actively stabilized wavelength (residual wavenumber fluctuation: $4 \times 10^{-5} \text{ cm}^{-1}$ -step-by-step acquisition mode(typical step size: 5×10⁻⁴ cm⁻¹) \Rightarrow high spectral resolution spectra IR laser source: lead-salt laser diode Three channels: -I₀: no cell -*I_{ref}* : absorption cell at room temperature $-I_t$: cold Herriott cell \Rightarrow I_{ref}/I₀ and I_{spl}/I₀ (precision ~5 ×10⁻⁴)

Spectral fitting

Acquired spectra = Absorption lines \otimes Laser emission profile Laser emission described with a Voigt profile and determined with the reference spectra at low pressure.

Absorption lines represented with complex profiles taking into account different physical effects (confinement narrowing (β), line mixing (ζ)...) Synthetic spectra are fitted on the acquired spectra with a global least-squares fit procedure.



Better residuals (Obs-Calc) ⇒ better determination of the fitted parameters

Application to atmospheric spectra

Atmospheric spectra obtained with LPMA (*Limb Profile Monitor of the Atmosphere*) a balloon-borne remote sensing FTIR instrument operating in absorption against the sun.



We normally write the temperature dependence of the pressure broadening parameter as

$$g(\mathbf{T}) = g(\mathbf{T}_{ref}) \begin{pmatrix} \overset{a}{\mathcal{C}} \frac{\mathcal{T}_{ref}}{\mathcal{T}_{\varnothing}} \\ \overset{{}_{e}}{\Theta} \end{pmatrix} \text{ or } \ln g(\mathcal{T}) = \ln g(\mathbf{T}_{ref}) + n_g \ln_{\mathcal{C}} \frac{\overset{a}{\mathcal{T}_{ref}}}{\mathcal{T}_{\varnothing}} \\ \overset{{}_{e}}{\Theta} \end{pmatrix}$$

or *y* = *a* + *bx*

If we include data between room temperature and temperatures down to 10 to 60 Kelvin, we find that we need to change the linear log - log function from a linear function to a 2nd order polyniomial as shown below in order to fit the data and to make precise extrapolations to other temperatures

$$g(\mathbf{T}) = g(\mathbf{T}_{ref}) \begin{pmatrix} \overset{a}{\mathbf{C}} \frac{\mathcal{T}_{ref}}{\mathcal{T}_{\emptyset}} \overset{o}{\mathbf{v}}_{g} \\ \overset{e}{\mathbf{C}} \frac{\mathcal{T}_{ref}}{\mathcal{T}_{\emptyset}} \overset{o}{\mathbf{v}}_{g} \end{pmatrix} \begin{pmatrix} \overset{e}{\mathbf{C}} \overset{a}{\mathbf{c}} \overset{a}{\mathbf{c}} \frac{\mathcal{T}_{ref}}{\mathcal{T}_{\emptyset}} \overset{o}{\mathbf{v}}_{g} \overset{o}{\mathbf{v}}_{g} \\ \overset{e}{\mathbf{c}} \overset{e}{\mathbf{c}} \frac{\mathcal{T}_{ref}}{\mathcal{T}_{\emptyset}} \overset{o}{\mathbf{v}}_{g} \overset{o}{\mathbf{v}}_{g} \end{pmatrix} \text{ or } \ln g(\mathcal{T}) = \ln g(\mathbf{T}_{ref}) + n_{g} \ln_{\mathbf{C}} \frac{\mathcal{T}_{ref}}{\mathcal{T}_{\emptyset}} \overset{o}{\mathbf{v}}_{g} + b_{2} \ln_{\mathbf{C}} \frac{\mathcal{T}_{ref}}{\mathcal{T}_{\emptyset}} \overset{o}{\mathbf{v}}_{g} \end{pmatrix}$$

or $\mathbf{y} = \mathbf{a} + \mathbf{b}_{1}\mathbf{x} + \mathbf{b}_{2}\mathbf{x}^{2}$



ln(γ(T))

Molec.	Band	B r	J	C N	Р	a u	<i>b</i> ₁	\boldsymbol{b}_2
		a n			e	r r		
		c h			t	e		
¹³ CO	1-0	R	0	—	He	-3.01□0.01	0.489□0.014	0.035 🗆 0.004
¹³ CO	1-0	P	2	_	He	-3.06□0.01	0.510□0.013	0.019□0.004
¹³ CO	1-0	R	0	_	Ar	-2.677 🗆 0.007	0.796 0.022	-0.018□0.016
¹³ CO	1-0	R	7	-	Ar	-3.073 \[] 0.002	0.721 \[] 0.007	0.057 🗆 0.005
¹² CH ₄	\square_3	Р	9	A2 1	N ₂	-2.860 \[] 0.003	0.783 0.016	0.039□0.013
¹² CH ₄		P	9	F2 1	N ₂	-2.842 \[] 0.002	0.760□0.011	0.069□0.009
¹² CH ₄		Р	9	F1 1	N ₂	-2.831□0.001	0.787 🗆 0.001	0.060□0.001
¹² CH ₄	\square_3	Р	9	A1 1	N ₂	-2.880 \[] 0.019	0.657 🗆 0.096	0.154□0.079

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MAJOR FINDINGS FROM THE LOW TEMPERATURE DIODE LASER STUDIES INCLUDE

1. NON LINEAR POWER LAW DEPENDENCE OF THE PRESSURE BROADENING COEFFICIENT AT TEMPERATURES BELOW APPROXIMATELY 150 TO 130 KELVIN.

2. TEMPERATURE DEPENDENT LINE MIXING IS IMPORTANT IN MODELLING METHANE ATMOSPHERIC SPECTRA.

3. MORE WORK , BOTH EXPERIMENTAL AND IN DEVELOPING MODELS DESCRIBING ABSORPTION LINE SHAPES MUST BE PURSUED IF ABSORPTION SPECTRA ARE MODELLED AT THE NOISE LEVEL

FT-IR Collaborators

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The v_9 band near 822 cm⁻¹ is observed in the composite unapodized CIRS spectrum (above) taken at medium resolution (1.7 cm⁻¹) at mid-latitudes. [A. Coustenis et al. Icarus 2007;189:35-62. doi:10.1016/j.icarus.2006.12.002].

COLD CELL INSIDE VAC BOX

COLD CELL

VAC SHIPPING BOX

PLATE

VACUUM COVER FOR

SAMPLE AREA

VAC BOX FOR COLD CELL



WHY ETHANE? WHY THE v₉ BAND?

1. 12-µm emission features of ethane are seen in the spectra from outer solar system bodies of Jupiter, Saturn, Neptune and Titan.

2. The v₉ band, especially the ${}^{R}Q_{0}$ sub-band (v₀ =~ 822 cm⁻¹) is of considerable interest due to its importance in molecular astrophysics and also because it is <u>often used in</u> <u>remote sensing applications.</u>

3. Laboratory measurements are required to convert the raw observational data of planetary observations into information useful for quantification,.

4. laboratory measurements normally include parameters such as line positions, intensities, pressure-broadened widths and shifts as a function of temperature.

The purpose of the present investigation is to provide new and accurate measurements of individual spectral line parameters for ${}^{R}Q_{0}$ AND several other Q, P, R sub-band transitions.

Titan's atmosphere consists predominantly of N_2 and measurable quantities of several organic molecules including ethane. Present investigations involve spectra of ethane and ethane broadened with nitrogen at various temperatures (298 K to 149 K), pressures and absorption path lengths.

Comparison of a Spectrum of Titan to our Laboratory spectrum



A few sub bands near the prominent ^RQ₀



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43 spectra fitted simultaneously. Tick marks at the top correspond to all transitions (>430) included in the fit. HB=HOT BAND $(v_9+v_4-v_4)$

No pressureinduced shifts, line mixing or speed dependence required to fit the spectra.



Examples of Torsional Splittings & Statistical Weights





Different sub-band series (^PQ, $^{R}P, ^{P}P)$ Effects of temperature and pressure upon the relative strengths of the various transitions



Well separated J,Ktransitions in this ^PP series vary from 7 to17(J") and 1 to 6 (K"). The torsional split components overlap at high pressures.

Hot-band transitions $(v_9 + v_4 - v_4)$ are marked with (*)

No pressure-induced shifts were required to fit even these wellseparated lines.

LINE INTENSITIES IN C2H6 V9 BAND

1. Intensity measurements in the most recent HITRAN and GEISA databases are based upon analysis by J. Vander Auwera, N. Moazzen-Ahmadi, Jean-Marie Flaud. Astrophys J. 2007;662:750-757. Those values are used as initial input in the present analysis.

2. Line Intensities measured in this work are lower by ~15% from HITRAN 2008 values.

3. Line intensities in the databases were normalized to the band intensity from a medium resolution spectrum recorded at PNNL based on the integrated area under the entire region of the band.

4. Intensities are based upon 43 high-resolution spectra recorded by TWO different Bruker FTS (PNNL and JPL). Measurements are obtained fitting all spectra simultaneously. Absolute uncertainties in intensity measurements are estimated to about $\pm 5\%$. Differences from the databases are probably due to the difficulty measuring the intensities in medium resolution spectrum?

Measured N₂- and Self-Widths vs. *M* (M=J'=J'' for Q sub-bands). Units of widths are cm⁻¹ atm⁻¹ at 296 K LEFT: ^rQ bands RED: Self-Widths BLUE: N₂-Widths

RIGHT: ^pQ bands RED: Self-Widths BLUE: N₂-Widths

> Ratio of Self-Widths to N₂-Widths =1.40±0.05





Comparison of Temperature Dependences (*n*) of Self-Widths: This Study vs. Nguyen et al. (J. Mol. Spectrosc. 2008;39:429-434)

Line	$\nu (\text{cm}^{-1})^{a}$	<i>n</i> (This work)	n
	. ()	Voigt profile ^a	Rautian profile ^b
^p Q(17,9)	798.93257(1)	0.602 ± 0.012	0.636 ± 0.123
^p Q(16,9)	798.97339(1)	0.592 ± 0.012	0.620 ± 0.104
^p Q(15,9)	799.01179(1)	0.583 ± 0.012	0.621 ± 0.110
^p Q(13,5)	809.13646(1)	0.579 ± 0.008	0.659 ± 0.119
^p Q(12,5)	809.16832(1)	0.566 ± 0.008	0.707 ± 0.113
^p Q(11,5)	809.19773(1)	0.552 ± 0.010	0.643 ± 0.133
^p Q(7,5)	809.29055(1)	0.497 ± 0.012	0.669 ± 0.104
pQ(6,5)	809.30729(1)	0.483 ± 0.014	0.742 ± 0.098
^p Q(13,2)	816.86769(1)	0.690 ± 0.008	0.735 ± 0.099
pQ(12,2)	816.90092(1)	0.686 ± 0.008	0.758 ± 0.128
^p Q(11,2)	816.93136(1)	0.682 ± 0.008	0.664 ± 0.115

^a This study. The error bars for positions and temperature dependence exponents are twice the standard deviation.

^b Nguyen et al. Reported temperature dependence exponents were calculated from their measured selfbroadened half-width coefficients at three different temperatures (242.2, 226.2 and 150.2 K). 1. 43 high-resolution (0.0016-0.005 cm⁻¹) spectra of pure and N₂-broadened C₂H₆ are fitted simultaneously to retrieve:

2. Positions, absolute intensities, N₂- and self-Widths and the temperature dependences of N₂- and self-Widths measured for over 1300 *J*, *K* transitions in 17 Q sub-bands and several ^pP, ^rR, ^rP and ^pR sub-bands.

3. Mean Ratio of Self-Widths to N_2 -Widths is 1.40±0.05

4. No pressure-induced shifts, line mixing or speed dependence were detected in the spectra.

SUMMARY & CONCLUSIONS

T-dependence exponents for N_2 -Widths are larger than for self-Widths and their values as well as ratios vary with *J*, *K* quanta. The "*n*" values are fitted to empirical linear relationship:

 $n = a + b \times (J-c),$

for each broadening gas in each sub-band structure.

Line intensities from this work are found to be ~15% lower than those listed in the HITRAN 2008 Database. The reason for this discrepancy has recently been investigated from measurements on a (new) spectrum recorded at JPL and the new intensities confirm our present measurements.

Importance of Present Laboratory Investigation

1. Using the parameters determined in this study the spectrum of ethane can be computed at any temperature below 296 K at infinite resolution.

2. From there one simply applies the instrument line shape to compare to a spectrum of Titan.

3. The importance of the intensity problem is that it affects the retrieved mixing ratio on a one to one basis.

4. Lorentz widths are temperature and pressure dependent and we have described that dependence with great accuracy.

5. We have also enough information (except for the unidentified lines) to describe the line intensity as a function of temperature-and no new lines will appear at lower temperatures than presently obtained (149 K).



Sung, et al , FT-IR measurements of cold C₃H₈ cross sections...for the Titan Atmosphere, ICARUS, submitted May

2013 Pure Propane spectrum at 297 and 160 K



□ What are pseudolines?

- 1)Aaverage transmission assumed for a freq. interval
- (uniformly)-spaced frequency bins as 'pseudolines'
- 2) Treat them as 'individual transitions'
 - *i.e.*, *S*, *Lorentz width*, and *E*"
- 3) Proved working in Earth remote sensing for heavy molecules (http://mark4sun.jpl.nasa.gov/data/spec/Pseudo/Readme)

□ Deriving the C₃H₈ pseudoline parameters at T₀=296 K

- Preset parameters spacing = 0.005 cm⁻¹; half widths = 0.12 (N₂) and 0.18 (self) Temp-dep. exponent n = 0.7 for N₂-broadening
- Voigt line profile was adopted
- Fit all laboratory spectra simultaneously to derive S and E''
- **Deriving band intensity**

"Band intensity computed by integrating band model absorption coefficients should be more accurate than those from measurements of integrated absorbance (Goldman et al. 1971; Giver at al. 1984)".


























Parameter	HITRAN08	PS (with LM)	PS (No LM)
Separation line 2-line 1 (cm ⁻¹)	0.007	0.00633 (3)	0.0641 (8)
Ratio of Int. line 2 to line 1	1.597	1.698 (2)	2.095 (9)
Separation line 3-line 1 (cm ⁻¹)	0.026	0.02557 (1)	0.02625 (5)
Ratio of Int. line 3 to line 1	2.506	2.772 (3)	3.429 (15)
Separation line 5-line 4 (cm ⁻¹)	0.0183	0.01846 (1)	0.01880 (5)
Ratio of Int. line 5 to line 4	1.0313	0.9962 (8)	1.002 (3)
Separation line 6-line 4 (cm ⁻¹)	0.0353	0.034923 (8)	0.03487 (3)
Ratio of Int. line 6 to line 4	1.0	0.9914 (5)	0.9296 915)

The following auxiliary parameters were included in the fitting.

These values were obtained using the path length L=21.681 m

Table 2

Retrieved line parameters for R(8) manifold in the 2v3 band of ¹²CH4

Line	Position (cm ⁻¹)	Intensity ^a	air W ^b	<i>n</i> (air)	air shift ^b	δ (air) ^c	SD ^d
9F22 ← 8F12	6096.167816 (7)	0.8205 (3)	0.0532 (1)	0.641 (4)	-0.01192 (8)	0.000070 (1)	0.144 (3)
9A21←8A11	6096.176862 (30)	0.4697 (3)	0.0497 (3)	0.825 (9)	-0.01084 (10)	0.000025 (1)	0.144 (3)
9E 2← 8E 2°	6096.180911 (32)	0.2461 (3)	0.0633 (5)	0.774 (7)	-0.00783 (9)	0.000060 (1)	0.133 (4)
9F12← 8F22	6096.372256 (5)	0.4511 (2)	0.0570 (1)	0.748 (3)	-0.01040 (4)	0.000052 (1)	0.118 (3)
9F21← 8F11 ^r	6096.423868 (5)	0.4471 (2)	0.0613 (1)	0.787 (4)	-0.00996 (7)	0.000056 (1)	0.119 (4)
9E 1←8E 1°	6096.485112 (10)	0.2980 (3)	0.04754 (2)	0.774 (7)	-0.00744 (9)	0.000060 (1)	0.133 (4)
9F11← 8F21 ^r	6096.500882 (7)	0.4408 (3)	0.0623 (1)	0.757 (5)	-0.00982 (8)	0.000050 (1)	0.154 (3)

^a10⁻²¹ cm/molecule at 296 K.

^bcm⁻¹ atm⁻¹ a 296 K.

ccm⁻¹ atm⁻¹ K⁻¹.

^dSpeed dependence (unitless).

e Line mixing in E species transitions

^f Line mixing in F species transitions





Simultaneous fit of 21 CO₂ spectra from Kitt Peak and JPL



SUMMARY

- TDL and FT-IR are complimentary
- Precise temperature dependent pressure parameters are essential for atmospheric modeling
- Complicated spectra are simplified by significant sample cooling
- Complicated molecules having clear spectral regions may be modeled with sufficient precision to be useful for astrophysical use.
- Cells with 100 meters path and stable temperatures as low as 50 Kelvin are feasible for TDL use, even for FT-IR use, where S/N is always an issue, with larger diameter and longer body cells
- Freq. comb lasers, properly used, may be the ultimate key to study sophisticated line shapes due to S/N and narrow emission profile, IF proper scanning is employed



see MANTZ et al, JMS 222(2007) 131-141

If interaction is governed by a potential of the form $V(R) \mu R^q$ this leads to a simple polynomial variation of pressure broadening cross sections, *S*, with the relative speed, v, of the collision partners ($S(v) \mu v^{-a}$) with $a = \frac{-2}{q-1}$.

Such a variation leads to a T^{-n} (with $n = \frac{q+1}{2q-2}$) So *n* continuously increases from 0.797 at room T to 0.904 at 90 K, for the P9 F1 1 transition, for example, thus a continuously DECREASING value of q.

so as T decreases the broadening is more sensitive to long range forces

Broadening temperature dependence



Temperature dependence

$$\gamma(T) = \gamma(T_{ref}) \left(\frac{T_{ref}}{T}\right)'$$

with n = (q+1)/(2q-2)Intermolecular potential V(R) $\propto R^{-q}$ $n \nearrow$ when T $\cong q \cong$ when T \cong **Collision broadening is more sensitive to the longrange attractive forces when the temperature**





Collisional cooling with the cold Herriott cell



The vertical level of the injector can be adjusted. The injector tip is heated to avoid freezing during injection of the gas **1280 cm pathlength** \Rightarrow access to weak absorption lines and not only to strong absorbers.











SAMPLE COMPARTMENT

The

= RISH

COLD CELL SYSTEM

VMR retrievals from atmospheric spectra



Differences up to 7% on the retrieved Volume Mixing Ratio were found comparing to an inversion model using only HITRAN04 spectroscopic parameters.



Line	Position (cm ³)	Intensity"	uir W ^e	n (air)	air shiff"	8 (nit?	SD
		~				-1010AN	
7E 1⊷ 6E 1	6676.927969 (13)	0.4469 (4)	0.0580 (2)	0.095 (6)	-0.01323 (13)	0.000099 (2)	0.090 (F
	.92737 (5)	8,369 (2)	0.0568 (0)	1.125(28)	-0.03779 (56)	8.468194 (9)	9.990 (F
	.9280	0.4893	0,0533	0.85	-0.010882	-	-
	.9280	Supp.Mat	0.0541		-0.0101 (3)		
7F12+- 6F22	6070.934296 (15)	0.7589 (4)	0.0598 (1)	0.728 (A)	-0.00951 (4)	6.000007(1)	0.101 (3)
	.93379 (4)	8.774(1)	0.0562 (1)	0.833 (6)	-0.02672 (11)	0.000122 (2)	0.090 (F
	.9350	0,7814	0.0549	0.85	-0.006971	-	
	.9350	Supp.Mat	0.0581 (4)		-0.0165 (0)	-	
7A11+-4A21*	6976,953537 (5)	1,2389 (4)	0,0684 (0)	8,821 (1)	-0.09883 (3)	9,600937 (0)	0.113(1)
	.95362 (2)	1.267 (1)	0.0540(1)	0.850(4)	-0.09699 (18)	0.000352 (1)	11.058 (3)
	.9540	1,226	0.0571	0.85	-0.001815	-	
	.9540	Supp.Mat	0.0583 (2)		-0.0917 (1)		
7F21← 6F11	6077,028450 (7)	0.7159(3)	0.0588(1)	0,778 (3)	-0.00951 (8)	9,000907(1)	0.101 (3)
	.02862 (2)	8,239 (1)	0,9562 (T)	9.833 (6)	-0.02672 (12)	9,900122 (2)	9,990 (7)
	.8283	0,7325	0.0532	11.85	-0.021226		
	.0283	Supp.Mnt	0.9561 (7)		-0.0199		
7F115 6F21	8677.046907(1)	4.7131 (5)	0.0540 (3)	0.806 (7)	-0.01621 (13)	.0.000132(1)	0.145 (7)
	.04742 (4)	8.740 (2)	0,0374 (3)	11.1154 (2)	-0.02128 (24)	0.00014614	0.090 (F)
	.0466	0,7554	9.9411	0.85	-0.021792	-	
	.0466	Sapp.Mat	0.0442		-0.0219 (2)	-	-
7A21+-6A11"	6077.063373 (5)	1.2282 (5)	0.0604 (0)	0.821 (1)	-0.09881 (3)	8,900937 (0)	0.113 (1)
	.16(349 (2)	1.178 (1)	1.1540 (1)	0.833.00	-0.02672 (12)	0.000122 (2)	9,010 (7



Ethane spectrum near 148 K Devi et al. 2010







2





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 	- 21		- 4
 	140	~ *	~

These values were obtained using the path length L=21.681 m

Table 2

Retrieved line parameters for R(6) manifold in the 2v3 hand of 12CH4

Line	Position (cm ⁻¹)	Intensity	air W ⁶	n (air)	air shift ^o	8 (air)	SD ^d
7E 1← 6E 1	6076.927969 (13)	0.4469 (4)	0.0580 (2)	0.695 (6)	-0.01323 (13)	0.000099 (2)	0.090 (F)
	00000	0.300 (7)	a nece (a)	1 135:30	0.01770.020	0.000104.00	0.000 (E)
	32737 (5)	0.369 (2)	0.0368 (6))	-0.05770 (50)	0.000134 (4)	0.090 (F)
	.9280	0.4893	0.0533	0.85	-0.010882		
	.9280	Supp.Mat	0.0525 (9)		-0.0101 (3)	1777 C	3 7777 8
7F12← 6F22	6076.934296 (15)	0.7589 (4)	0.0588 (1)	0.778 (3)	-0.00951 (6)	0.000007 (1)	0.101 (3)
	.93379 (4)	0.774 (1)	0.0562 (1)	0.833 (6)	-0.02672 (12)	0.000122 (2)	0.090 (F)
	.9350	0.7814	0.0549	0.85	-0.00697		
	.9350	Supp.Mat	0.0563 (6)		-0.0065 (0)		
7A11⊷6A21°	6076.953537 (5)	1.2389 (4)	0.0604 (0)	0.821 (1)	-0.00881 (3)	0.000037 (0)	0.113 (1)
	.95362 (2)	1.267 (1)	0.0540 (1)	0.850 (4)	-0.00690 (10)	0.000052 (1)	0.058 (5)
	.9540	1.226	0.0571	0.85	-0.001815		
	.9540	Supp.Mat	0.0565 (2)		-0.0017 (1)		
7F21← 6F11	6077.028450 (7)	0.7159 (3)	0.0588 (1)	0.778 (3)	-0.00951 (6)	0.000007(1)	0.101 (3)
	.02862 (2)	0.739(1)	0.0562 (1)	0.833 (6)	-0.02672 (12)	0.000122 (2)	0.098 (F)
	.0283	0,7325	0.0532	0.85	-0.021226		
	.0283	Supp.Mat	0.0545 (7)		-0.0198	- <u></u>	
7F11← 6F21	6077.046907 (1)	0.7131 (5)	0.0540 (3)	0.808 (7)	-0.01621 (13)	0.000132(1)	0.145 (7)
	.04742 (4)	0.740 (2)	0.0374 (3)	0,854 (2)	-0.02120 (24)	0.000148 (4)	0.090 (F)
	.9466	0.7554	0.0411	0.85	-0.021792		
	.0466	Supp.Mat	0.0428 (9)		-0.0219 (2)		
7A21⊷6A11'	6077.063373 (5)	1.2282 (5)	0.0604 (0)	0.821 (1)	-0.00881 (3)	0.000037 (0)	0.113 (1)
	.06349 (2)	1,178 (1)	0.0540 (1)	0.833 (6)	-0.02672 (12)	0.000122 (2)	0.090 (F)