10 μm High-Resolution Spectra of Acrolein (*trans*-form)

assignments for ν_{14} and ν_{16} bands

$$H_2C=C(H)-C(H)=O \qquad (C_S)$$
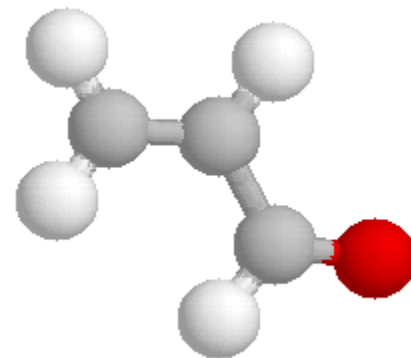
Objective - to provide benchmark high-resolution laboratory data in the 10 μm region for smoke detection

X.J. Jiang, J.M. Fisher, Li-Hong Xu

Centre for Laser, Atomic and Molecular Sciences (CLAMS),
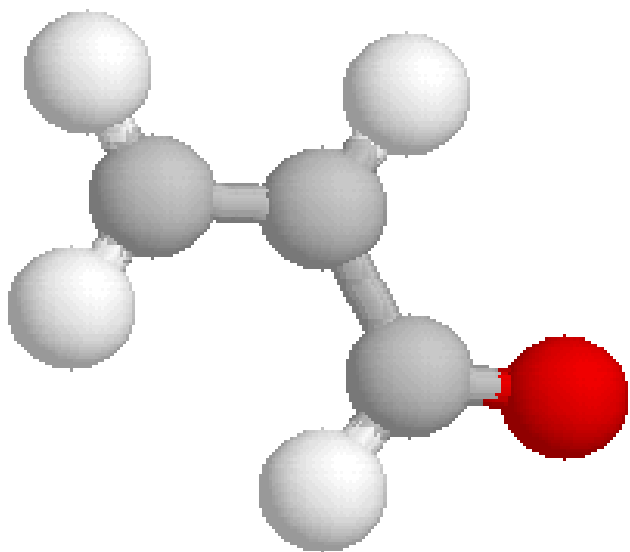Dept of Physical Sciences, Univ. of New Brunswick, Saint John, NB, Canada

A.R.W. McKellar

Steacie Institute for Molecular Sciences, National Research Council of Canada,
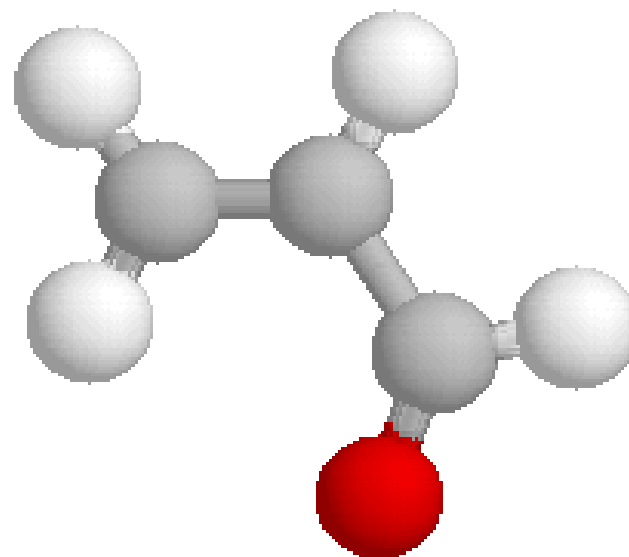Ottawa, Canada

Acrolein $H_2C=C(H)-C(H)=O$ C_s symmetry

trans-form

cis-form

$E_{elec.} = -191.9742621$ (Hartree)

$E_{elec.} = -191.9707933$ (Hartree)

$\Delta E_{ele} \sim 760 \text{ cm}^{-1}$

1 Hartree = 219474 cm^{-1}

Based on *ab initio* calculation at B3LYP/6-311++G** using Gaussian03

Introduction - environmental and health concerns

➢ Acrolein plays an important role in pollution and is listed in
US-EPA 188 Hazardous Air Pollutants (HAPs)

➢ It is one of the priority mobile air toxics
(Acetaldehyde, Acrolein, Benzene, 1,3-Butadiene, Formaldehyde,
Diesel Particulate Matter + Diesel Exhaust Organic Gas
Source: J. Wilson, FHWA Air Toxics Workshop, Chicago, IL, May 12, 2003

➢ It is principally used as a chemical intermediate in the production of
acrylic acid and its esters

➢ Combustion of fossil fuels and tobacco smoke contribute to
the environmental prevalence of acrolein

Hazardous Air Pollutants (HAP) Detection Methods

- GC-MS

- MS-MS

- Proton Transfer MS

- FTIR (low resolution IR)
  - Open path atmospheric P

- **Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS)**
  - Extractive sampling, low P
  - Continuous
  - High Speed < 1 s
  - High Resolution
  - High Sensitivity
  - Absolute Concentrations

Aerodyne Research, Inc. & Philip Morris Research Center, VA.

- Sub-List of HAPs Most Applicable to TILDAS Detection Methods
  - Acetaldehyde   *
  - Acrolein   *
  - Acrylonitrile
  - 1-3 Butadiene   *
  - Benzene
  - Carbonyl Sulfide
  - Ethylene Oxide
  - Formaldehyde
  - Formic Acid
  - Hydrazine
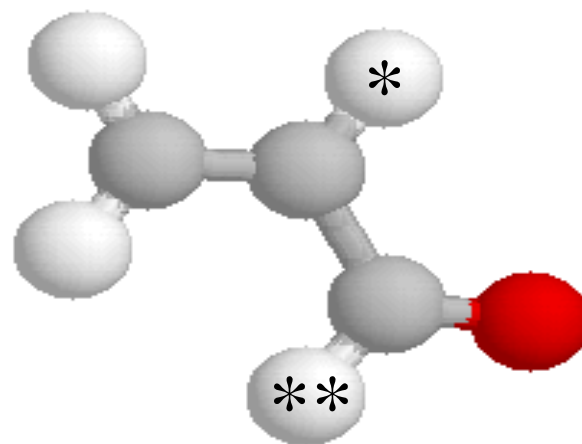 - Methanol   *

  * currently targeted molecules

High resolution data are needed, and are not yet available in literature

Vibrational modes of acrolein (*trans*-form)

A'	Description	Obs (cm^{-1})
ν_1	=CH$_2$ a-str	3103
ν_2	CH* str	3069
ν_3	=CH$_2$ s-str	2998
ν_4	CH** str	2800
ν_5	C=O str	1742
ν_6	C=C str	1625
ν_7	=CH$_2$ sci	1420
ν_8	CH** bend	1360
ν_9	CH* bend	1275
ν_{10}	C-C str	1158
ν_{11}	**=CH$_2$ i/p**	**912**
ν_{12}	CCO bend	564
ν_{13}	CCC bend	324

Vib. degrees of freedom:

3x8 - 3T - 3R = 18

A''	Description	Obs (cm^{-1})
ν_{14}	**=CH$_2$ twist**	**993**
ν_{15}	CH** o/p	972
ν_{16}	**=CH$_2$ o/p**	**959**
ν_{17}	CH* o/p	593
ν_{18}	C-C tor	158

Ref. Y. Hamada, Y. Nishimura, M. Tsuboi, *Chem. Phys.* **100** (1985) 365-375.

Survey spectrum of Acrolein - Pacific Northwest National Laboratory

Sample: Acrolein at 25C
Composite spectrum (1 ppm-meter at 296K)
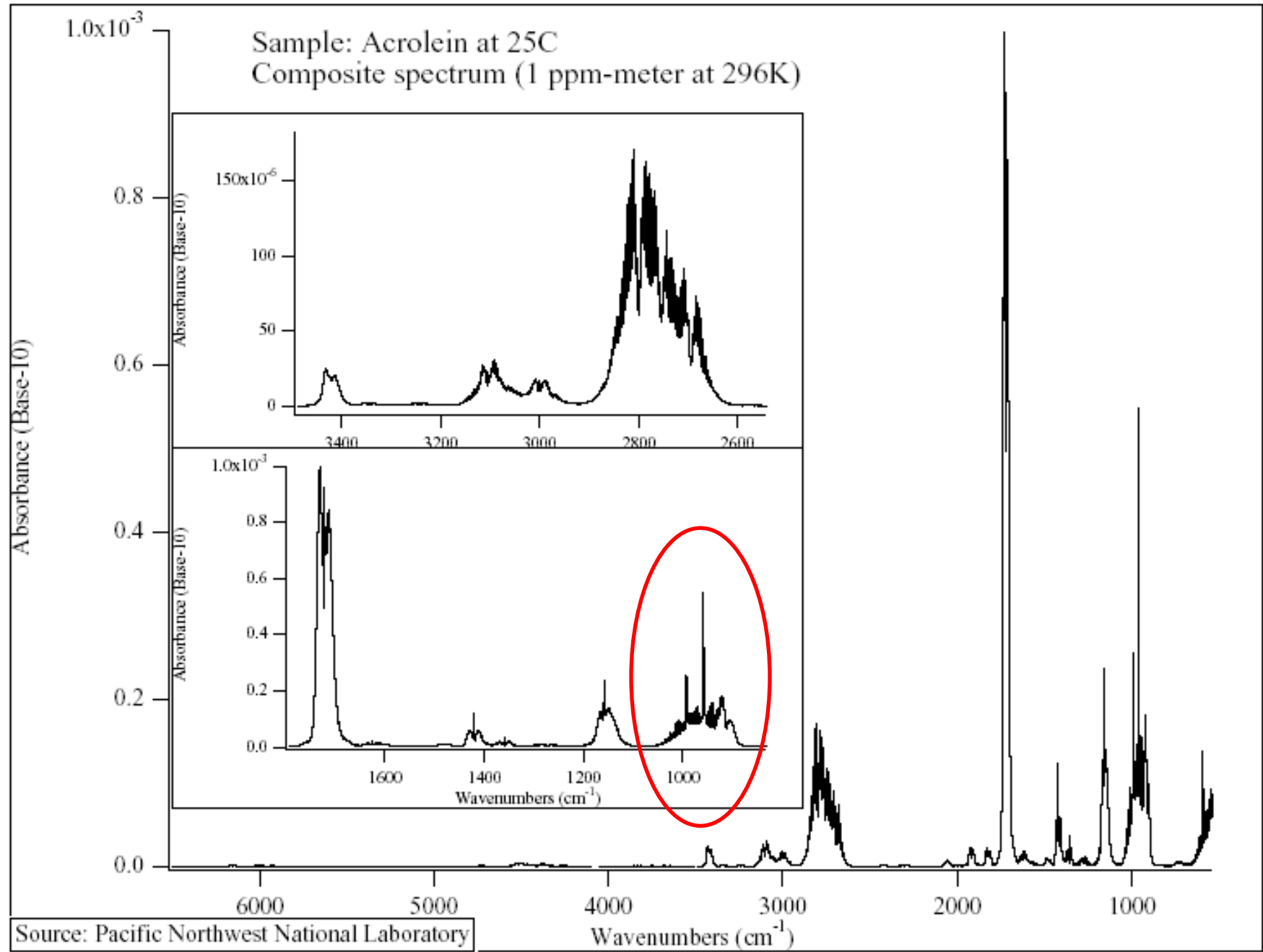
Acrolein (*trans*-form): High Resolution Spectroscopy

➢ Low energy *trans*-form has been studied extensively by microwave spectroscopy;

➢ No previous high-resolution studies exist for the 10 μm region;

➢ High-resolution FTIR spectra have been recorded at the National Research Council of Canada from 800 – 1100 cm^{-1} @ 0.002 cm^{-1} resolution at room and cooled temp.
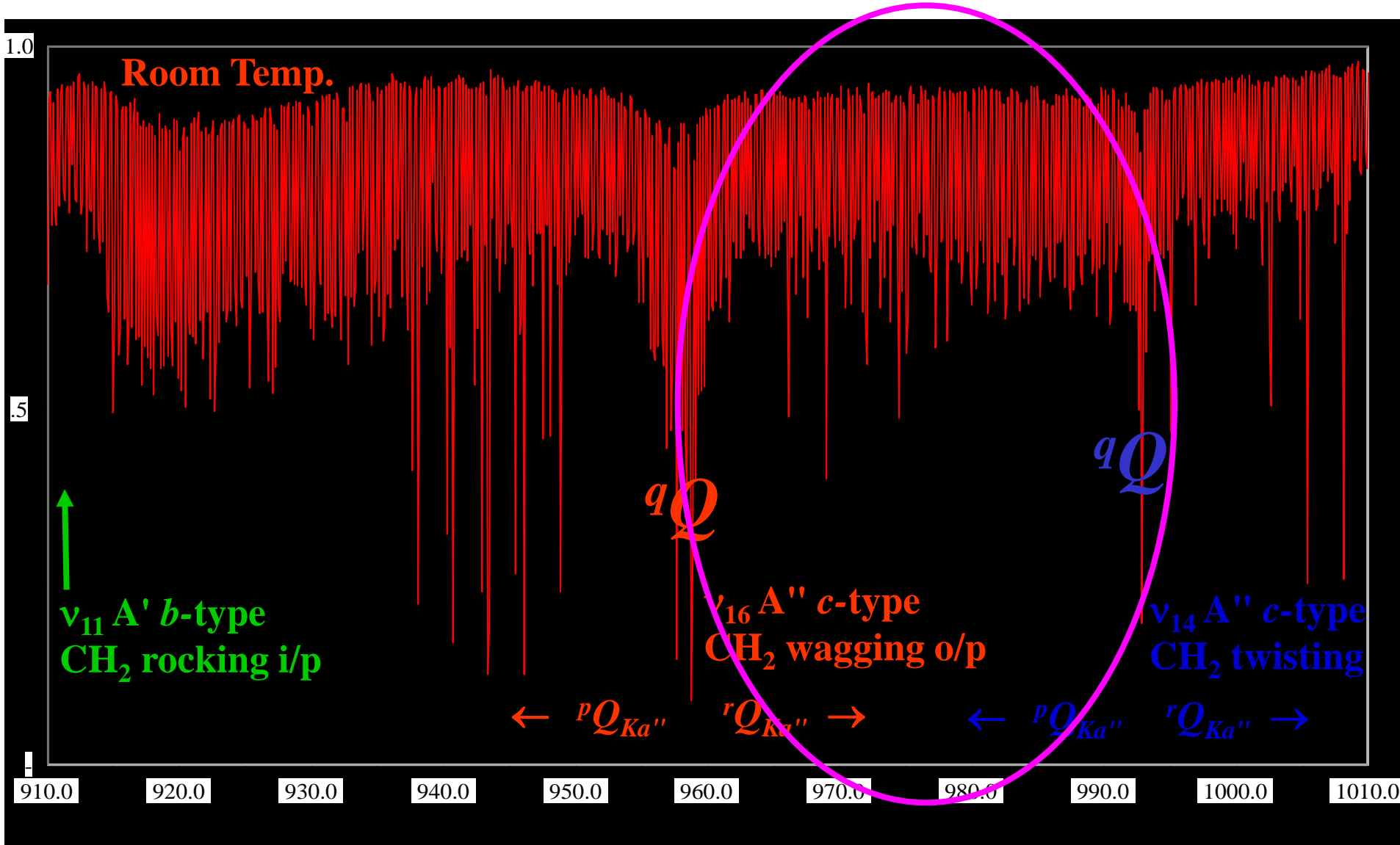
    Spectrum I: 295K, 30 cm multi-pass cell set to 4 transits, ~500 mTorr

    Spectrum II: 180K, 2 m multi-pass cell set to 4 transits, ~60 mTorr
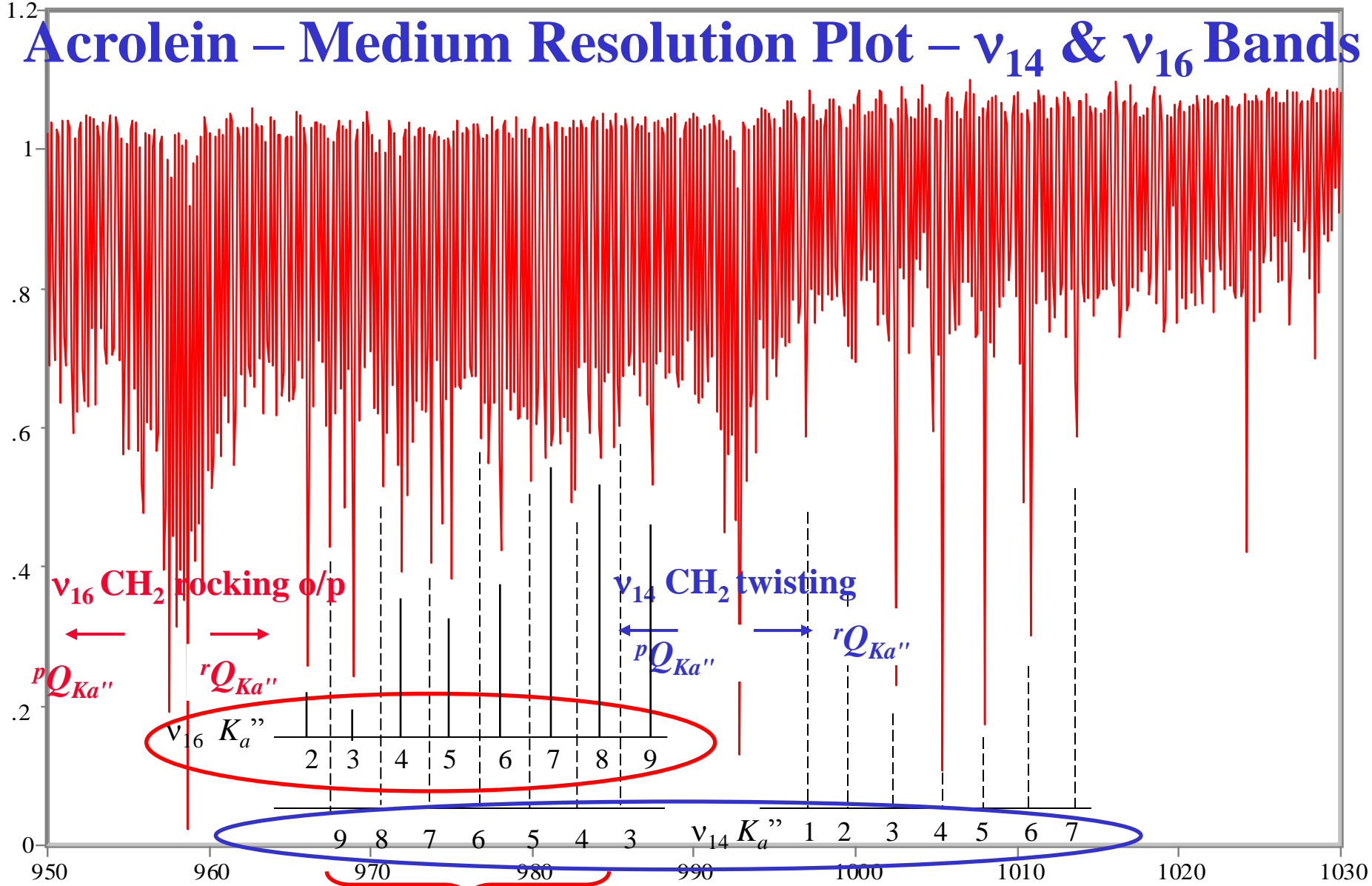
cover at least the ν_{11} (A' CH_2 rocking, in-plane),   912 cm^{-1}

                      ν_{16} (A" CH_2 wagging, out-of-plane)   959 cm^{-1}

                      ν_{14} (A" CH_2 twisting)   993 cm^{-1}

➢ Rotational analyses of the

        ν_{16} and ν_{14} bands – both c-types   are reported here.

Acrolein – Low Resolution Plot – $\nu_{11}, \nu_{16}, \nu_{14}$ modes

Acrolein – Medium Resolution Plot – ν_{14} & ν_{16} Bands

ν_{16} CH$_2$ rocking o/p

ν_{14} CH$_2$ twisting

$^pQ_{Ka''}$ $^rQ_{Ka''}$

$^pQ_{Ka''}$ $^rQ_{Ka''}$

ν_{16} K_a'' 2 3 4 5 6 7 8 9

ν_{14} K_a'' 9 8 7 6 5 4 3   1 2 3 4 5 6 7

Transmission / Wavenumber (cm-1)

Paged   X-Zoom CURSOR

File # 1 = AP2804~1

4/28/2004 4:59 PM Res=.0021

2m cell ,4pass, 0.06 Torr acrolein

^rQ of ν_{16} and ^pQ of ν_{14} overlap to some extent

High Resolution Display

$\nu_{16}^{\ 3\leftarrow4}P$

P25   P24   P23

$\nu_{16}^{\ 4\leftarrow5}P$

P17   P16   P15   P14

$\nu_{16}^{\ 5\leftarrow6}P$ $\nu_{16}^{\ p}P$

P8   P7   P6

941.0   941.1   941.2   941.3   941.4   941.5   941.6   941.7   941.8   941.9   942.0   942.1

P29   P28   P27   P26 $\nu_{14}^{\ 3\leftarrow4}P$ $\nu_{14}^{\ p}P$

P9   P8   P7   P6 $\nu_{14}^{\ 5\leftarrow6}P$

$\nu_{16}^{\ 6\leftarrow5}Q$

ν_{16}
$^{2\leftarrow1}R27_{1,27}$

$\nu_{16}^{\ 4\leftarrow3}R$

R16   R17   R18   R19

$\nu_{16}^{\ 5\leftarrow4}R$ R6   R7   R8   R9

$\nu_{16}^{\ 3\leftarrow2}R$ R25 $\nu_{16}^{\ r}R$ R26   R27

974.0   974.1   974.2   974.3   974.4   974.5   974.6   974.7   974.8   974.9   975.0   975.1

Wavenumber (cm^{-1})
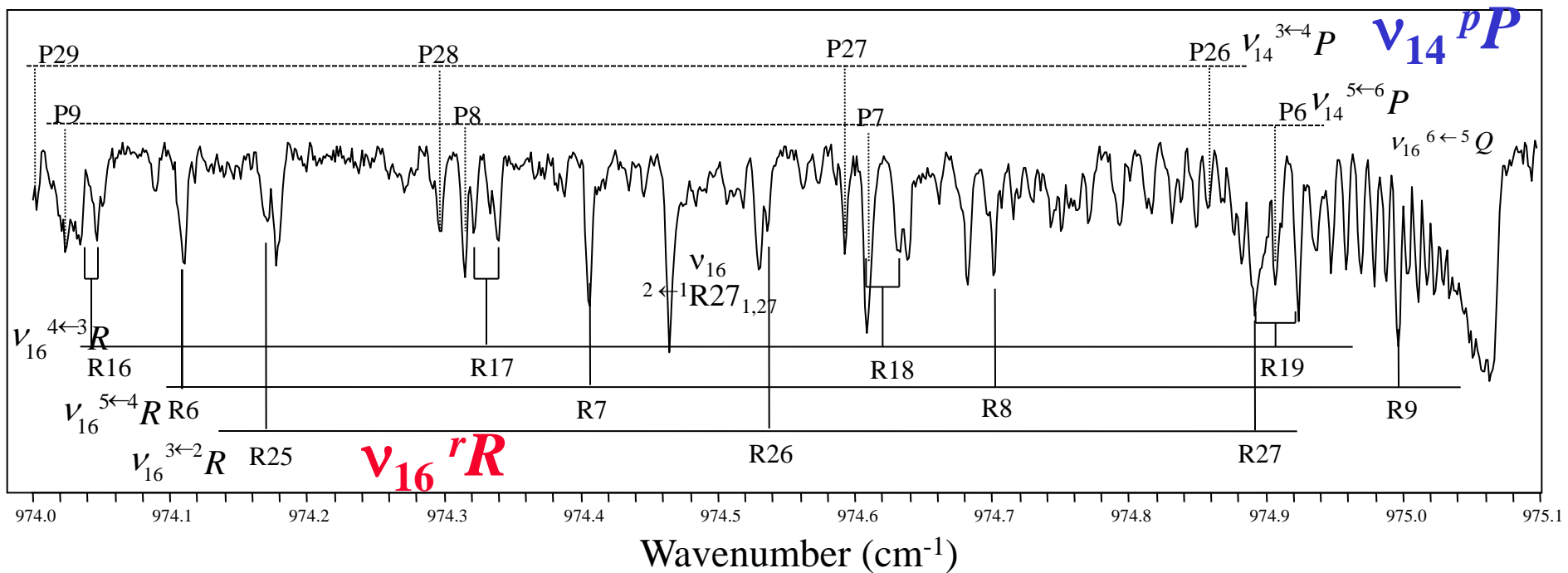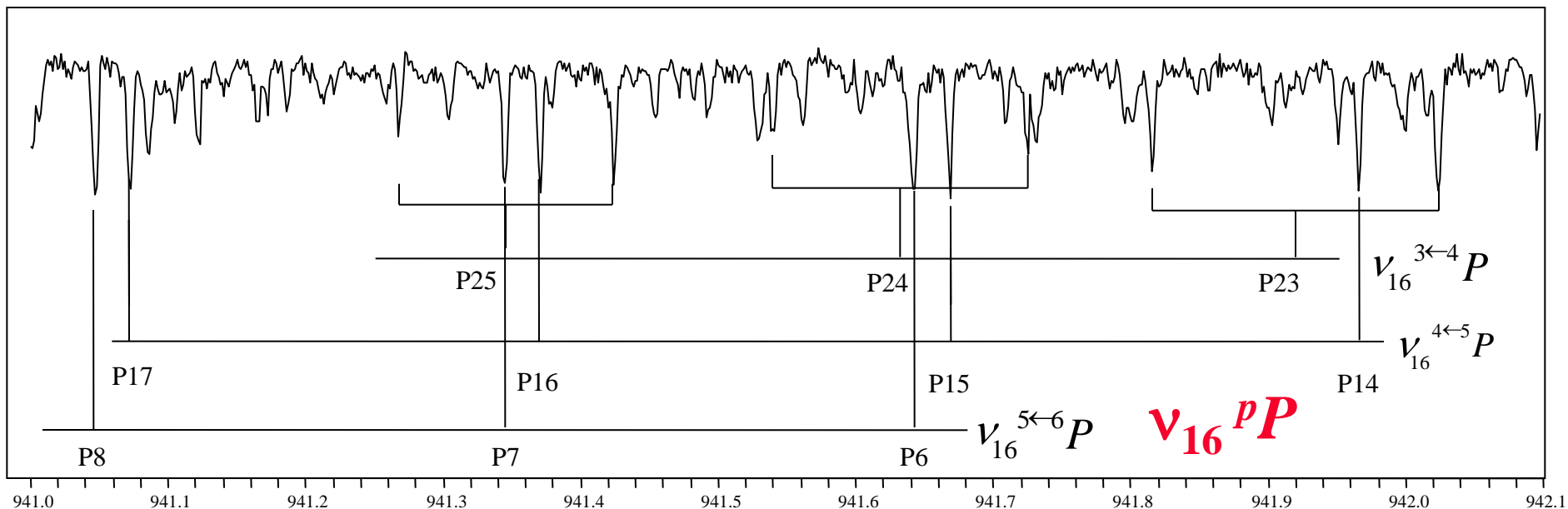
Modeling – Watson Asymmetric Rotor Hamiltonian (isolated band approach)

➢ ν_{18} (ground state):

  - 270 MW transitions were previously measured in the literature.

  - They were refitted for refined ground state parameters.

➢ ν_{16} (A$''$ CH$_2$ out-of-plane wagging):

  - Upper states have been identified for $K_a' = 0$ to 10.

  - Small asymmetry splittings for $K_a' < 5$ have been observed.

  - The band has been modeled by a Watson asymmetric rotor Hamiltonian with $K_a' = 7$ and 8 excluded.

➢ ν_{14} (A$''$ CH$_2$ twisting):

  - Upper states have been identified for $K_a' = 1$ to 9.

  - Small asymmetry splittings for $K_a' < 5$ have been observed.

  - The band has been modeled by a Watson asymmetric rotor Hamiltonian with $K_a' = 1$-3 excluded.

Molecular Parameters

	Ground State[a]	ν_{16} (CH$_2$ wagging)	ν_{14} (CH$_2$ twisting)
ν_{vib}	0.0	958.74075(11)	992.65739(69)
A	1.57954994(15)	1.596714(10)	1.570188(54)
B	0.1554241692(67)	0.15529624(80)	0.155220(16)
C	0.1415208986(73)	0.14152245(82)	0.141938(19)
Δ_K x10^5	1.2023(16)	2.506(26)	0.76(13)
Δ_{JK} x10^6	-0.292890(96)	-0.286(13)	1.058(63)
Δ_J x10^7	0.34750(12)	0.3543(31)	
δ_J x10^8	0.39988(35)	0.458(30)	
δ_K x10^5	0.0193(89)	0.1026(76)	-1.000(19)
H_K x10^7		-0.137(19)	-0.385(95)
H_{KJ} x10^8	-0.001594(34)	-0.571(10)	1.688(50)
H_{JK} x10^{10}	-0.0029(18)	-0.146(69)	
# of lines	270	962 (K$_a$'=7,8 excluded)	552 (K$_a$'=1-3 excluded)
RMS	0.017 MHz	0.0010 cm^{-1}	0.0013 cm^{-1}

[a] Ground state parameters have been converted to cm^{-1} for ready comparison.

J-Reduced Energy Diagram

(cm^{-1})

ν_{16} ν_{14}

Ka Ka

J values
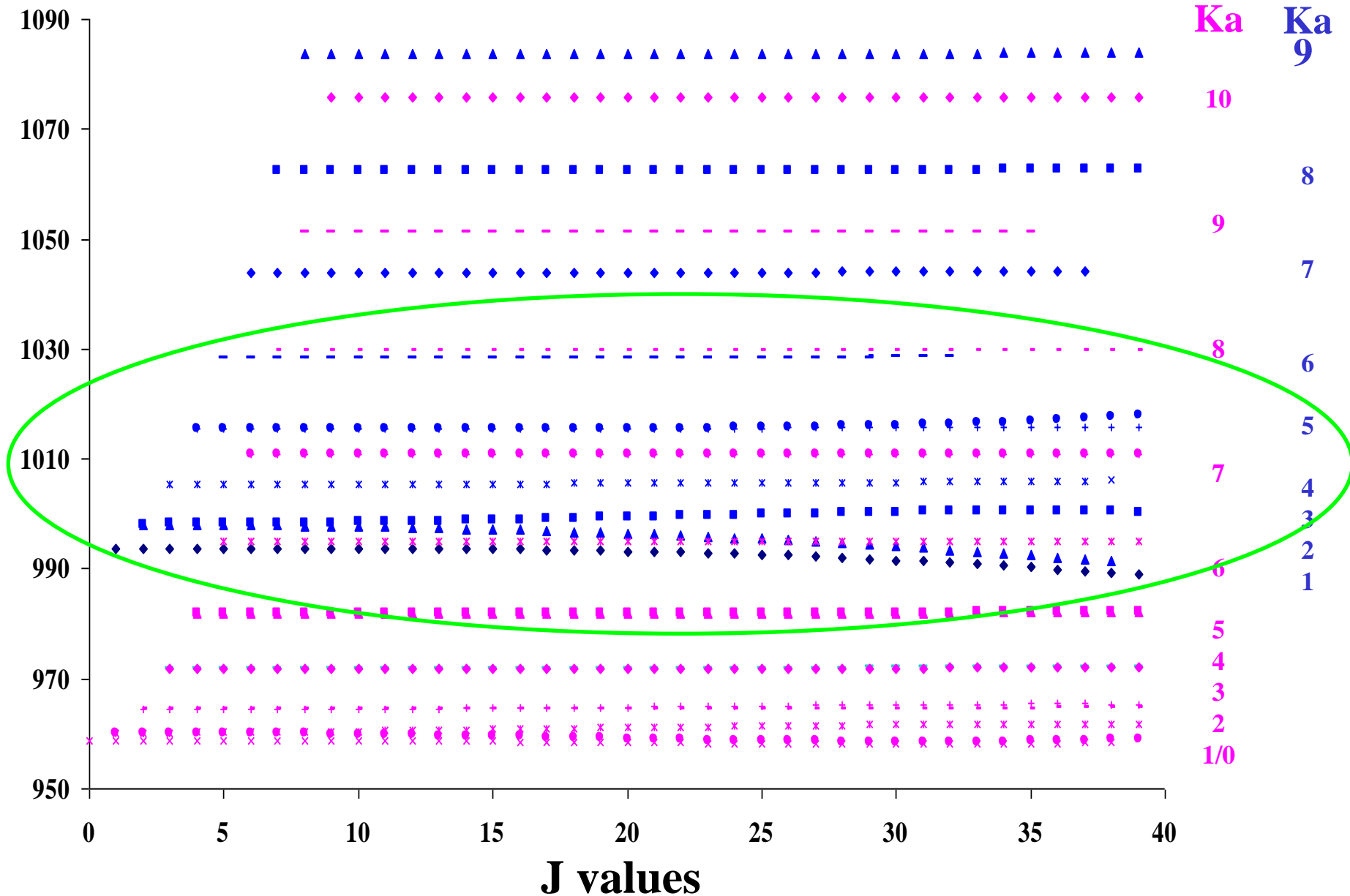
Summary and Future

➢ To a large extent, the **ν_{16} (A") c-type CH$_2$ out-of-plane wagging band** (959 cm^{-1}) and **ν_{14} (A") c-type CH$_2$ twisting band** (993 cm^{-1}) can be modeled by a Watson asymmetric rotor Hamiltonian, treating each state separately with some subbands excluded (we believe states excluded are perturbed);

➢ We plan to carry out analysis for the **ν_{11} (A') CH$_2$ in-plane rocking mode** (912 cm^{-1}) next, as state interactions are expected between ν_{11}, ν_{16} and ν_{14}. Indeed, we have observed some irregular J and K patterns in ν_{16} and ν_{14}. In order to treat the spectra properly, it might be helpful to use an interacting band model;

➢ We have just started to model the ν_{14} and ν_{16} states simultaneously with inclusion of symmetry allowed terms between the ν_{14} and ν_{16}.

➢ In future, further low temp FTIR spectra would be really helpful with the new Bruker IFS125 HR FTS (0.0009 cm^{-1} unapodized max. res.) at the **Canadian Light Source** in Saskatoon.

Line Intensity Calculation

$$S_{ij} = \varepsilon \frac{8\pi^3}{3hc} \nu_{ij} \, \text{☺} \, \frac{T_o}{TZ_v Z_t Z_r} [1 - e^{-\frac{hc\nu_{ij}}{kT}}] e^{-\frac{hcE_i}{kT}}$$

$$|<\mu>|^2 \, A <J'K' \leftarrow J''K''>$$

ε: Nuclear spin statistical weight
ν_{ij}: Transition frequency
⌂: Loschmidt's number
T: Temperature
Z: Partition functions (vib, tors, rot)
$|<\mu>|^2$: Transition moment - vibrational
A: Honl-London factor – rot. overlap

Ab initio Dipole Derivative Calculation

➤ Structure & frequency calculation with Gaussian 03 at B3LYP/6-311++G**

- **Eigenvectors (displacements) for each normal mode**
  (standard orientation, normalized, not orthogonal):
  multiplied by $(m_{rd\_n})^{1/2} \Rightarrow$ **PAM**

$$\{\frac{dx}{dQ_n}, \frac{dy}{dQ_n}, \frac{dz}{dQ_n}\}_{i=1 \, to \, N} \quad (n = 1 \text{ to } 3N\text{-}6)$$

- **Dipole derivative**
  (in z-matrix orientation) $\Rightarrow$ PAM

$$\{\frac{d\mu_g}{dx}, \frac{d\mu_g}{dy}, \frac{d\mu_g}{dz}\}_{i=1 \, to \, N} \quad (g = x, y, z)$$

- **Dipole derivatives**
  for each normal mode
  in PAM system

$$\frac{d\mu_g}{dQ_n} = \{\{\frac{d\mu_g}{dx}, \frac{d\mu_g}{dy}, \frac{d\mu_g}{dz}\}_i\} \bullet \{\{\frac{dx}{dQ_n}, \frac{dy}{dQ_n}, \frac{dz}{dQ_n}\}_i\}$$

Vibrational modes of acrolein (*trans*-form)

A'	Description	Obs (cm^{-1})
ν_1	=CH$_2$ a-str	3103
ν_2	CH* str	3069
ν_3	=CH$_2$ s-str	2998
ν_4	CH** str	2800
ν_5	C=O str	1742
ν_6	C=C str	1625
ν_7	=CH$_2$ sci	1420
ν_8	CH** bend	1360
ν_9	CH* bend	1275
ν_{10}	C-C str	1158
ν_{11}	**=CH$_2$ i/p**	**912**
ν_{12}	CCO bend	564
ν_{13}	CCC bend	324

High-resolution FTIR spectra have also been recorded at NRC in FIR region

Convering:

Low frequency vibrations and ν_{18} hot band Analysis is in progress - A.R.W. McKellar NRC

A"	Description	Obs (cm^{-1})
ν_{14}	**=CH$_2$ twist**	**993**
ν_{15}	CH** o/p	972
ν_{16}	**=CH$_2$ o/p**	**959**
ν_{17}	CH* o/p	593
ν_{18}	C-C tor	158

Ref. Y. Hamada, Y. Nishimura, M. Tsuboi, *Chem. Phys.* **100** (1985) 365-375.

10 μm High-Resolution Spectra of 1,3-Butadiene $H_2C=C(H)-C(H)=CH_2$ (C$_{2h}$)
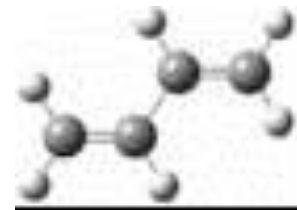
Acrolein $H_2C=C(H)-C(H)=O$ (C$_S$)
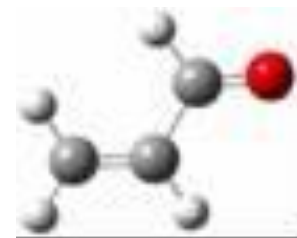
Objective - to provide and extend benchmark high-resolution laboratory data for the two molecules in the 10 μm region

Li-Hong Xu, X.J. Jiang, J. Fisher, Z.D. Sun, R.M. Lees
Centre for Laser, Atomic and Molecular Sciences (CLAMS),
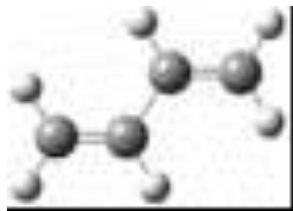Dept of Physical Sciences, Univ. of New Brunswick, Saint John, NB, Canada

N.C. Craig
Dept. of Chemistry,
Oberlin College,
Ohio, U.S.A.

A.R.W. McKellar
Steacie Institute for Molecular Sciences,
National Research Council of Canada,
Ottawa, Canada

1,3-Butadiene $H_2C=C(H)-C(H)=CH_2$


C_{2h} symmetry

➤ Lower energy planar *trans*-form belongs to the C_{2h} symmetry group.

➤ Normal isotopic species is non-polar, prohibiting traditional MW spectroscopy.

➤ **1,3-Butadiene, ν_{11} (a_u) CH_2 wagging mode - centred in 11 μm region**

- FTIR spectrum has been recorded in Giessen at 0.00186 cm^{-1} (~60 MHz) resolution and rotationally analyzed by N.C. Craig *et al., J. Mol. Struct.* **695-696** (2004) 59-69.

- Many medium and low *J Q*-branch component lines are not resolved in the Doppler limited Fourier transform spectra.

- We have applied the **saturation Lamb-dip technique** (~200 kHz) to the present case (using **CO₂/MWSB**). Several ^rQ-branches have been completely resolved.

- For intensity information, a line list with position and intensity has been compiled using *ab initio* **dipole derivative** & rotational constants from high resol'n analysis, Z.D. Sun *et al., J. Mol. Struct.* **742** (2005) 69-76.

1,3-Butadiene $H_2C=C(H)-C(H)=CH_2$

➢ used in the production of rubber and plastics.

➢ detected in ambient air (released from motor vehicle exhaust) - 0.3 ppb.

➢ expected in the cigarette smoke matrix (1 of the 4 target molecules in 2004).

➢ at Aerodyne Research Inc. & Philip Morris Research Center, quantum cascade laser system is commissioned – **reliance on lab benchmark database**.
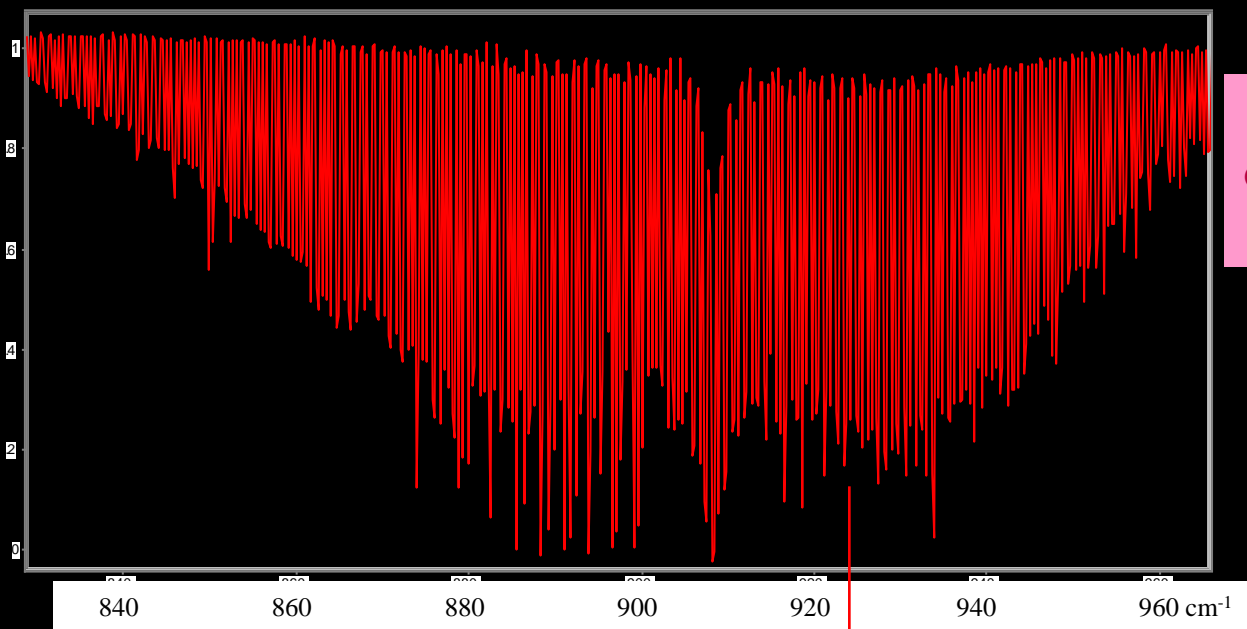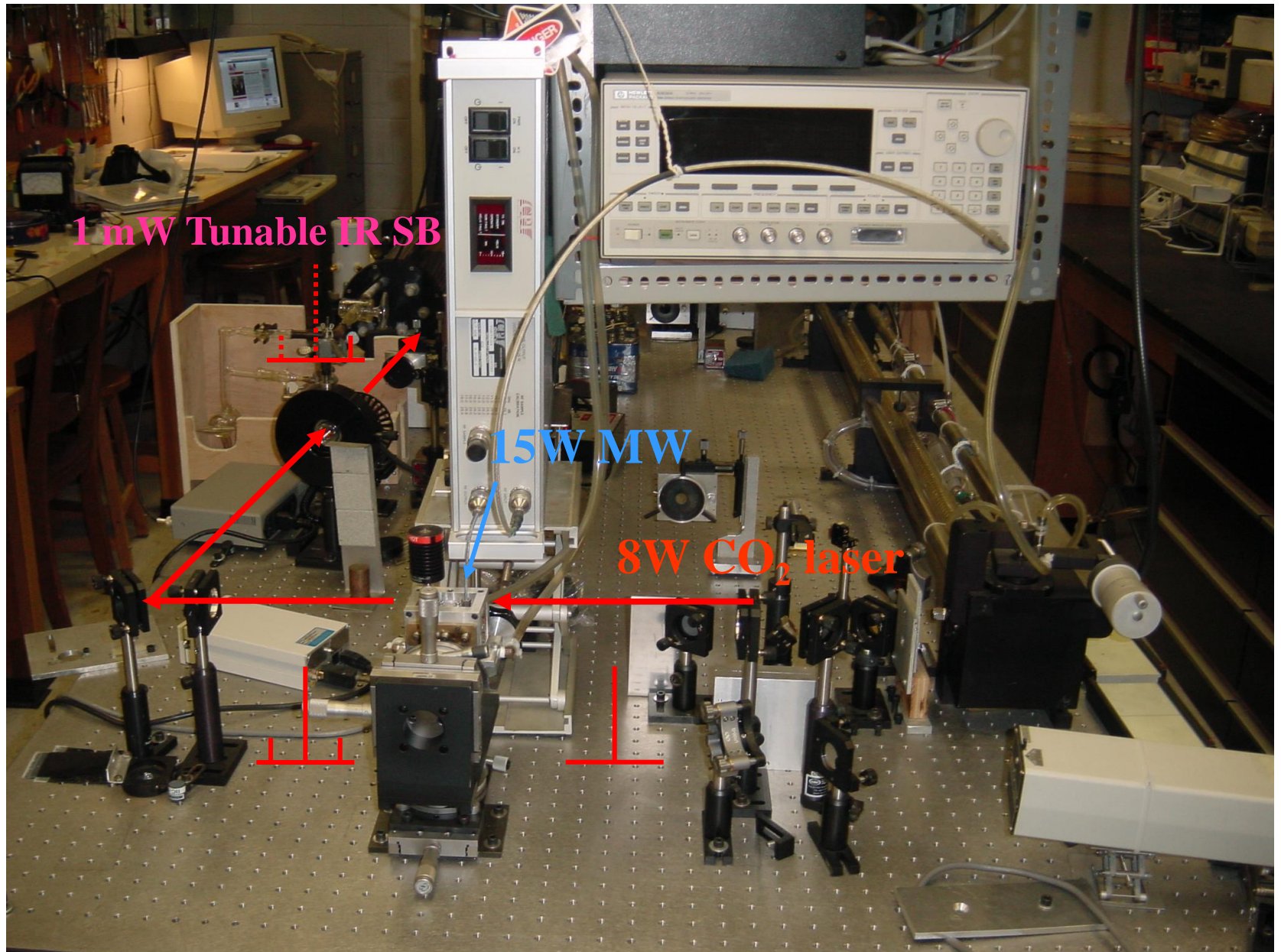

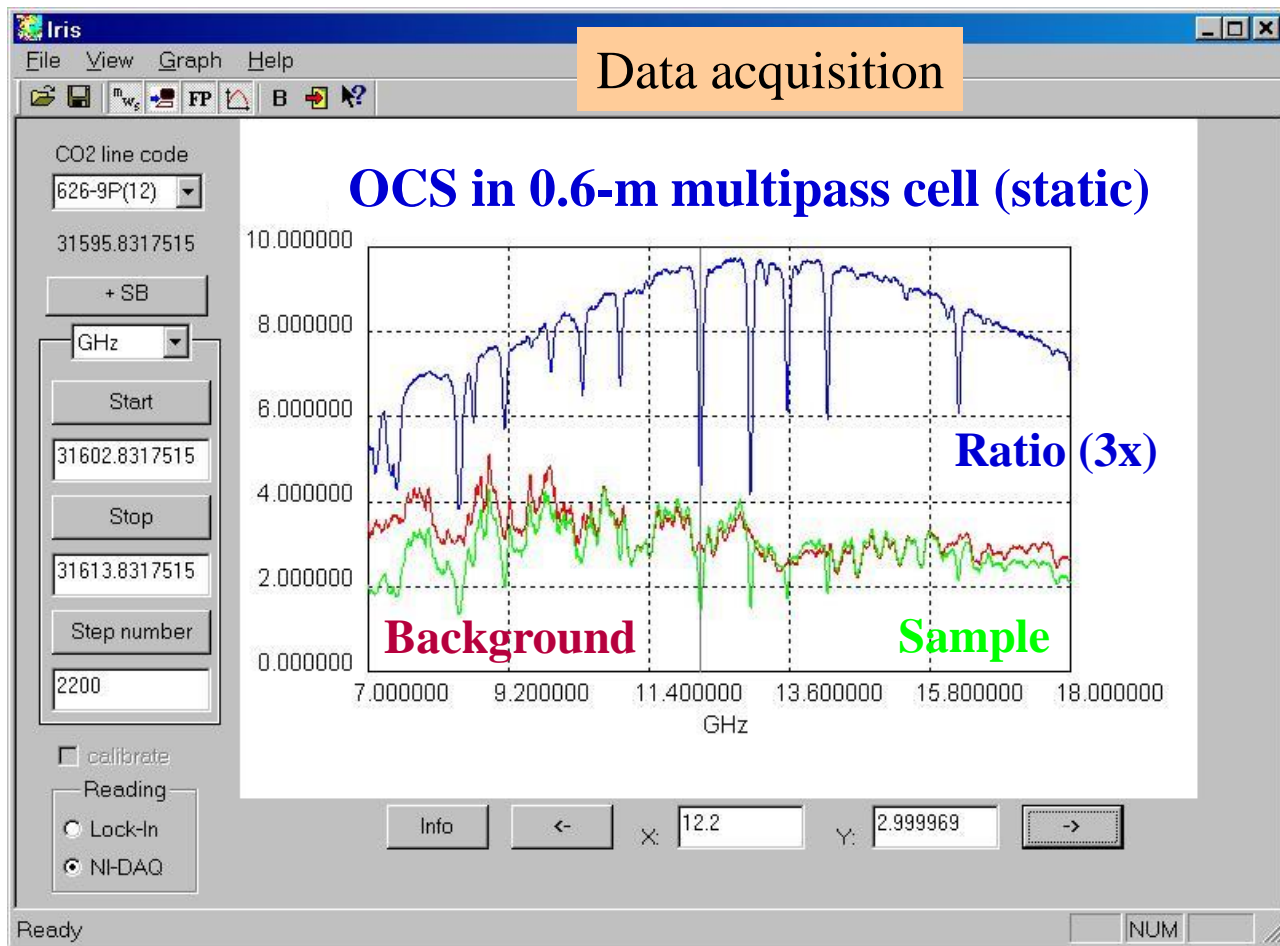with our sub-Doppler tech. overlapped features – resolved $K_a = 7 \leftarrow 6$ Q-branch

> 10 lines
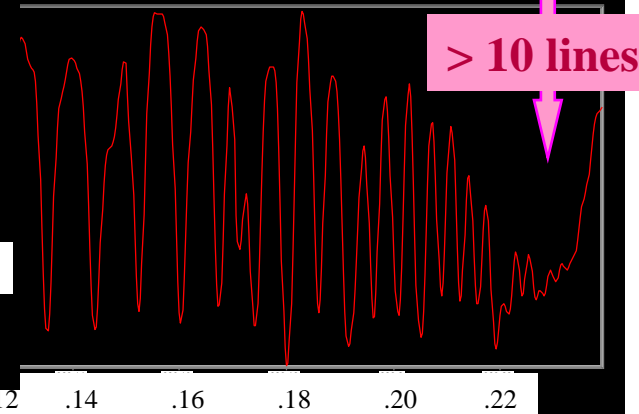
Giessen FTIR at 0.00186 cm^{-1} (~60 MHz) resolution
N.C. Craig et al., J. Mol. Struct. 695-696 (2004) 59-69.

Optical Table Layout

1 mW Tunable IR SB

15W MW

8W CO_2 laser

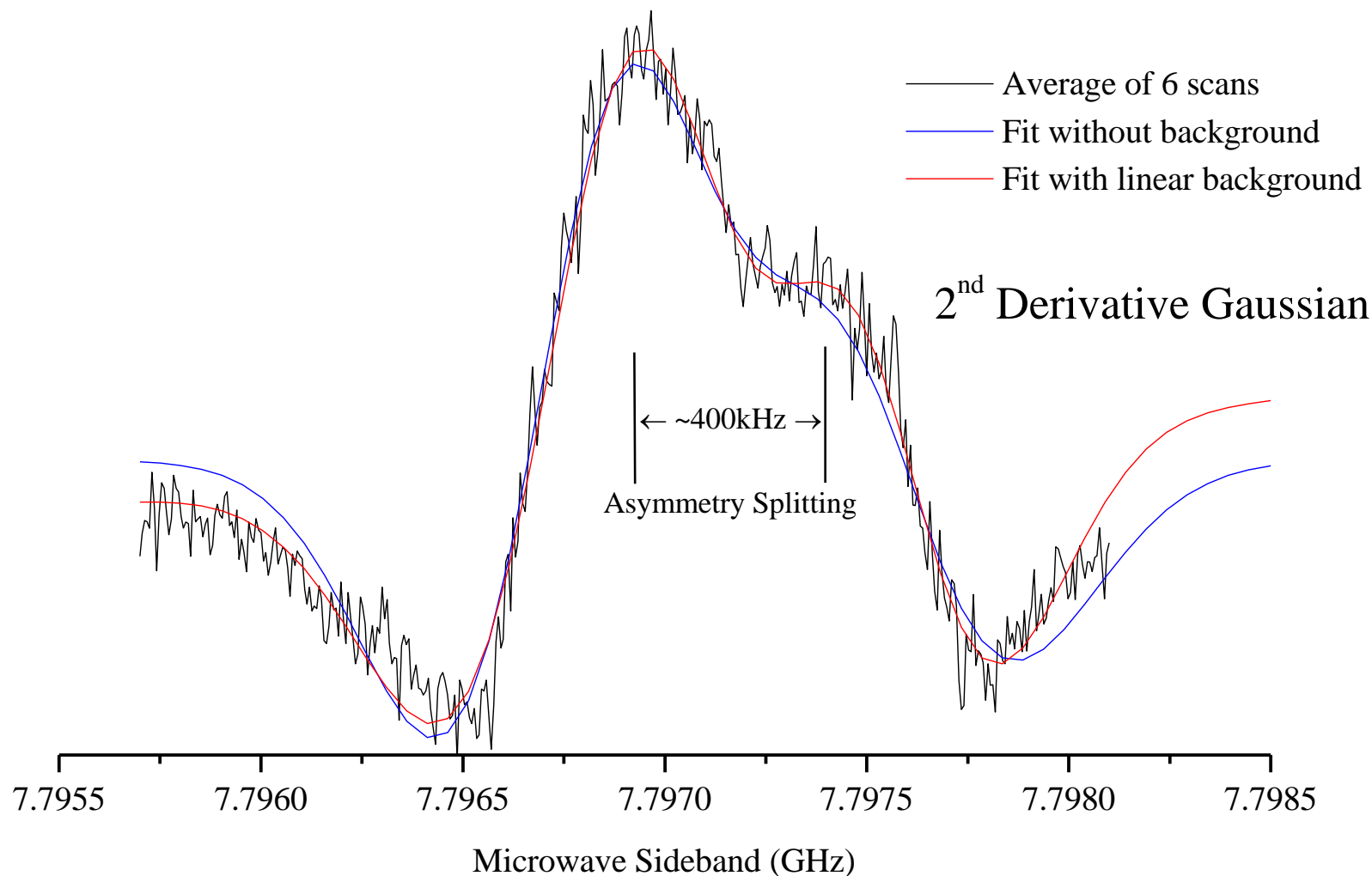# Frequency Sweeping, PZT Tuning & Data Acquisition

Saturation Lamb-dip experiments
@ sub-Doppler resolution (~ 200 kHz)

Methanol (CH_3OH), OCS, Butadiene (C_4H_6)
in collaboration with colleagues in NNOV-Russia

10P42 CO$_2$ Laser Line + SB in Up MW Scanning Direction
K$_a$ = 7 ← 6, J = 27

Average of 6 scans
Fit without background
Fit with linear background

2nd Derivative Gaussian

← ~400kHz →

Asymmetry Splitting

Microwave Sideband (GHz)

Lamb-Dip Measurements - Completely Resolved Q-Branches

$K_a = 7 \leftarrow 6$ Q branch $10P(42) + SB$ 922.914293 cm^{-1}

(Ka+Kc = J ← Ka+Kc = J+1)

J	LDO MHz	LDO cm^{-1}	FTS cm^{-1}	O-C MHz	LDO MHz	O-C MHz	Δ MHz
7	9668.64	923.236804		5.38			
8	9638.97	923.235815		5.21			
9	9604.94	923.234680		5.09			
10	9566.22	923.233388		4.95			
11	9522.58	923.231932		4.87			
12	9473.55	923.230297		4.71			
13	9418.75	923.228469		4.41			
14	9358.03	923.226444		4.19			
15	9290.98	923.224207		4.05			
16	9216.79	923.221732		3.61			
17	9135.46	923.219019	923.219410	3.37			
18	9046.38	923.216048	923.216096	3.18			
19	8949.01	923.212800	923.212837	3.00			
20	8842.65	923.209252	923.209270	2.74			
21	8726.84	923.205389	923.205322	2.47			
22	8601.08	923.201194	923.201094	2.29			
23	8464.56	923.196641	923.196657	2.09			
24	8316.60	923.191705	923.191976	1.84			
25	8156.48	923.186364	923.186381	1.48	**(Ka+Kc = J+1 ← Ka+Kc = J)**		
26	7983.64	923.180599	923.180423	1.23			
27	*7797.45*	923.174388	923.174366	1.18	*7797.03*	1.21	**0.42**
28	*7596.73*	923.167693	923.167702	0.99	*7596.07*	1.02	**0.66**
29	*7380.82*	923.160491	923.160603	0.78	*7379.76*	0.77	**1.06**
30	*7148.85*	923.152753	923.152763	0.55	*7147.26*	0.55	**1.59**

⬆ small Δ splittings have been observed ⬆

Ab initio Dipole Derivative for the ν_{11} Band of BDE

➤ Structure & frequency calculation with Gaussian 03 at B3LYP/6-311++G**

➤ *Ab initio* frequency calculation gives:

- Eigenvectors for each normal mode
(standard orientation, normalized, not orthogonal):
$$\Phi_n = \{\{\frac{dx}{dQ_n}, \frac{dy}{dQ_n}, \frac{dz}{dQ_n}\}_{i=1\,to\,10}$$ $(n = 1$ to $15)$
multiplied by $(m_{rd\_n})^{1/2} \Rightarrow$ PAM

- Dipole derivative in z-matrix orientation:
$\Rightarrow$ **PAM**
$$\frac{d\mu_g}{dk} = \{\frac{d\mu_g}{dx}, \frac{d\mu_g}{dy}, \frac{d\mu_g}{dz}\}_{i=1\,to\,10}$$ $(g$ and $k =$ x, y, z$)$

- Dipole derivatives for each normal mode in PAM system
$$\frac{d\mu_g}{dQ_n} = \{\{\frac{d\mu_g}{dx}, \frac{d\mu_g}{dy}, \frac{d\mu_g}{dz}\}_i\} \bullet \{\{\frac{dx}{dQ_n}, \frac{dy}{dQ_n}, \frac{dz}{dQ_n}\}_i\}$$

Ab initio results for 4 Au modes ν_{11}

Ab initio output	Harmonic Frequencies (cm^{-1})	172.39	534.49	937.36	1051.21
	IR Intensities (km/mol)	0.6983	14.2316	95.8243	36.8438
Our calc	dμ_C/dQ (Debye)	**0.02676**	**-0.1208**	**-0.3135**	**-0.1944**
	sum(dμ/dQ)^2 * cvt	0.6982	14.2313	95.8172	36.8419

Acrolein *J*-Reduced Energy Diagram
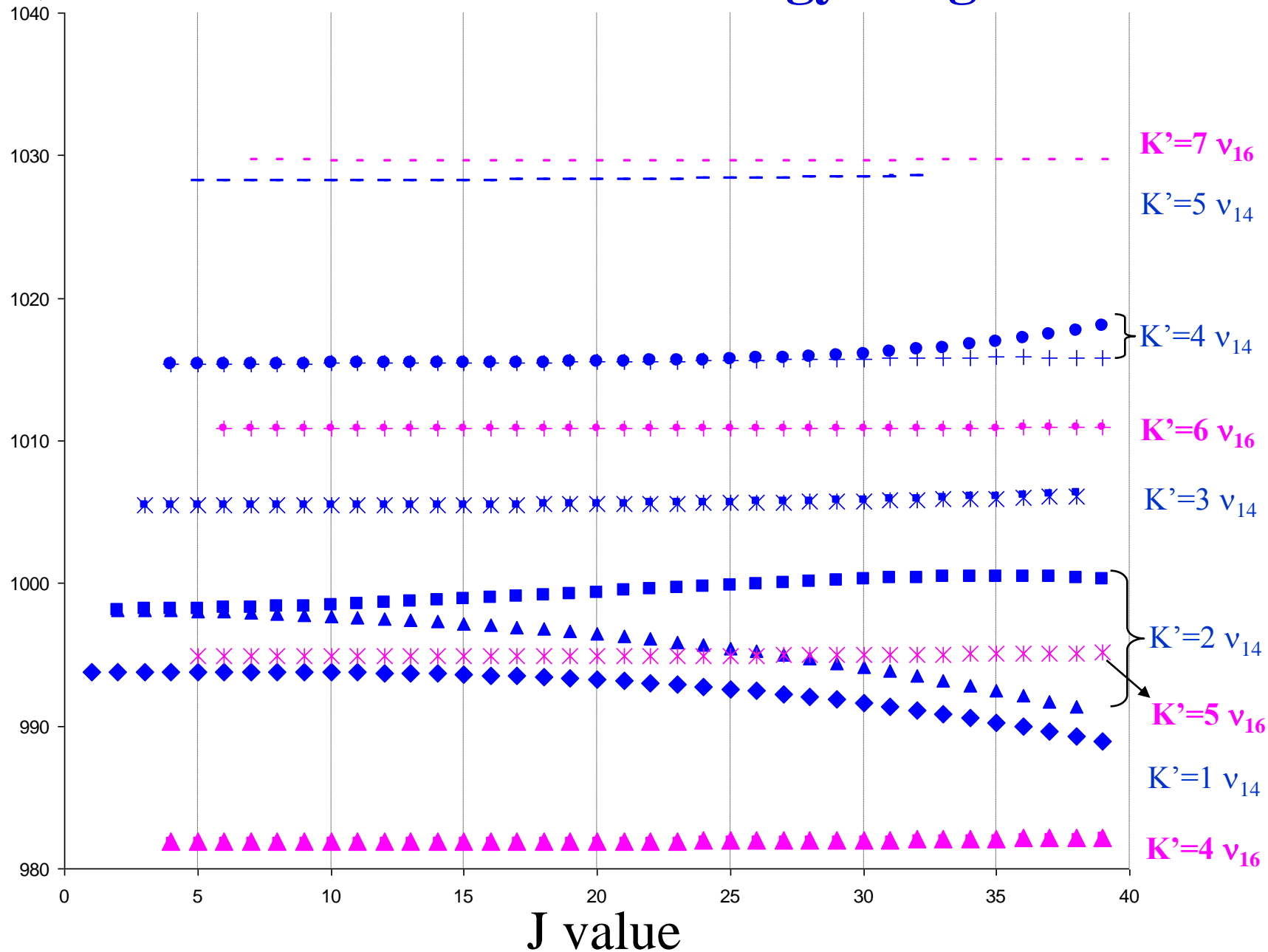
Acrolein *J*-Reduced Energy Diagram (Calculated)

Our hi-resolution analyses of ν_{16} and ν_{14} bands have revealed several possible perturbations. Interaction partners are yet to be identified.

This diagram shows possible interaction pairs between nearby vibrational states.

ν_{14} CH$_2$ twist

ν_{15} CH** wag o/p

ν_{16} CH$_2$ wag o/p

ν_{11} CH$_2$ rock i/p

Legend:
- ν_{14} CH$_2$ twist
- ν_{16} CH$_2$ wag o/p
- ν_{11} CH$_2$ rock i/p
- ν_{15} CH** wag o/p

Calculated *J*-Reduced Energy (cm^{-1})

K value
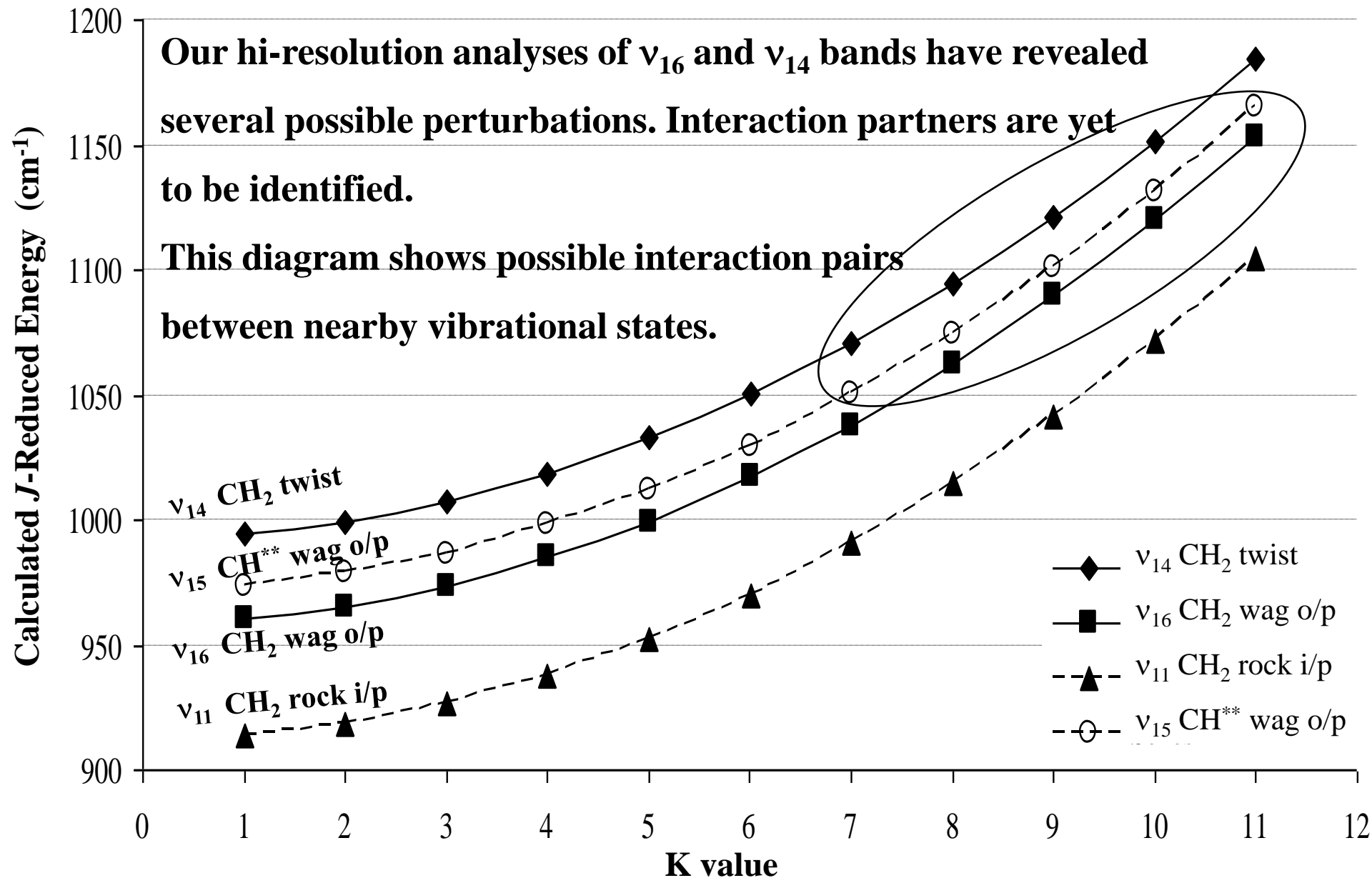
US-EPA 188 Hazardous Air Pollutants (HAPs)

Acetaldehyde	2-Chloroacetophenone	2,4-Dinitrotoluene	Methoxychlor	1,3-Propane sultone
Acetamide	Chlorobenzene	1,4-Diethyleneoxide	Methyl bromide	beta-Propiolactone
Acetonitrile	Chlorobenzilate	1,2-Diphenylhydrazine	Methyl chloride	Propionaldehyde
Acetophenone	Chloroform	Epichlorohydrin	Methyl chloroform	Propoxur
2-Acetylaminofluorene	Chloromethyl methyl ether	1,2-Epoxybutane	Methyl ethyl ketone	Propylene dichloride
Acrolein	Chloroprene	Ethyl acrylate	Methyl hydrazine	Propylene oxide
Acrylamide	Cresols/Cresylic	Ethyl benzene	Methyl iodide	1,2-Propylenimine
Acrylic acid	o-Cresol	Ethyl carbamate	Methyl isobutyl ketone	Quinoline
Acrylonitrile	m-Cresol	Ethyl chloride	Methyl isocyanate	Quinone
Allyl chloride	p-Cresol	Ethylene dibromide	Methyl methacrylate	Styrene
4-Aminobiphenyl	Cumene	Ethylene dichloride	Methyl tert butyl ether	Styrene oxide
Aniline	2,4-D, salts and esters	Ethylene glycol	4,4-Methylene bis(2-chloroaniline)	2,3,7,8-Tetrachlorodibenzo-p-dioxin
o-Anisidine	DDE	Ethylene imine		
Asbestos	Diazomethane	Ethylene oxide	Methylene chloride	
Benzene	Dibenzofurans	Ethylene thiourea	Methylene diphenyl diisocyanate	1,1,2,2-Tetrachloroethane
Benzidine	1,2-Dibromo-3-chloropropane	Ethylidene dichloride		Tetrachloroethylene
Benzotrichloride	Dibutylphthalate	Formaldehyde	4,4-Methylenedianiline	Titanium tetrachloride
Benzyl chloride	1,4-Dichlorobenzene(p)	Heptachlor	Naphthalene	Toluene
Biphenyl	3,3-Dichlorobenzidene	Hexachlorobenzene	Nitrobenzene	2,4-Toluene diamine
Bis(2-ethylhexyl)phthalate	Dichloroethyl ether	Hexachlorobutadiene	4-Nitrobiphenyl	2,4-Toluene diisocyanate
	1,3-Dichloropropene	Hexachlorocyclopentadiene	4-Nitrophenol	o-Toluidine
Bis(chloromethyl)ether	Dichlorvos	Hexachloroethane	2-Nitropropane	Toxaphene
Bromoform	Diethanolamine	Hexamethylene-1,6-diisocyanate	N-Nitroso-N-methylurea	1,2,4-Trichlorobenzene
1,3-Butadiene	N,N-Diethyl aniline		N-Nitrosodimethylamine	1,1,2-Trichloroethane
Calcium cyanamide	Diethyl sulfate	Hexamethylphosphoramide	N-Nitrosomorpholine	Trichloroethylene
Caprolactam	3,3-Dimethoxybenzidine	Hexane	Parathion	2,4,5-Trichlorophenol
Captan	Dimethyl aminoazobenzene	Hydrazine	Pentachloronitrobenzene	2,4,6-Trichlorophenol
Carbaryl	3,3'-Dimethyl benzidine	Hydrochloric acid	Pentachlorophenol	Triethylamine
Carbon disulfide	Dimethyl carbamoyl chloride	Hydrogen fluoride	Phenol	Trifluralin
Carbon tetrachloride	Dimethyl formamide	Hydrogen sulfide	p-Phenylenediamine	2,2,4-Trimethylpentane
Carbonyl sulfide	1,1-Dimethyl hydrazine	Hydroquinone	Phosgene	Vinyl acetate
Catechol	Dimethyl phthalate	Isophorone	Phosphine	Vinyl bromide
Chloramben	Dimethyl sulfate	Lindane (all isomers)	Phosphorus	Vinyl chloride
Chlordane	4,6-Dinitro-o-cresol, and salts	Maleic anhydride	Phthalic anhydride	Vinylidene chloride
Chlorine	2,4-Dinitrophenol	Methanol	Polychlorinated biphenyls	Xylenes
Chloroacetic acid				

National Air Toxics Assessment 32-Compound Sub-list in red

"Pseudo" line lists from TDL spectra: Acrolein
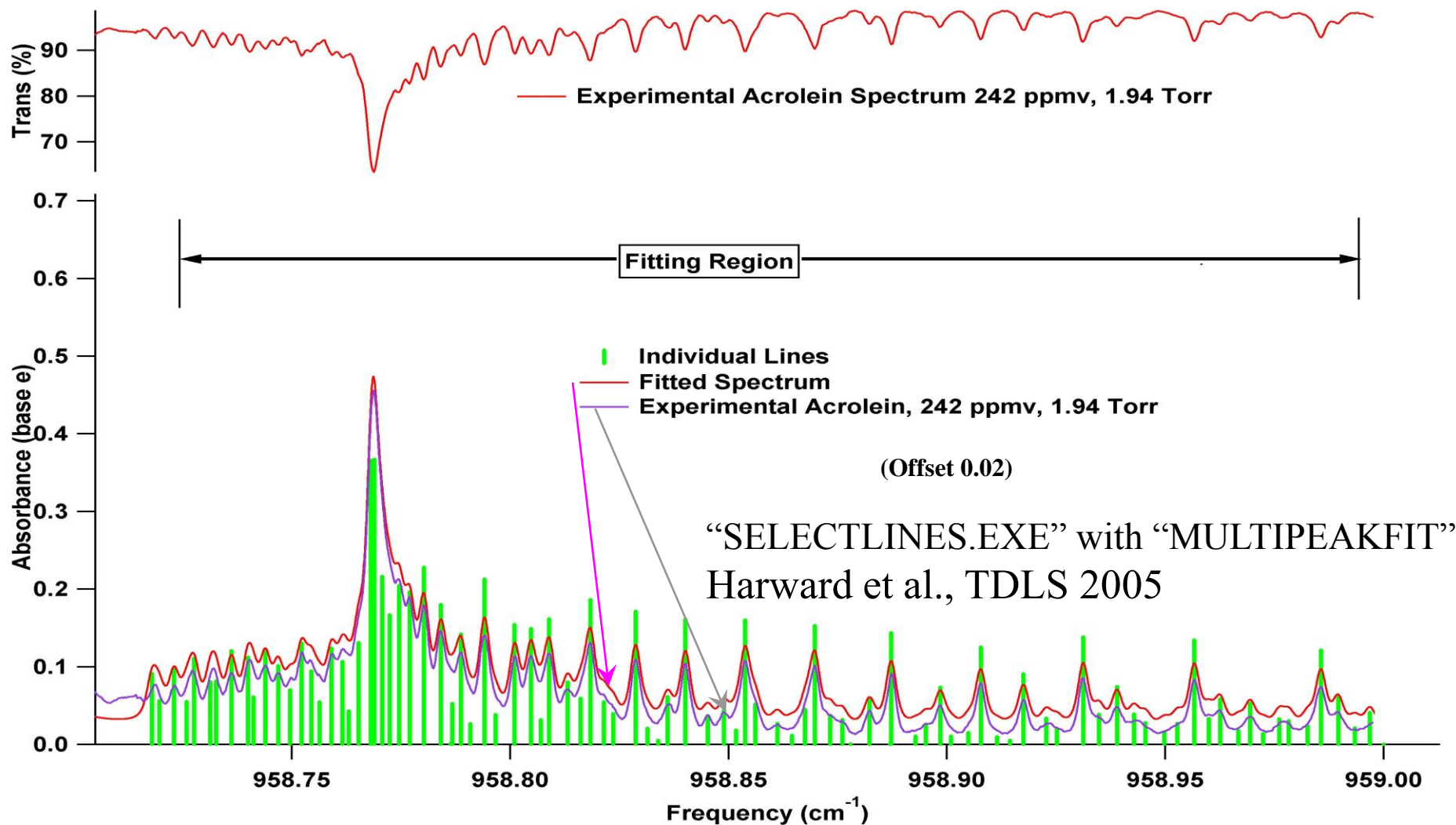
For better intensity information from the hi-resolution spectra by "scaling"
to the low resolution TDL spectra where intensity information is known accurately.

Acrolein Detection Scheme

High resolution FTIR Spectrum obtained from NRC (scaled to low TDL od spectra)

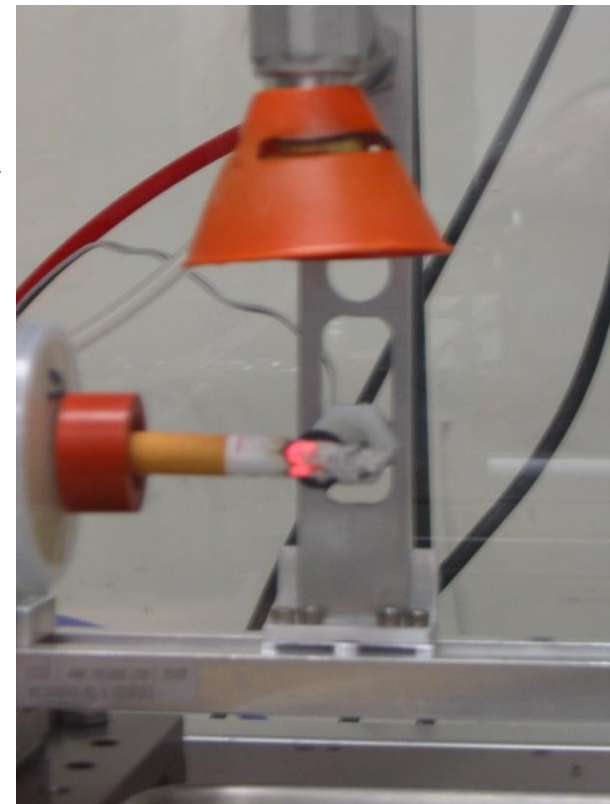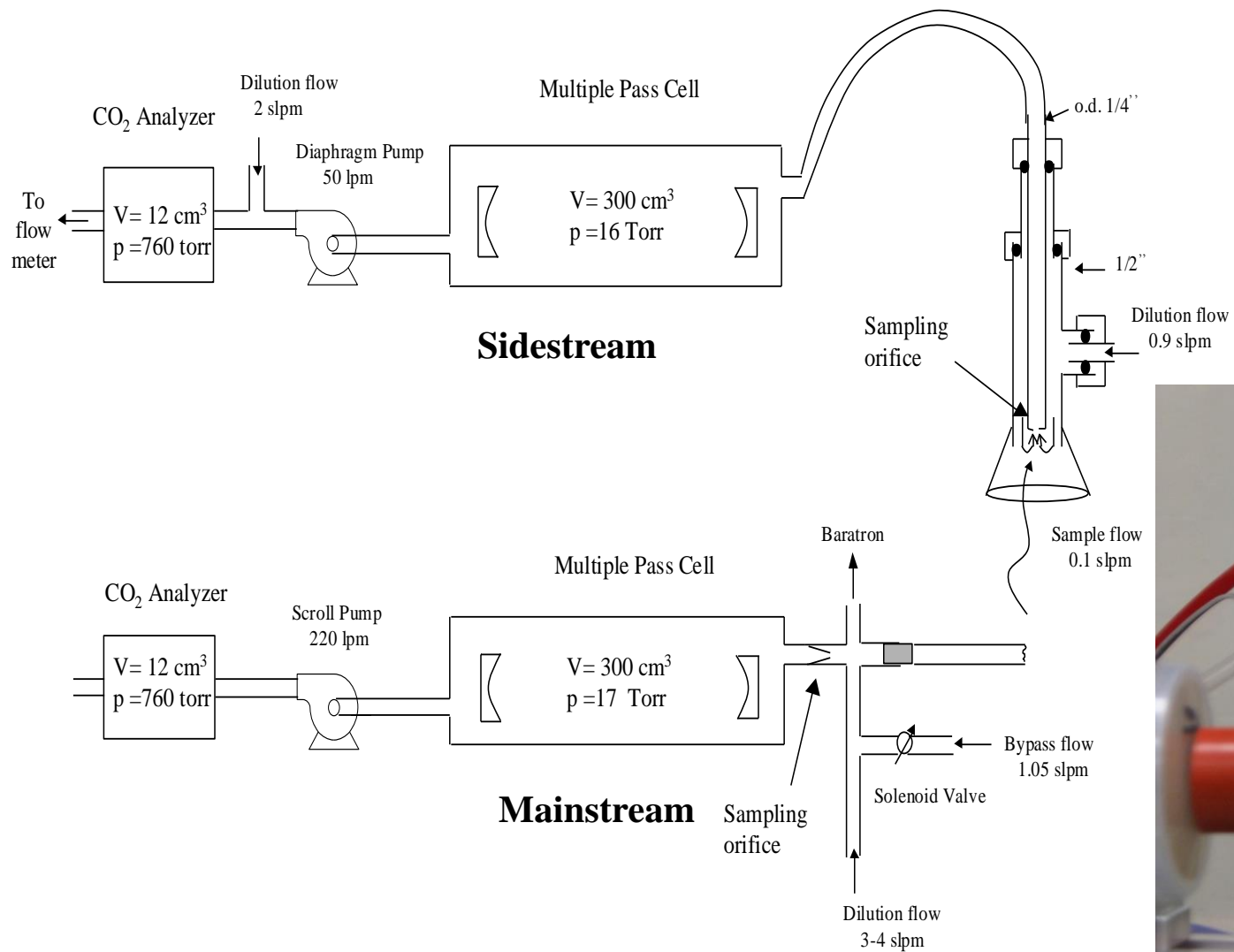Linestrengths from Harward et al. (2005), scaled to 76 m, 1 ppb, 50 Torr Abs max: 3×10^{-5}

Strongest features at 958 cm^{-1} with atmospheric background CO_2, H_2O

Background subtracted spectrum with Ethylene, 1 ppb

Acrolein Detection limit:
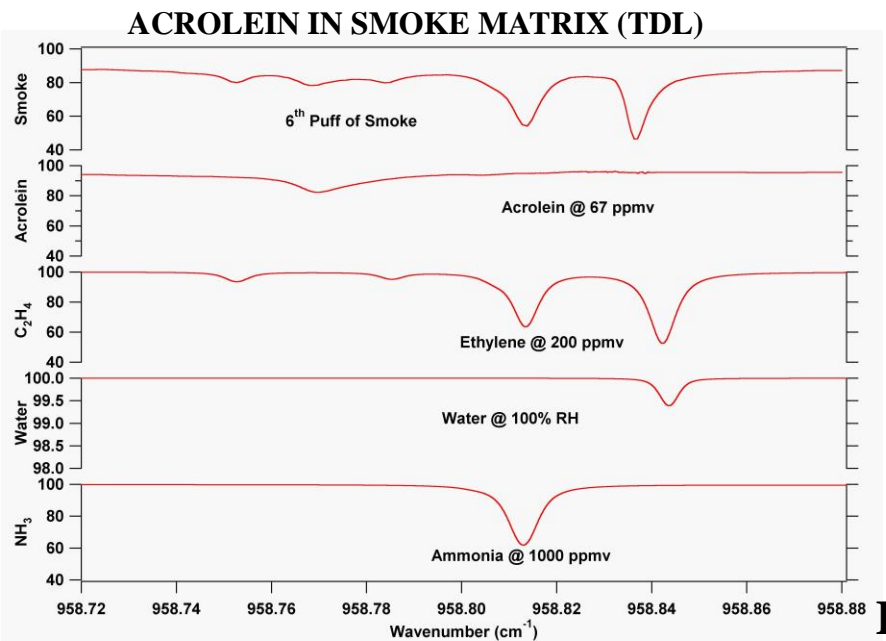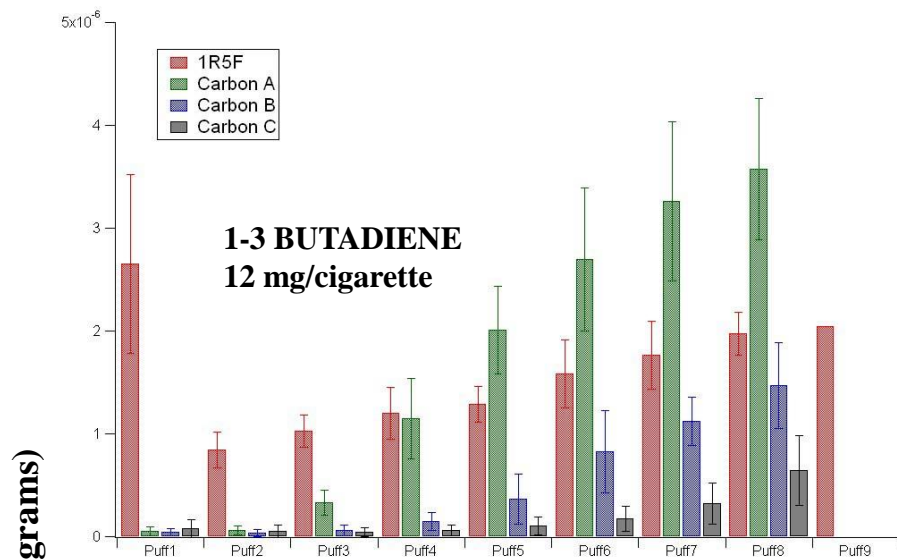   0.4 ppb (2s, 60 s)

Cigarette Smoke Analysis

Shi et al., Anal. Chem. 2003
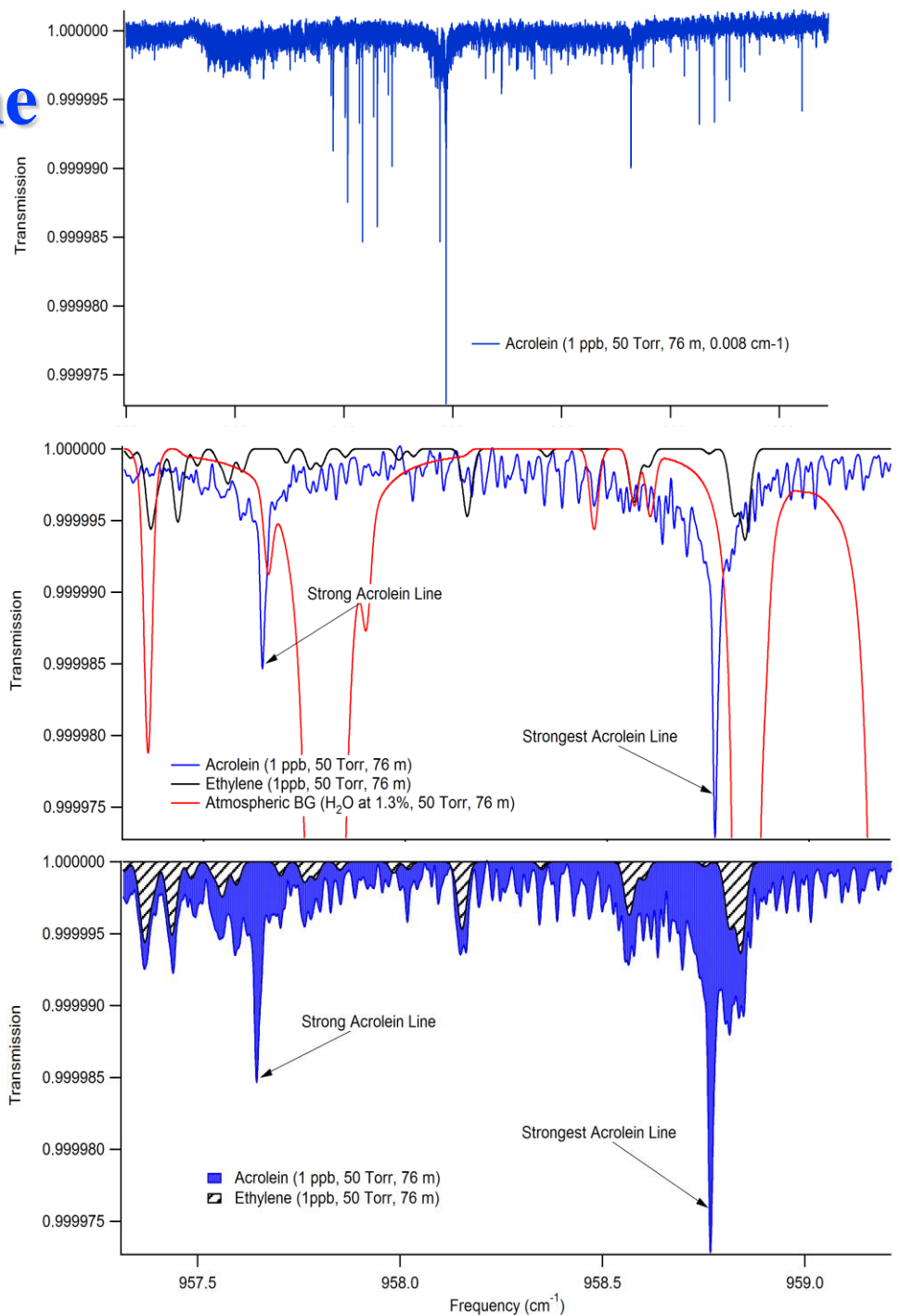
Cigarette Smoke Analysis with QCLs
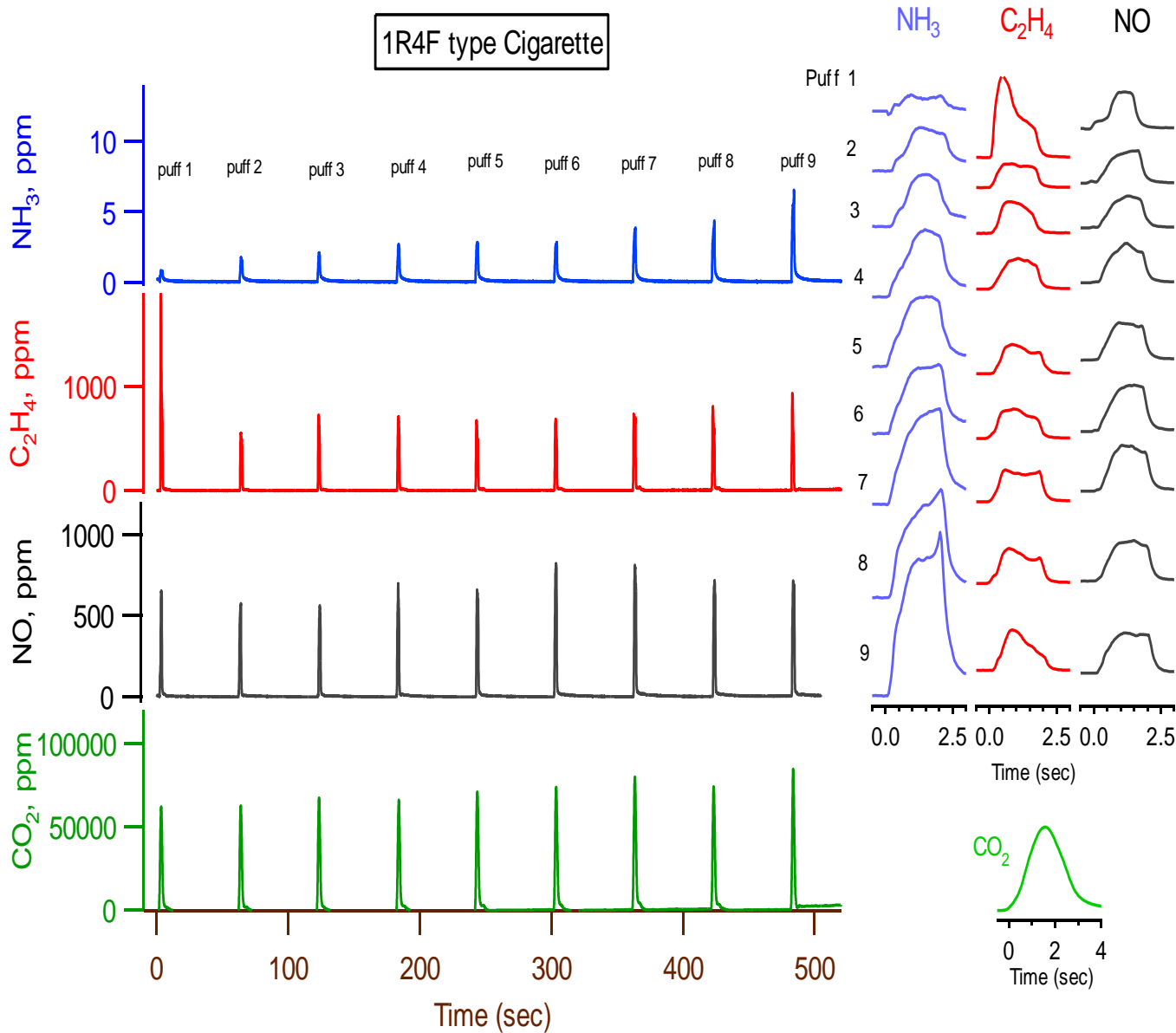
Acrolein Cigarette Smoke (TDL Spectra)
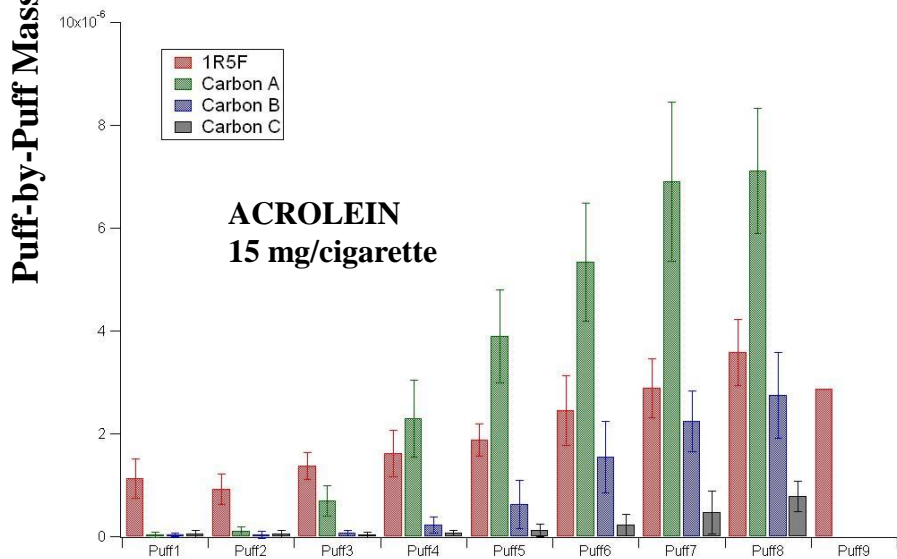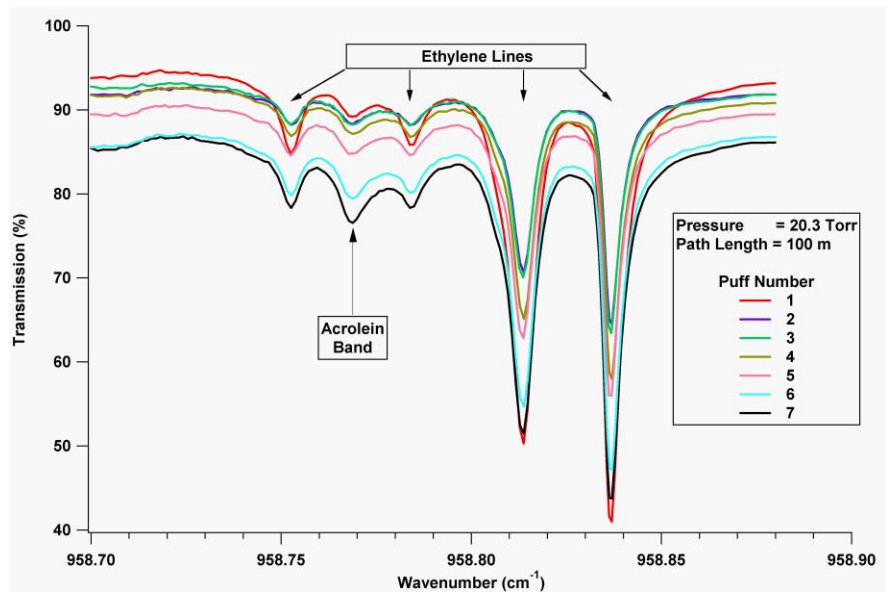
Ref: Harward, Thweatt, Parrish; TDLS 2005