Saddle Point Localization of Molecular Wavefunctions

G. Ch. MELLAU

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Padua, 22.05.2018

Outline

Molecules in highly excited states

1. Intuitive understanding of molecules and the [H,C,N] molecular system

FT-IR spectroscopy of the highly excited states

1. FT-IR Hot GAs Molecular Emission (HOTGAME) spectroscopy
2. Analysis of the high resolution very dense emission spectra of HCN and HNC

Complete eigenenergy list

1. Complete eigenenergy structure of the [H,C,N] molecular system
2. "Spectroscopy" of the *ab initio* [H,C,N] eigenenergies

Classical to Quantum correspondence at the saddle point

1. Classical and quantum frequencies at the barrier for Morse and quartic potential
2. New approximate analytical model and the [H,C,N] eigenenergies at the barrier

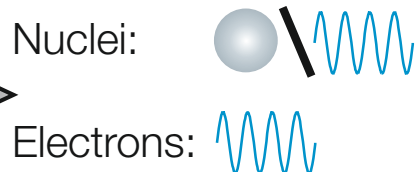## Saddle Point Localization

1. Saddle point localization of the wavefunctions for the quartic potential
2. Molecular saddle point localized states
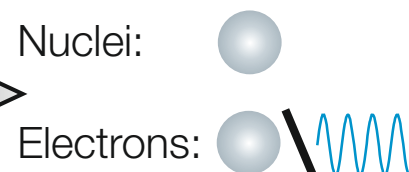
Intuitive understanding of molecules

Exact quantum mechanics

Nuclei:

Electrons:

Born-Oppenheimer model

Nuclei:

Electrons:

Classical coupling of electrons

Nuclei:

Electrons:

Physics → *Chemistry*

Molecular quantum mechanics	Quantum chemistry	Quasi-electron theory of molecules

H

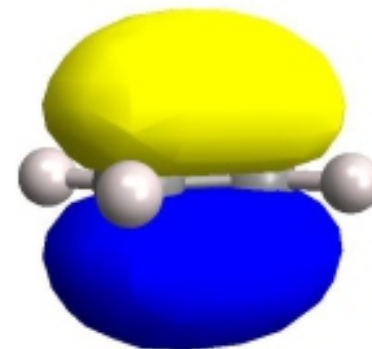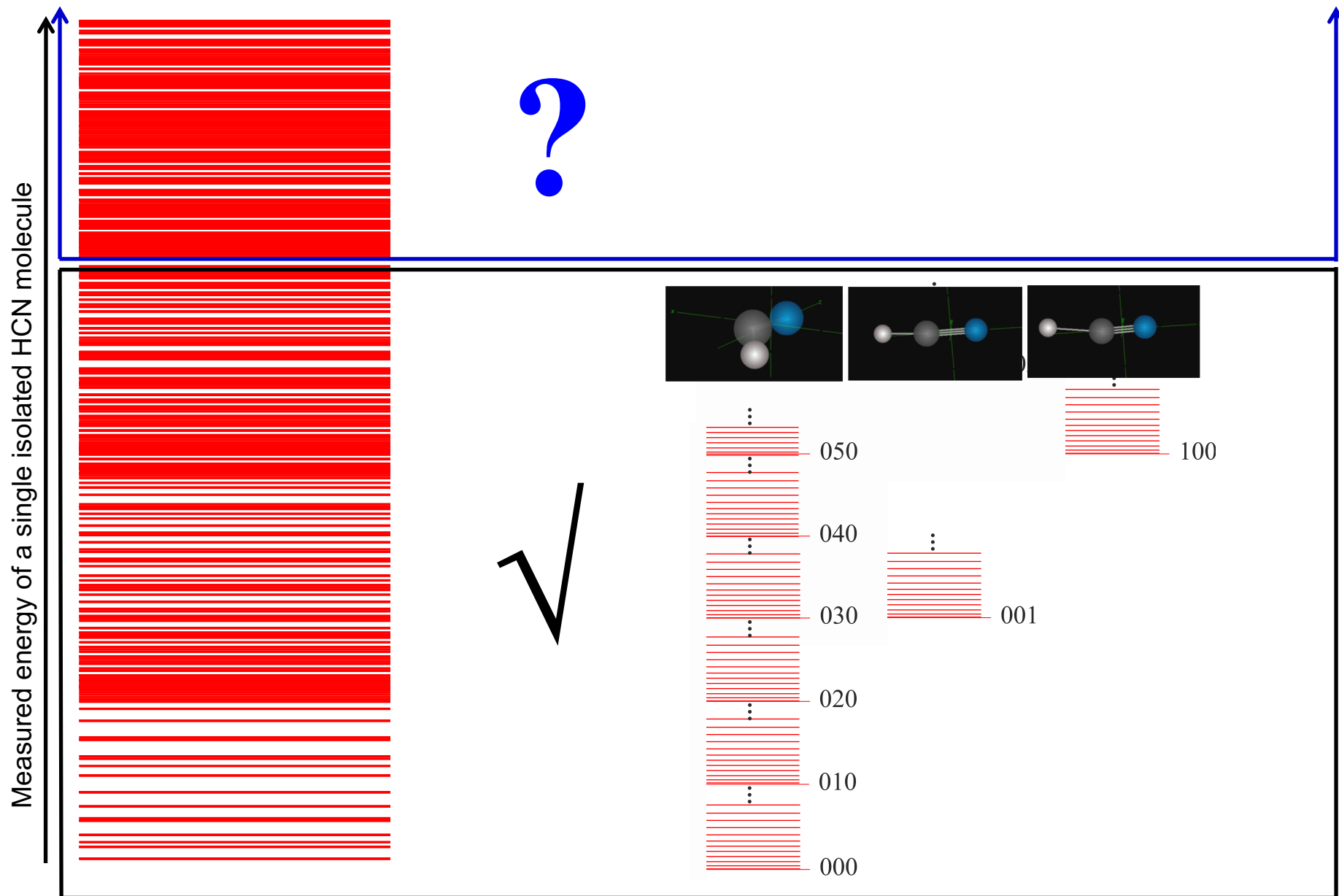H   C   C   H

H
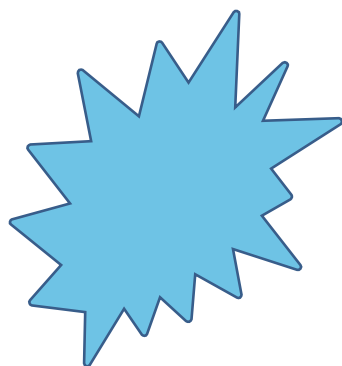
Molecules described by the molecular formula
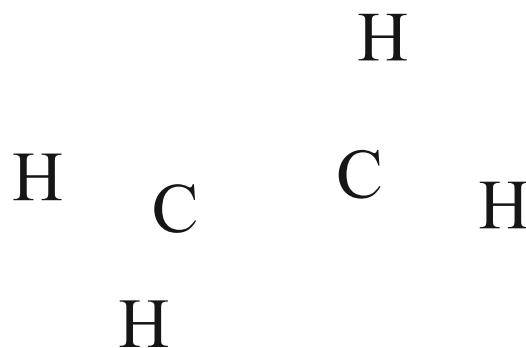
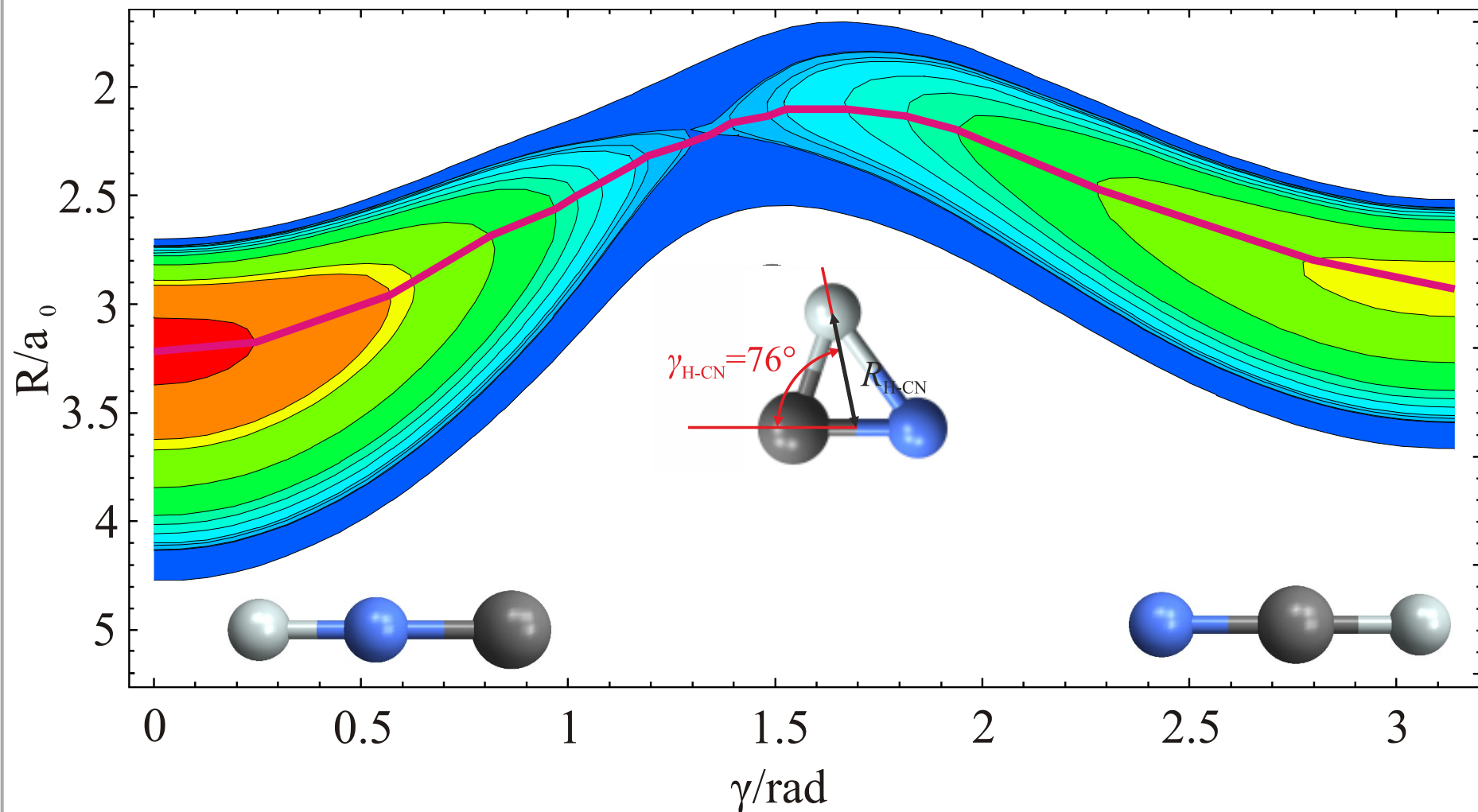Molecules with a shape described through the geometry of the nuclear configuration

Molecules with a shape made up from individual quasi-electrons

H. Primas, *Chemie in unserer Zeit, 19*, 109 (1985), G. Ch. Mellau, in preparation

Rovibrational states: What we understand

?

√

Measured energy of a single isolated HCN molecule

050

040

030

020

010

000

001

100

[H,C,N] molecular system

$\gamma_{\text{H-CN}} = 76°$

$R_{\text{H-CN}}$

R/a_0

γ/rad

Potential function form: Mourik *et al. J. Chem. Phys.*, **2001**, *115*, 3706-3718

[H,C,N] Molecular Eigenenergies
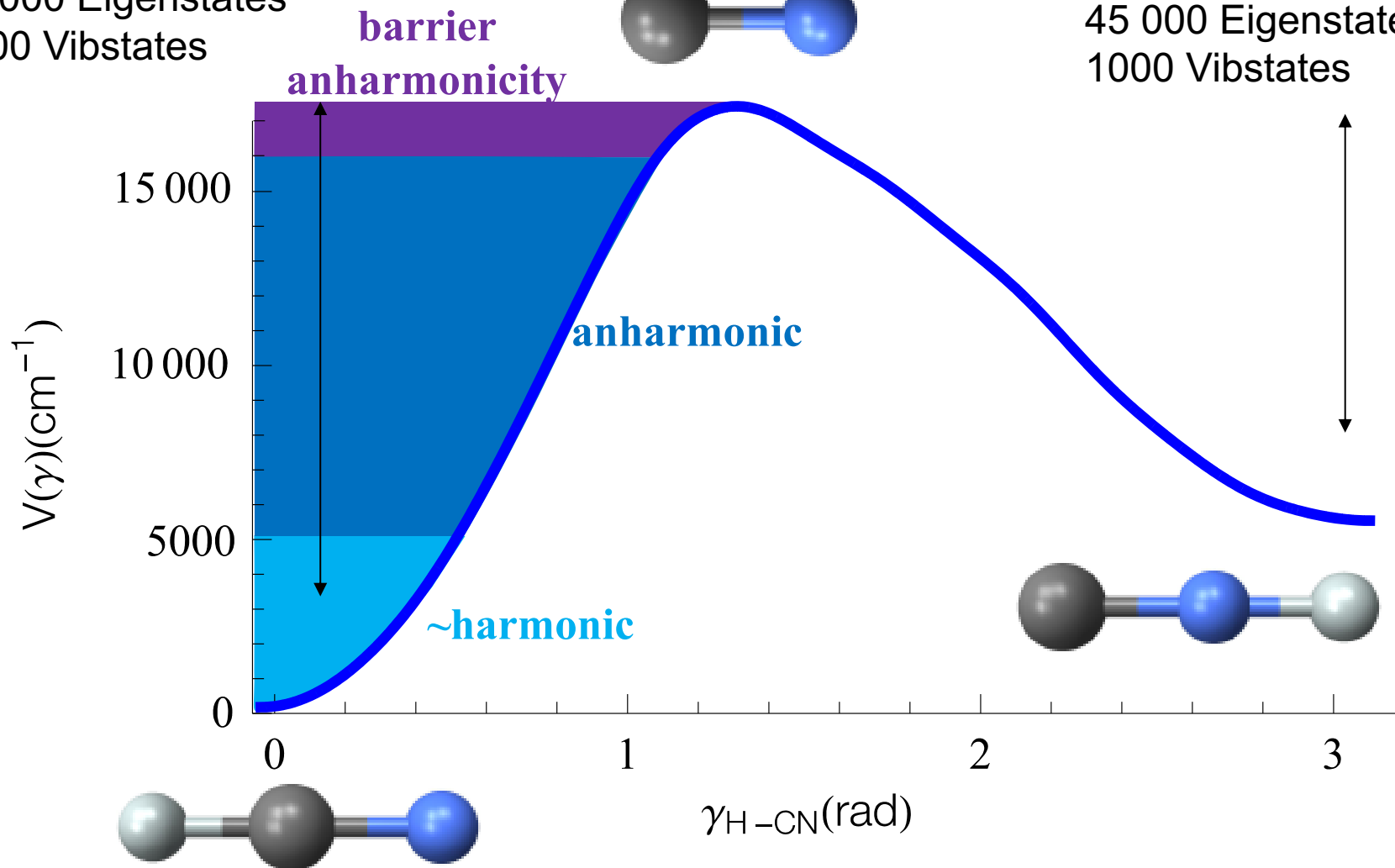
Isomerisation as bond-breaking "vibration"

H−CN

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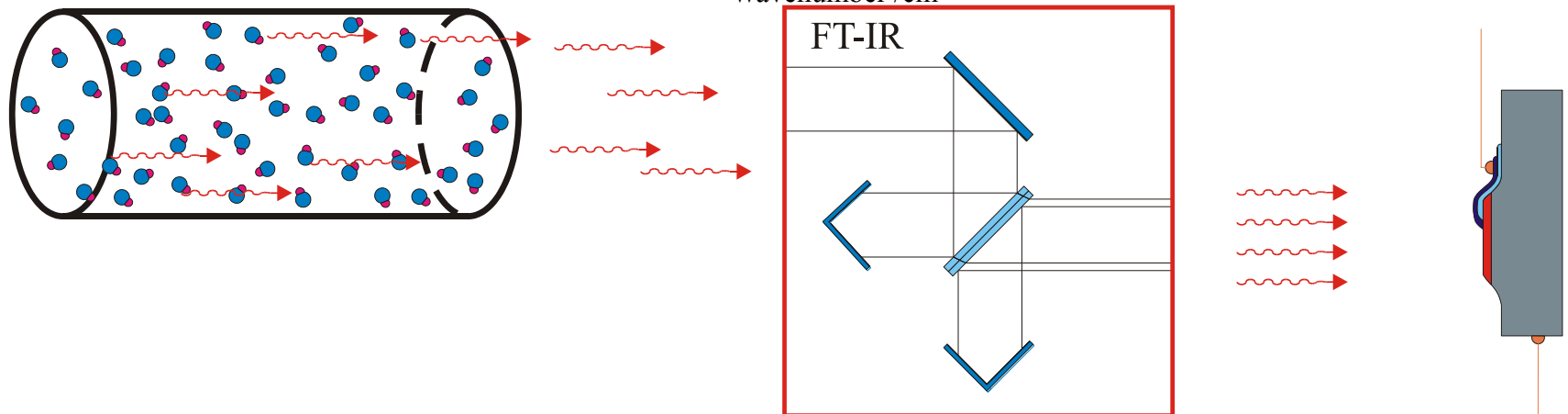2. New approximate analytical model and the [H,C,N] eigenenergies at the barrier
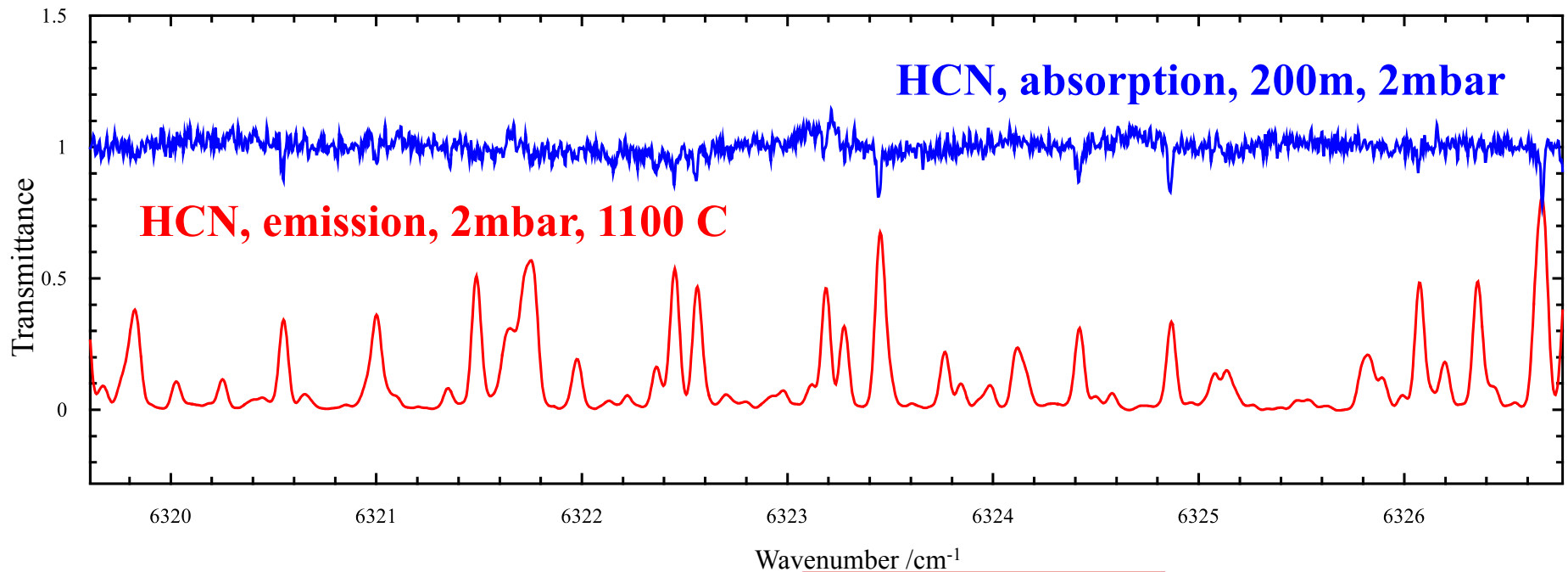
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FTIR absorption spectroscopy
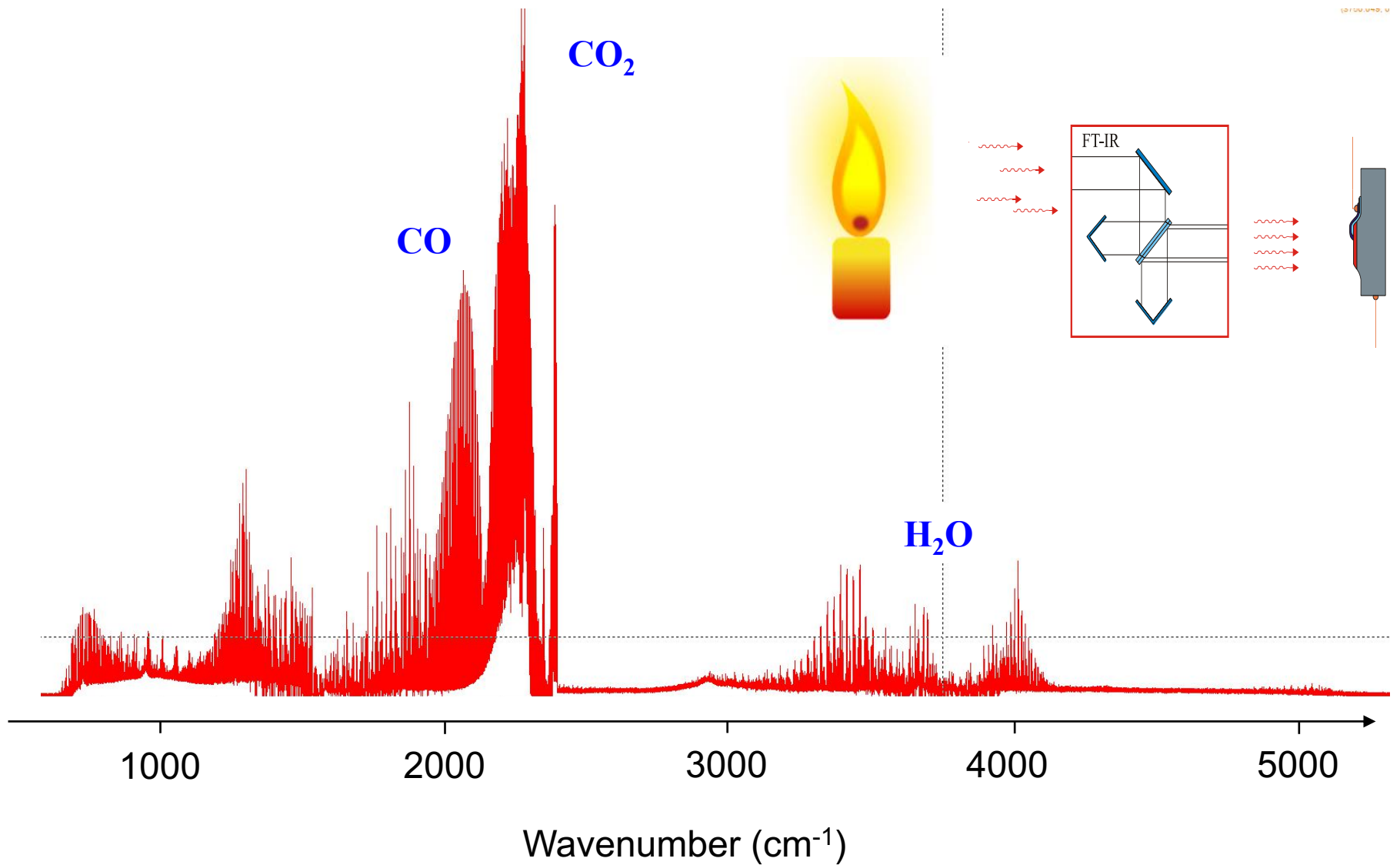
HCN, absorption, **200m**, 2mbar
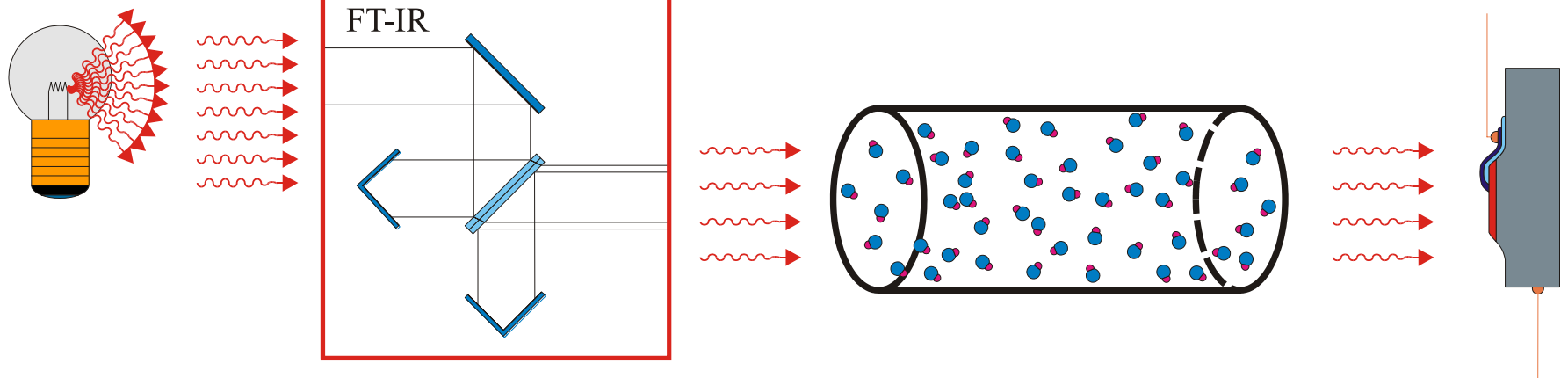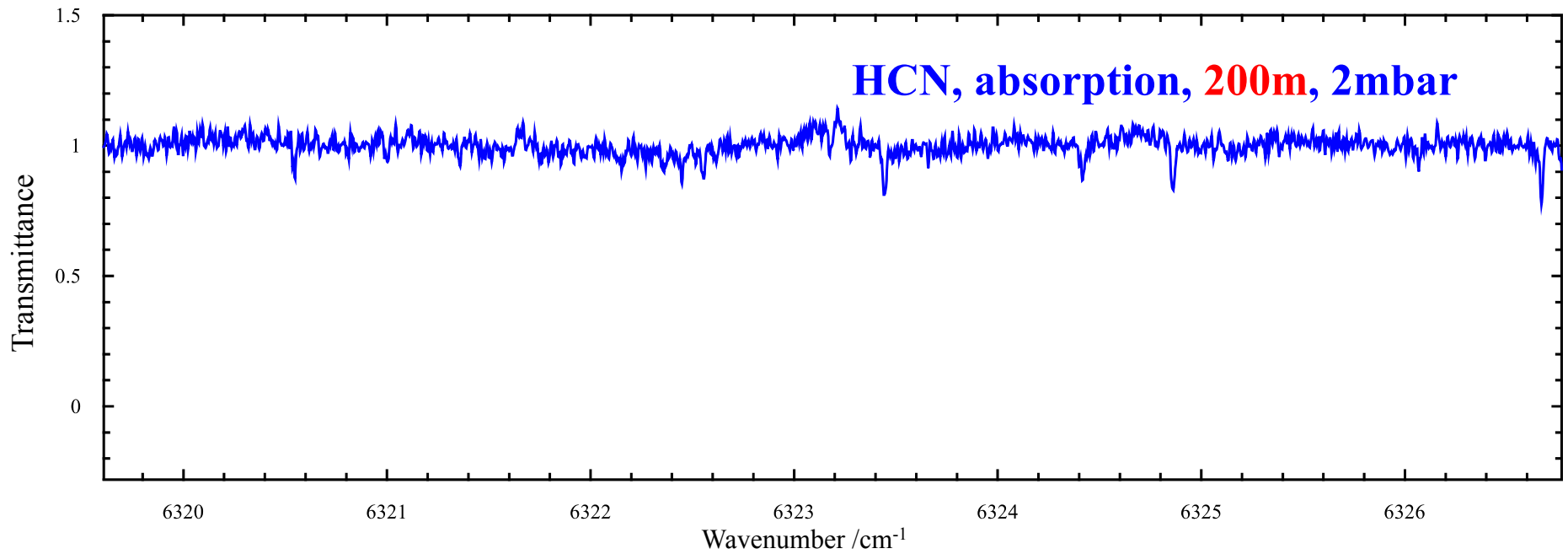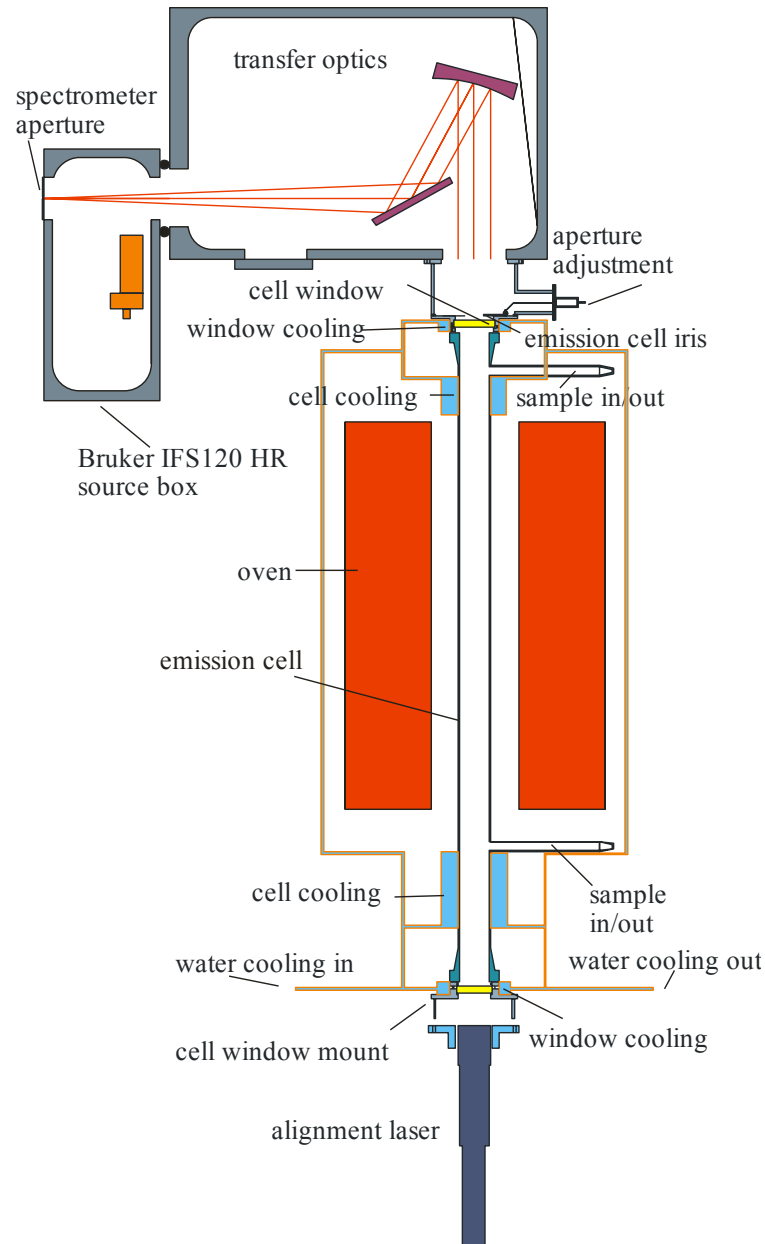
Absorption ↔ Emission

Hot gas infrared emission (HOTGAME) spectra are extremely rich in transitions in comparison with even very long path absorption measurements (G. Mellau and M. Winnewissser , 1997)
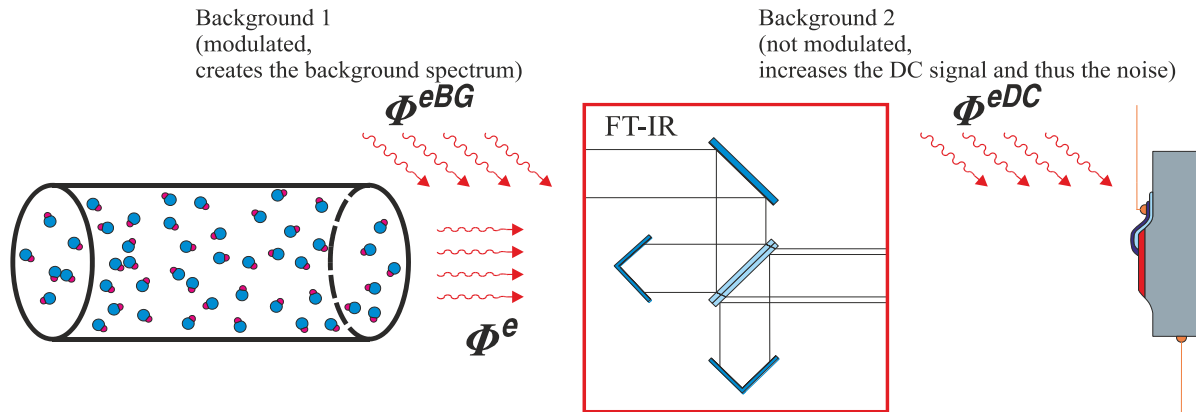
Emission spectrum of a candle

CO$_2$

CO

H$_2$O

FT-IR

Wavenumber (cm^{-1})

Hot gas molecular emission (HOTGAME)

transfer optics

spectrometer aperture

aperture adjustment

cell window

window cooling

emission cell iris

cell cooling

sample in/out

Bruker IFS120 HR source box

oven

emission cell

cell cooling

sample in/out

water cooling in

water cooling out

cell window mount

window cooling

alignment laser

HOTGAME spectroscopy

Background 1
(modulated,
creates the background spectrum)

Background 2
(not modulated,
increases the DC signal and thus the noise)

Φ^{eBG}

FT-IR

Φ^{eDC}

Φ^e

$$\Phi^e_{p\tilde{\nu}} + \Phi^{eBG}_{p\tilde{\nu}} + \Phi^{eDC}_{p\tilde{\nu}} = \Phi^{eS}_{p\tilde{\nu}}$$

HOTGAME spectroscopy

Background 1
(modulated,
creates the background spectrum)

Φ^{eBG}

FT-IR

Background 2
(not modulated,
increases the DC signal and thus the noise)

Φ^{eDC}

Φ^e

$$\Phi^e_{p\tilde{\nu}} + \Phi^{eBG}_{p\tilde{\nu}} + \Phi^{eDC}_{p\tilde{\nu}} = \Phi^{eS}_{p\tilde{\nu}}$$

HCN Emission experiments

1997   1100 °C

2007   1300 °C.

HCN

HNC
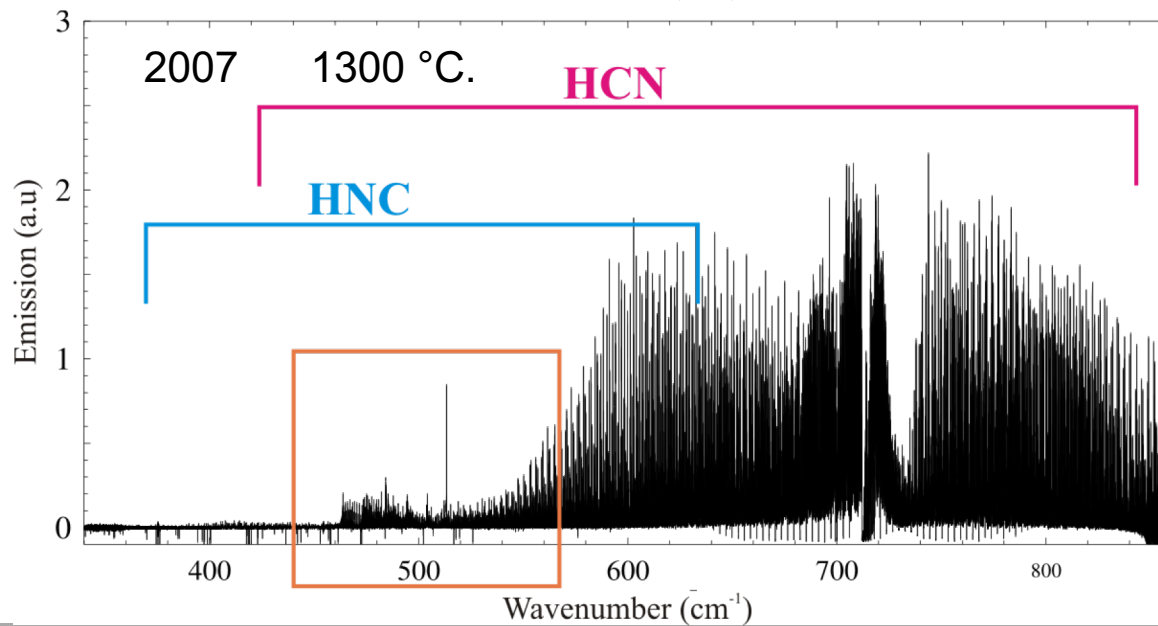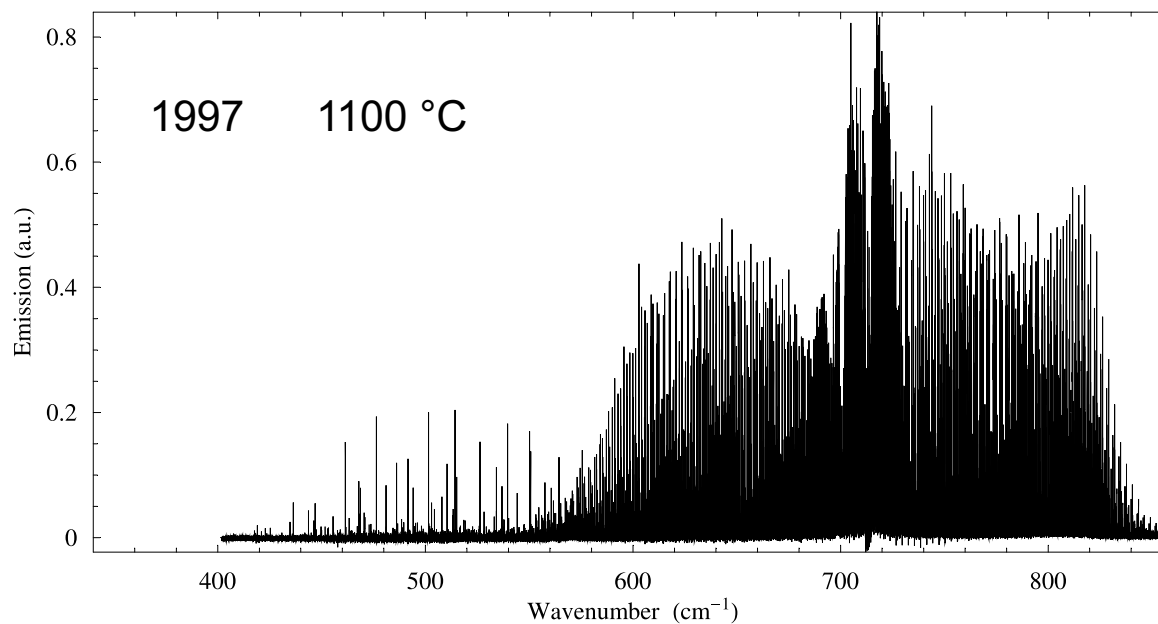
HCN/HNC emission spectra

HOTGAME spectroscopy of CO$_2$

T=1923 K

R(146)

2378.4479 cm^{-1} R(198)

[c] D. Bailly, C. Camy-Peyret, R. Lanquetin, Temperature Measurement in Flames through CO$_2$ and CO Emission: New Highly Excited Levels of CO$_2$, J.Mol.Spectrosc.182,10 (1997).
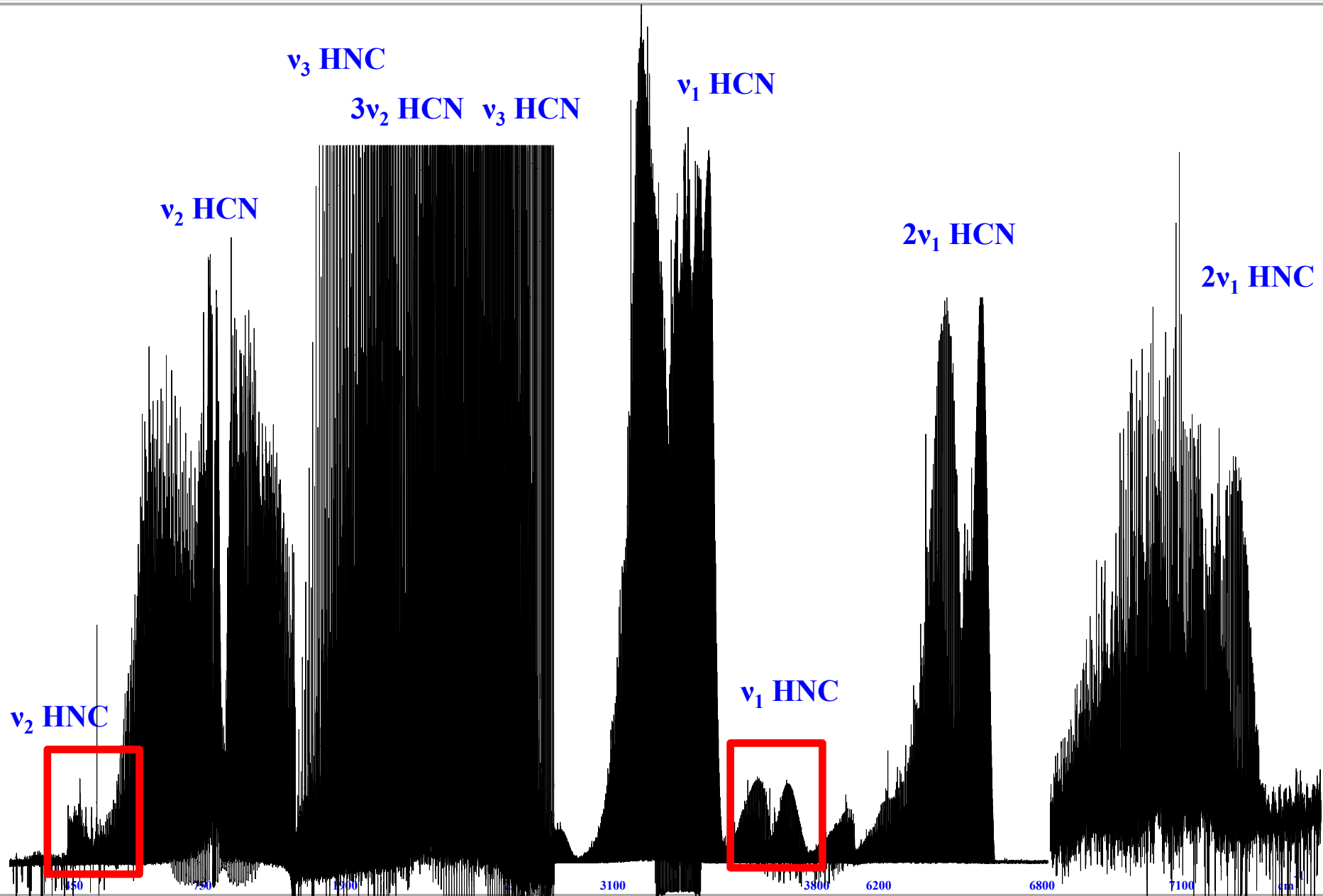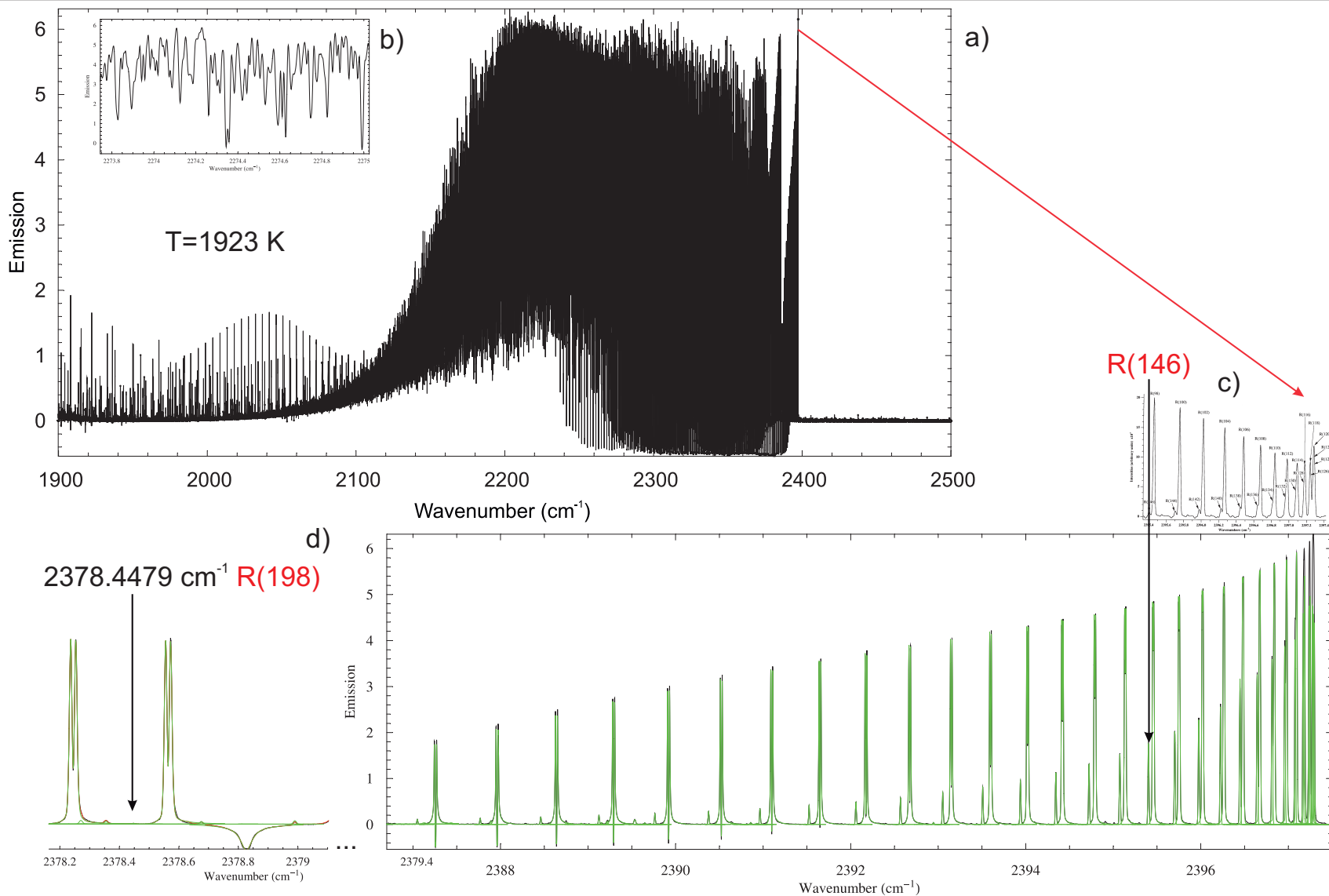
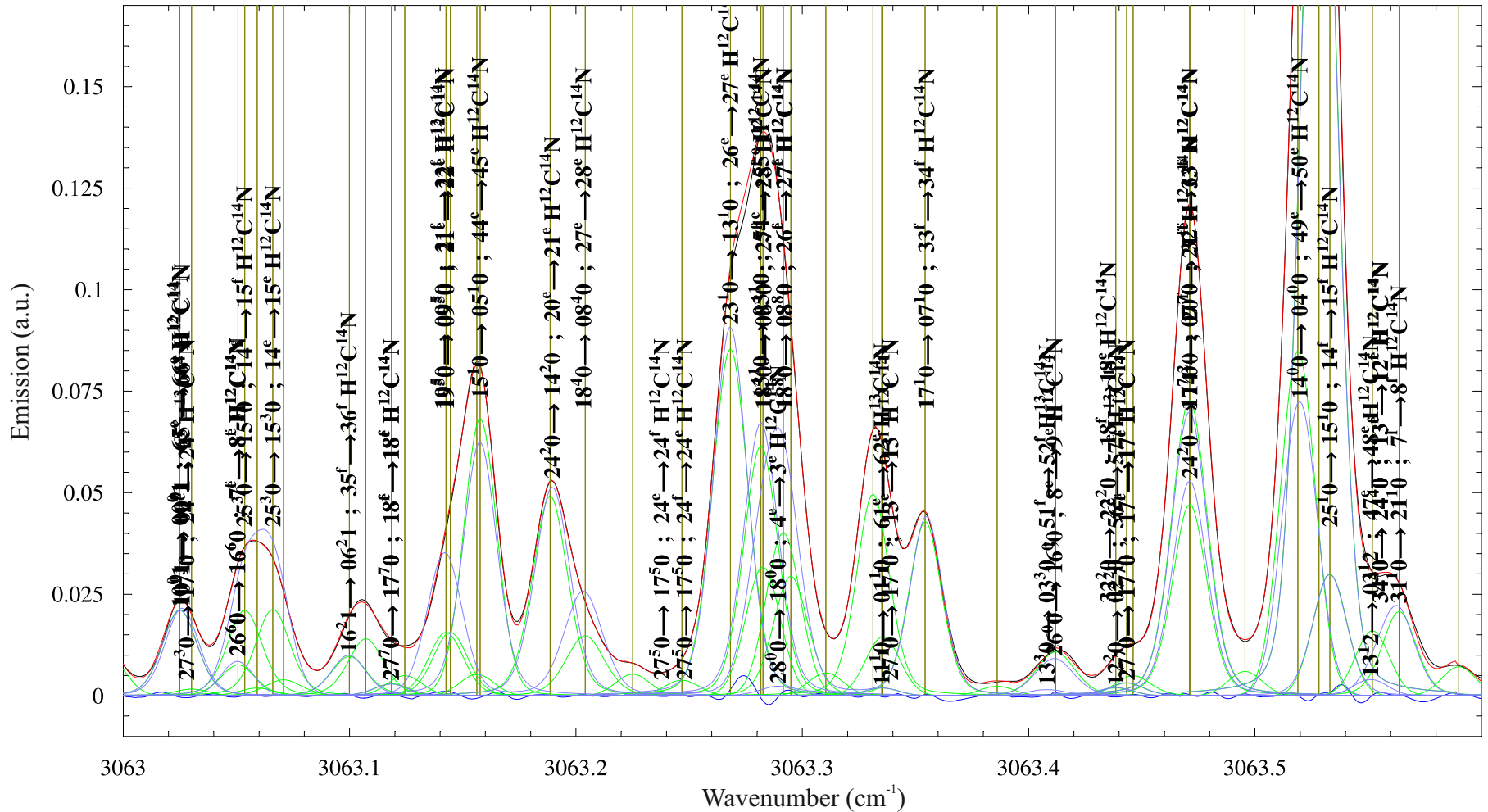# HOTGAME spectroscopy of H_2O
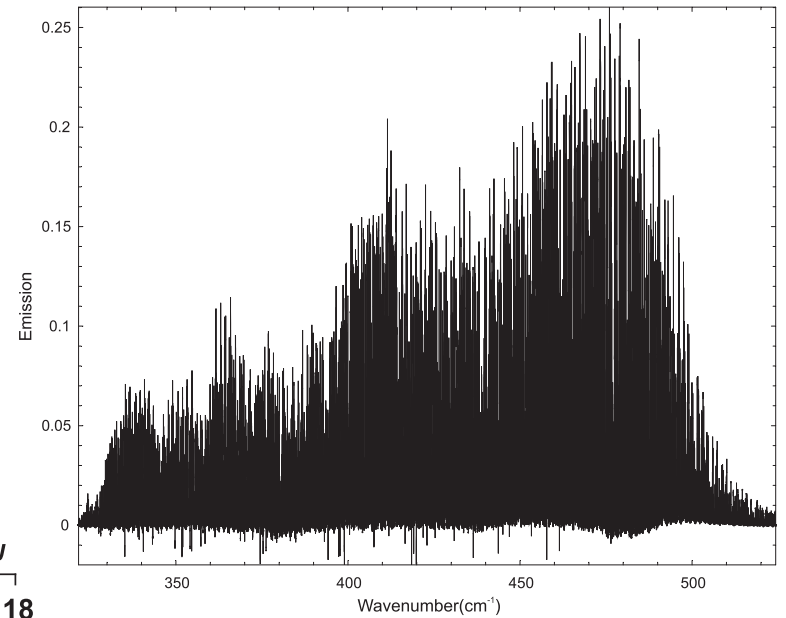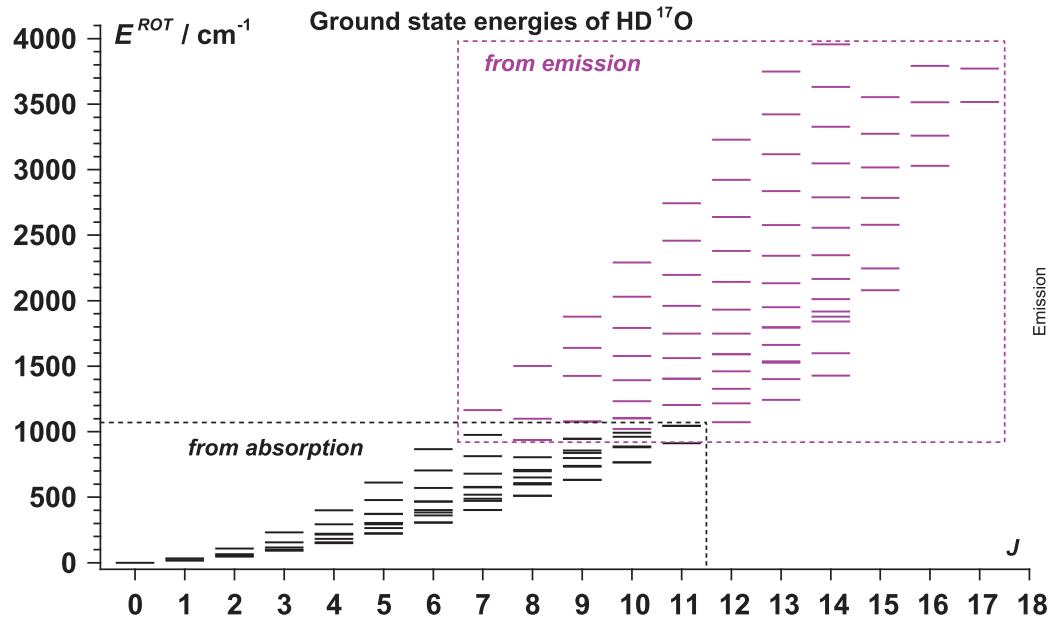
Analysis

I skipped this in fact very important part due to the time limit: To assign these spectra some very complex assignment program is needed where the (x,y) data points of the spectrum are linked directly to the eigenvalues of the Energy Matrix. In this way it is possible to achieve a perfect deconvolution of the overlapping lines. This is a screenshot of the analysis program.

HNC: The ν_1 band system

G. Ch. Mellau, *J. Mol. Spectrosc. 264*, 2 (2010)

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Complete eigenenergy list

25.000 + 20.000 eigenstates

HCN

HNC

complete

complete

E (cm^{-1})

0 γ π

15000

10000

5000

0
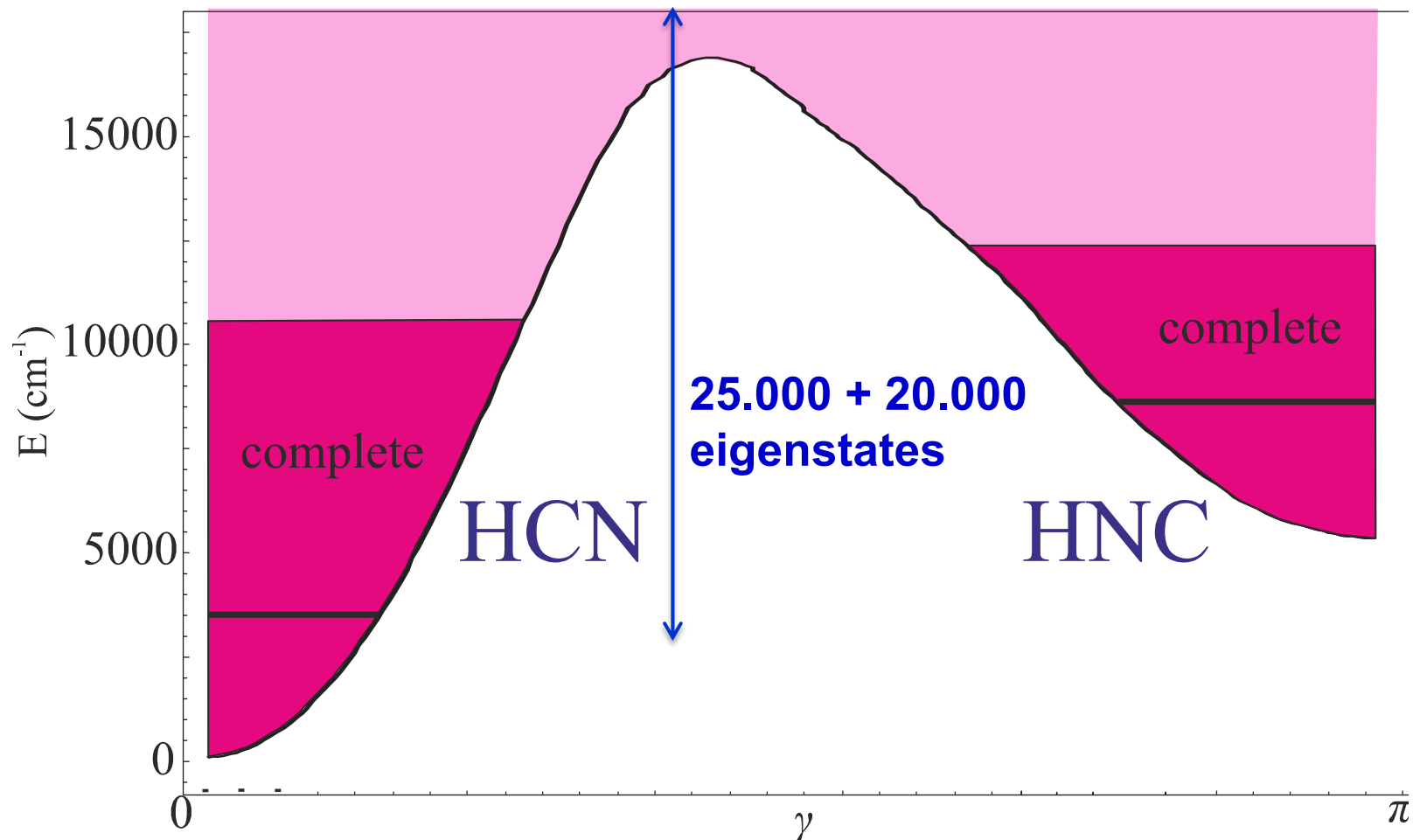
G.Ch. Mellau, *J. Chem. Phys*. 133, 164303 (2010),
G.Ch. Mellau, *J. Chem. Phys*. 134, 234303 (2011),… 14 papers and some in preparation

Complete eigenenergy list

Rovibrational eigenenergy structure of the [H,C,N] molecular system

Georg Ch. Mellau[a)]
Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany

Fundamental understanding of the structure and dynamical evolution of molecules can be extracted from high resolution spectra. The list of possible rovibrational eigenenergies is the main result obtained from these experiments. In principle, these eigenenergies could be determined to any precision by theoretical calculations if the molecular Schrödinger equation, which describes the correlated motions of the electrons and nuclei could be solved exactly. This is, however, not possible, because while this multi-dimensional eigenvalue differential equation is extremely simple to formulate, it is impossible to solve. For polyatomic molecules we can obtain theoretical eigenenergies for the molecular motion of the nuclei only within the Born-Oppenheimer approximation using a highly accurate potential energy surface (PES). But even using such an exact PES the eigenenergies observed do not reach the accuracy of the high resolution experiments. In fact in high resolution spectroscopy we reverse the situation described: we use experiments to solve the molecular Schrödinger equation. The analysis of the observed

Accurate partition functions

The internal partition function Q_{int} of a free molecule is

$$Q_{int}(T) = \sum_i g_i(2J_i + 1)\mathrm{e}^{-\frac{c_2 E_i}{T}} \equiv \text{Complete Eigenenergy List}$$

where c_2 is the second radiation constant, J_i is the rotational quantum number and g_i is the degeneracy factor. The relative accuracy of the partition function at temperature T calculated by summing over the E_i high resolution eigenenergies is

$$\frac{u(Q_{int})}{Q_{int}}(T) \approx \frac{u(E_i)[\mathrm{cm}^{-1}]}{T[K]}$$

where $u(E_i)$ is the measurement uncertainty of energy levels given in cm^{-1}. All levels up to ~16*T excitation energy in cm^{-1} must be measured and included in the sum. For HCN the complete eigenenergy list is very accurate with $u(E_i)$=0.0005 - 0.00001 cm^{-1} resulting in
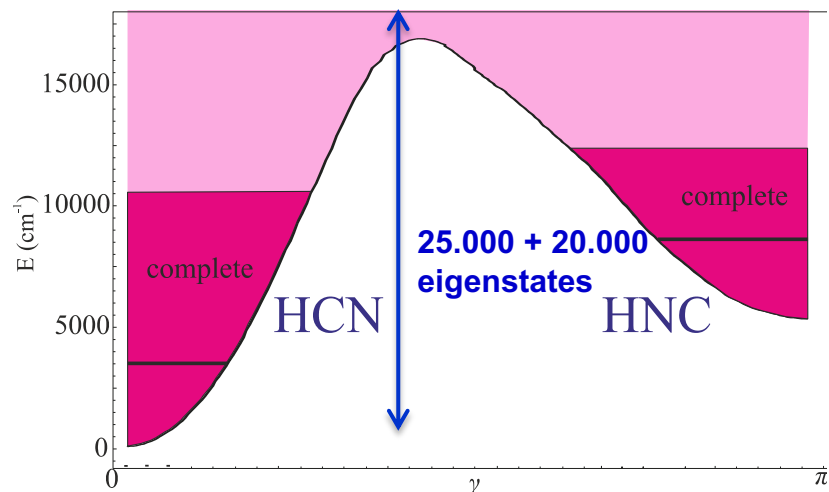
$$Q_{\mathrm{HCNint}}(298\mathrm{K}) = 148.70043(5)$$

where the uncertainty has been calculated based on the specific mean uncertainty of each rovibrational data set. The best values published before are 148.72 and 148.5(5). Theoretical first principle calculations are limited to $u(Q_{int})/Q_{int}$=10^{-2}-10^{-4}. The accuracy of Q_{int} is in fact related to the question up to which excitation energy is the measured eigenenergy list complete.

Ab initio [H,C,N] eigenenergies: $v_1 v_2^l v_3$?

e, $J=0$	e, $J=1$	f, $J=1$	…		e, $J=60$	f, $J=60$
0.0000	2.9100		00^00		5376.5455	
	718.7979	718.8120…	01^10		6091.7720	6118.0706
1414.9159	1417.8414		02^00		6797.5744	
2100.5823	2103.4725		02^20		6852.9351	6832.6549
2801.4591	2117.2600	2117.2909…			7440.7011	7535.3291
3307.7458	2804.4008	2816.9020…			7494.9722	7582.0682
3510.9917	2816.8871	3496.8648…			7568.2503	8179.3270
4176.2430	3310.6353	4007.1891…			8153.0590	8231.9466
4181.4534	3496.8172	4210.5491…			8187.3730	8300.5555
4686.2843	3513.8969	4865.8119…			8268.2633	8891.0365
…	…	…			…	…
		…				
18754.768	18150.834	18029.4513 …			18033.7293	18057.3009
18770.643	18159.392	18051.2290…			18036.1204	18063.0370
18795.017	18165.387	18087.2527…			18039.4689	18091.6386
18817.187	18165.677	18096.2871…			18055.2306	18102.6992

HCN/HNC eigenenergy and eigenvector data sets

from experiments

E (cm^{-1})

15000

10000

5000

0

complete

complete

HCN

HNC

complete

25.000 + 20.000 eigenstates

0   γ π

3

60 000 HCN/HNC peaks!

HCN

HNC

Emission (a.u)

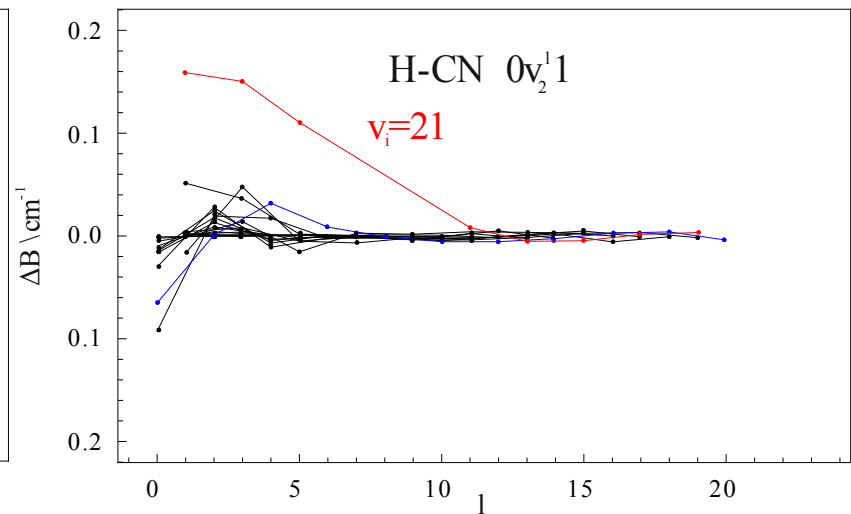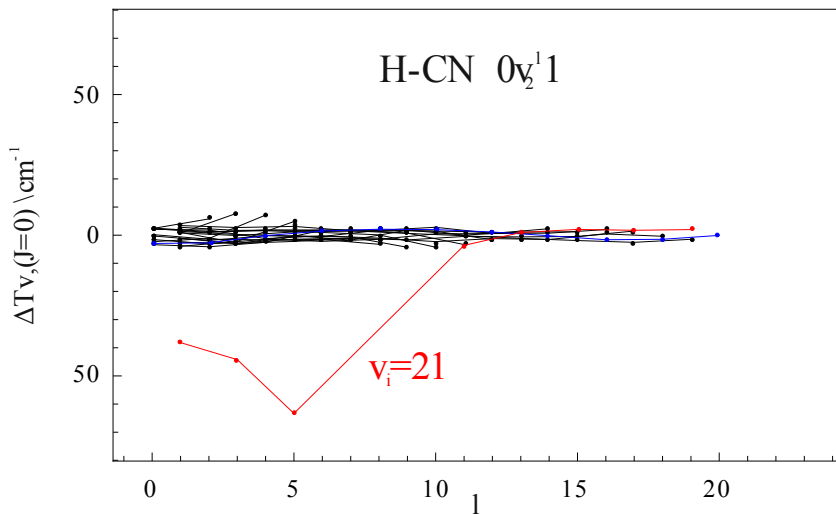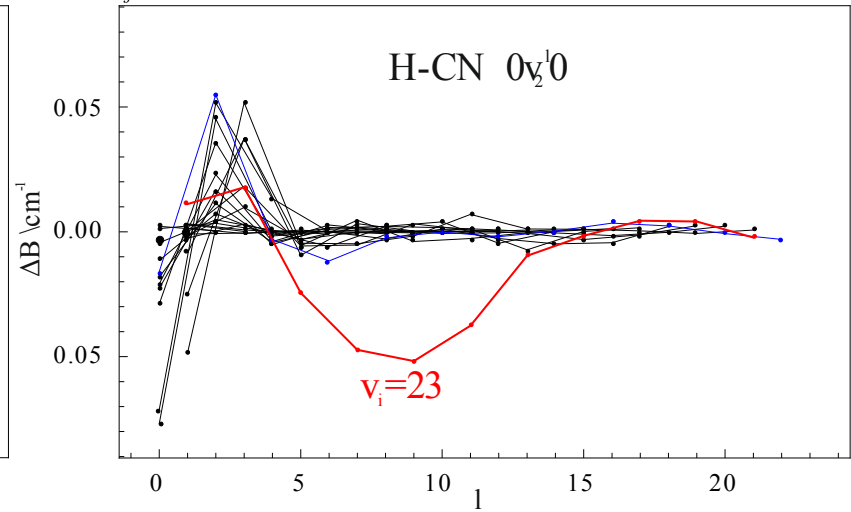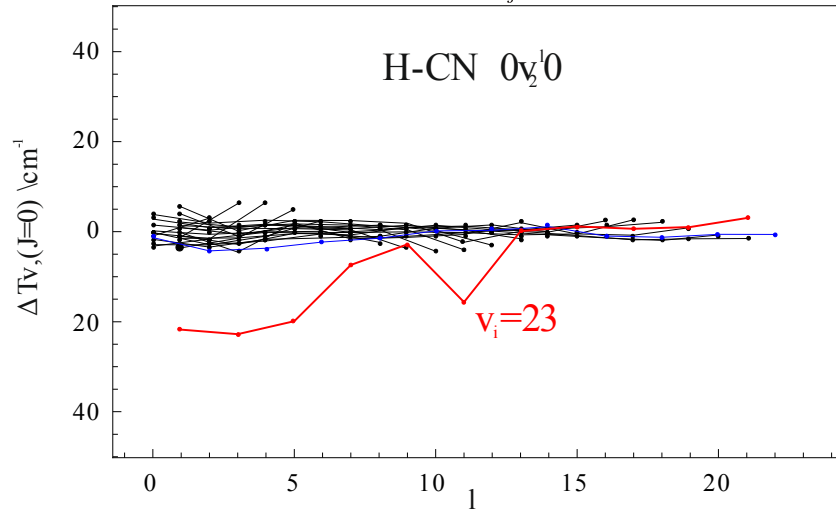400   500   600   700   800

Wavenumber (cm^{-1})

G.Ch. Mellau, *J. Chem. Phys.* 133, 164303 (2010),
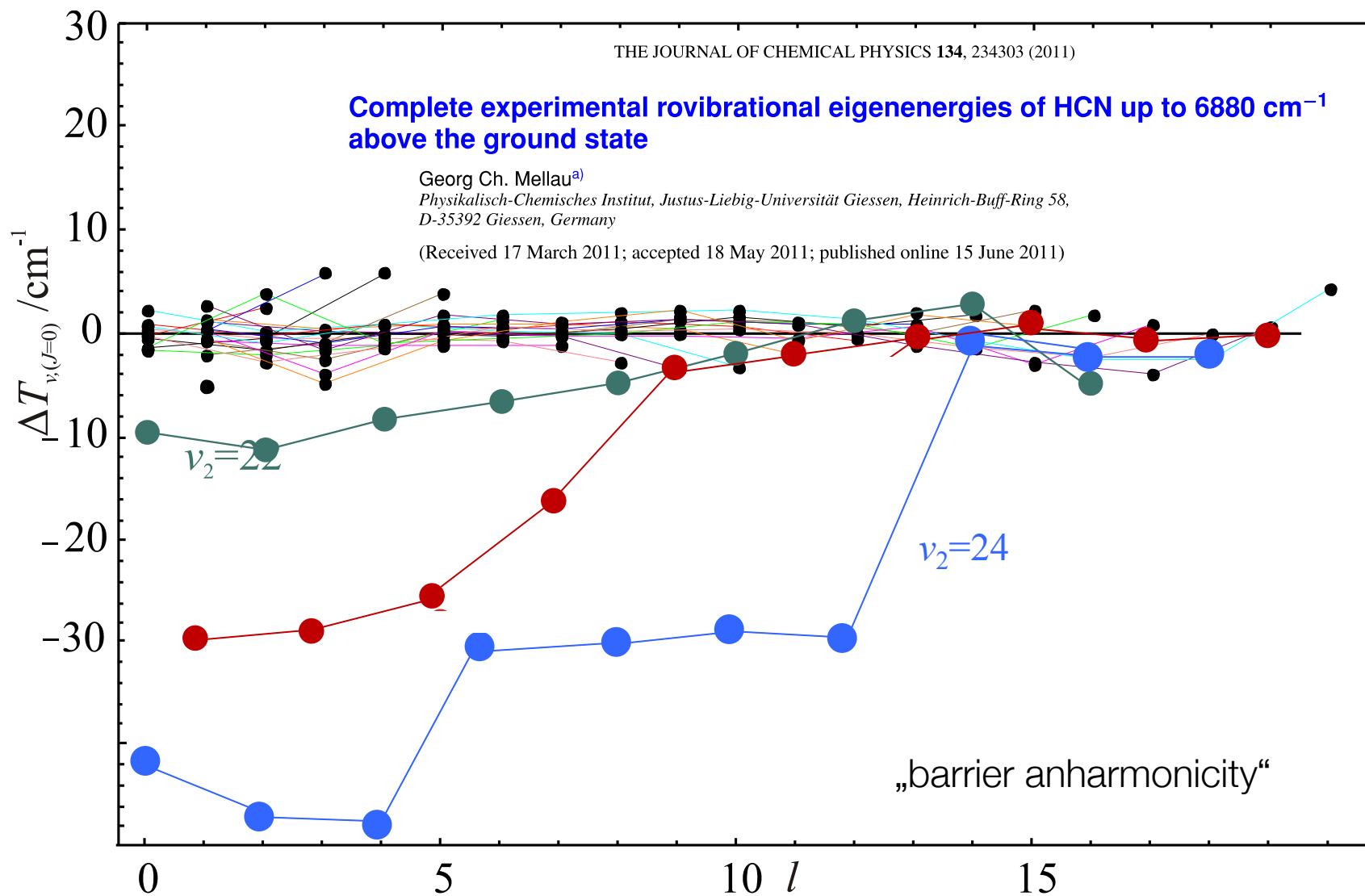G.Ch. Mellau, *J. Chem. Phys.* 134, 234303 (2011),… 14 papers

Complete (v_1,v_2,v_3,l) assigned ab initio up to the isomerization barrier

e, $J=0$	e, $J=1$		e, $J=60$	f, $J=60$
0.0000	2.9100	00^00	5376.5455	
	718.7979	01^10	6091.7720	6118.0706
1414.9159	1417.8414	02^00	6797.5744	
2100.5823	2103.4725	02^20	6852.9351	6832.6549
…	…		…	…
18754.768	18150.834	?????	18033.7293	18057.3009
18770.643	18159.392	?????	18036.1204	18063.0370

Complete pattern based assignment of all 168.110 ab initio rotation-vibration eigenenergies

G.Ch. Mellau, *J. Chem. Phys.*, 134, 234303 (2011)

Source 1): UCL Exomol ab initio list

Mourik *et al. J. Chem. Phys.* 115, 3706 (2001), G. J. Harris *et al.*, *MNRAS* 367, 400 (2006)

Source 2): extended 1) to higher energies with stored eigenvectors and improved convergence (A. Kyuberis, O. Polyansky, N. F. Zobov)
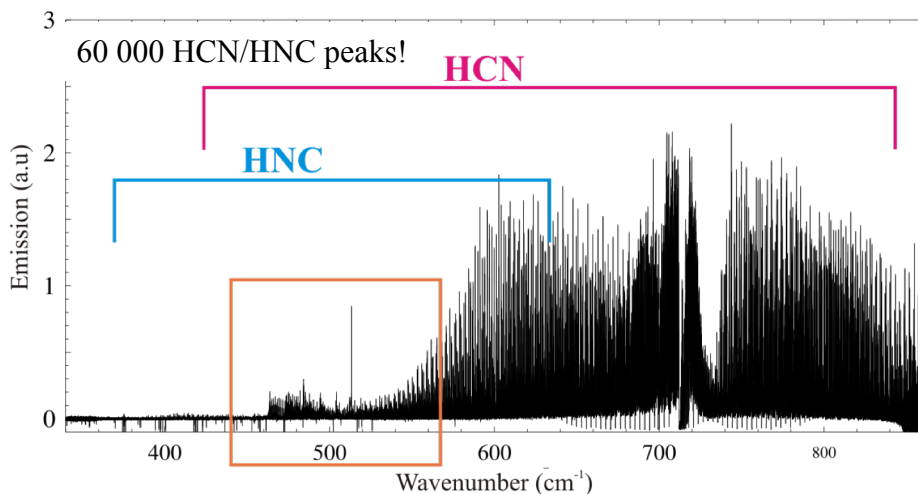
Onset of isomerization: $0v_20 \Rightarrow 23$ and $0v_21 \Rightarrow 21$

$$\sum_{i=1}^{3} \omega_i \left(\frac{d_i}{2} + v_i\right) - \sum_{i=1}^{3} \frac{d_i \omega_i}{2} + l^2 g_{2,2} + \sum_{i=1}^{3}\sum_{j=i}^{3} \left(\frac{d_i}{2} + v_i\right)\left(\frac{d_j}{2} + v_j\right) x_{i,j} - \sum_{i=1}^{3}\sum_{j=i}^{3} \frac{1}{4}\left(d_i d_j\right) x_{i,j} + \sum_{i=1}^{3} l^2 \left(\frac{d_i}{2} + v_i\right) y_{i,l,l} + \ldots$$

G. Ch. Mellau, in preparation

Vibrational signature of the isomerization
Vibrational signature of a transition state

Complete experimental rovibrational eigenenergies of HCN up to 6880 cm^{-1} above the ground state

Georg Ch. Mellau[a)]
Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany

$v_2=22$

$v_2=24$

„barrier anharmonicity"

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Morse classical to quantum correspondence

$$E_0' - E_0'' = \omega_e \left(1 - \frac{\frac{\omega_e}{2} + \frac{E_0' + E_0''}{2}}{D_e} \right)^{\frac{1}{2}}$$

$$\omega_c(E) = \omega_e \left(1 - \frac{E}{D_e} \right)^{\frac{1}{2}}$$
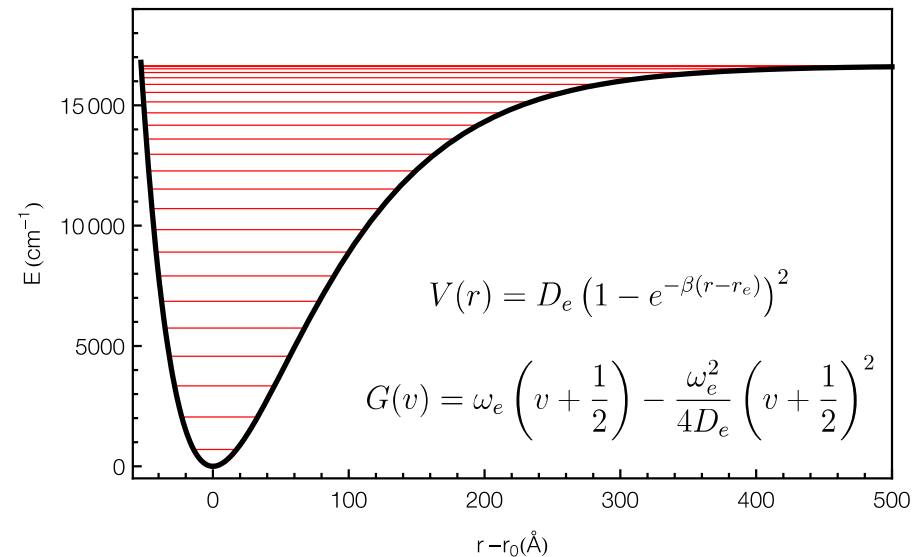
$$V(r) = D_e \left(1 - e^{-\beta(r - r_e)} \right)^2$$

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \frac{\omega_e^2}{4 D_e} \left(v + \frac{1}{2} \right)^2$$

$\hbar \omega_c(E)$ **classical frequency**

$\Delta E_n(E_n)$ **quantum frequency**

$$\hbar \omega_c(E) \approx \Delta E_n(E_n)$$

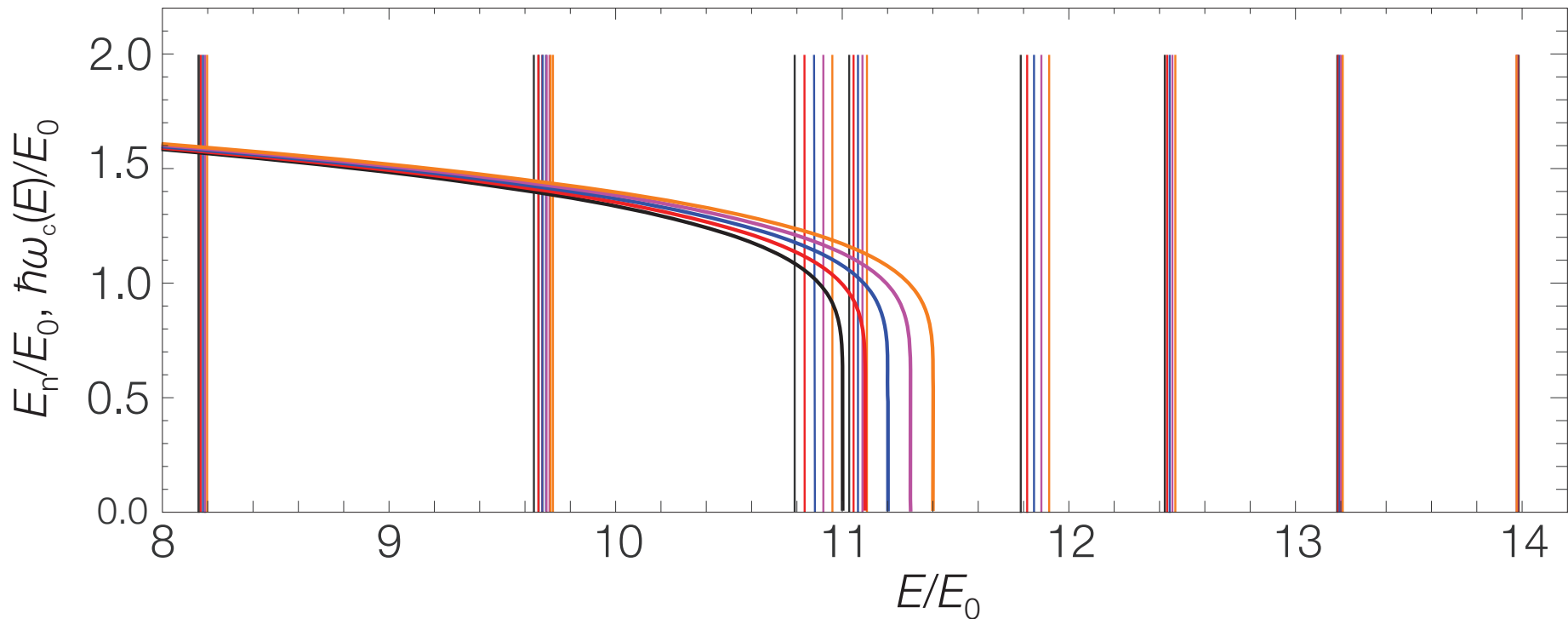$$E \longleftrightarrow E_n = \frac{\omega_e}{2} + \frac{E_0' + E_0''}{2}$$

J. R. Nielsen (ed.), Niels Bohr Collected Works, Vol. 3: The Correspondence Principle (1918–1923), Amsterdam: North-Holland Publishing(1976).

Morse classical to quantum correspondence

$$\omega_c(E) = \omega_e \left(1 - \frac{E}{D_e}\right)^{\frac{1}{2}}$$

$$E \longleftrightarrow E_n = \frac{\omega_e}{2} + \frac{E'_0 + E''_0}{2}$$

$$\hbar\omega_c(E) = \Delta E_n(E_n)$$

$\hbar\omega_c(E)$ **classical frequency**

$\Delta E_n(E_n)$ **quantum frequency**

Mg-NC bending potential

M. Fukushima and T. Ishiwata, J.Chem.Phys. 13 ,124311 (2011)

Mg-NC bending potential

Mellau et al., Saddle point localization of molecular wavefunctions, *Scientific Reports* **6**, 33068 (2016)
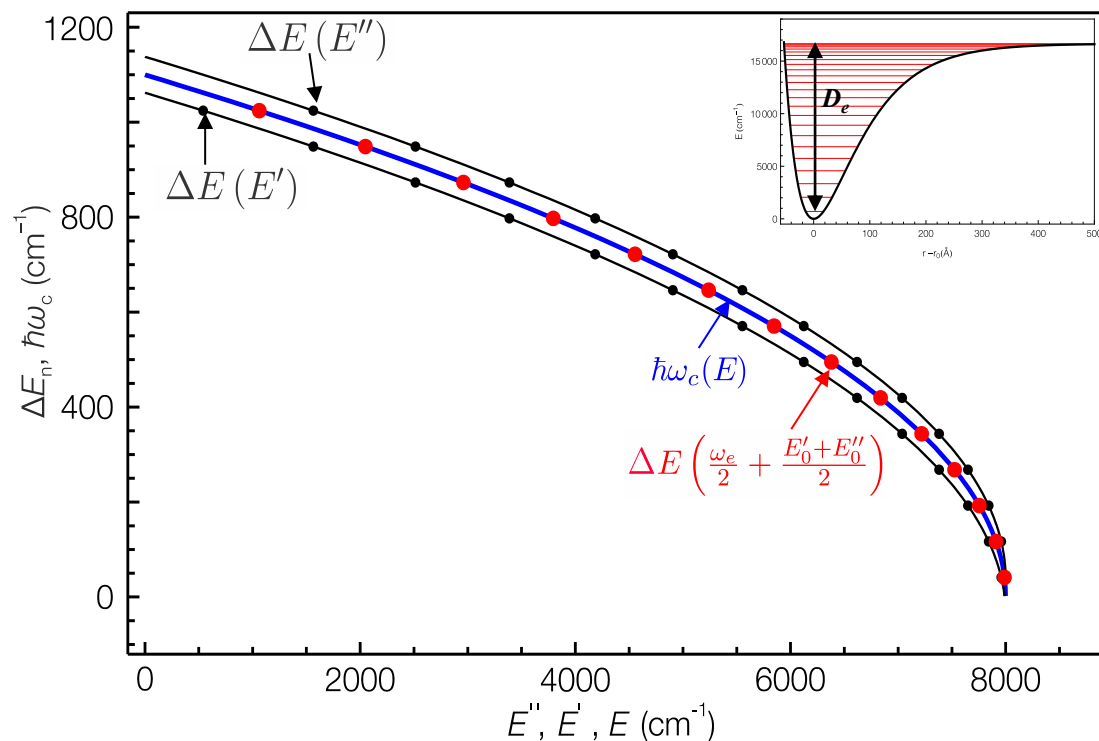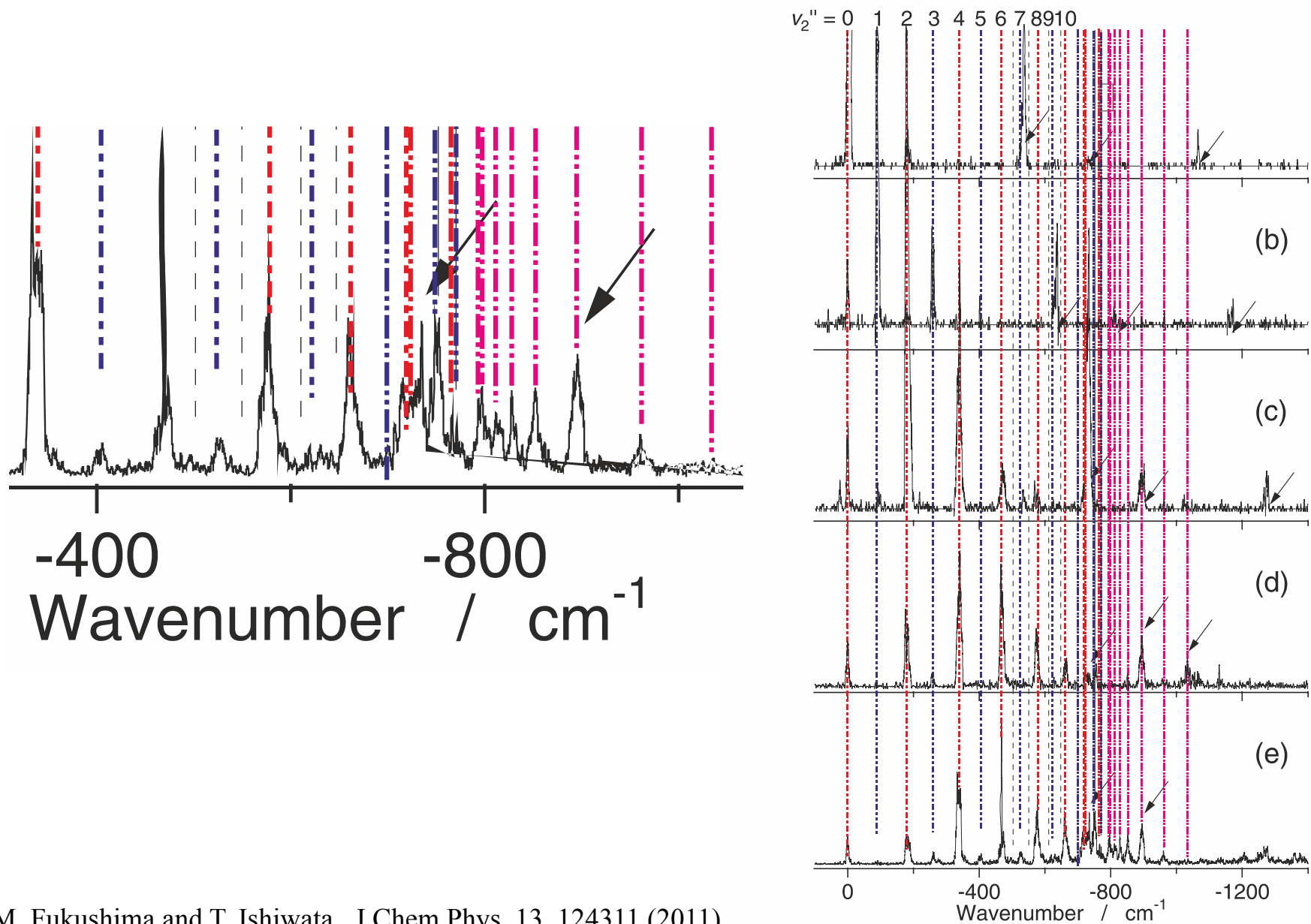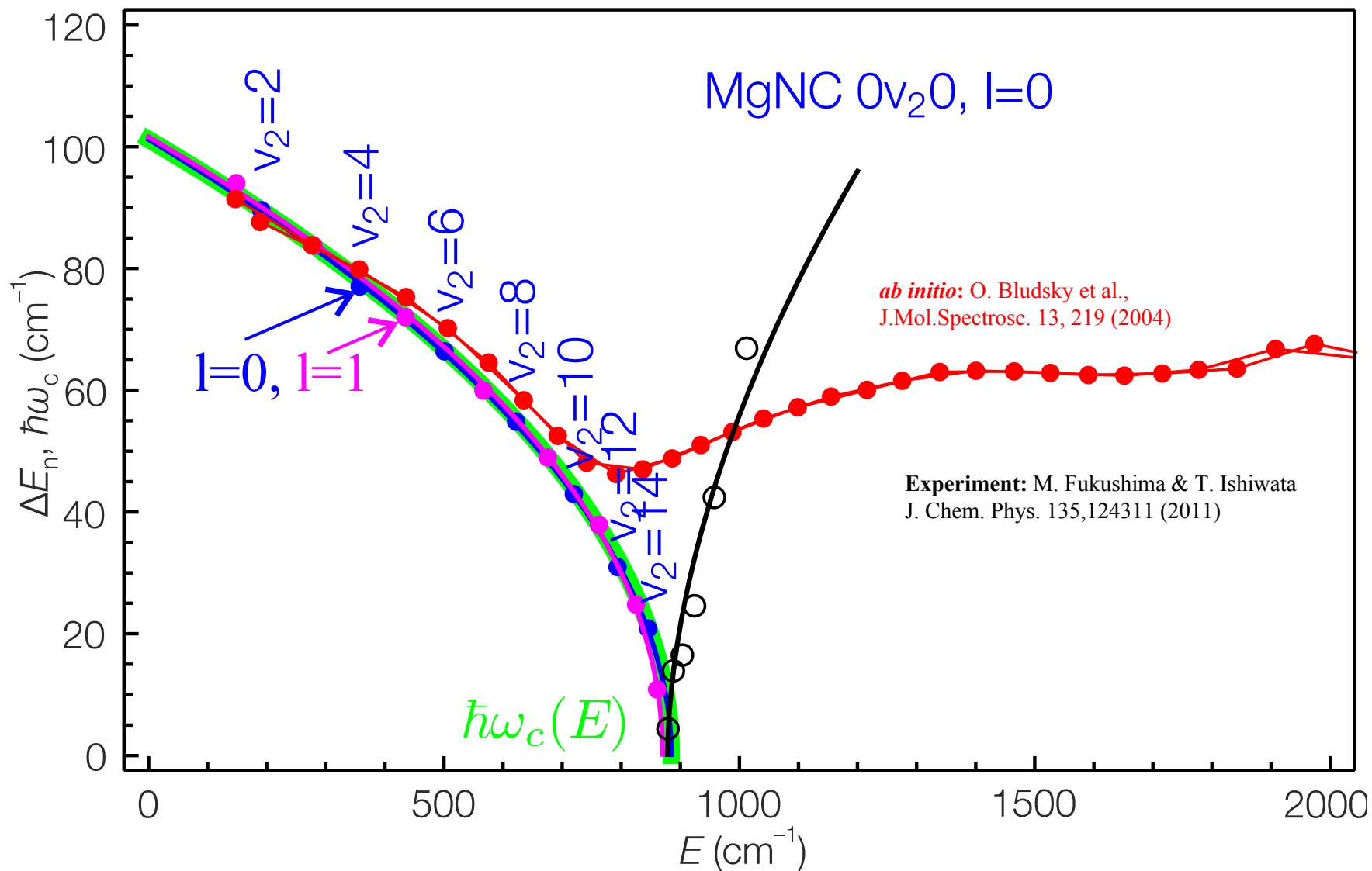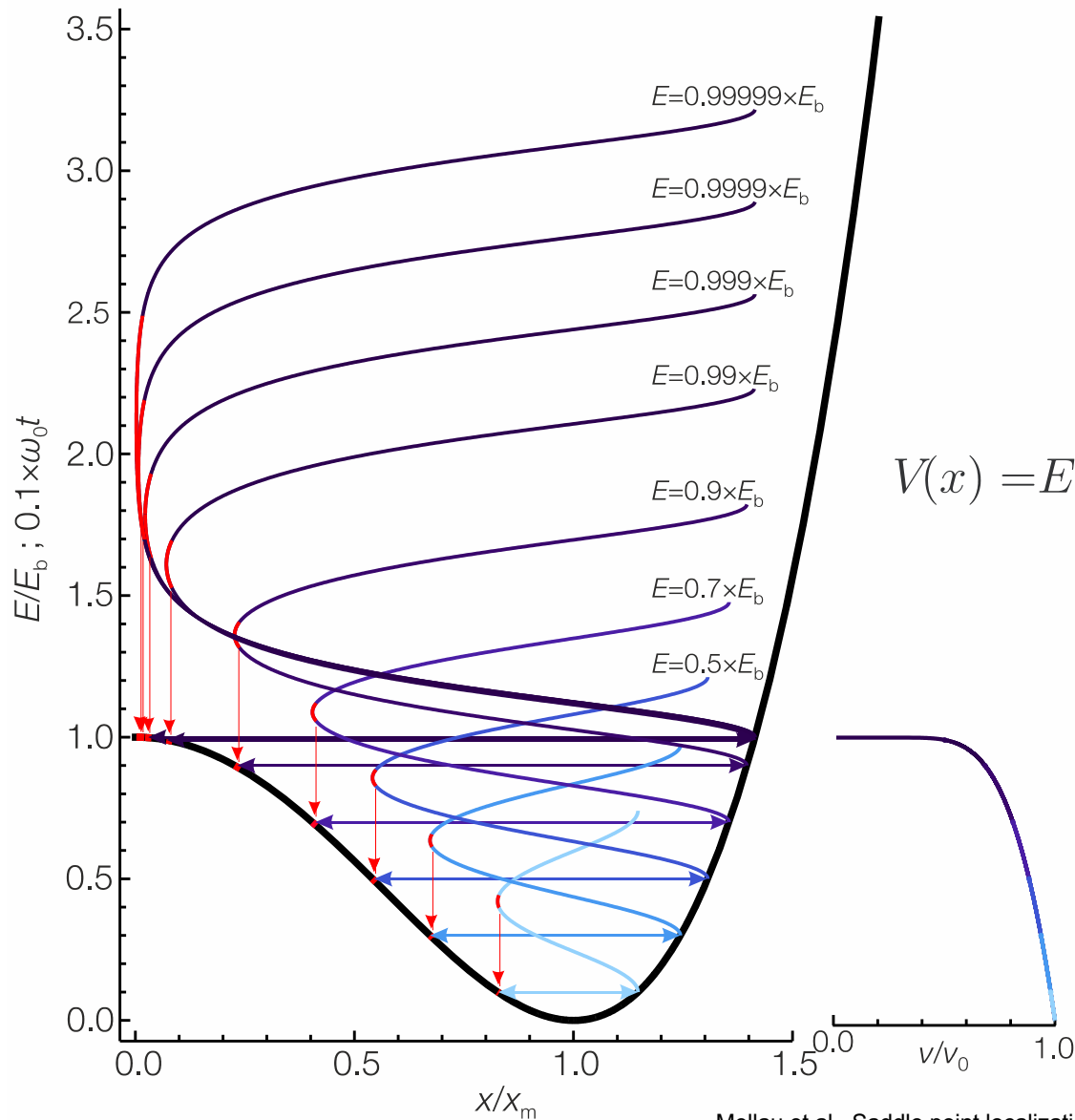
Classical motion at the saddle point

$$V(x) = E_b + E_b \left(-2 \left(\frac{x}{x_m} \right)^2 + \left(\frac{x}{x_m} \right)^4 \right)$$

Mellau et al., Saddle point localization of molecular wavefunctions, *Scientific Reports* **6**, 33068 (2016)
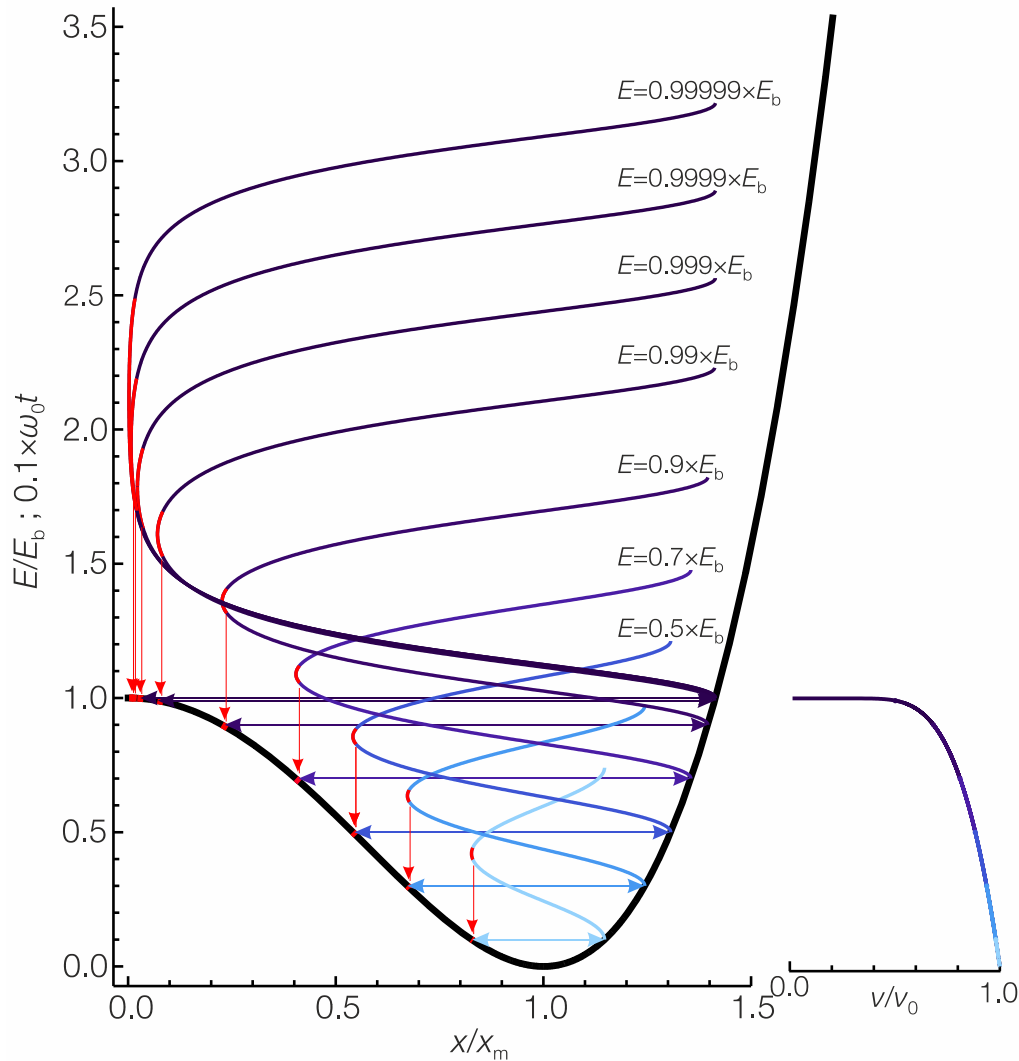
Classical motion at the saddle point

E_0 harmonic zero point energy

$$\hbar\omega_u(E) = \frac{\sqrt{2}\pi E_0 \sqrt[4]{\frac{E-E_b}{E_b}+1}}{K\left(\frac{1}{2}\left(1+\frac{1}{\sqrt{\frac{E-E_b}{E_b}+1}}\right)\right)}$$

$$\hbar\omega_l(E) = \frac{\pi E_0 \sqrt{\sqrt{\frac{E-E_b}{E_b}+1}+1}}{K\left(\frac{2}{1+\frac{1}{\sqrt{\frac{E-E_b}{E_b}+1}}}\right)}$$

$\hbar\omega_c(E)$ **classical frequency**

$$V(x) = E_b + E_b\left(-2\left(\frac{x}{x_m}\right)^2 + \left(\frac{x}{x_m}\right)^4\right)$$

Y. Onodera, *Prog. Theor. Phys.* 44, 1477 (1970)
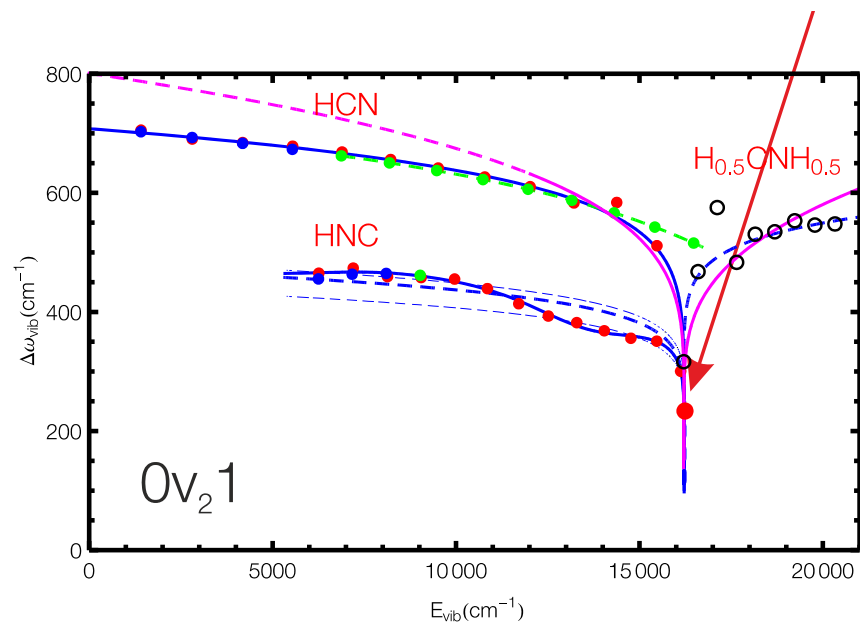
Classical to quantum correspondence at the saddle point
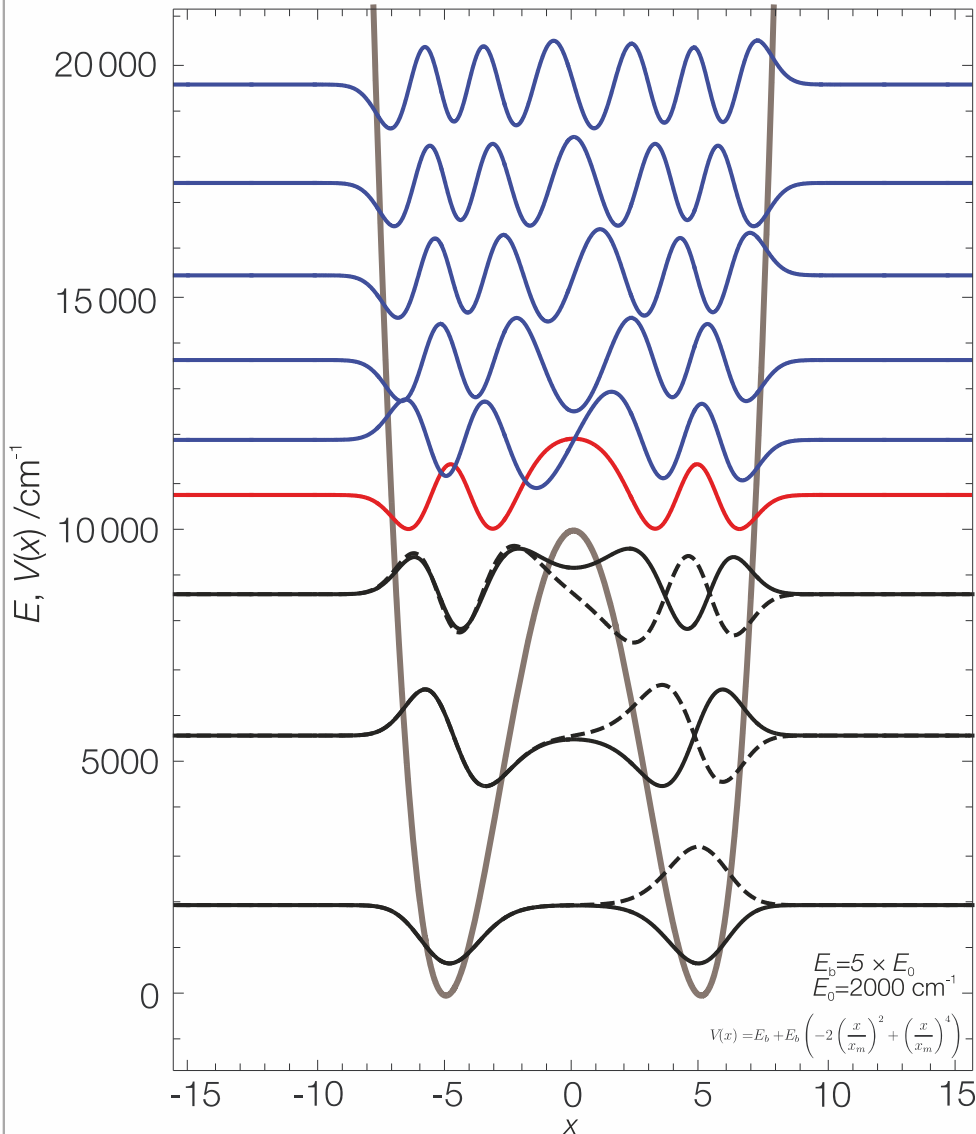
$$\hbar\omega_u(E) = \frac{\sqrt{2}\pi E_0 \sqrt[4]{\frac{E-E_b}{E_b}+1}}{K\left(\frac{1}{2}\left(1+\frac{1}{\sqrt{\frac{E-E_b}{E_b}+1}}\right)\right)}$$

$$\hbar\omega_l(E) = \frac{\pi E_0 \sqrt{\sqrt{\frac{E-E_b}{E_b}+1}+1}}{K\left(\frac{2}{1+\frac{1}{\sqrt{\frac{E-E_b}{E_b}+1}}}\right)}$$

$$E \longleftrightarrow E_n = E_{0,harm} + \frac{E_0' + E_0''}{2}$$

$E_b = 5 \times E_0$
$E_0 = 2000 \text{ cm}^{-1}$

$V(x) = E_b + E_b\left(-2\left(\frac{x}{x_m}\right)^2 + \left(\frac{x}{x_m}\right)^4\right)$

Mellau et al., Saddle point localization of molecular wavefunctions, *Scientific Reports* **6**, 33068 (2016)

Frequency correspondence

The eigenenergy spectrum depends only from E_b/E_0
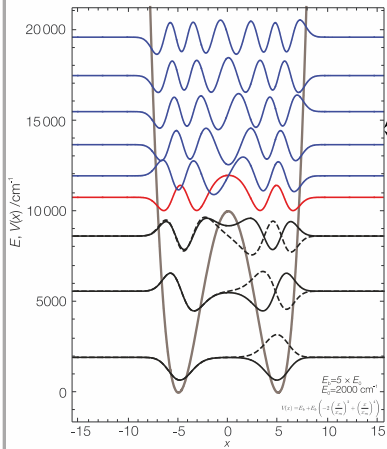
$\hbar\omega_c(E)$ classical frequency

$\Delta E_n(E_n)$ quantum frequency

$$\hbar\omega_c(E) \approx \Delta E_n(E_n)$$

$$E \longleftrightarrow E_n = \frac{\omega_e}{2} + \frac{E_0' + E_0''}{2}$$

$$E(n) = E(0) + \sum_{i=0}^{n} \hbar\omega_c(E_0 - E(0) + (E(i) + E(i-1))/2)$$

Mellau et al., Saddle point localization of molecular wavefunctions, *Scientific Report*s **6**, 33068 (2016)
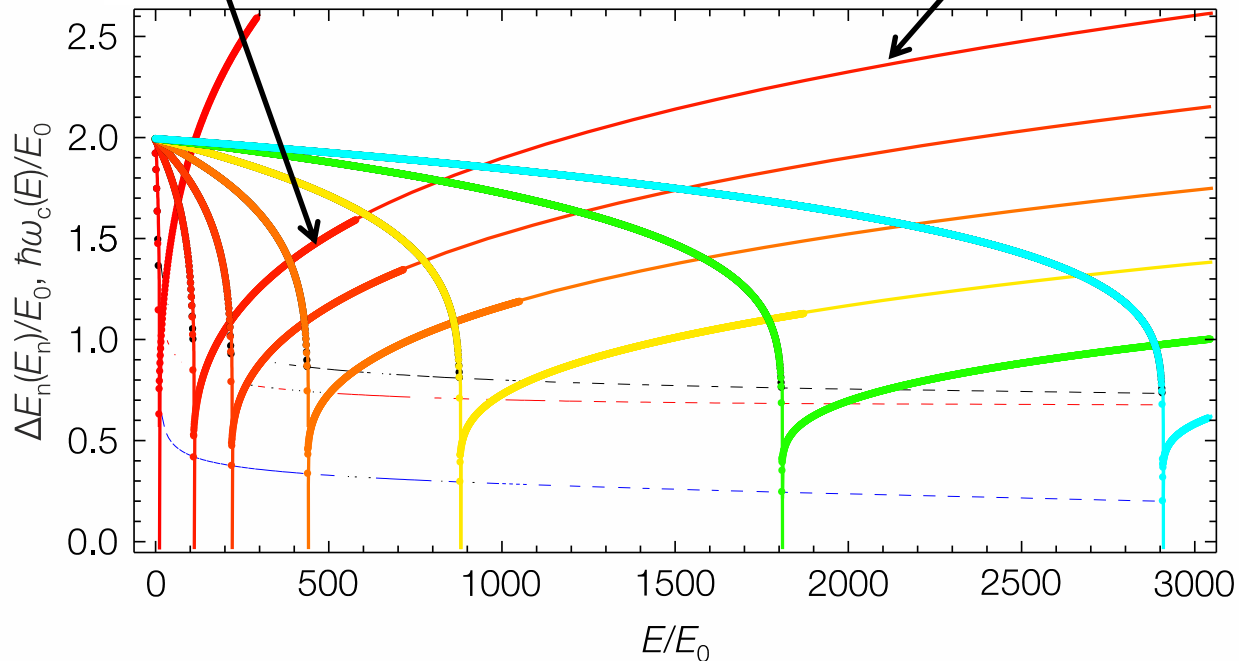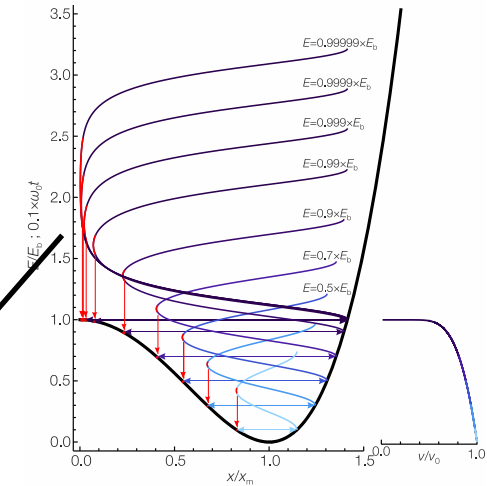
The saddle point frequency pattern
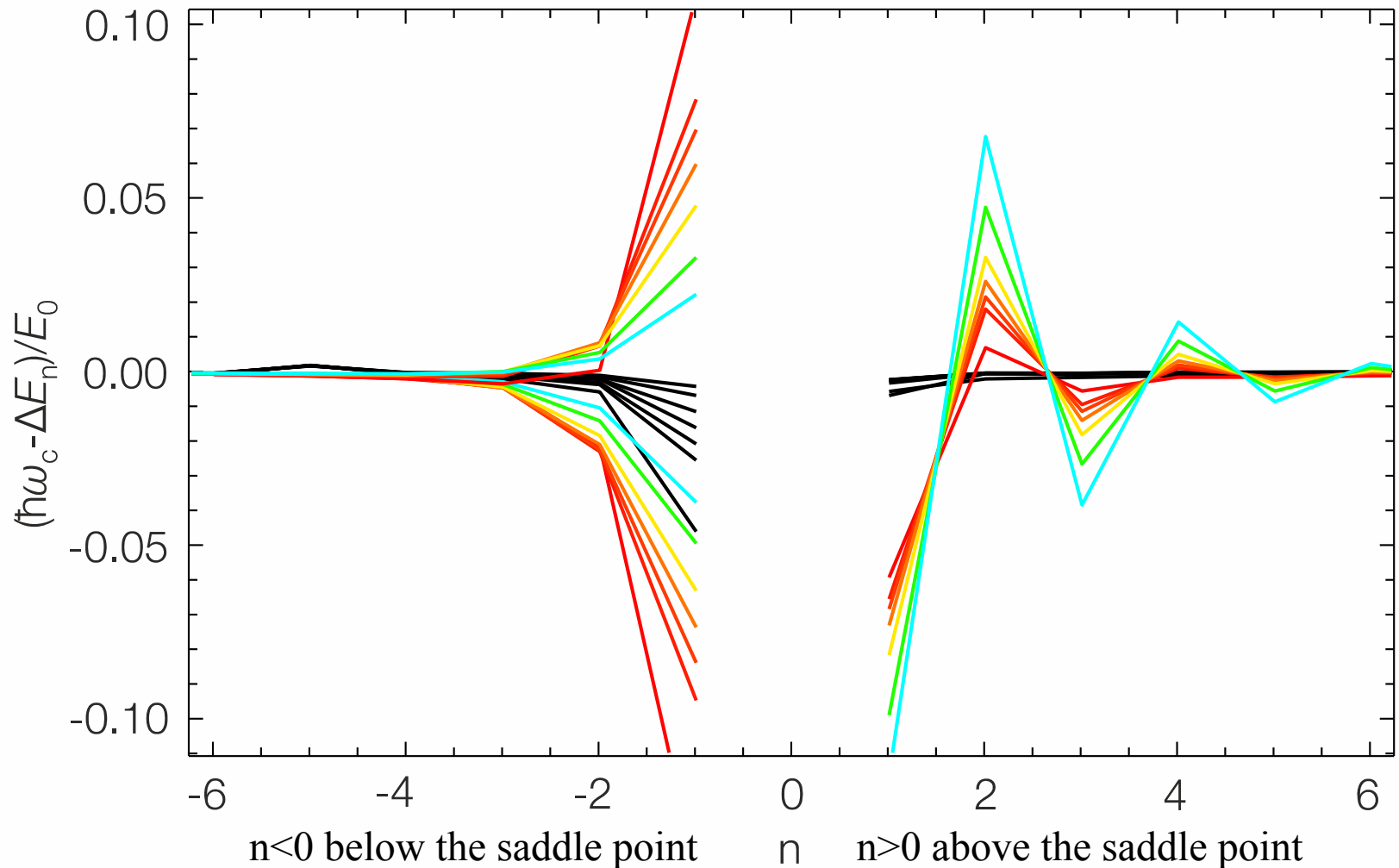
The difference between the classical and quantum frequencies in the neighborhood of the saddle point for increasing barrier height. Black curves show the semiclassical case

Mellau et al., Saddle point localization of molecular wavefunctions, *Scientific Report*s **6**, 33068 (2016)

The saddle point frequency pattern

The eigenenergies and the classical frequencies for quartic potentials with $E_b = i \times E_0$ with $i = 11.0$ to 11.4.
Eigenenergies at the saddle point change their position to avoid low quantum frequencies.

Vibrational signature of the isomerization
Vibrational signature of a transition state

Complete experimental rovibrational eigenenergies of HCN up to 6880 cm⁻¹ above the ground state

Georg Ch. Mellau[a]
Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany
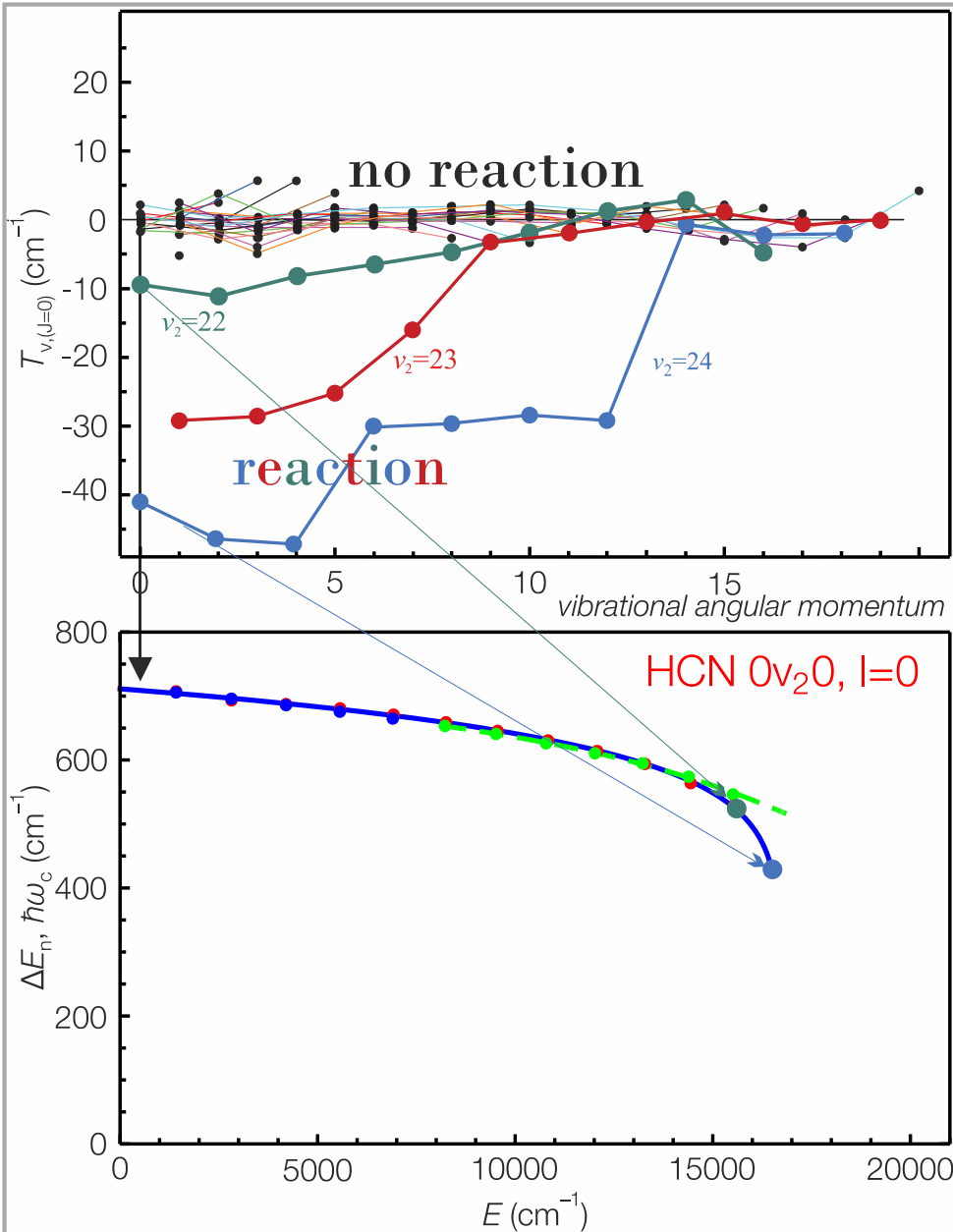
„barrier anharmonicity"

Transition state spectroscopy ↔ "frequency analysis"

New methods to extract chemically relevant saddle point energies from spectroscopically measured quantities

2672 cm^{-1} 4979 cm^{-1}
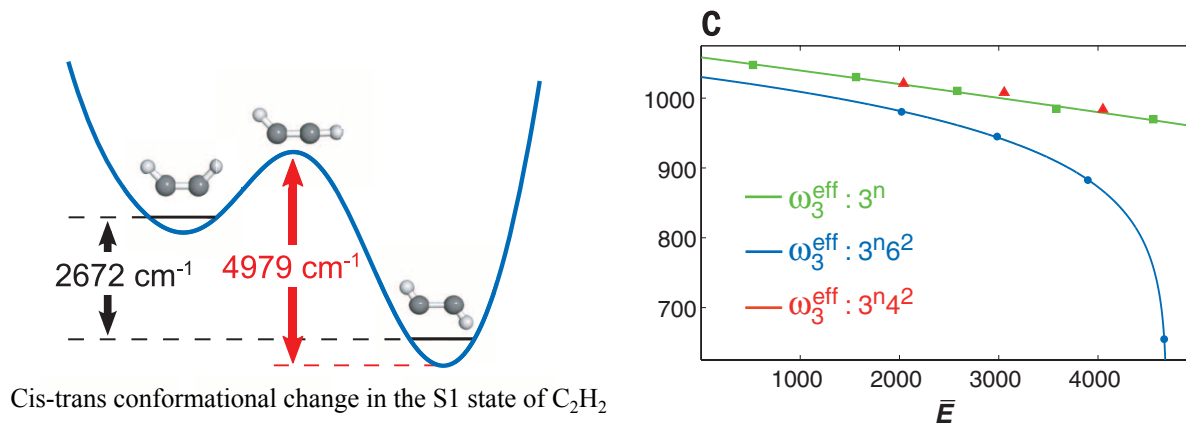
Cis-trans conformational change in the S1 state of C_2H_2

$\omega_3^{eff} : 3^n$
$\omega_3^{eff} : 3^n6^2$
$\omega_3^{eff} : 3^n4^2$

11517 cm^{-1}

16798 cm^{-1}

HCN
16686(17) cm^{-1}
16344 cm^{-1}

HNC
10986(40) cm^{-1}
10924 cm^{-1}

J. H. Baraban, P. B. Changala, G. C. Mellau, J. F. Stanton, A. J. Merer, and R. W. Field, Science, 350, 1338 (2015)
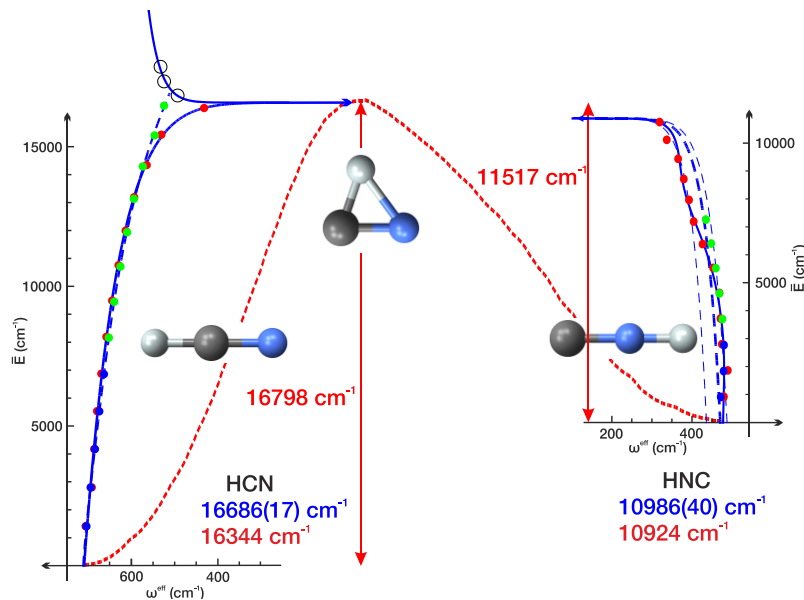
1/m frequency formula
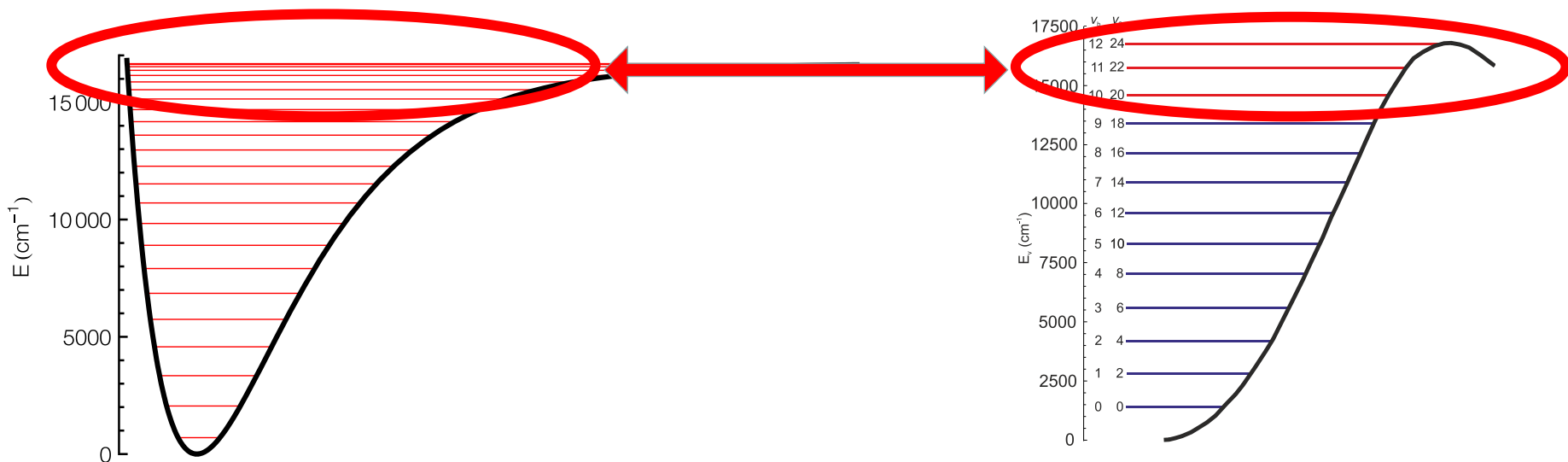
$$\omega^{\text{eff}}(\overline{E}) = \omega_0 \left(1 - \frac{\overline{E}}{E_{\text{TS}}}\right)^{1/m}$$

$$\omega^{\text{eff}}(n) = \frac{\partial E}{\partial n} = \frac{\Delta E}{\Delta n}$$

R. W. Field group, MIT, Cambridge

$$\omega_c(E) = \omega_0 \left(1 - \frac{E_0(0) + \frac{E_0'' + E_0'}{2}}{E_b}\right)^{\frac{1}{m}}.$$

Mellau et al., Saddle point localization of molecular wavefunctions, *Scientific Reports* **6**, 33068 (2016)

Frequencies for $0v_20$ pure bending series
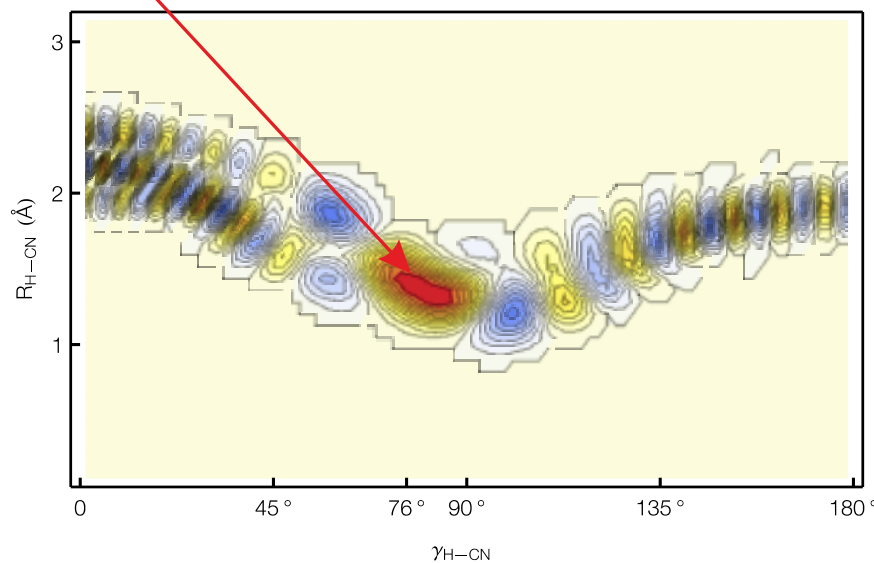

measured
spectroscopic predicted
ab initio

$$\hbar\omega_u(E) = \frac{\sqrt{2}\pi E_0 \sqrt[4]{\frac{E-E_b}{E_b}+1}}{K\left(\frac{1}{2}\left(1+\frac{1}{\sqrt{\frac{E-E_b}{E_b}+1}}\right)\right)}$$

$$\hbar\omega_l(E) = \frac{\pi E_0 \sqrt{\sqrt{\frac{E-E_b}{E_b}+1}+1}}{K\left(\frac{2}{1+\frac{1}{\sqrt{\frac{E-E_b}{E_b}+1}}}\right)}$$

HCN

$\pi / \ log(\frac{64E_b}{E_b-E})$ NH$_{0.5}$

HNC

$\pi / \log(\frac{64E_b}{E_b-E}$

$$\omega_c(E) = \omega_0 \left(1 - \frac{E_0(0)+\frac{E_0''+E_0'}{2}}{E_b}\right)^{\frac{1}{m}}$$

$0v_20$

$\Delta\omega_{vib}$(cm^{-1})

E_{vib}(cm^{-1})
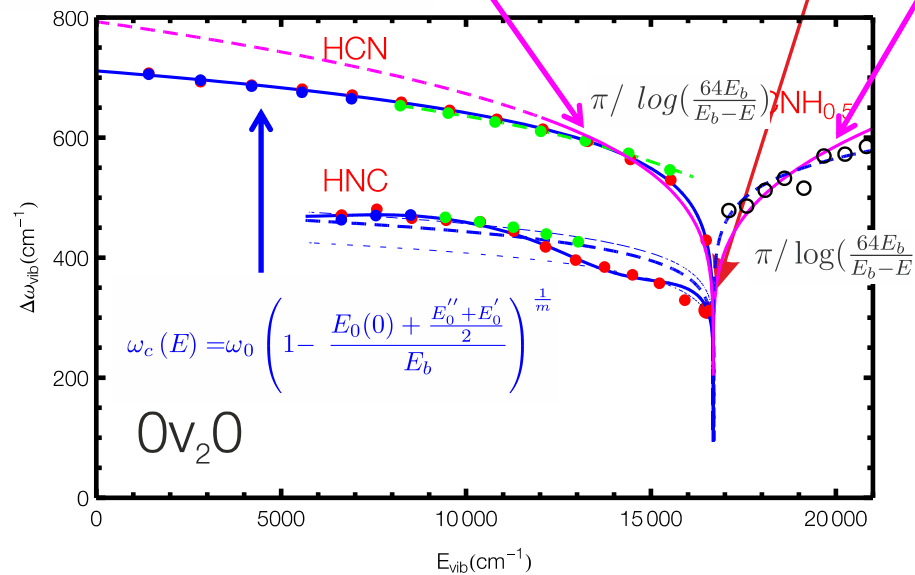
Frequencies for $0v_22$: 2 x CN stretch + bending series
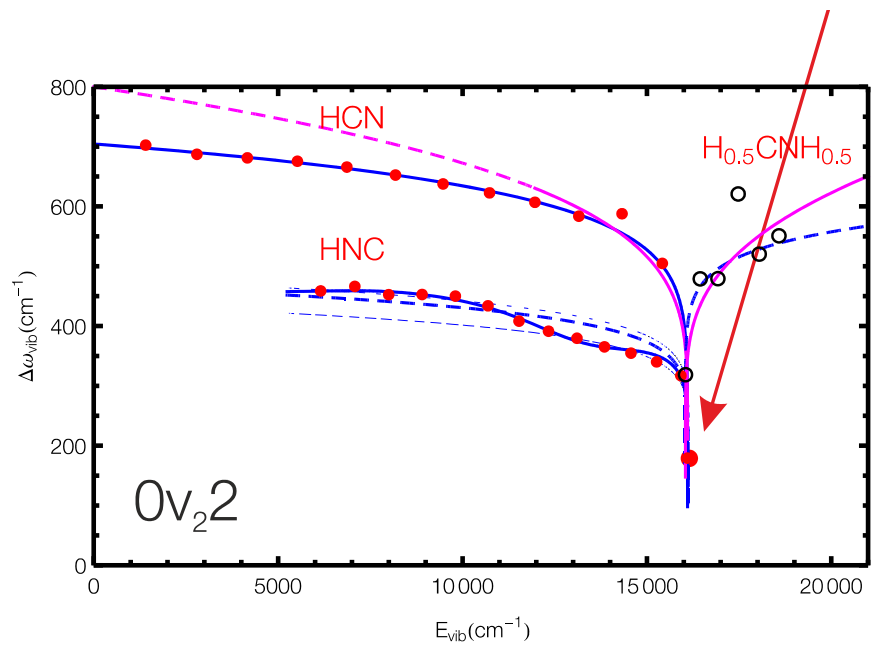
Nearly separable isomerizing system
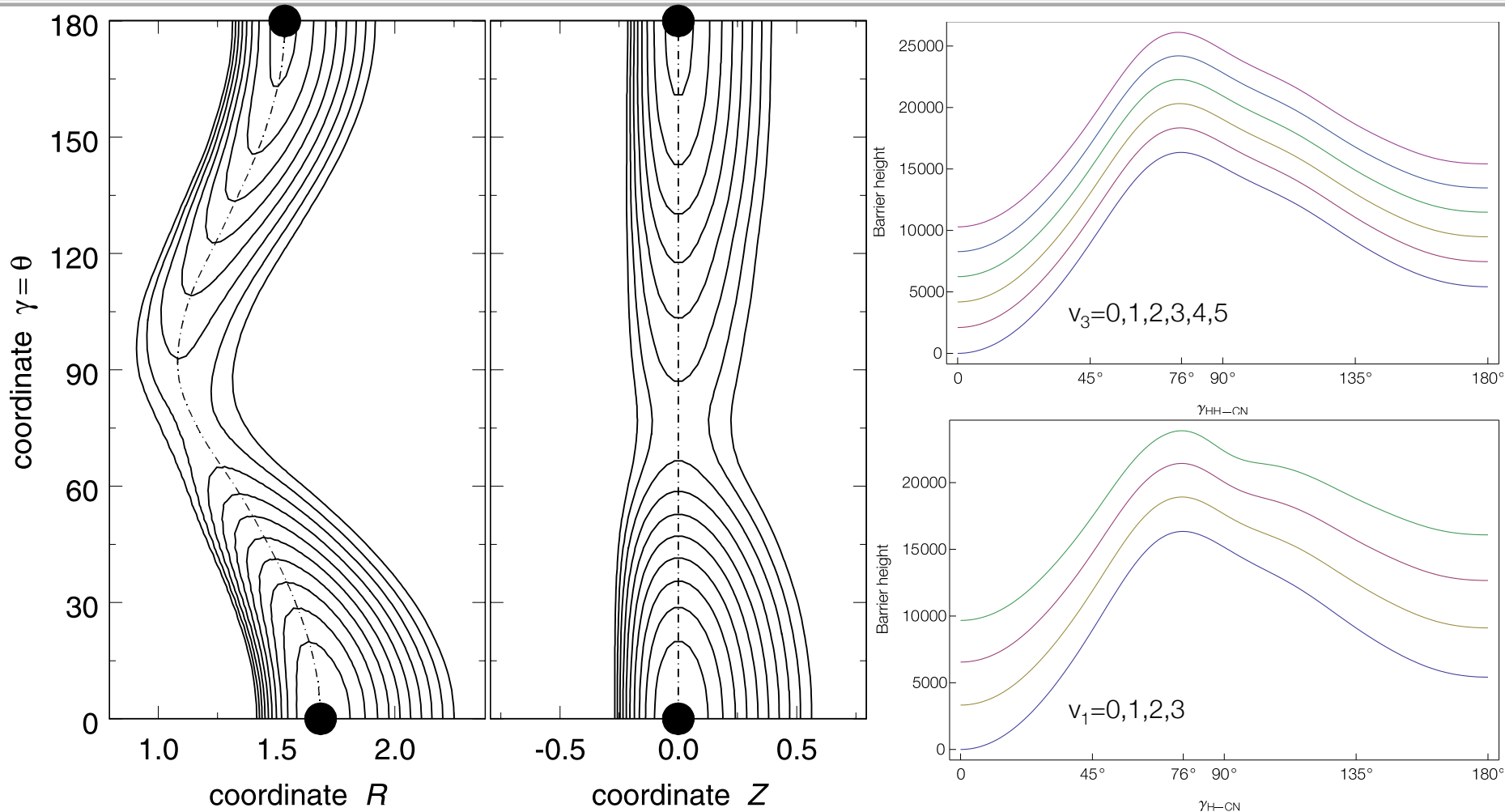
Canonical Perturbation Theory

Separation of motion: one-dimensional Hamiltonian in the bending angle parameterized by the v_1 and v_3 stretch quantum numbers -> $V_{v1;v3}(\gamma)$ pseudopotentials

M. Joyeux et al. *Adv. Chem. Phys.* **136** 267 (2005)   Z. Bacic and J.C. Light, J. Chem. Phys. 86 3065 (1987)

The spectroscopic (v_1, v_2, l) isomerization barrier

from HNC side

$0 x v_3$

$v_1 x 0$

$v_1 = 0,1,2,3$

$v_3 = 0,1,2,3,4,5$
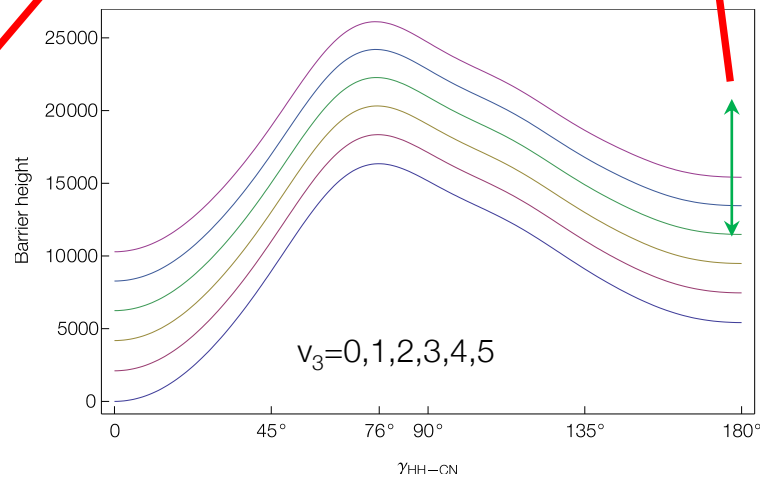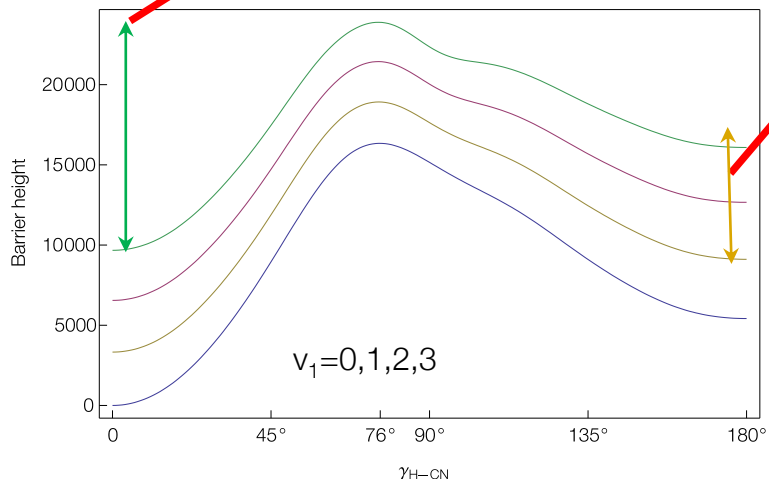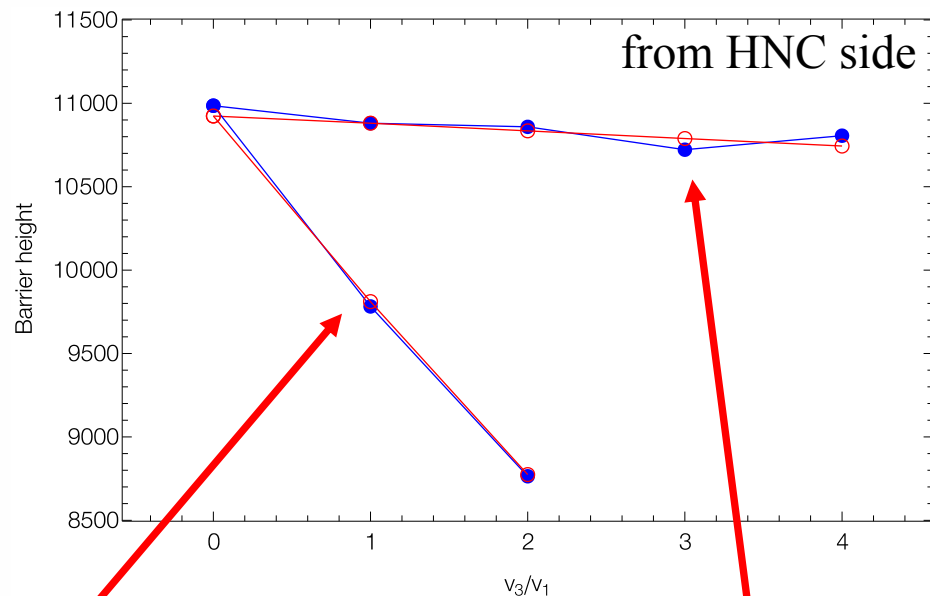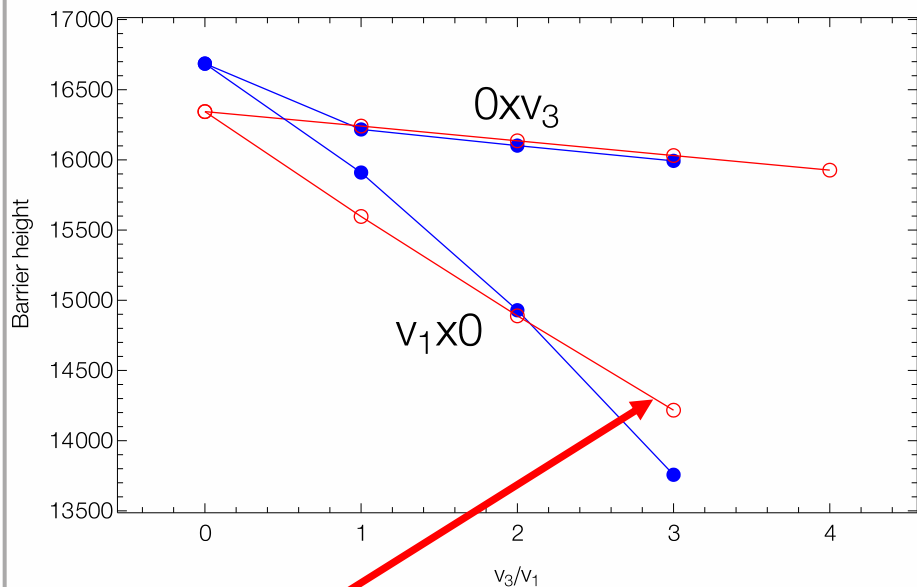
● Eigenenergy fit

● M. Joyeux et al. *Adv. Chem. Phys.* **136** 267 (2005)

Outline

Molecules in highly excited states

1. Intuitive understanding of molecules and the [H,C,N] molecular system

FT-IR spectroscopy of the highly excited states

1. FT-IR Hot GAs Molecular Emission (HOTGAME) spectroscopy
2. Analysis of the high resolution very dense emission spectra of HCN and HNC

Complete eigenenergy list

1. Complete eigenenergy structure of the [H,C,N] molecular system
2. "Spectroscopy" of the *ab initio* [H,C,N] eigenenergies

Classical to Quantum correspondence at the saddle point

1. Classical and quantum frequencies at the barrier for Morse and quartic potential
2. New approximate analytical model and the [H,C,N] eigenenergies at the barrier

Saddle Point Localization

1. Saddle point localization of the wavefunctions for the quartic potential
2. Molecular saddle point localized states

Low barrier case
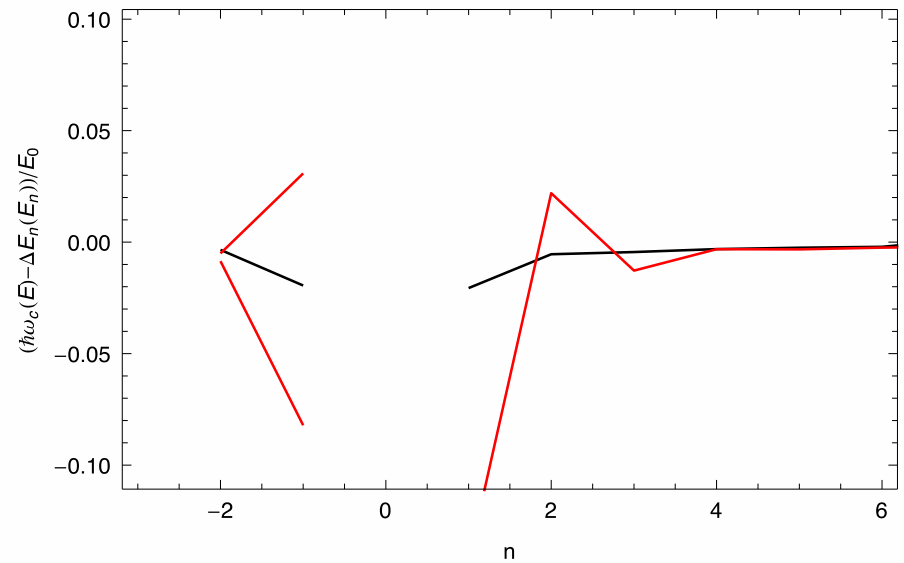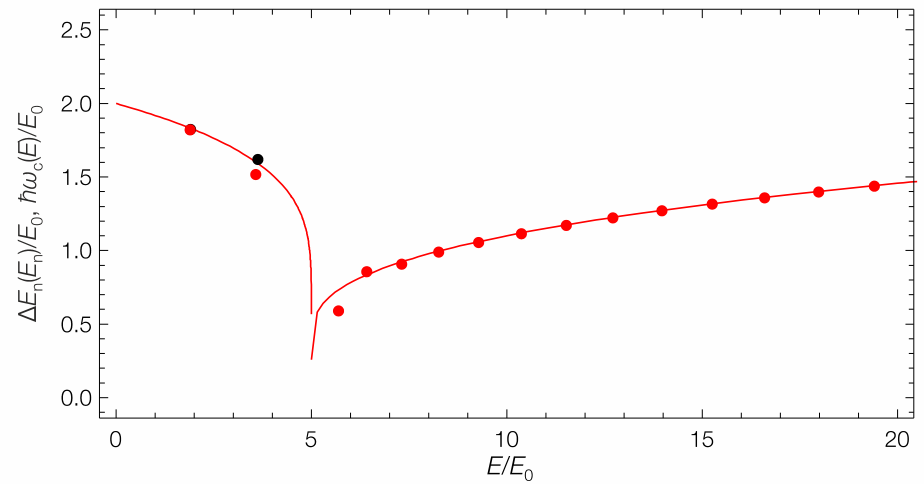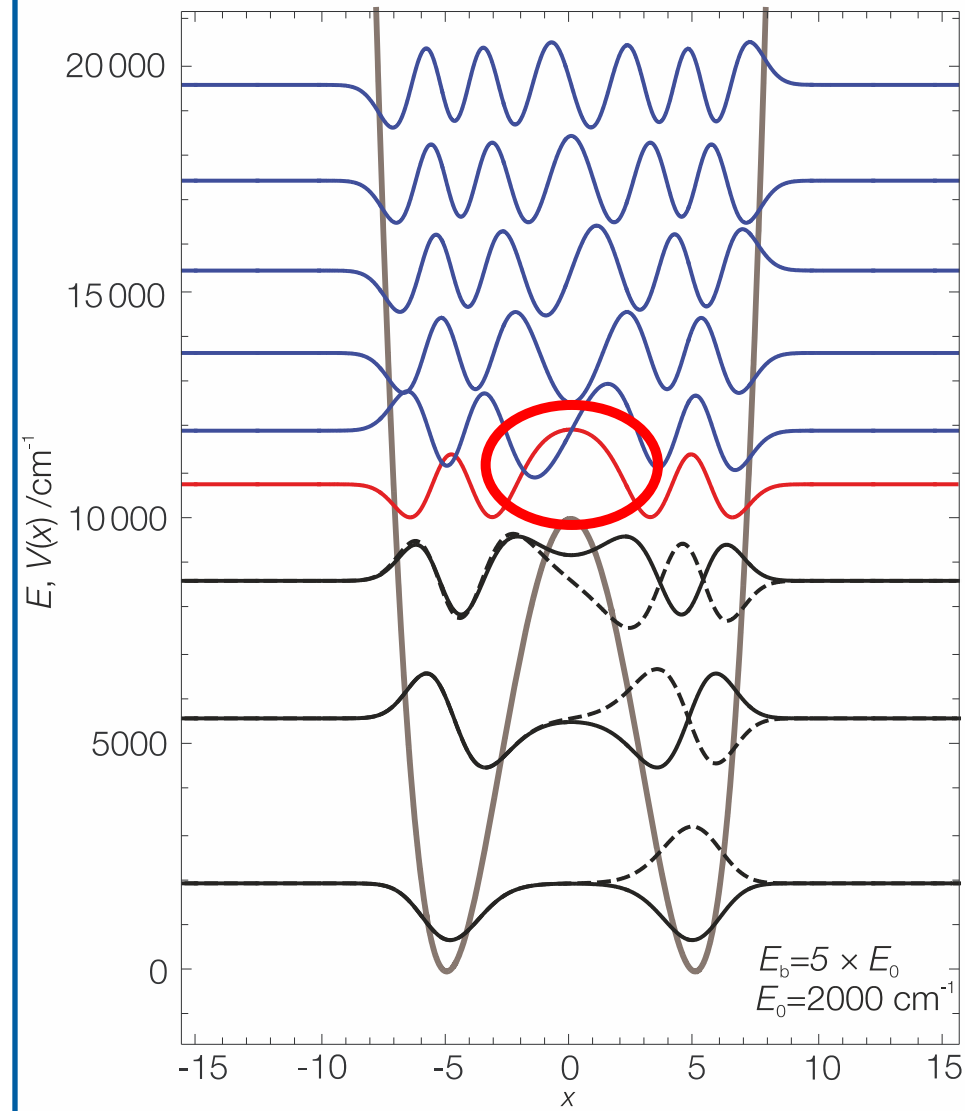
$E_b = 5 \times E_0$
$E_0 = 2000 \text{ cm}^{-1}$

Localization of the eigenstates at the barrier

Nr	E_n	E	$\Delta E_n(E)$	$\hbar\omega_c(E)$	$|\Psi(x)|^2$	$\Psi(x)$
125	106.640	107.230	1.172	1.174		
126	106.640	107.230	1.173	1.174		
127	107.820	108.370	1.117	1.121		
128	107.820	108.380	1.120	1.121		
129	108.930	109.450	1.030	1.053		
130	108.940	109.470	1.059	1.051		
131	109.960	110.390	0.854	0.949		
132	109.990	110.500	1.007	0.929		
133	110.820					
134	111.000					
135	111.590	111.800	0.424	0.489		
136	112.010	112.280	0.534	0.516		
137	112.540	112.810	0.528	0.538		
138	113.070	113.350	0.557	0.556		
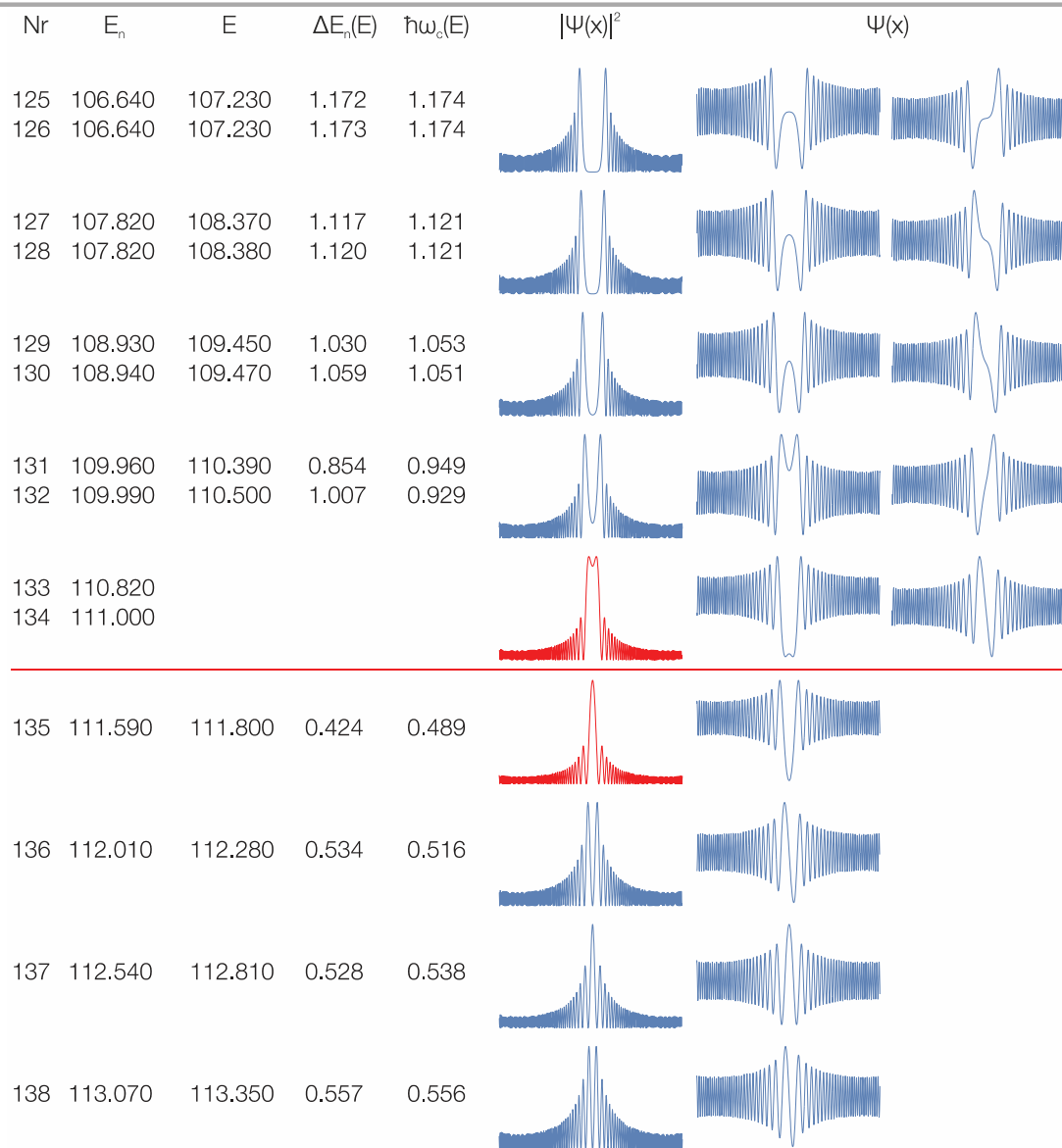
Localization of the eigenstates at the barrier
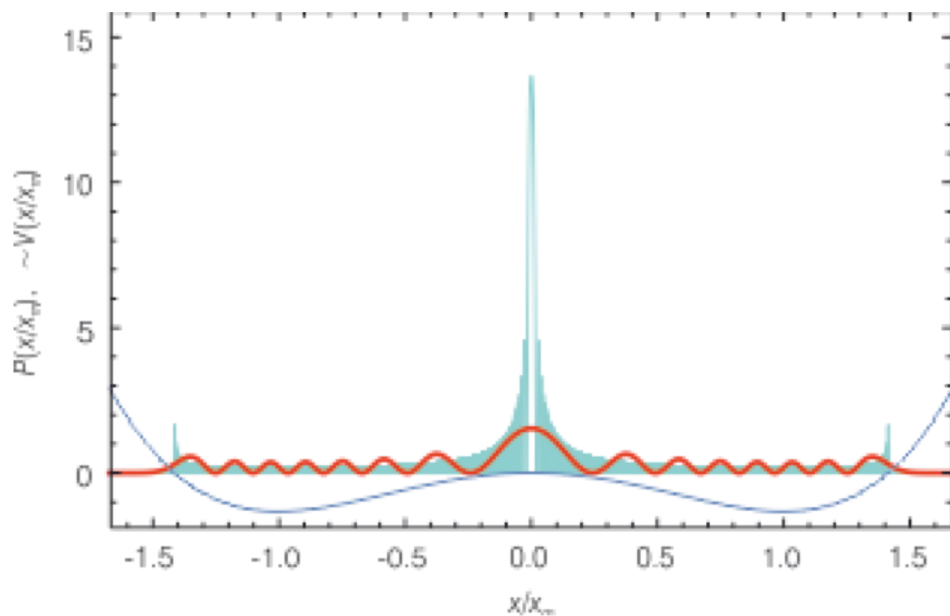
Case of $E_b = 11 \times E_0$ and $E_b = 2911 \times E_0$
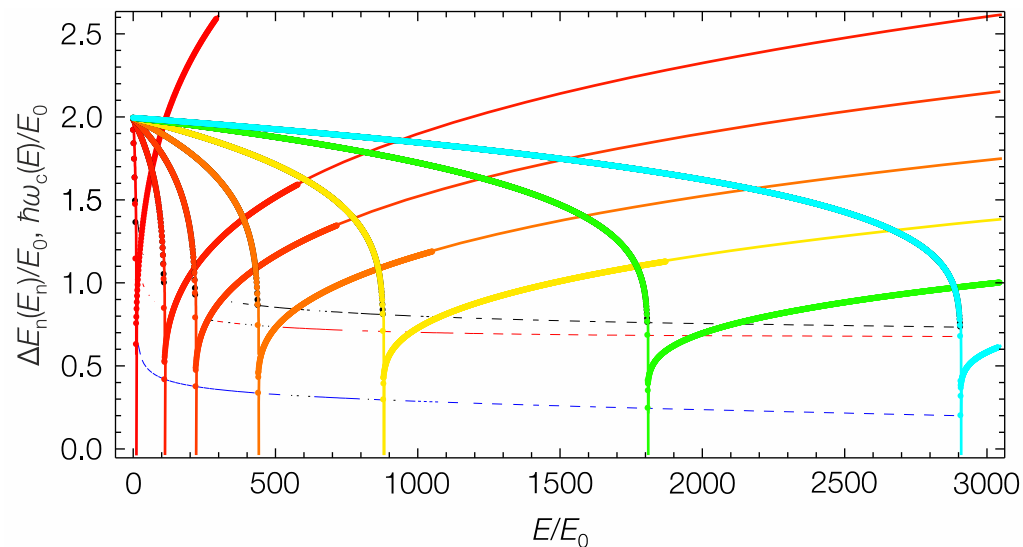
P. Dutta, SP. Bhattacharyya, Phys. Lett. A 163, 193 (1992)

J.R. Henderson, H.A. Lam, J. Tennyson J. Chem. Soc.Faraday Trans.88, 3287 (1992)

Mellau et al., Saddle point localization of molecular wavefunctions, *Scientific Report*s **6**, 33068 (2016)

Localization for $0v_20$ pure bending series

measured
spectroscopic predicted
ab initio

Mellau et al., Saddle point localization of molecular wavefunctions, *Scientific Reports* **6**, 33068 (2016)
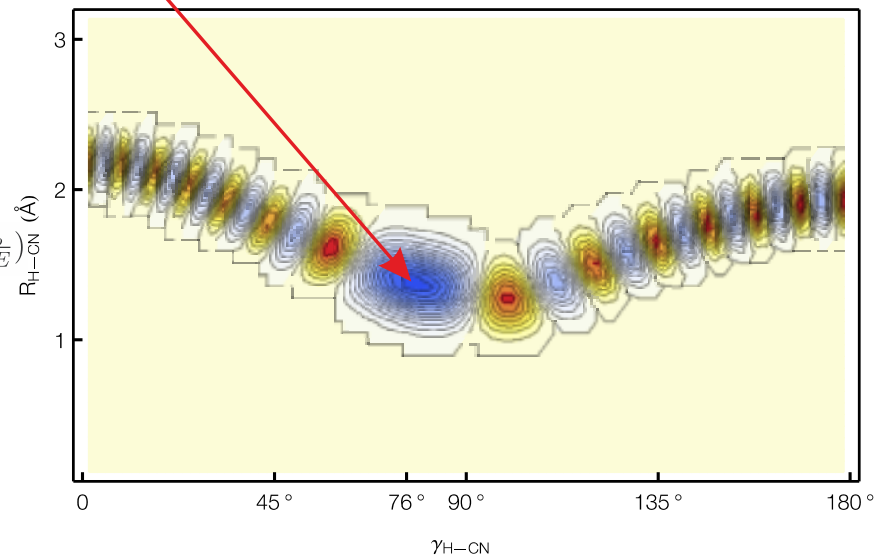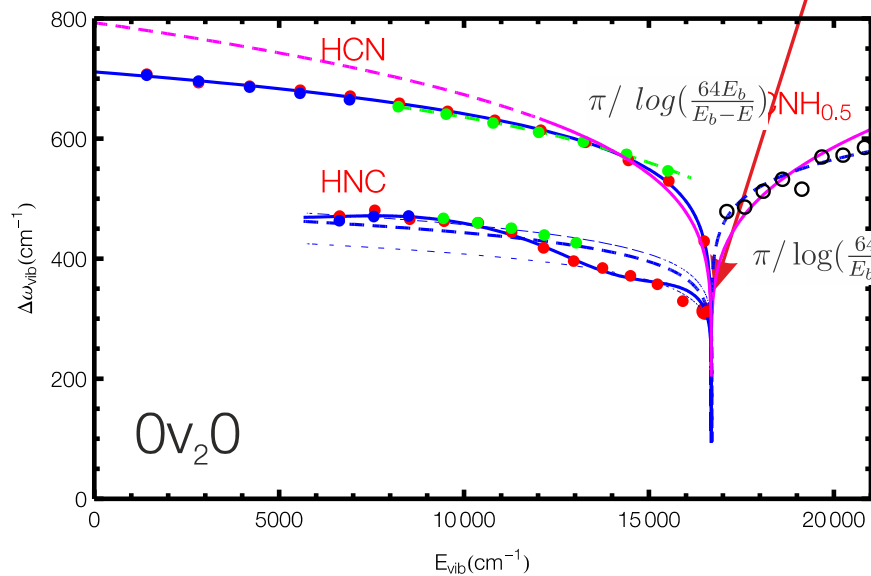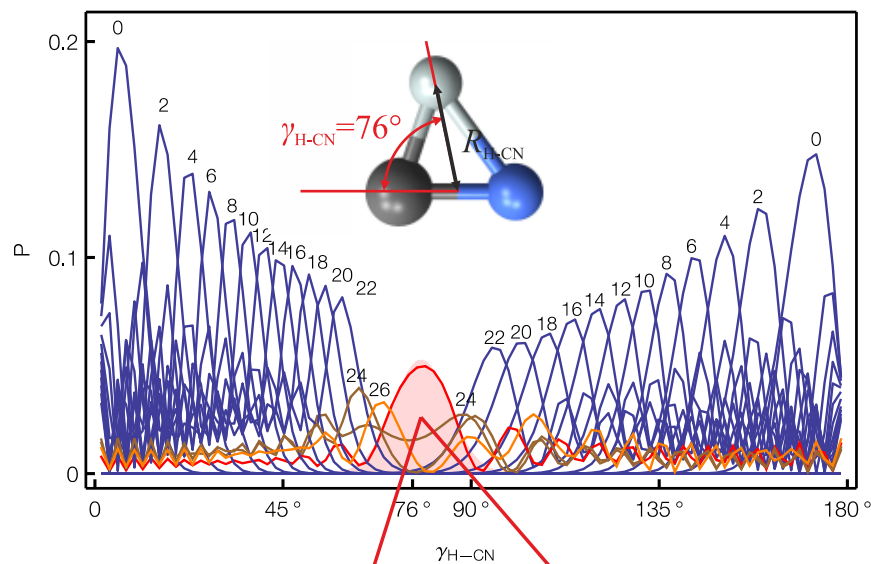
Localization for $0v_21$: CN stretch + bending series
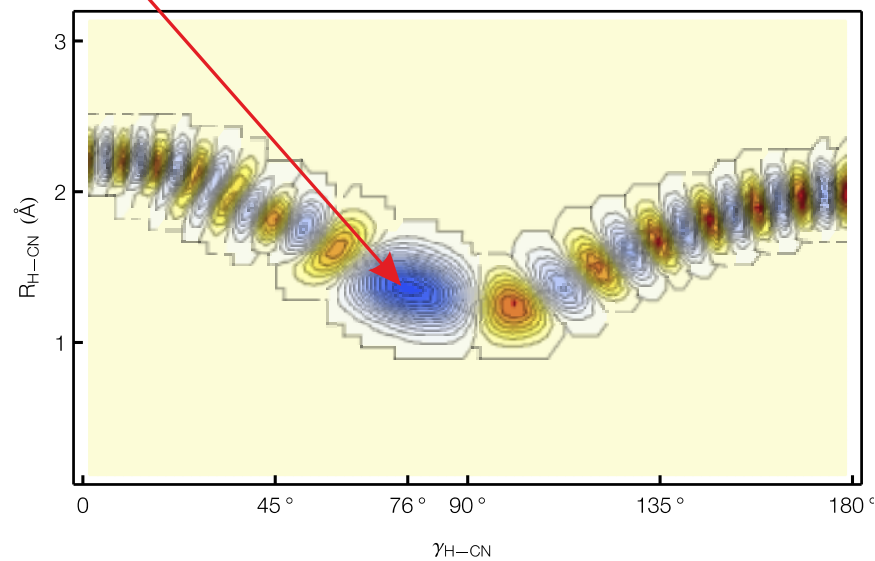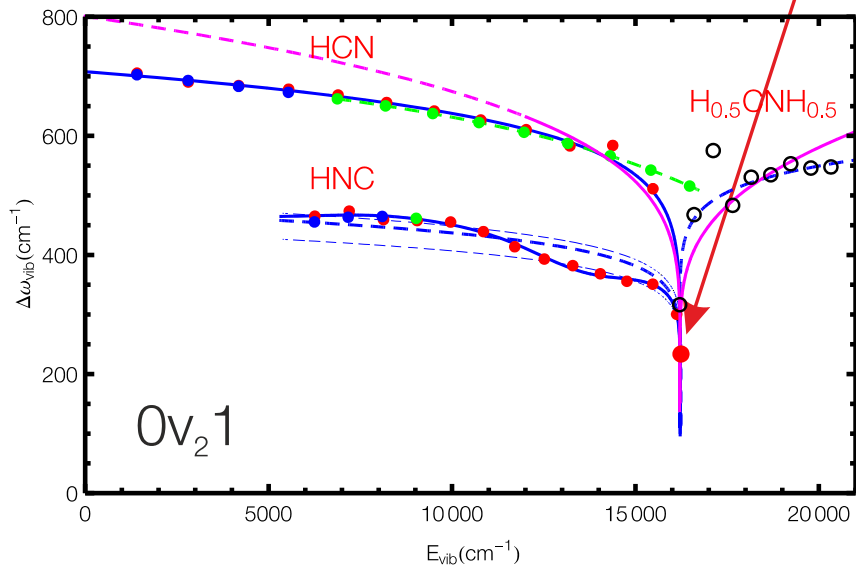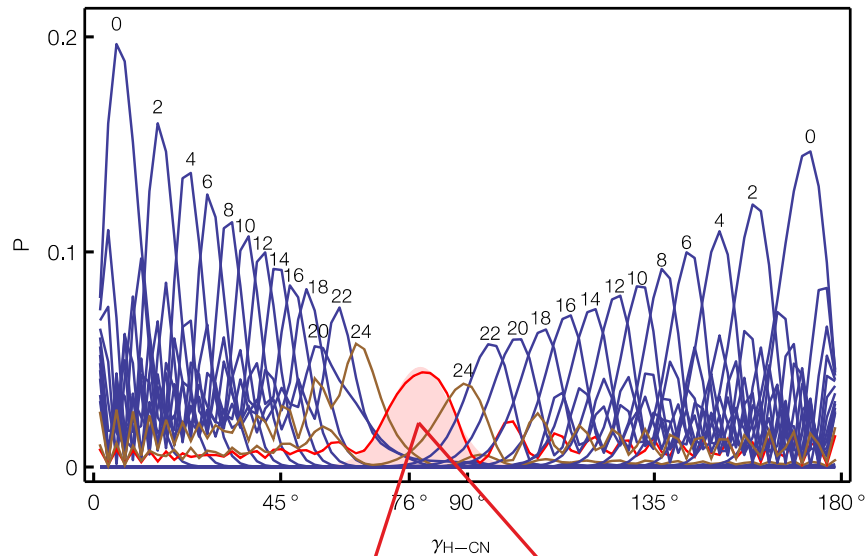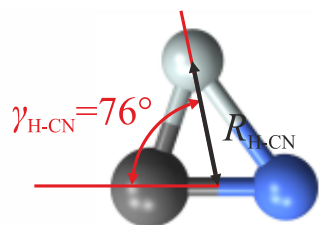
Localization for 0v₂2: 2 x CN stretch + bending series

Quantum number dependence of the localization

$$V(x) = E_0 \times (x/x_m)^2$$

Mellau et al., Saddle point localization of molecular wavefunctions, *Scientific Reports* **6**, 33068 (2016)

Quantum number dependence of the localization

$E_b = 5 \times E_0$
$E_0 = 2000$ cm^{-1}

Mellau et al., Saddle point localization of molecular wavefunctions, *Scientific Reports* **6**, 33068 (2016)

Acknowledgments

Shown and explained the existence of the saddle point localization effect and its application in molecular physics.
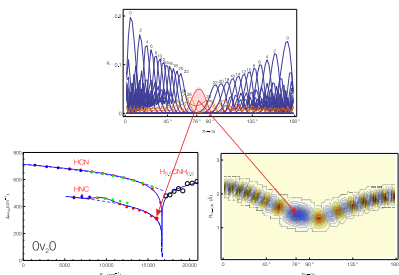
Shown the full dimensional vibrational angular momentum dependent dip of the vibrational energies as the vibrational excitation approaches the saddle point.
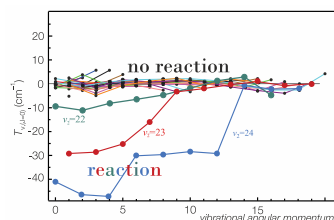
Internal dynamic effect for HCN,HNC,DCN (and probably general to HAB linear molecules): *effect of highly excited vibrational momentum*
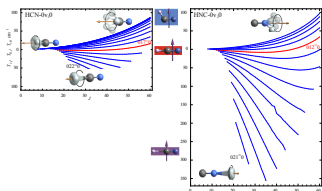
The first time a complete experimental/theoretical analysis of the rovibrational spectrum of a polyatomic molecule has been achieved in an extended excitation region.
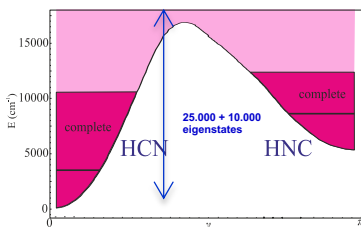
Interaction between stretch and internal rotation
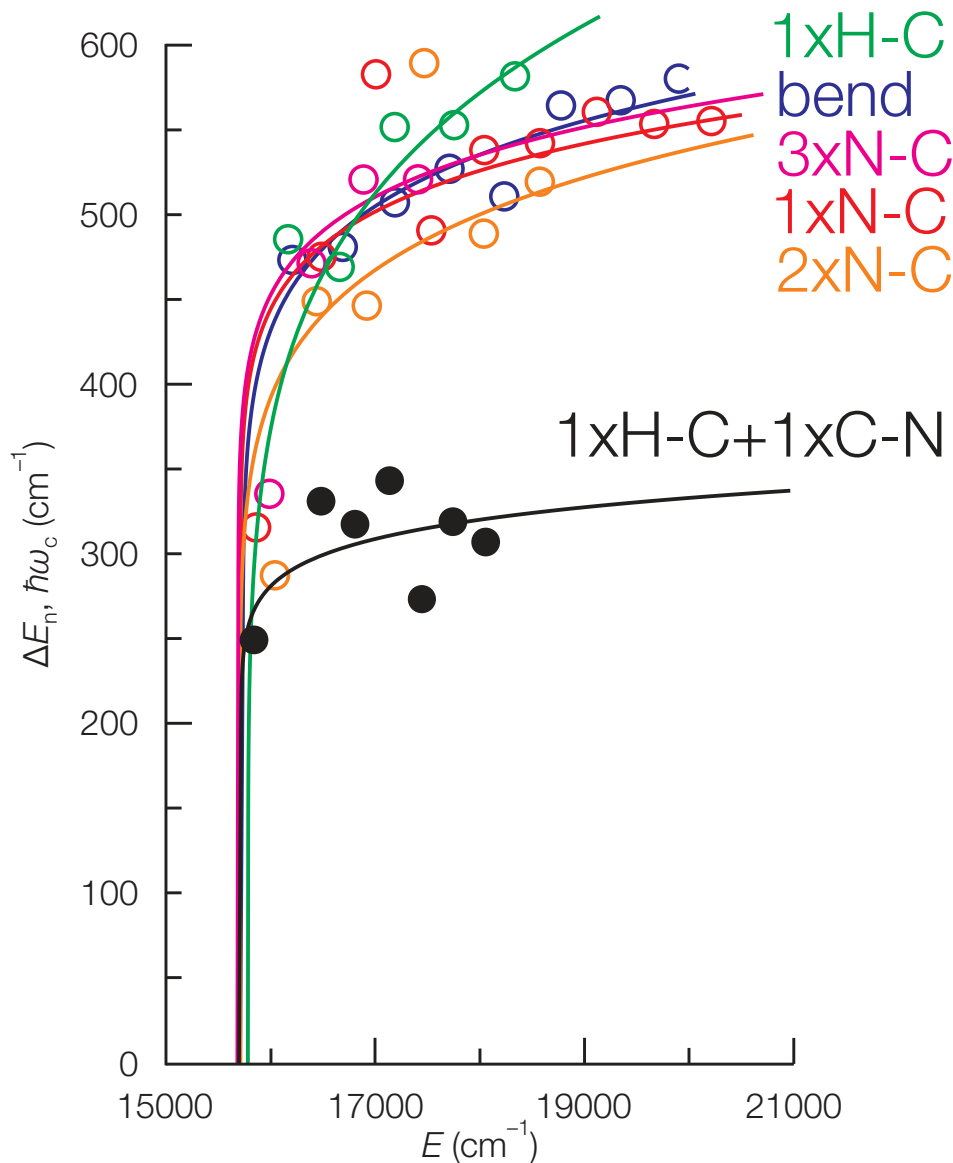
Dynamic degeneracy of *l*=0 states
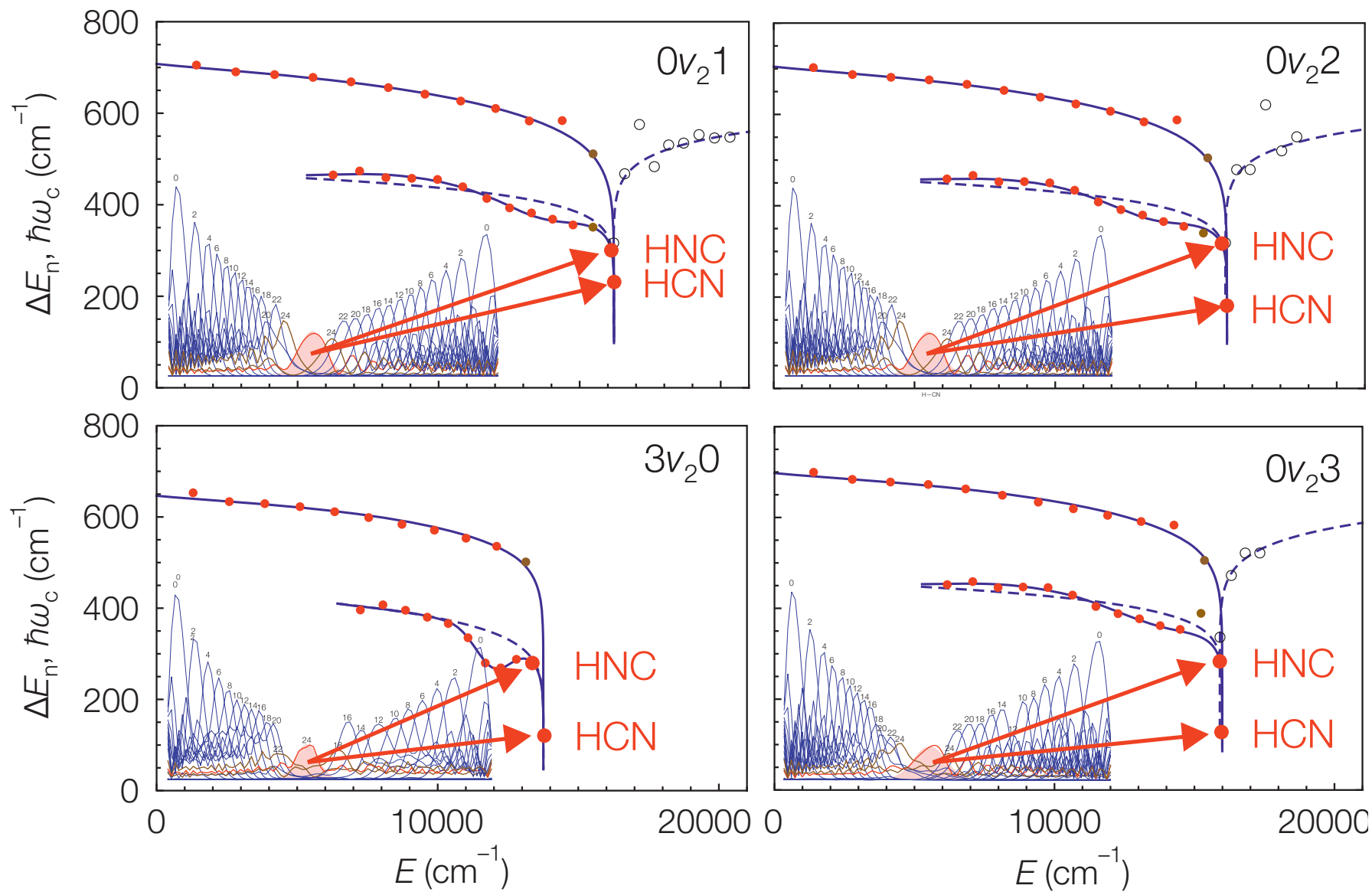
HCN $0v_20$ l=3... bending series
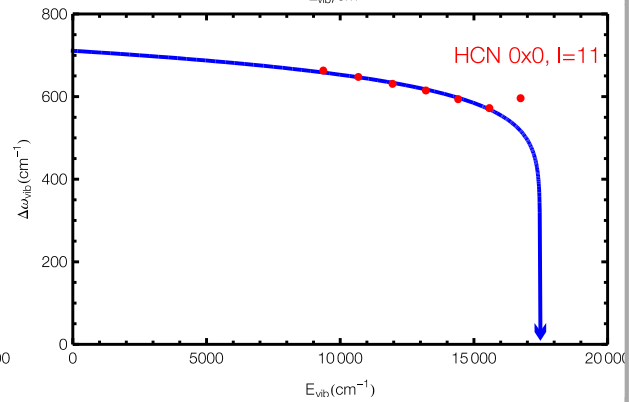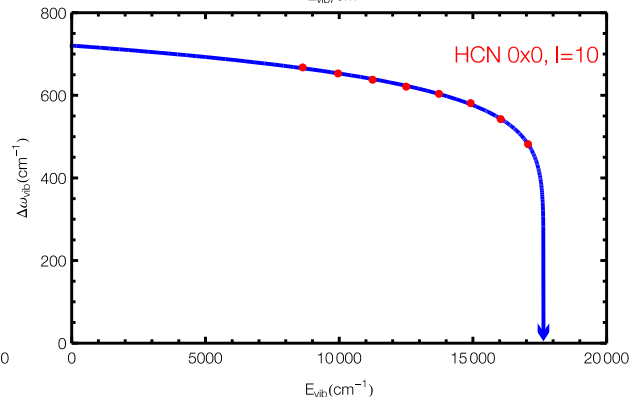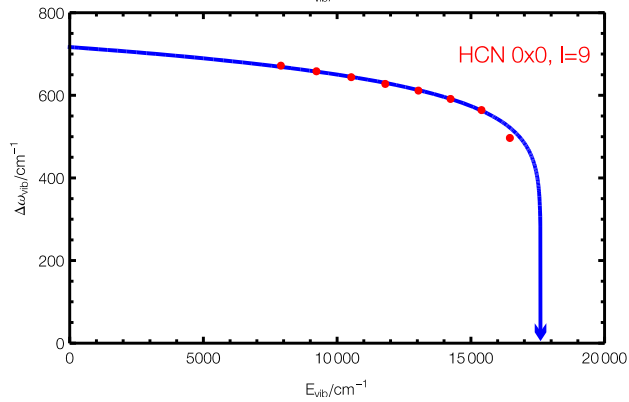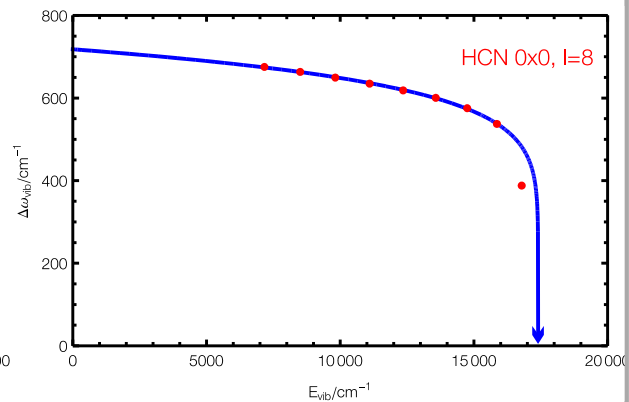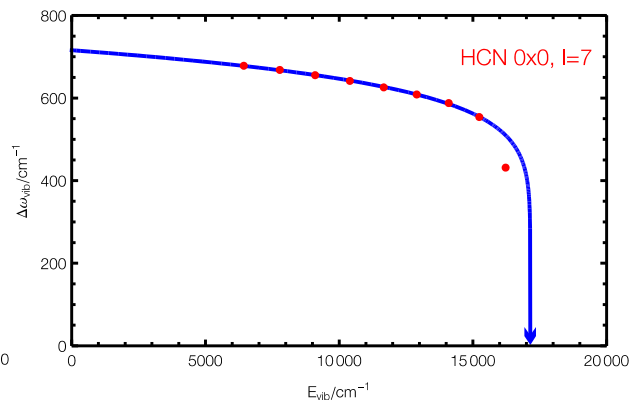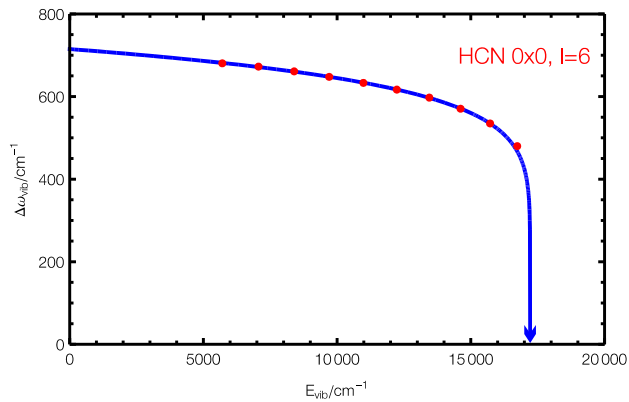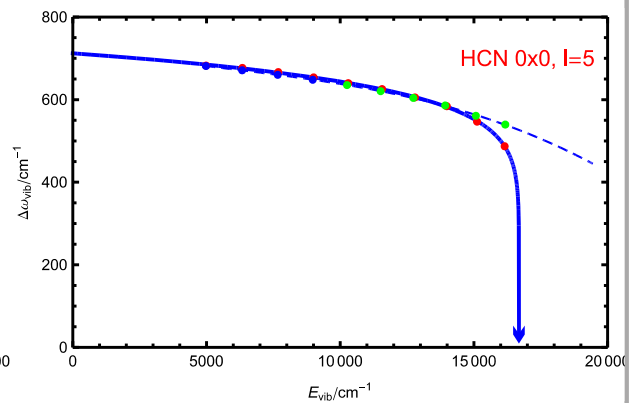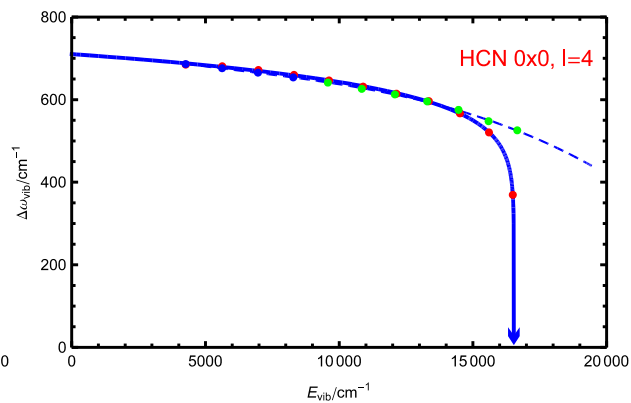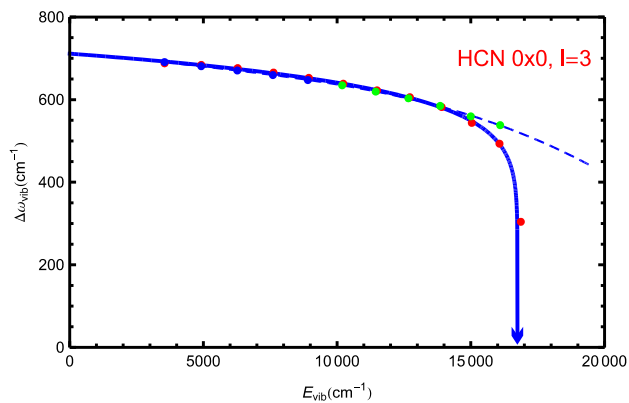
Potential kinks
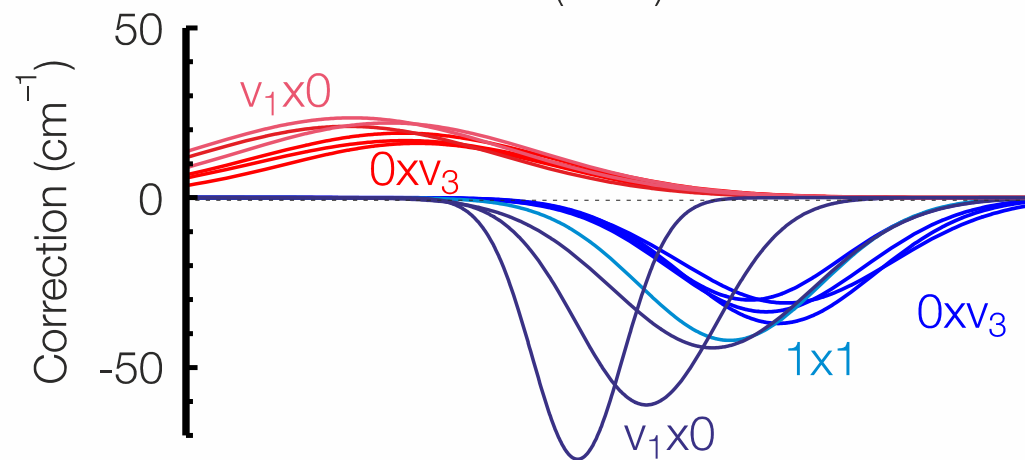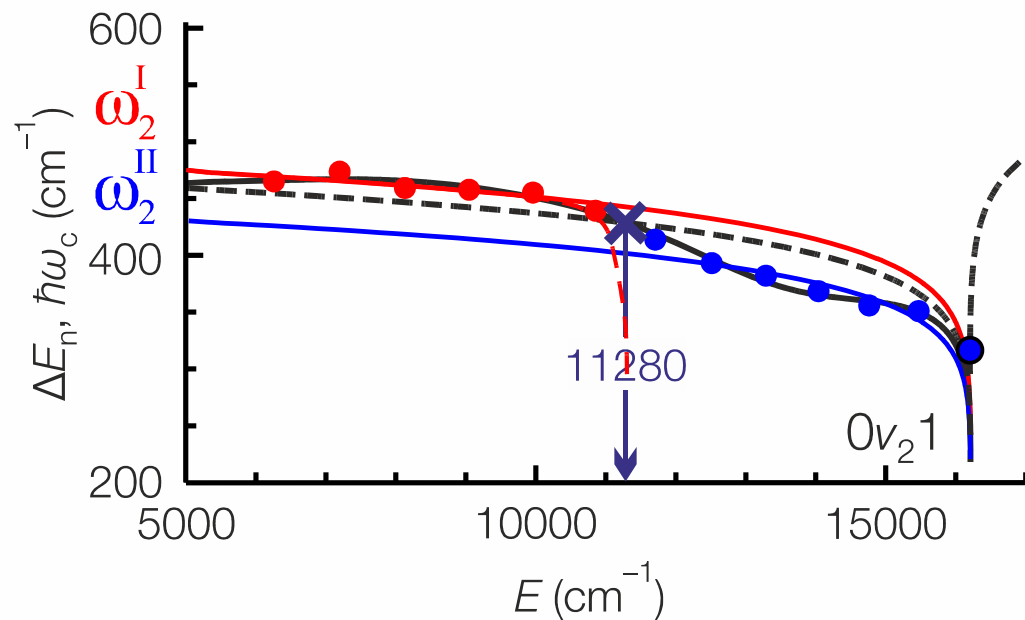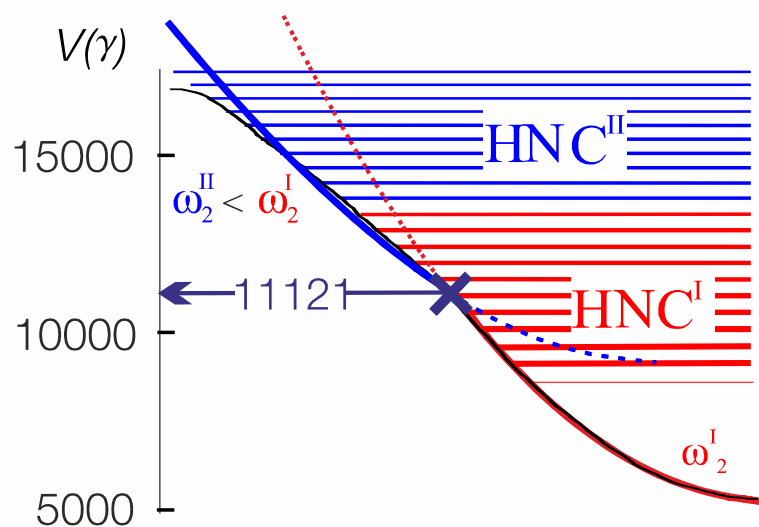
HCN→HNC delocalization ↔ Width of the dynamic barrier