

Theoretical rovibronic spectroscopy of small molecules



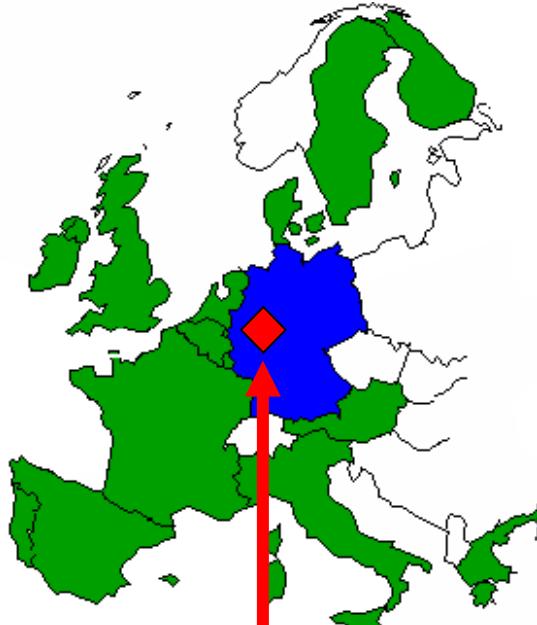
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***Where is
Wuppertal?***





Bergische Universität Wuppertal





132

5

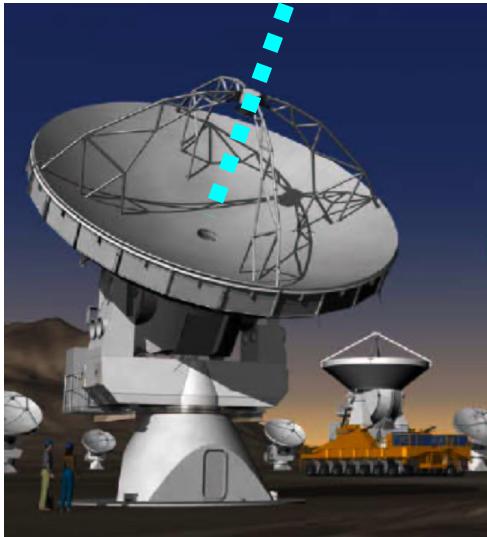
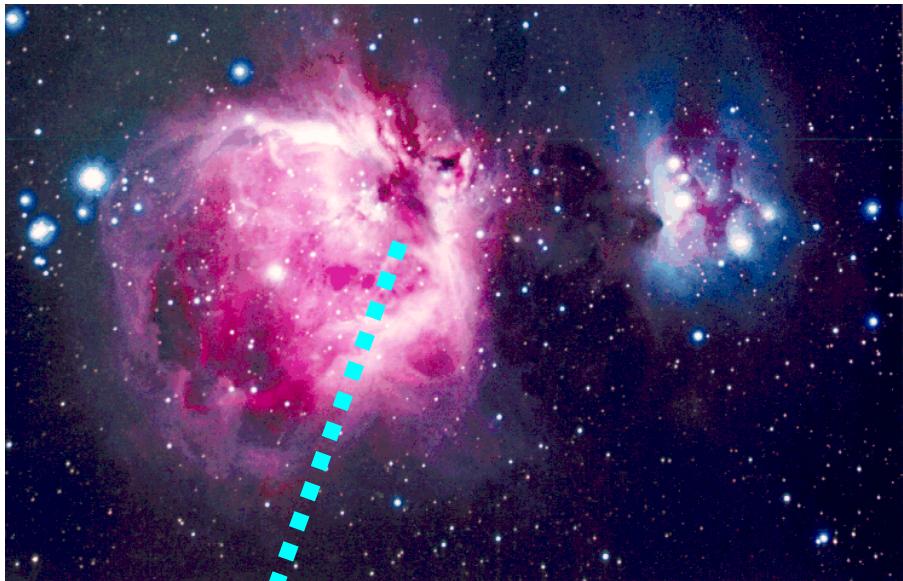
133



The Schwebebahn (monorail) in Wuppertal

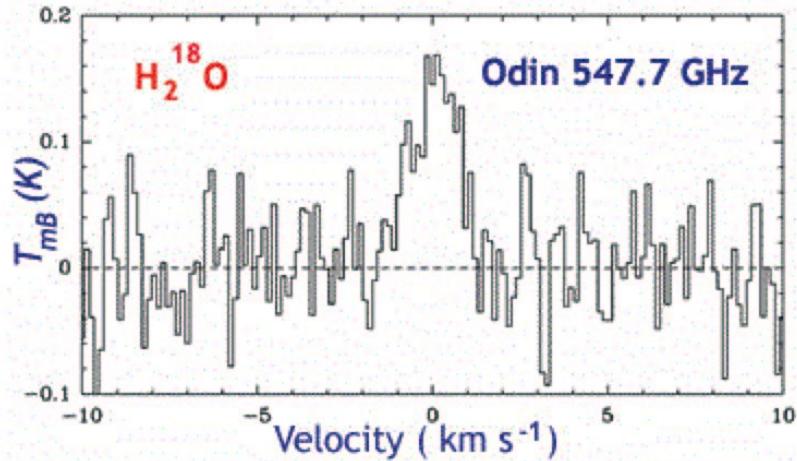


Remote sensing experiments



*....astrophysics/chemistry
....atmospheric research*

C/2002 C1 (Ikeya-Zhang): 24 - 28 April 2002



Determine *what is there*

Determine *how much is there*

Remote sensing experiments

To determine *how much is there*, we must know the line strengths of the rovibronic transitions in question.

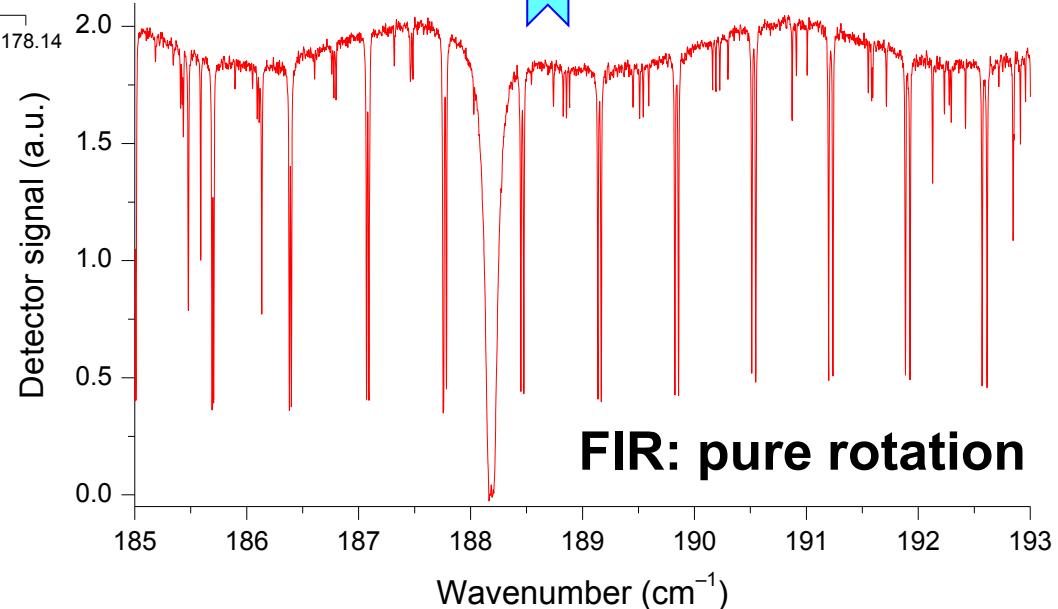
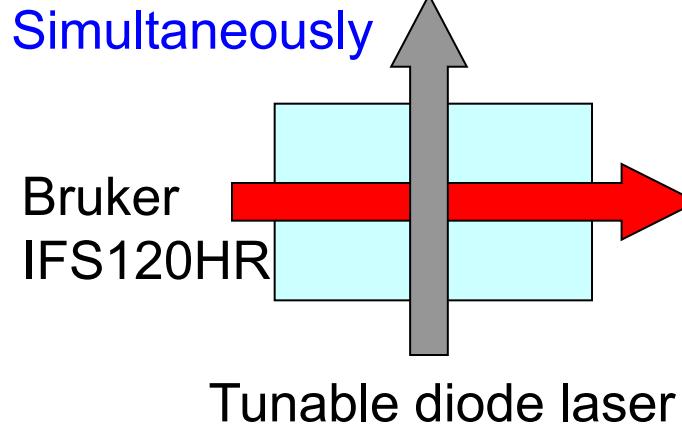
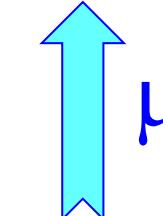
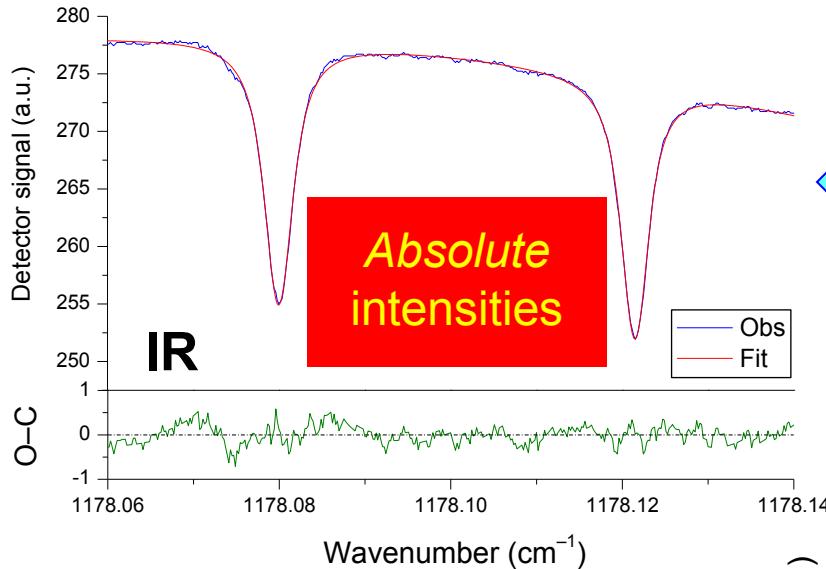
Line strength: Molecule-intrinsic transition probability

$$S(f \leftarrow i) = g_{\text{ns}} \sum_{m_f, m_i} \sum_{A=X,Y,Z} \left| \left\langle \Phi_{\text{rv}}^{(f)} \Phi_{\text{elec}}^{(f)} | \mu_A | \Phi_{\text{elec}}^{(i)} \Phi_{\text{rv}}^{(i)} \right\rangle \right|^2$$

Line strengths can be measured by laboratory spectroscopy of molecules at known concentrations.

An example ...

J. Vander Auwera, Université Libre de Bruxelles, B
A. Perrin, Université Paris 12, F
T. F. Giesen, University of Cologne, D
W. Stahl, University of Aachen, D



Remote sensing experiments

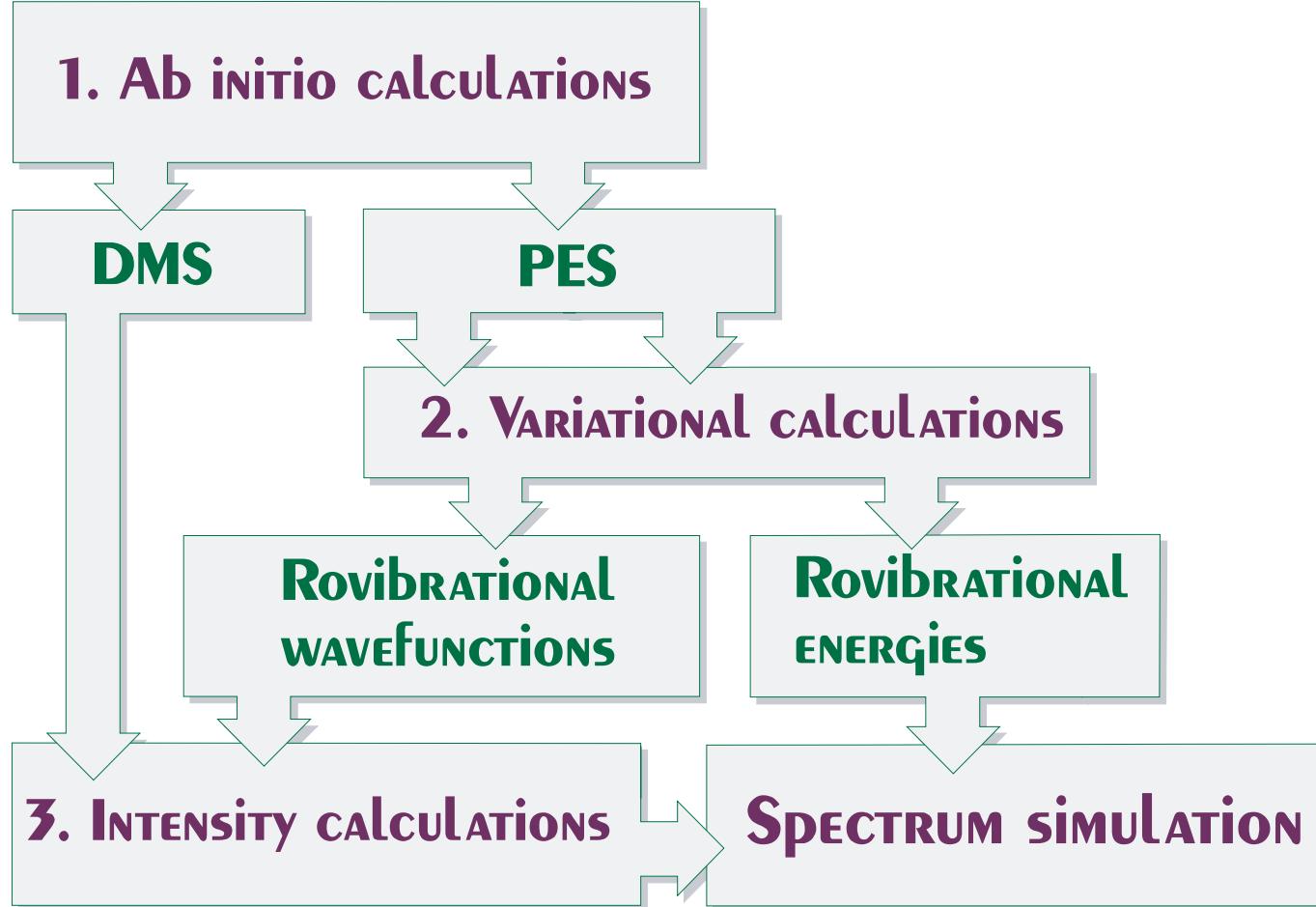
The experiments, in particular the determination of concentrations for unstable molecules, are difficult.

So what about theoretical calculations of line strengths?

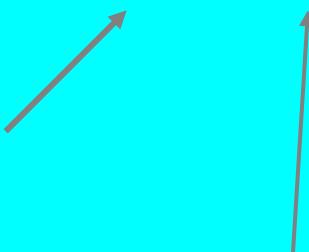
Ingredients:

- Ab initio* potential energy surfaces (PES)
- Ab initio* dipole moment surfaces (DMS)

Computation of rovibrational spectra

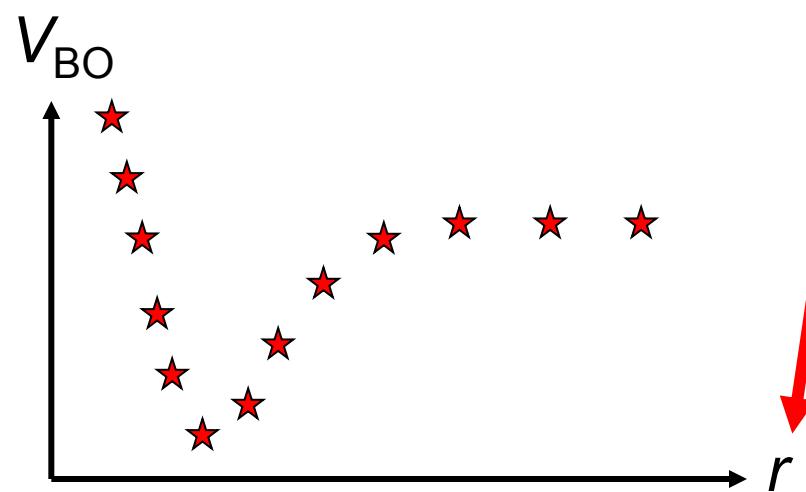
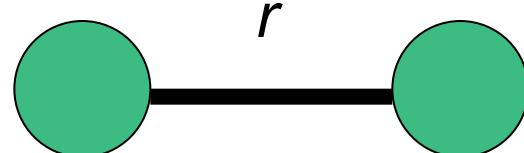


Starting point: The Born-Oppenheimer Approximation



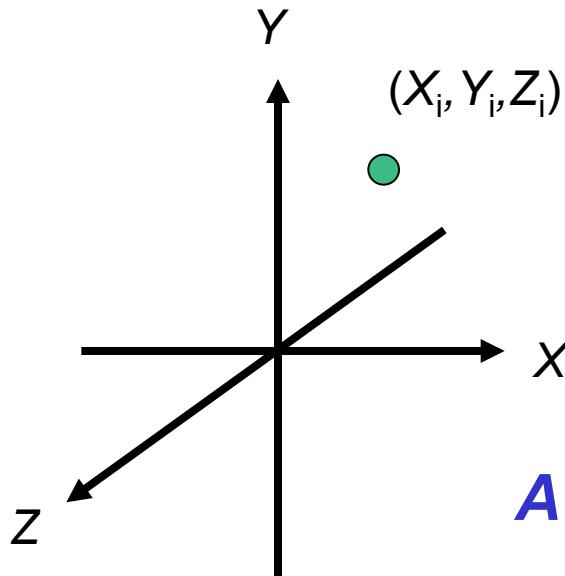
Ab initio (electronic structure) calculation

nuclear positions fixed in space



Ab initio calculation of dipole moment components

Expectation value of dipole moment operator for electronic wavefunction



$$A = X, Y, Z$$

Nuclear-motion calculation

from *ab initio* calculation

$$\hat{H}_n \psi_n^{(j)}(\mathbf{R}_n) = E_{ne}^{(j)} \psi_n^{(j)}(\mathbf{R}_n)$$

„observable“ energy

„ansatz“ for the wavefunction

known basis function
(harmonic oscillator, rigid rotor...)

Variational nuclear-motion calculation



is an eigenvalue of the matrix with the elements

The eigenvector coefficients are

Energies/wavefunctions from variational rotation-vibration calculations

Basis functions:

$$|\Psi_{Basis}\rangle = |J, K, m\rangle |v_{inv}, J, K\rangle \Psi_{v_1}^{MO}(\xi_1) \times \Psi_{v_2}^{MO}(\xi_2) \times \Psi_{v_3}^{MO}(\xi_3) \times \Psi_{V,l}^{HO}(\xi_{4a}, \xi_{4b})$$

Rigid rotor
eigenfunctions

Morse oscillators

Two-dimensional
isotropic harmonic
oscillators for doubly
degenerate bending
vibrations

Numerov-Cooley
solution of inversion
Schrödinger
equation for

$$V_0(\rho) = V(\rho, \xi_\lambda = 0)$$

**Hougen-Bunker-Johns theory:
Eckart & Sayvetz conditions**
 $\Rightarrow \widehat{T}_{\text{nuc}} = \text{expansion in the } \xi_i$

[1] H. Lin *et al.*, *J. Chem. Phys.* **117**, 11265 (2002)

[2] S.N. Yurchenko *et al.*, *Mol. Phys.* **103**, 359 (2005) and references given there.

Variational rotation-vibration calculations for NH₃

$J \leq 18$

Vibrational basis set:

$$2(\nu_1 + \nu_2 + \nu_3) + \nu_{inv} + V_{bend} \leq 8$$

Dipole moment surfaces:

CCSD(T)/aug-cc-pVTZ, 14400 points [1]

Frozen-core-approximation

Numerical finite-difference procedure

Potential energy surface:

CCSD(T)/aug-cc-pVTZ, 51816 points [2]
extrapolated to CBS+ level (3814 points,
complete basis set, relativistic effects)

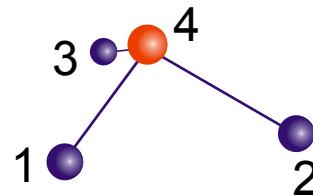
[1] S. N. Yurchenko, M. Carvajal, H. Lin, J. J. Zheng, W. Thiel, and P. Jensen, *J. Chem. Phys.* **122**, 104317 (2005).

[2] H. Lin, J. J. Zheng, S. N. Yurchenko, P. Jensen, and W. Thiel, *in preparation*.

Electronically averaged dipole moment for NH₃ expressed as

“Molecular Bond” representation [1] for general use

$$\bar{\mu} = \mu_1^{\text{Bond}} e_1 + \mu_2^{\text{Bond}} e_2 + \mu_3^{\text{Bond}} e_3$$



$$e_j = \frac{\mathbf{r}_j - \mathbf{r}_4}{|\mathbf{r}_j - \mathbf{r}_4|}$$

μ_j^{Bond} is a parameterized function of internal vibrational coordinates

Expansion in linearized displacement coordinates (¹⁴NH₃) for use in present calculations

All parameter values are available on request!

Vibrational transition moments for $^{14}\text{NH}_3$

States		ν_{fi}/cm^{-1}	Obs. μ_{fi}/D	$Ab initio \mu_{fi}/\text{D}$		
f	i	Exp.		Pracna 1989	Marquardt 2003	Present work
0 ⁻	0 ⁺	0.79	1.47193(1) ^d	1.536	1.574	1.4564
ν_2^+	0 ⁻	931.64	0.248(7)	0.269	0.2183	0.2445
ν_2^-	0 ⁺	968.12	0.236(4)	0.258	0.2075	0.2347
$2\nu_2^+$	0 ⁻	1596.68	0.02036(25)	0.027	0.0091	0.0202
$2\nu_2^-$	0 ⁺	1882.18	0.003256(35)	0.007	0.0261	0.0026
$3\nu_2^+$	0 ⁻	2383.36	0.00496(13)	0.004	0.0261	0.0054
$3\nu_2^-$	0 ⁺	2895.51	0.002856(40)	0.003	0.0155	0.0027
$4\nu_2^+$	0 ⁻	3461				0.0020
$4\nu_2^-$	0 ⁺	4055				0.0009
ν_1^+	0 ⁻	3335.23	0.0262(1)		0.0366	0.0269
ν_1^-	0 ⁺	3337.08	0.0262(1)		0.0366	0.0270
$(\nu_1 + \nu_2)^+$	0 ⁻	4293.72	0.0079		0.0067	0.0087
$(\nu_1 + \nu_2)^-$	0 ⁺	4320.06	0.0079		0.0066	0.0083
ν_3^+	0 ⁺	3443.68	0.0182(1)		0.0915	0.0181
ν_3^-	0 ⁻	3443.20	0.0182(1)		0.0915	0.0180
$(\nu_2 + \nu_3)^+$	0 ⁺	4416.91	0.0206		0.0128	0.0246
$(\nu_2 + \nu_3)^-$	0 ⁻	4434.61	0.0206		0.0127	0.0244
ν_4^+	0 ⁺	1626.28	0.08408(34)		0.0839	0.0828
ν_4^-	0 ⁻	1626.58	0.08408(34)		0.0838	0.0827
$2\nu_4^{0,+}$	0 ⁻	3215.23	0.00920(6)			0.0073
$2\nu_4^{0,-}$	0 ⁺	3217.59	0.00920(6)			0.0074
$2\nu_4^{\pm 2,+}$	0 ⁺	3240.18	0.00920(6)			0.0091
$2\nu_4^{\pm 2,-}$	0 ⁻	3240.82	0.00920(6)			0.0090
$(\nu_2 + \nu_4)^+$	0 ⁺	2540.53	0.002358(36)		0.0077	0.0091
$(\nu_2 + \nu_4)^-$	0 ⁻	2585.34	0.002182(82)		0.0080	0.0094

[1] P. Pracna, V. Špirko, and W. P. Kraemer, *J. Mol. Spectrosc.* **136**, 317 (1989).

[2] R. Marquardt, M. Quack, I. Thanopulos, and D. Luckhaus, *J. Chem. Phys.* **119**, 10724 (2003).

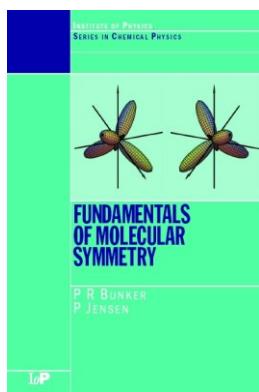
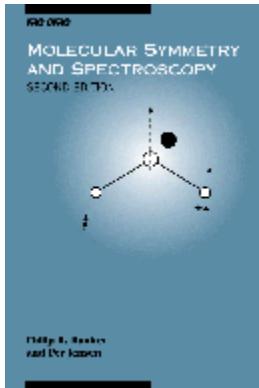
Vibrational transition moments for $^{14}\text{NH}_3$

States		ν_{fi}/cm^{-1}	Obs. μ_{fi}/D	<i>Ab initio</i> μ_{fi}/D		
f	i	Exp. ^a		Pracna 1989	Marquardt 2003	Present work
ν_2^-	ν_2^+	35.69	1.2448(23)	1.305	1.355	1.2376
$2\nu_2^+$	ν_2^-	629.35		0.557	0.5084	0.5144
$2\nu_2^-$	ν_2^+	949.75	0.285(10)	0.313	0.2698	0.2855
$3\nu_2^+$	ν_2^-	1416.03	0.0737(16)	0.089	0.0288	0.0738
$3\nu_2^-$	ν_2^+	1963.08	0.00081(11)	0.004	0.0416	0.0011
ν_1^+	ν_2^-	2367.90	0.0040		0.0157	0.0002
ν_1^-	ν_2^+	2404.65	0.0040		0.0159	0.0008
ν_3^+	ν_2^+	2511.25	0.02286(29)		0.0080	0.0178
ν_3^-	ν_2^-	2475.87	0.02286(29)		0.0080	0.0181
$2\nu_4^{\pm 2,+}$	ν_2^+	2307.75	0.00672(15)			0.0044
$2\nu_4^{\pm 2,-}$	ν_2^-	2273.49	0.00672(15)			0.0048
$2\nu_4^{0,+}$	ν_2^-	2247.90	0.00085			0.0036
$2\nu_4^{0,-}$	ν_2^+	2285.16	0.00085			0.0031
$(\nu_2 + \nu_4)^+$	ν_2^+	1608.10	0.0888(12)		0.0867	0.0911
$(\nu_2 + \nu_4)^-$	ν_2^-	1618.01	0.0843(27)		0.0856	0.0876
ν_1^-	ν_1^+	1.06	1.47912(14)		1.599	1.4626
$2\nu_2^-$	$2\nu_2^+$	284.71	1.02(18)	0.995	1.047	0.9383
$3\nu_2^+$	$2\nu_2^-$	501.97	1.05(34)	0.898	0.9430	0.8876
$3\nu_2^-$	$2\nu_2^+$	1298.04		0.113	0.0830	0.1116
$3\nu_2^-$	$3\nu_2^+$	511.36		1.037	1.039	0.9671
$4\nu_2^+$	$3\nu_2^-$	566				0.9933
$4\nu_2^-$	$3\nu_2^+$	1671				0.0343
$4\nu_2^-$	$4\nu_2^+$	593		1.107	1.072	1.0199
ν_3^+	ν_3^-	0.31	1.5094		1.626	1.4885
ν_4^+	ν_4^-	1.09	1.4554(32)		1.574	1.4422

[1] P. Pracna, V. Špirko, and W. P. Kraemer, *J. Mol. Spectrosc.* **136**, 317 (1989).

[2] R. Marquardt, M. Quack, I. Thanopulos, and D. Luckhaus, *J. Chem. Phys.* **119**, 10724 (2003).

Absorption intensity simulation: XY₃ molecules



$$I(f \leftarrow i) = \int_{\text{Line}} \epsilon(\tilde{\nu}) d\tilde{\nu}$$

$$= \frac{8\pi^3 N_A \tilde{\nu}_{if}}{(4\pi\epsilon_0)3hc} \frac{e^{-E_i/kT}}{Q} [1 - \exp(-hc\tilde{\nu}_{if}/kT)] S(f \leftarrow i)$$

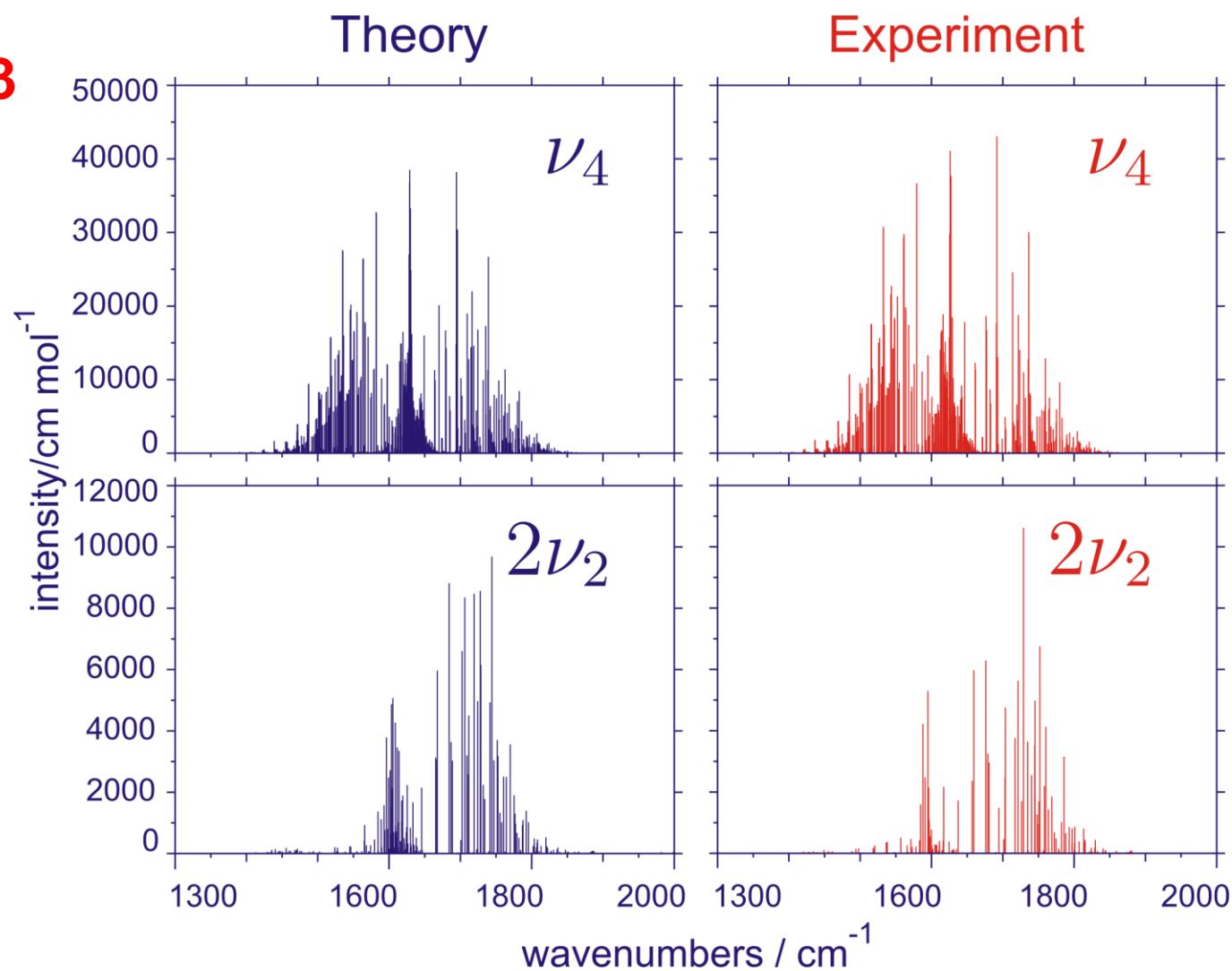
$$S(f \leftarrow i) = g_{ns} \sum_{m_f, m_i} \sum_{A=X,Y,Z} \left| \langle \Phi_{rv}^{(f)} \Phi_{elec}^{(f)} | \mu_A | \Phi_{elec}^{(i)} \Phi_{rv}^{(i)} \rangle \right|^2$$

$$S(f \leftarrow i) = g_{ns} (2J' + 1) (2J'' + 1) \left| \sum_{V' K' \tau'_{\text{rot}}} \sum_{V'' K'' \tau''_{\text{rot}}} C_{V' K' \tau'_{\text{rot}}}^* C_{V'' K'' \tau''_{\text{rot}}} (-1)^{\tau''_{\text{rot}} - \tau'_{\text{rot}}} (-1)^{\sigma'_{\text{rot}} + \sigma''_{\text{rot}} + K'} \right. \\ \times \begin{pmatrix} J'' & 1 & J' \\ K'' & (K' - K'') & -K' \end{pmatrix} \left\{ \delta_{K' K''} (1 - \delta_{\tau'_{\text{rot}}, \tau''_{\text{rot}}}) (\tau''_{\text{rot}} - \tau'_{\text{rot}}) \langle V' | \bar{\mu}_z | V'' \rangle \right. \\ + (1 - \delta_{K' K''}) [-\delta_{\tau'_{\text{rot}}, \tau''_{\text{rot}}} \langle V' | \bar{\mu}_y | V'' \rangle \\ + (1 - \delta_{\tau'_{\text{rot}}, \tau''_{\text{rot}}}) (\tau''_{\text{rot}} - \tau'_{\text{rot}}) (K'' - K') \langle V' | \bar{\mu}_x | V'' \rangle] \\ \left. \times \left[\delta_{K' + K'', 1} + \frac{1}{\sqrt{2}} (1 - \delta_{K' + K'', 1}) \right] \right\}^2,$$

[1] S. N. Yurchenko, M. Carvajal, H. Lin, J. J. Zheng, W. Thiel, and P. Jensen, *J. Chem. Phys.* **122**, 104317 (2005).

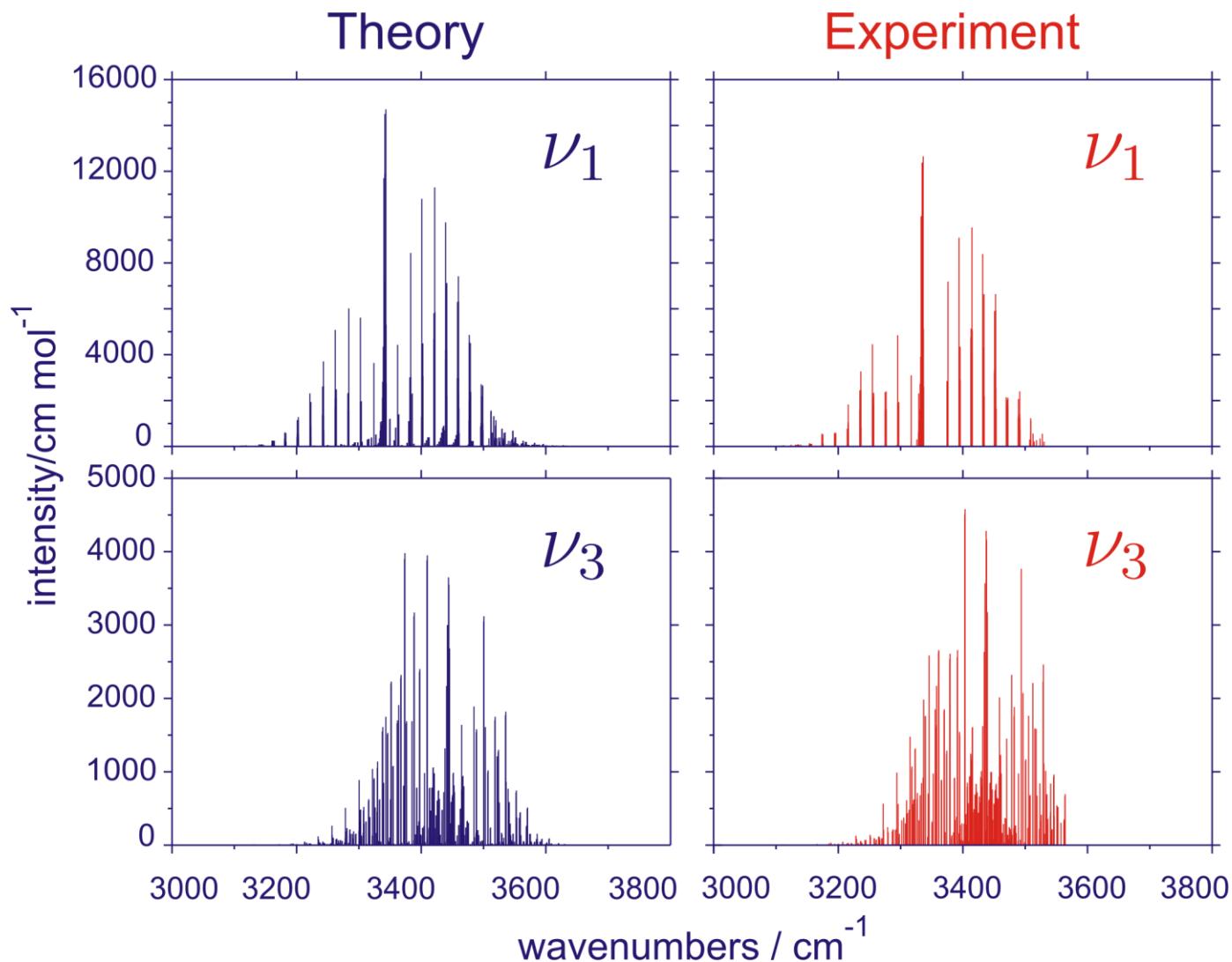
[2] S. N. Yurchenko, W. Thiel, M. Carvajal, H. Lin, and P. Jensen, *Adv. Quant. Chem.*, in press.

The ν_4 and $2\nu_2$ absorption bands of $^{14}\text{NH}_3$



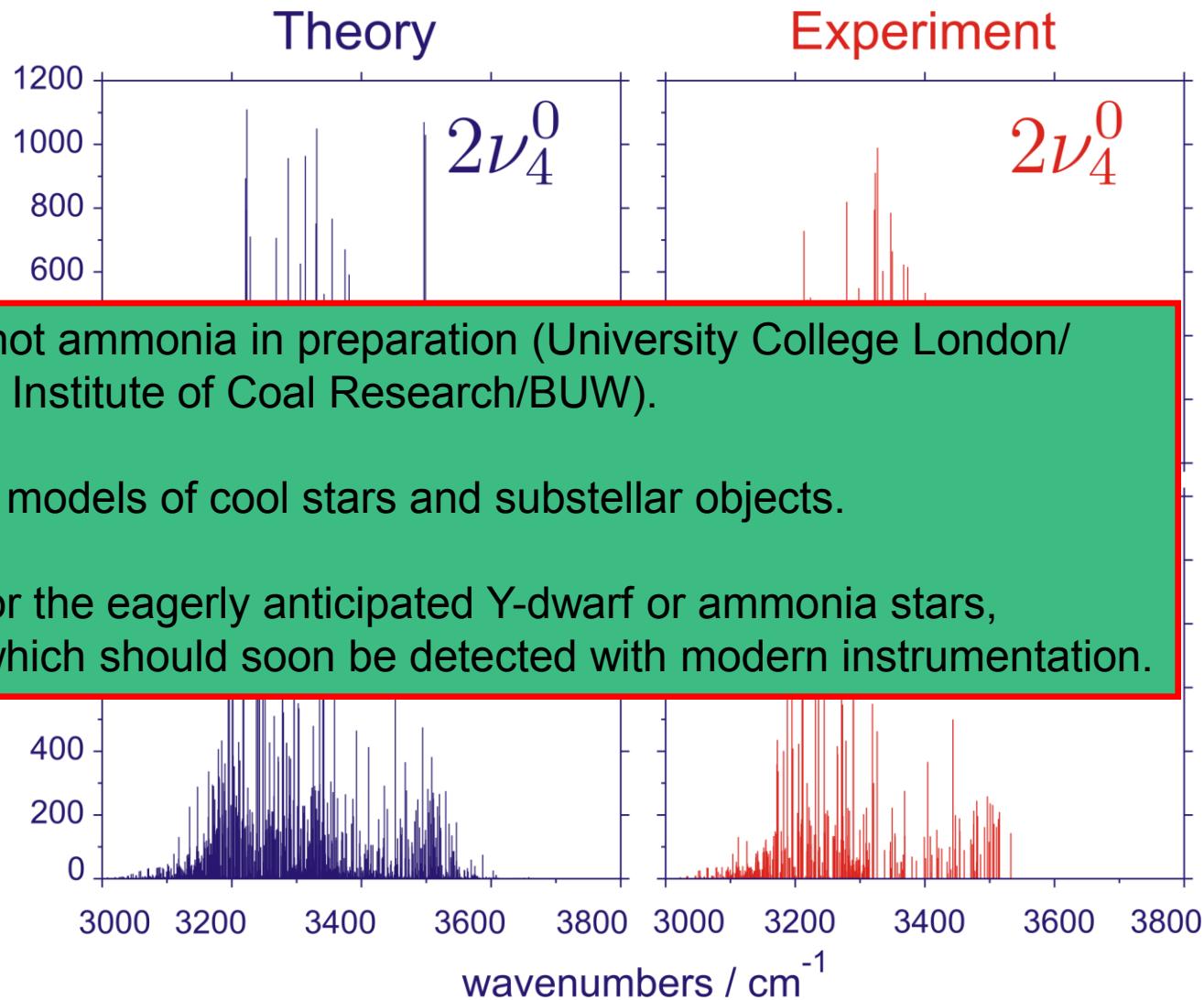
Experiment: C. Cottaz, G. Tarrago, I. Kleiner, L. R. Brown, J. S. Margolis, R. L. Poynter, H. M. Pickett, T. Fouchet, P. Drossart, and E. Lellouch, *J. Mol. Spectrosc.* **203**, 285 (2000).

The ν_1 and ν_3 absorption bands of $^{14}\text{NH}_3$



Experiment: I. Kleiner, L. R. Brown, G. Tarrago, Q.-L. Kou, N. Picqué, G. Guelachvili, V. Dana, and J.-Y. Mandin, *J. Mol. Spectrosc.* **193**, 46 (1999).

The $2\nu_4^0$ and $2\nu_4^{\pm 2}$ absorption bands of $^{14}\text{NH}_3$



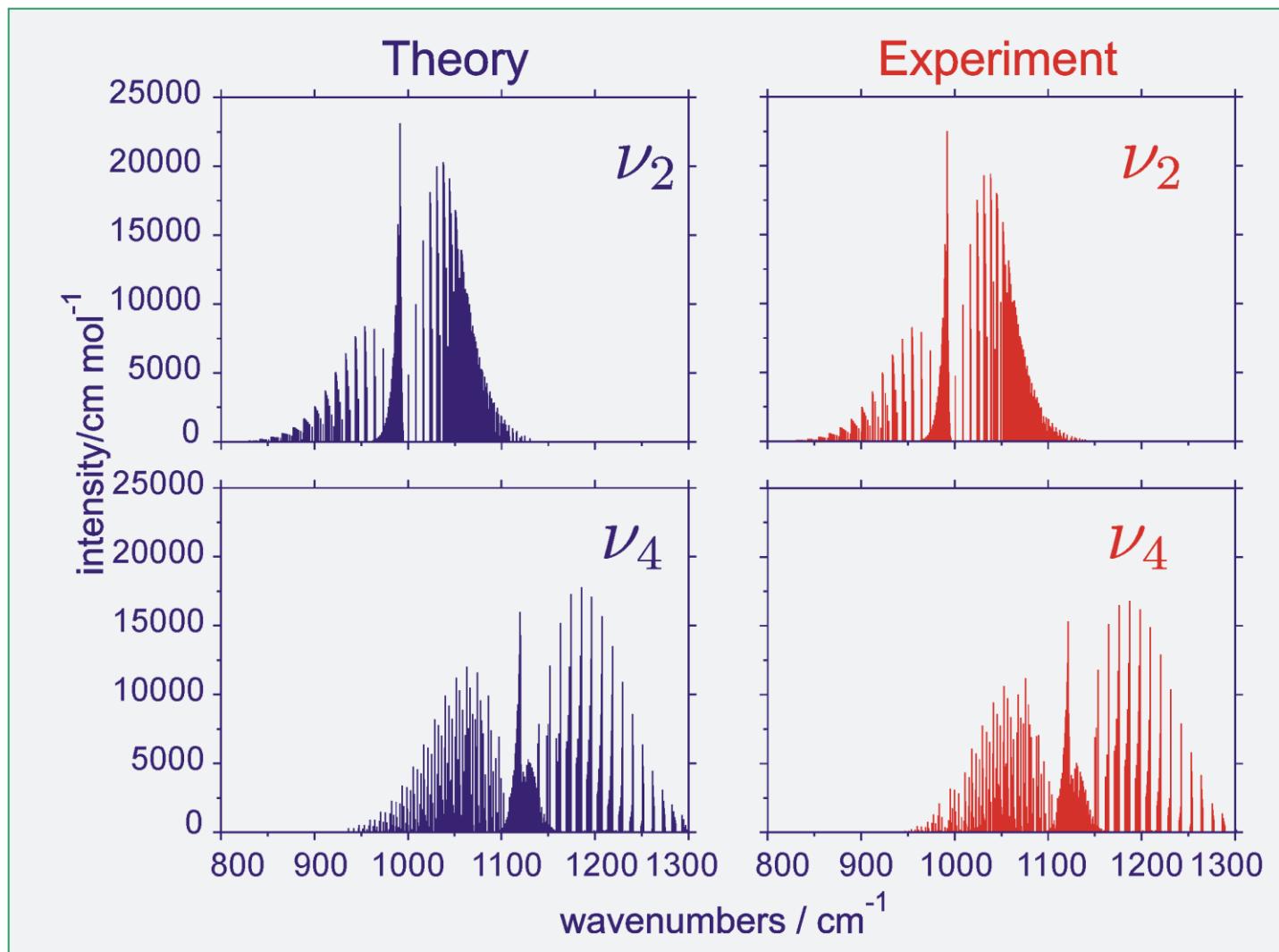
Linelist for hot ammonia in preparation (University College London/
Max Planck Institute of Coal Research/BUW).

Suitable for models of cool stars and substellar objects.

Important for the eagerly anticipated Y-dwarf or ammonia stars,
faint stars which should soon be detected with modern instrumentation.

Experiment: I. Kleiner, L. R. Brown, G. Tarrago, Q.-L. Kou, N. Picqué, G. Guelachvili, V. Dana, and J.-Y. Mandin, *J. Mol. Spectrosc.* **193**, 46 (1999).

The ν_2 and ν_4 absorption bands of PH_3

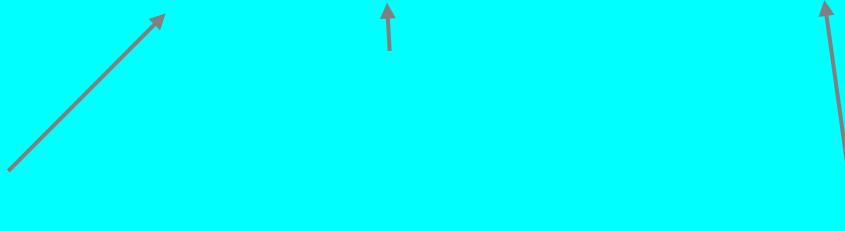


Experiment: L.R. Brown, R.L. Sams, I. Kleiner et al., *J. Mol. Spectrosc.* 215, 178 (2002)

Theory: S. N. Yurchenko, M. Carvajal, W. Thiel, and P. Jensen, *J. Mol. Spectrosc.* 239, 71 (2006)

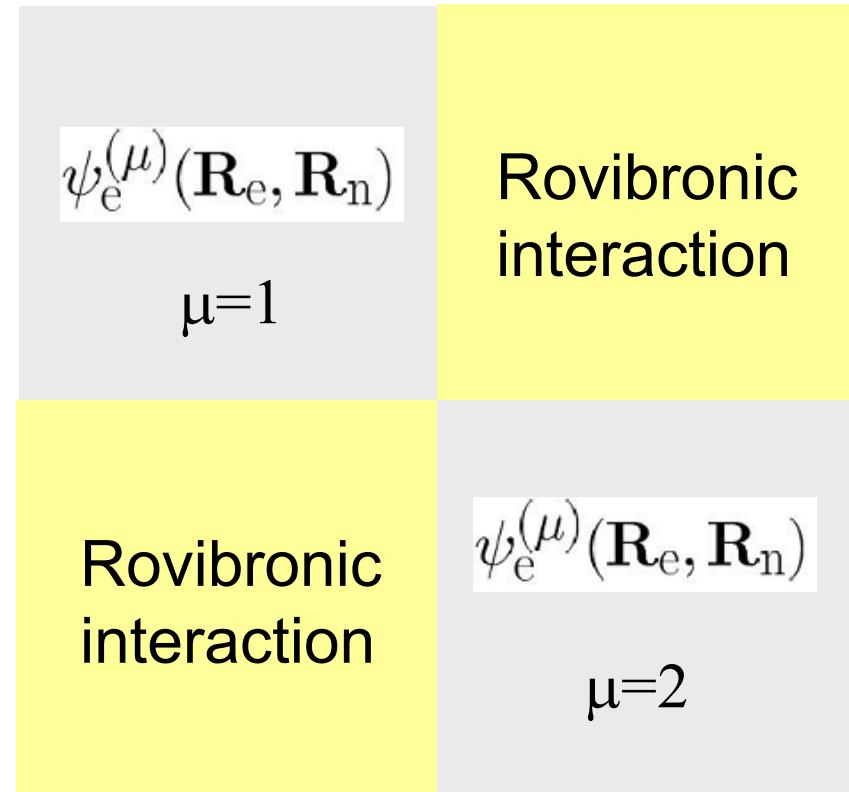
Born-Oppenheimer Approximation

**Beyond
the Born-Oppenheimer Approximation**

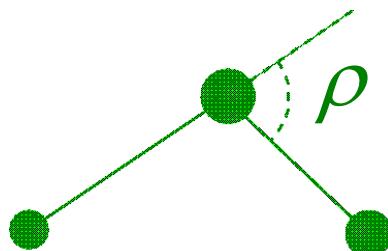


Beyond the Born-Oppenheimer Approximation

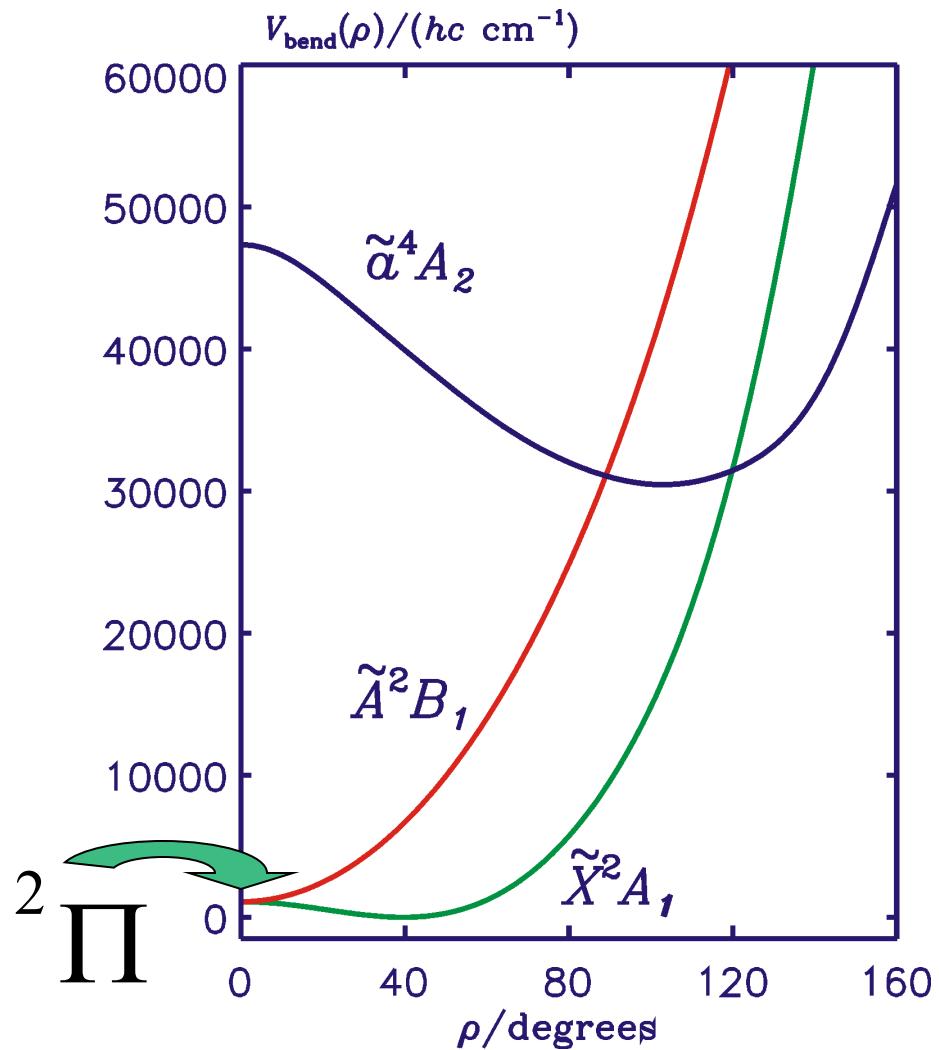
matrix representation
of rovibronic Hamiltonian
for two interacting
electronic states



CH_2^+ RENNER EFFECT



Λ
—
(0 Σ)
1 Π
2 Δ
3 Φ
...
 2Π



Rovibronic wavefunctions for Renner-degenerate states

Isolated electronic state (Born-Oppenheimer approximation):

Renner-degenerate states:

Interaction between $\psi_e^{(-,S)}$ and $\psi_e^{(+,S)}$ caused by \tilde{L}_z .

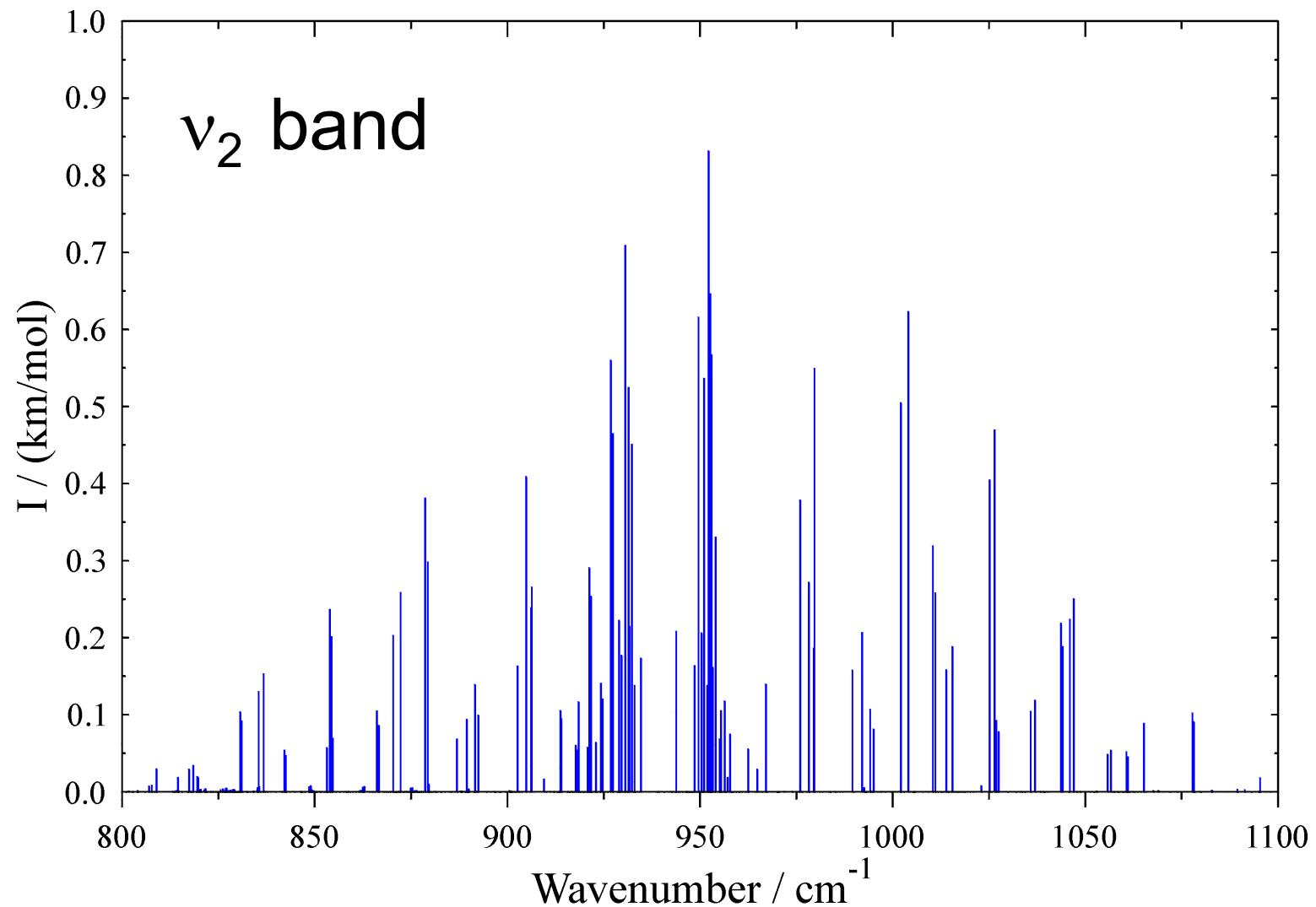
CH_2^+ Calculations

- Ab initio potential energy functions from W. P. Kraemer, Per Jensen, and P. R. Bunker, *Can. J. Phys.* 72, 871-878 (1994)
- One parameter of the potential energy function has been adjusted to obtain agreement with experiment for the v_3 vibrational term value in the $\tilde{X}^2\text{A}_1$ state.

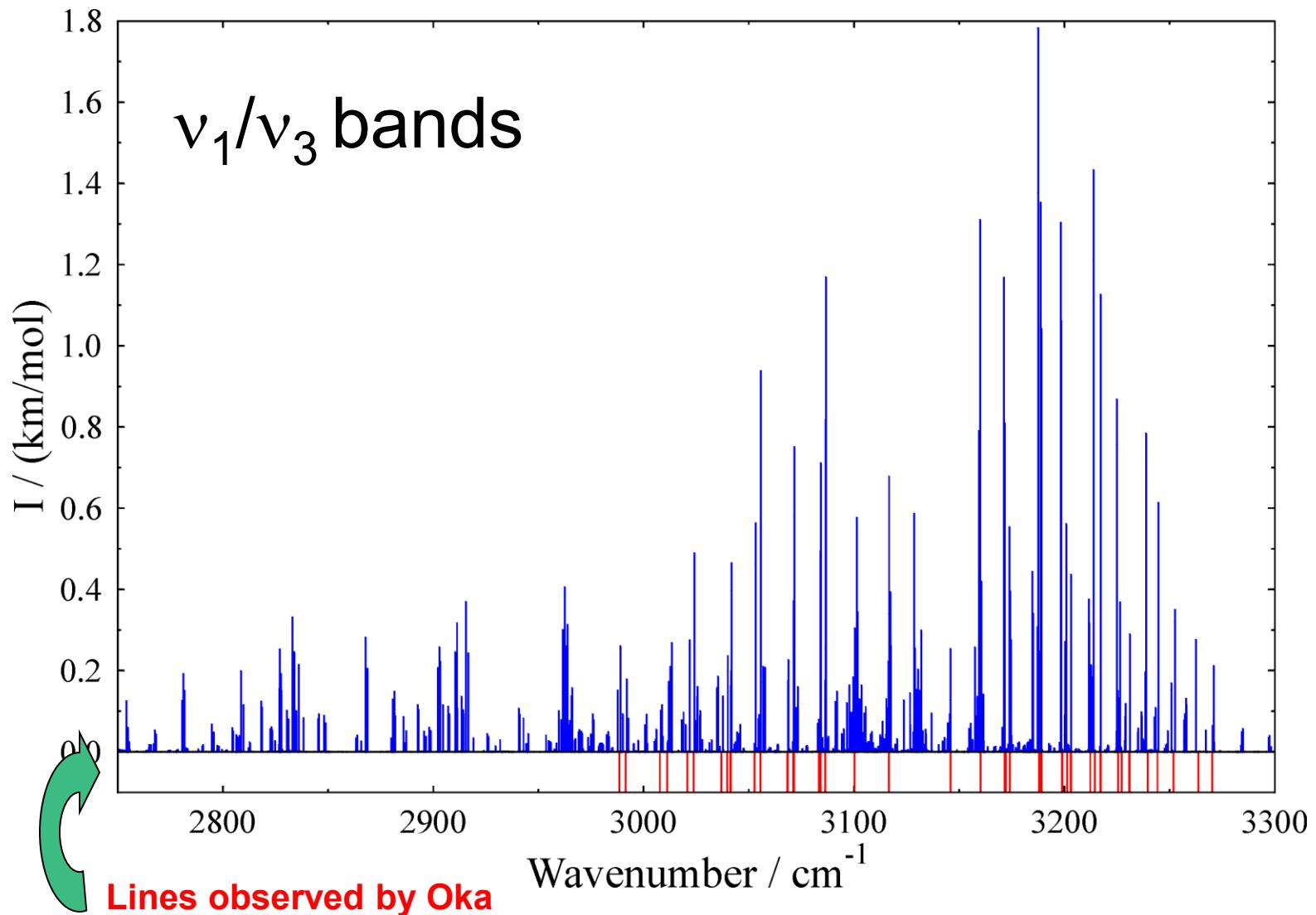
CH_2^+ Experiment

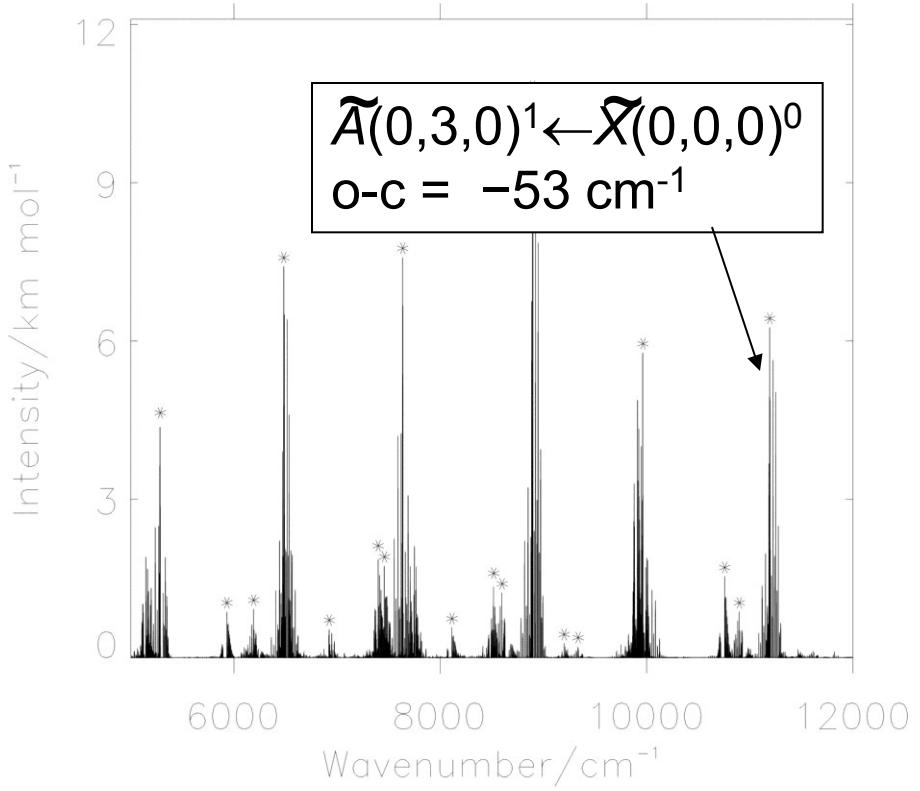
- $\tilde{X}^2\text{A}_1 v_3$ band ($K_a = 0 \leftarrow 0$ and $1 \leftarrow 1$) measured by M. Rösslein, C. M. Gabrys, M.-F. Jagod, and T. Oka, *J. Mol. Spectrosc.* 153, 738-740 (1992).
- Photoelectron spectrum of CH_2 ; S. Willitsch and F. Merkt: *J. Chem. Phys.* 118, 2235-2241 (2003).
- $\tilde{A}^2\text{B}_1 \leftarrow \tilde{X}^2\text{A}_1$ electronic spectrum; J. L. Gottfried and T. Oka, *J. Chem. Phys.* 121, 11527 (2004)

CH_2^+ $\tilde{\chi}^2A_1$ $N \leq 10$ $T = 300 \text{ K}$

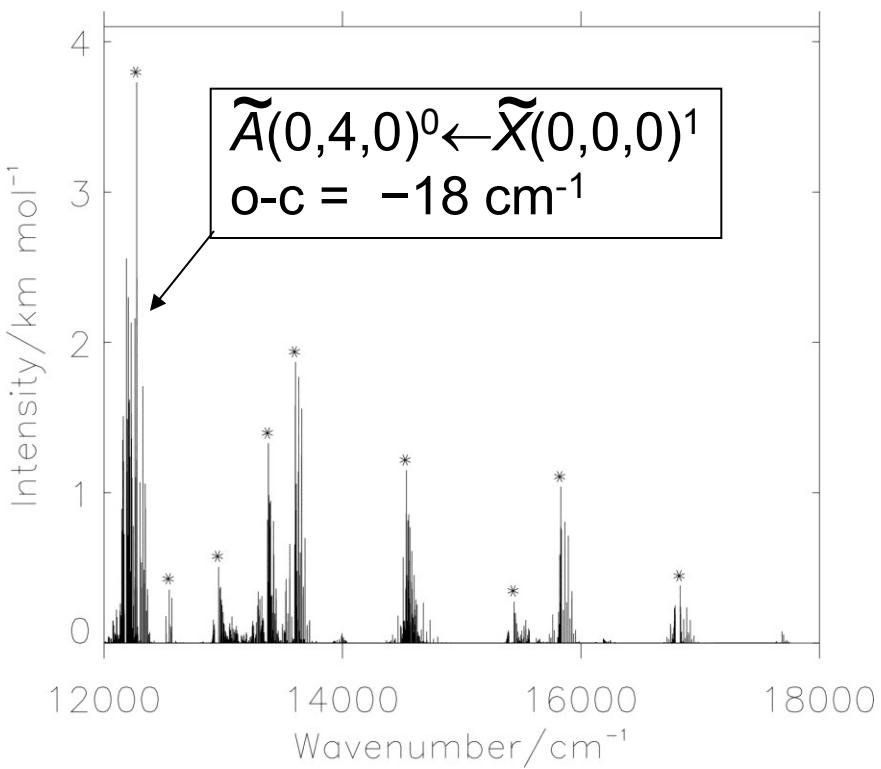
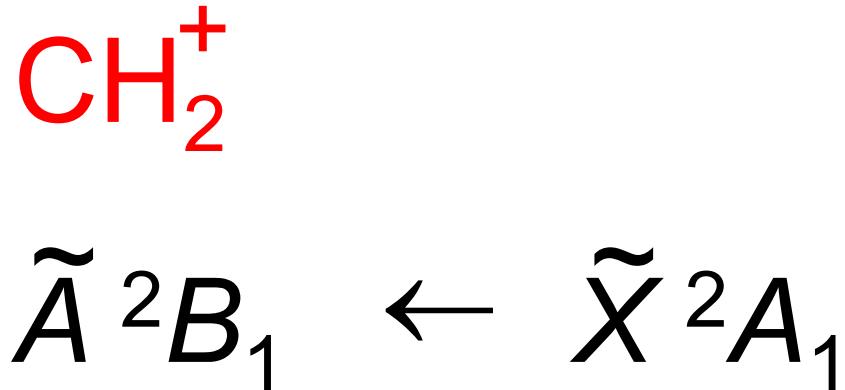


CH_2^+ \tilde{X}^2A_1 $N \leq 10$ $T = 300 \text{ K}$

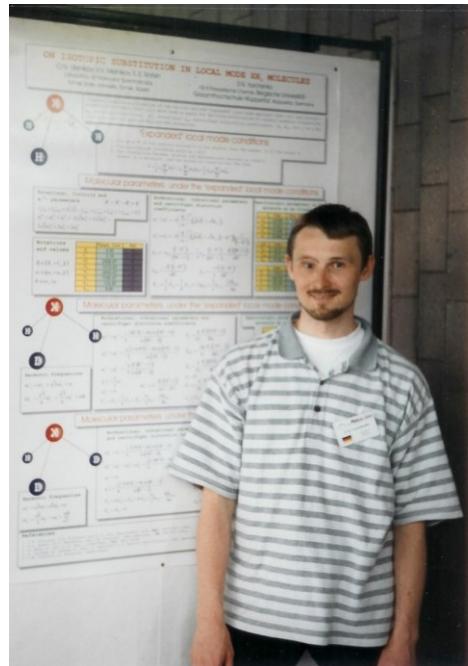




J. L. Gottfried and T. Oka,
***J. Chem. Phys.* 121, 11527 (2004)**



Thanks & Acknowledgments



The principal doer:

Sergei N. Yurchenko, Wuppertal, Ottawa,
Mülheim, Dresden

Other doers:

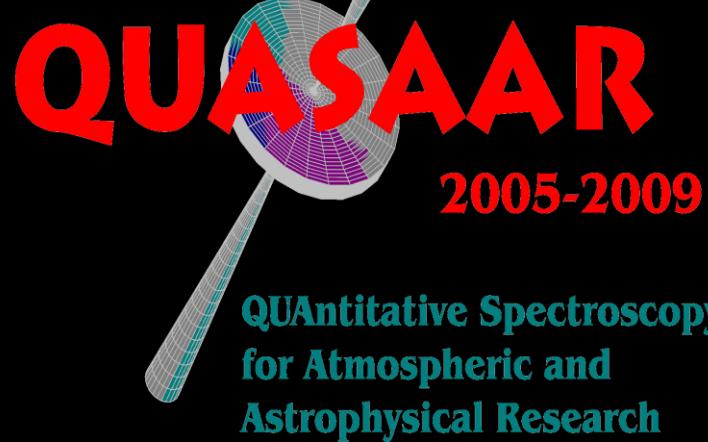
Miguel Carvajal, Huelva
Wolfgang P. Kraemer, Munich
Hai Lin, Denver
Jing Jing Zheng, Mülheim

Fellow ponderers:

P. R. Bunker, Ottawa
Walter Thiel, Mülheim

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Marie Curie Research
Training Network



Vacant
positions for
PhD students and
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