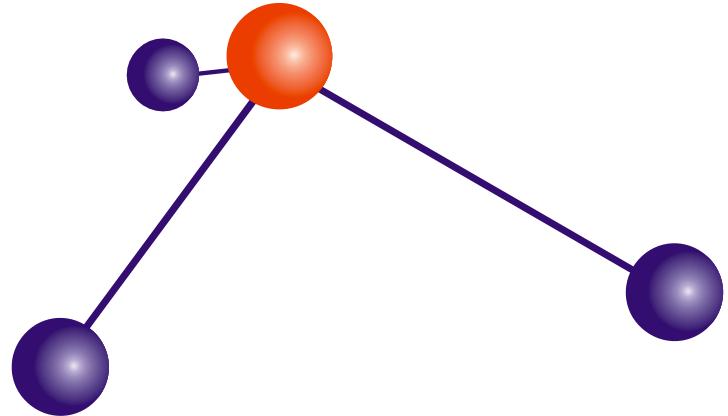


Simulation of rovibrational absorption spectra for XY_3 molecules

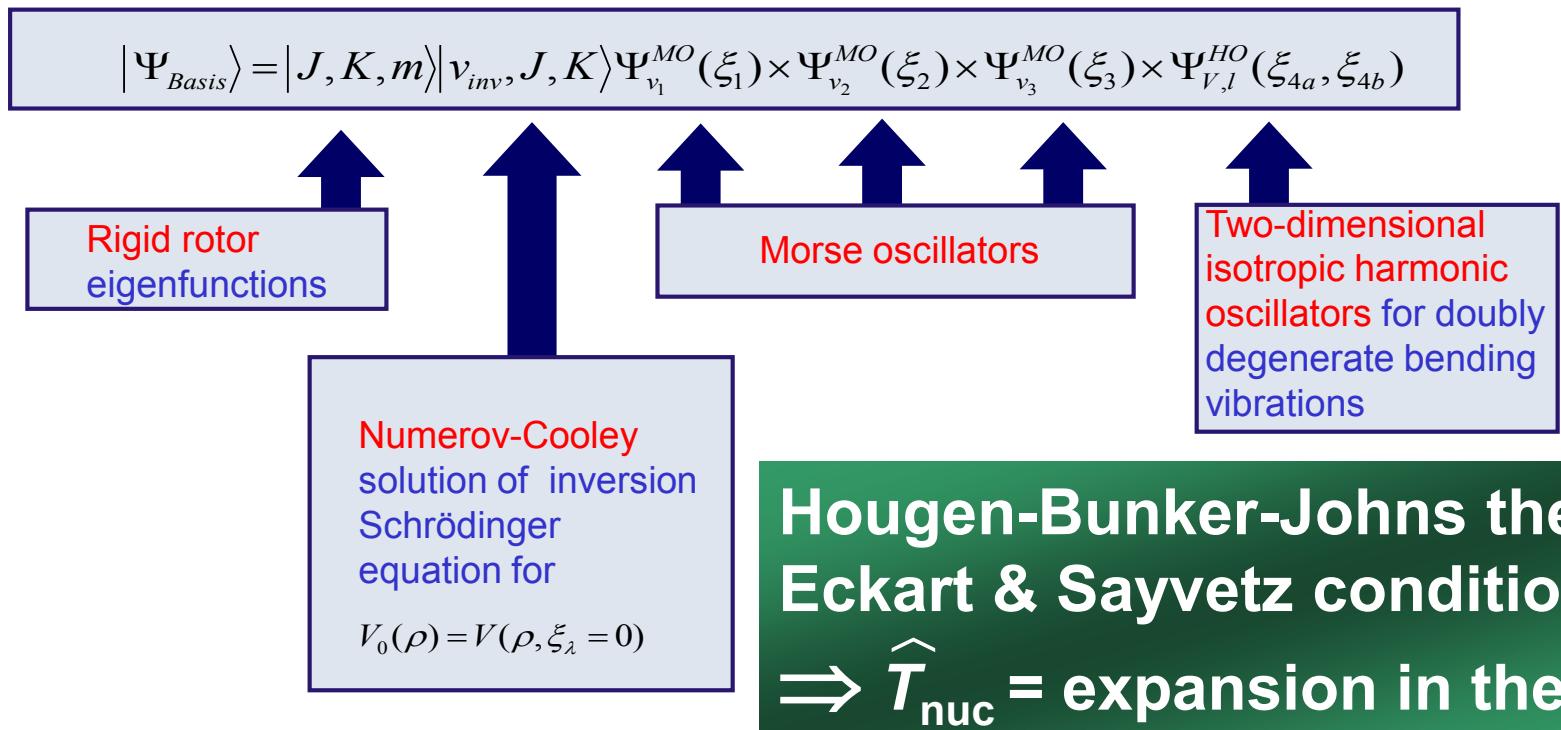
Ingredients:

- Potential energy surface
- Dipole moment surfaces
- (Rovibrational energies and wavefunctions)



Energies/wavefunctions from variational rotation-vibration calculations

Basis functions:



[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)

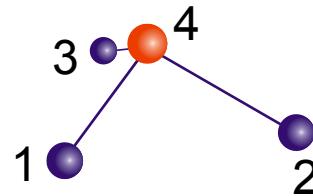
[1] S. N. Yurchenko, M. Carvajal, H. Lin, J. J. Zheng, W. Thiel, and P. Jensen, *J. Chem. Phys.* **122**, 104317 (2005).

[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).

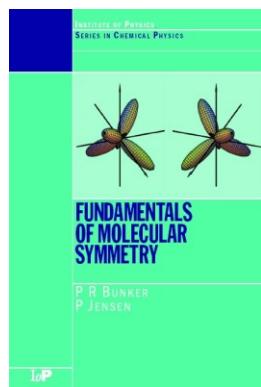
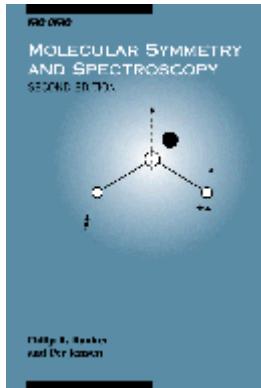
Vibrational transition moments for $^{14}\text{NH}_3$

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



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

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

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

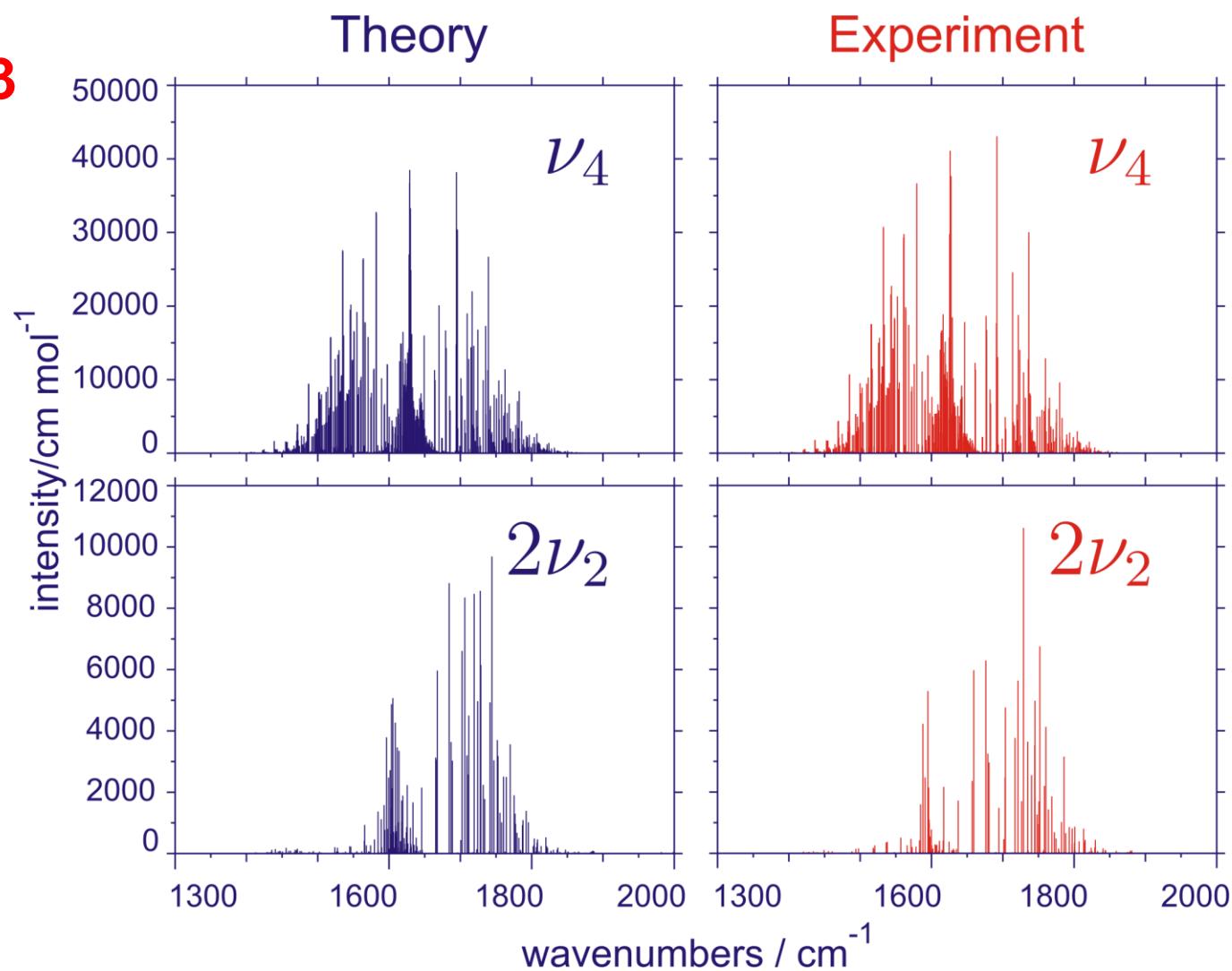
$$S(f \leftarrow i) = g_{ns} (2J' + 1) (2J'' + 1)$$

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

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

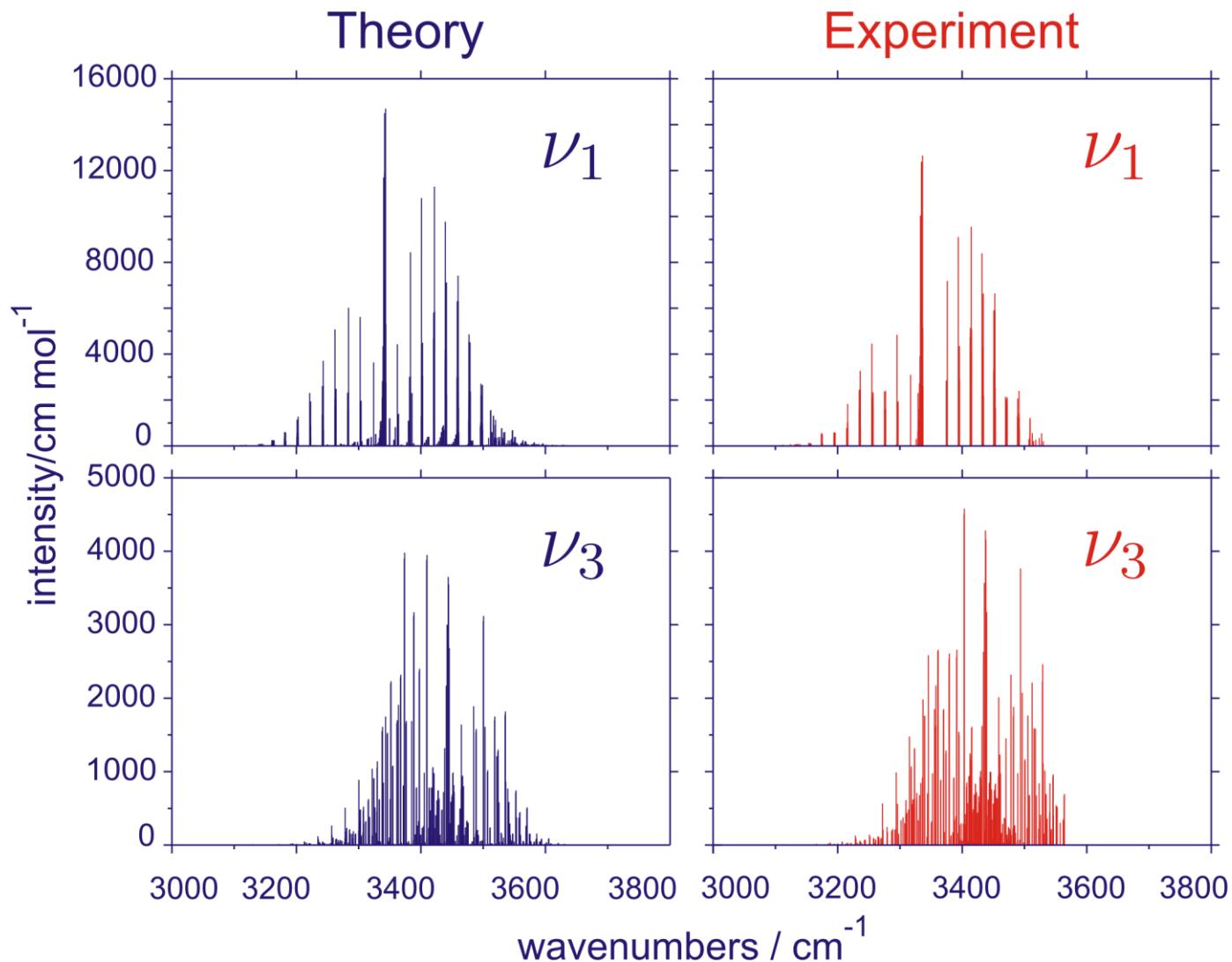
[2] S. N. Yurchenko, W. Thiel, M. Carvajal, H. Lin, and P. Jensen, *Adv. Quant. Chem.*, *in press*.

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



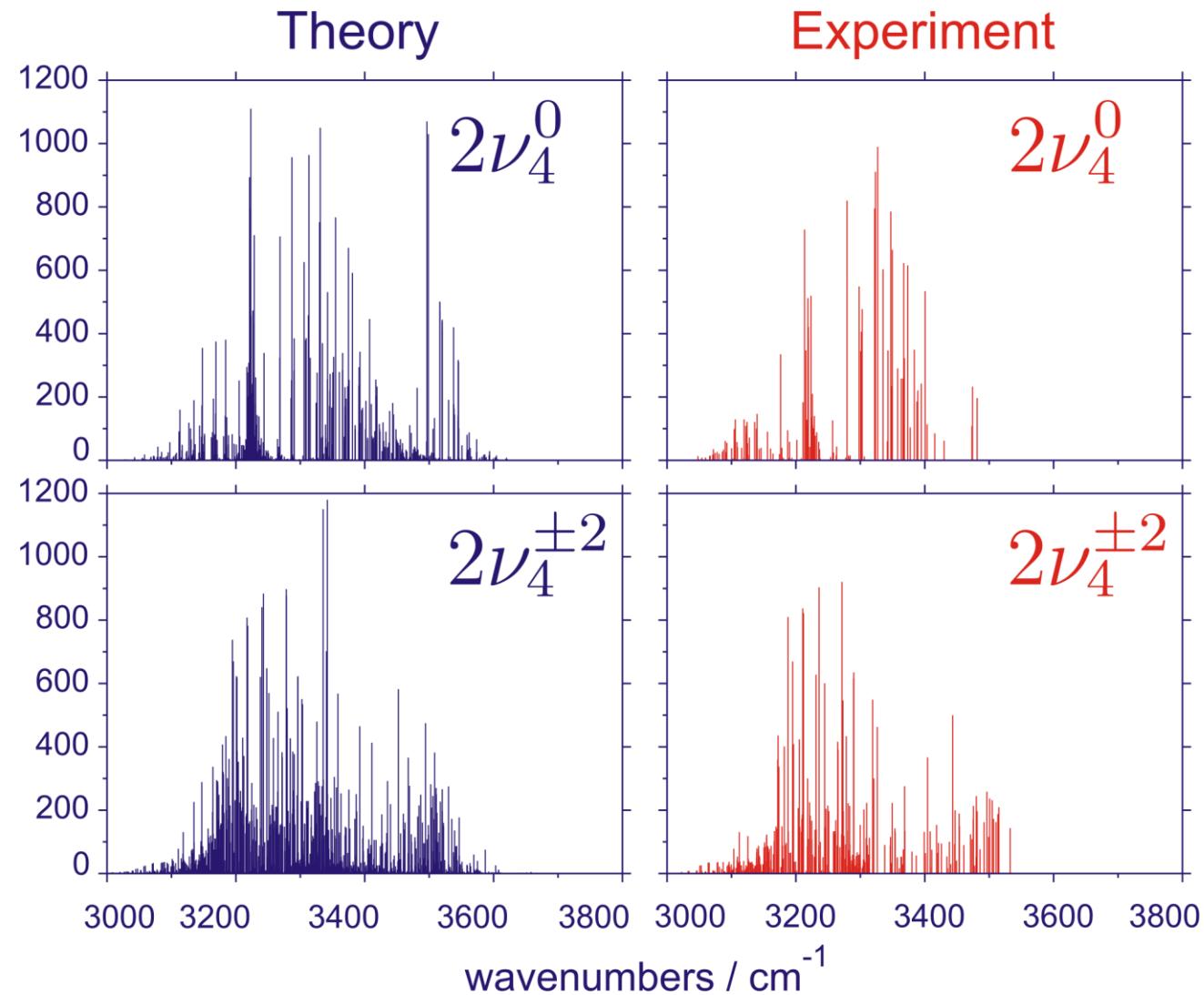
Experiment: C. Cottaz, G. Tarrago, I. Kleiner, L. R. Brown, J. S. Margolis, R. L. Poynter, H. M. Pickett, T. Fouchet, P. Drossart, and E. Lellouch, *J. Mol. Spectrosc.* **203**, 285 (2000).

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 $^{14}\text{NH}_3$



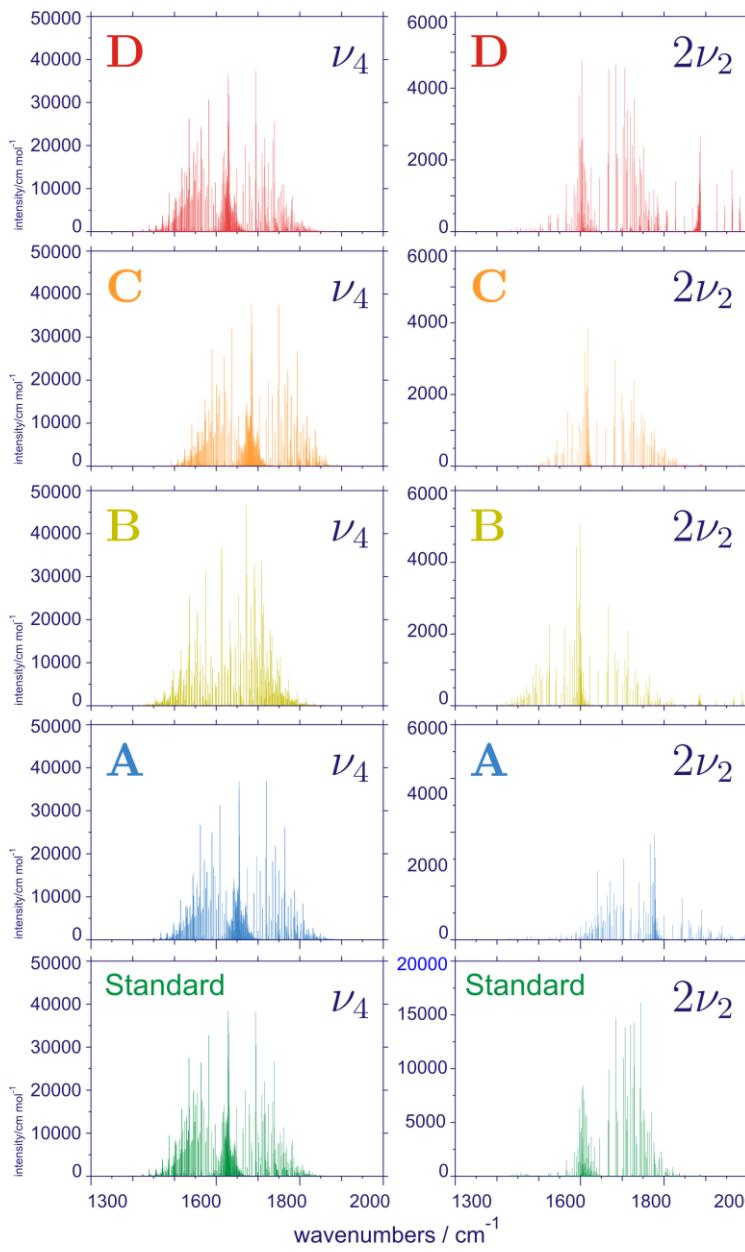
Experiment: I. Kleiner, L. R. Brown, G. Tarrago, Q.-L. Kou, N. Picqué, G. Guelachvili, V. Dana, and J.-Y. Mandin, *J. Mol. Spectrosc.* **193**, 46 (1999).

D. Simplification of the dipole moment function.

The dipole moment components are given by only the leading terms:

$$\bar{\mu}_x = \mu_{4a}^x \xi_{4a}, \bar{\mu}_y = \mu_{4a}^x \xi_{4b}, \bar{\mu}_z = \mu_0^z \cos \rho;$$

There is no noticeable change in the structure of the ν_4 band. However, the $2\nu_2$ band, whose upper state is an excited inversion state, has completely lost its original structure.



C. Simplification of the potential energy function.

The potential energy function is truncated after the second-order terms:

$$V = V^{(0)}(\rho) + \sum_k V_k^{(1)}(\rho) \xi_k^\ell + \sum_{kl} V_{kl}^{(2)}(\rho) \xi_k^\ell \xi_l^\ell$$

The effect of the potential-energy truncation is noticeable but minor for the ν_4 band while very pronounced in the case of the $2\nu_2$ band.



B. Simplification of the kinetic energy operator.

Kinetic energy operator truncated at the zero-order term. The effect of the kinetic energy simplification is drastic: The simulated $2\nu_2$ band changes so much that it is hardly recognizable and the ν_4 band is also altered significantly from the standard simulation.



A. Basis set reduction.

$$P = 2(n_1 + n_2 + n_3) + n_i + n_b \leq 2.$$

Both the absolute intensities and the line positions undergo serious changes.



Standard. No simplification.

a. The basis set.

$$P = 2(n_1 + n_2 + n_3) + n_i + n_b \leq 8.$$

b. The kinetic energy operator is truncated after 4th order.
c. The expansion of the potential energy function V is taken to 6th order.

d. The expansion of the dipole moment components is taken to 6th order.



Doubly harmonic approximation

The simplest model for rovibrational intensities:
the rotation as a rigid symmetric rotor;
the vibrational motion as uncoupled harmonic oscillators;
the dipole moment as a first-order expansion in
normal coordinates. There are drastic changes for the $2\nu_2$
band, which carries no intensity in this approximation.

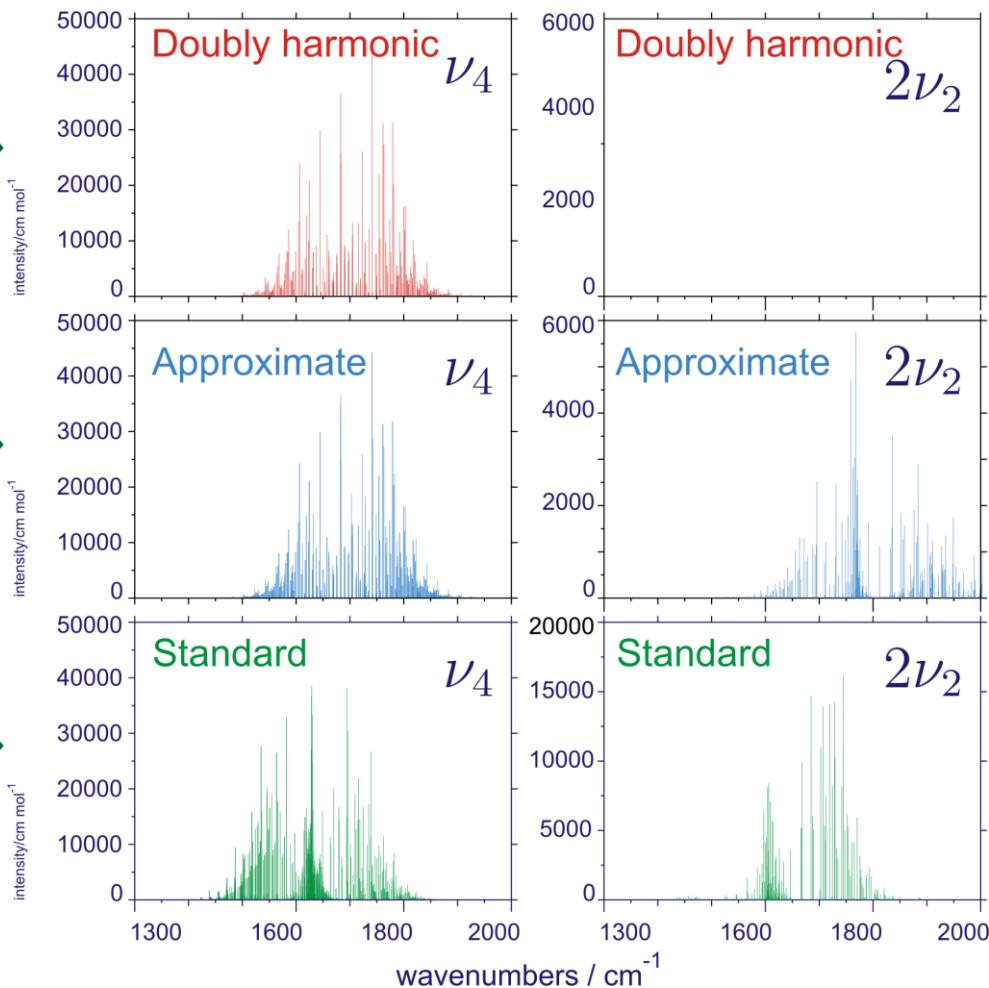
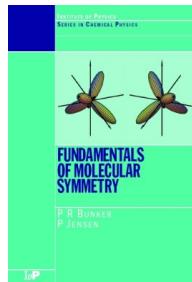
Approximate

A+B+C+D simplifications

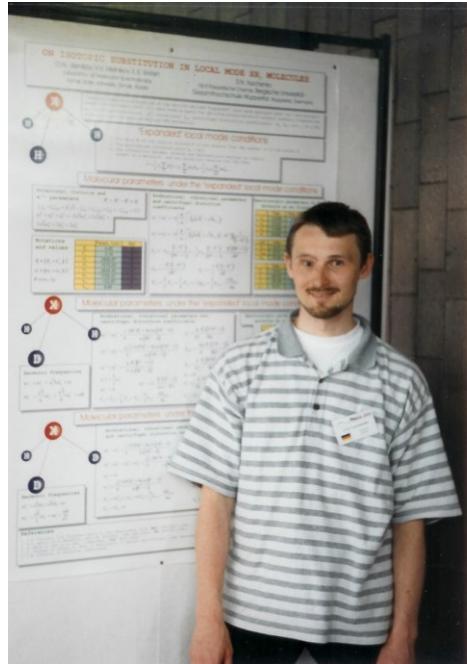
The simulations are altered significantly relative to those obtained in the standard approximation, and the effect is much larger for the weak $2\nu_2$ band.

Standard. No simplification.

- The basis set.
 $P = 2(n_1 + n_2 + n_3) + n_i + n_b \leq 8$.
- The kinetic energy operator is truncated after 4th order.
- The expansion of the potential energy function V is taken to 6th order.
- The expansion of the dipole moment components is taken to 6th order.



Thanks & Acknowledgments



The principal doer:

Sergei N. Yurchenko, Wuppertal, Ottawa,
Mülheim

Other doers:

Miguel Carvajal, Huelva
Hai Lin, Minneapolis
Jing Jing Zheng, Mülheim

A fellow ponderer:

Walter Thiel, Mülheim

Thanks for support from the European Commission,
the German Research Council (DFG), and the Foundation
of the German Chemical Industry (Fonds der Chemie).