Global Analysis of the NH_2 Radical Rotational, Vibrational, and Electronic Transitions

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Introduction

- The NH_2 radical, first observed a long time ago,[1] is a benchmark molecule for the Renner-Teller effect[2]

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[1] Herzberg & Ramsay, *J. Chem. Phys.* **20** (1952) 347

[2] Dressler and Ramsay, *Phil. Trans. R. Soc. A* **25** (1959) 553

[3] van Dishoeck, Jansen, Schilke, & Phillips, *Astr. Phys. J.* **416** (1993) L83

[4] Kawakita, Ayani, & Kawabata, *Publ. Astr. Soc. Japan* **52** (2000) 925

[5] Jungen & Merer, *Molec. Phys.* **40** (1980) 1; Duxbury & Dixon, *Molec. Phys.* **43** (1981) 255; and Jensen, Odaka, Kraemer, Hirano, & Bunker, *Spectrochim. Acta Part A* **58** (2002) 763

[6] Jensen, Kraemer, & Bunker, *Molec. Phys.* **101** (2003) 613

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- Molecule of astrophysical interest detected in the ISM and in comets[3,4]

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- Large number of experimental and theoretical[5] investigations

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- Molecule of astrophysical interest detected in the ISM and in comets[3,4]
- Large number of experimental and theoretical[5] investigations
- Only one global analysis carried out[6]

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Introduction-*continued*

Two analyses of the NH_2 data are carried out

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Analysis	I	II
Data set	$J \leq 4$ levels up to 14 000 cm^{-1}	$J \leq 25$ lines Ground & (010) states
Approach	Exact 3-D + Rot.	Effective 1-D + Rot.
Effect	Renner-Teller	Anomalous distortion

Outline

- The available data

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- Analysis I
    - Theoretical approach
    - Results

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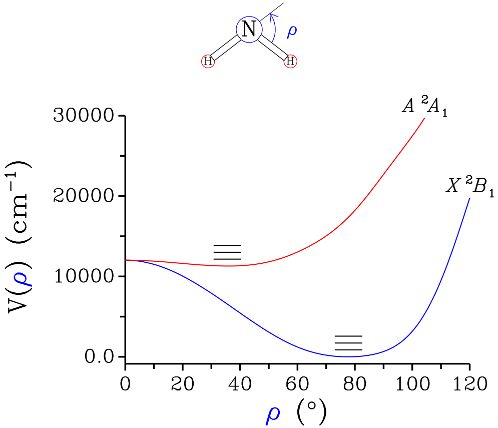
Simplified energy level diagram



Available data

$X\,{}^2B_1$	
(000)	0
(010)	1 497
(020)	2 961
(100)	3 219
⋮	
(0,10,0)	13 448
21 states	

$A\,{}^2A_1$	
(000)	11 122
(010)	12 280
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(120)	17 073
6 states	

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Rovibronic basis set functions

The rovibronic wavefunctions are expanded using[1,2]

$$\chi^{+}(R_1, R_2, t)\,|{+\Lambda}\rangle \quad \& \quad \chi^{-}(R_1, R_2, t)\,|{-\Lambda}\rangle$$

---

[1] Mitrushchenkov, *J. Chem. Phys.* **136** (2012) 024108

[2] Coudert, Gans, Holzmeier, Loison, Garcia, Alcaraz, Lopes, & Röder, *J. Chem. Phys.* **149** (2018) 224304

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where

$$\begin{cases} \chi^{+},\ \chi^{-} & \text{vibrational wavefunctions} \\ |{+\Lambda}\rangle,\ |{-\Lambda}\rangle & \text{eigenfunctions of } L_z \\ R_1,\ R_2,\ t = \cos\tilde{\theta} & \text{Radau coordinates} \end{cases}$$

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Taking the singularities into account

The vibrational wavefunctions are expanded[1]

$$\chi^{\pm}(R_1, R_2, t) = (1-t)^{\frac{\alpha^{\pm}}{2}}(1+t)^{\frac{\beta^{\pm}}{2}} \sum_{n=0} P_n^{(\alpha^{\pm},\beta^{\pm})}(t)\phi_n(R_1, R_2)$$

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Singularity at the linear configuration and the Renner coupling are taken into account

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Vibrational matrix elements are evaluated using Gaussian quadratures

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Potential energy surface

For the $X = \begin{cases} B_1 & \text{lower} \\ A_1 & \text{upper} \end{cases}$ electronic substates[1]

$$V^X(r_1, r_3, \rho) = V_0^X(\rho) + \sum_j F_j^X(\rho) y_j + \sum_{j \le k} F_{jk}^X(\rho) y_j y_k + \cdots$$

where $j, k = 1$ or 3, $y_j = 1 - \exp[-a(r_j - r_0)]$, and

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f_{jk} and $f_{jk}^{i,X}$ are adjusted to the data.

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Data set & analysis results

Experimental energy levels up to $J = 4$ and $\left\{ \begin{array}{l} (310)\ \tilde{X}\,^2B_1 \\ (010)\ \tilde{A}\,^2A_1 \end{array} \right.$

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24 vibrational states & 753 rotational energy levels[1–3]

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Varying 20 potential energy parameters, level energies were reproduced with an RMS of 2 cm^{-1}

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Observed minus calculated table (000) of $\tilde{X}\,^2B_1$

J	K_a	K_c	$F_{1,2}$	Obs.	O−C	J	K_a	K_c	$F_{1,2}$	Obs.	O−C
1	0	1	F_1	21.109	0.140	3	2	1	F_1	184.612	0.697
1	0	1	F_2	21.143	0.174	3	2	1	F_2	185.023	0.497
1	1	1	F_1	31.773	0.044	3	3	1	F_1	243.849	−0.215
1	1	1	F_2	32.005	−0.061	3	3	1	F_2	244.650	−0.396
1	1	0	F_1	36.535	0.141	3	3	0	F_1	244.064	−0.206
1	1	0	F_2	36.800	0.069	3	3	0	F_2	244.872	−0.378
2	0	2	F_1	62.042	0.370	4	0	4	F_1	195.685	0.862
2	0	2	F_2	62.099	0.412	4	0	4	F_2	195.780	0.838
2	1	2	F_1	69.263	0.251	4	1	4	F_1	197.560	0.805
2	1	2	F_2	69.411	0.062	4	1	4	F_2	197.674	0.570
2	1	1	F_1	83.536	0.550	4	1	3	F_1	243.460	1.711
2	1	1	F_2	83.740	0.417	4	1	3	F_2	243.672	1.555
2	2	1	F_1	115.398	−0.003	4	2	3	F_1	262.165	0.970
2	2	1	F_2	115.927	−0.141	4	2	3	F_2	262.523	0.655
2	2	0	F_1	116.669	0.056	4	2	2	F_1	277.231	1.558
2	2	0	F_2	117.196	−0.069	4	2	2	F_2	277.594	1.366
3	0	3	F_1	120.742	0.615	4	3	2	F_1	330.403	0.390
3	0	3	F_2	120.822	0.638	4	3	2	F_2	331.070	0.081
3	1	3	F_1	124.727	0.509	4	3	1	F_1	331.875	0.500
3	1	3	F_2	124.849	0.291	4	3	1	F_2	332.537	0.203
3	1	2	F_1	153.001	1.099	4	4	1	F_1	417.347	−0.612
3	1	2	F_2	153.204	0.957	4	4	1	F_2	418.427	−0.816
3	2	2	F_1	178.793	0.445	4	4	0	F_1	417.380	−0.609
3	2	2	F_2	179.203	0.187	4	4	0	F_2	418.460	−0.812

Observed minus calculated table (040) of $\tilde{X}\,^2B_1$

J	K_a	K_c	$F_{1,2}$	Obs.	O−C
0	0	0	F_1	5785.567	1.422
1	0	1	F_1	5806.678	1.216
1	0	1	F_2	5806.725	1.263
1	1	1	F_1	5830.312	1.294
1	1	1	F_2	5831.195	0.987
1	1	0	F_1	5836.131	1.727
1	1	0	F_2	5837.049	1.454
2	0	2	F_1	5847.945	0.701
2	0	2	F_2	5848.046	0.785
2	1	2	F_1	5866.827	0.524
2	1	2	F_2	5867.337	−0.157
2	1	1	F_1	5884.309	1.882
2	1	1	F_2	5884.905	1.281
2	2	1	F_1	5953.463	1.083
2	2	1	F_2	5955.335	0.742
2	2	0	F_1	5954.402	1.210
2	2	0	F_2	5956.255	0.867
3	0	3	F_1	5907.585	−0.363
3	0	3	F_2	5907.684	−0.341
3	1	3	F_1	5920.935	−0.778
3	1	3	F_2	5921.350	−1.560
3	1	2	F_1	5955.709	1.925
3	1	2	F_2	5956.206	1.211
3	2	2	F_1	6017.126	0.599
3	2	2	F_2	6018.484	−0.264
3	2	1	F_1	6021.662	1.229
3	2	1	F_2	6023.012	0.435
3	3	1	F_1	6141.579	0.363
3	3	1	F_2	6144.156	−0.047
3	3	0	F_1	6141.579	0.283
3	3	0	F_2	6144.292	0.010
4	0	4	F_1	5983.645	−2.184
4	0	4	F_2	5983.797	−2.224
4	1	4	F_1	5992.090	−2.661
4	1	4	F_2	5995.419	−0.542
4	1	3	F_1	6049.329	1.745
4	1	3	F_2	6049.830	1.006
4	2	3	F_1	6101.024	−0.242
4	2	3	F_2	6102.102	−1.400
4	2	2	F_1	6113.607	1.433
4	2	2	F_2	6114.735	0.519
4	3	2	F_1	6228.159	−0.289
4	3	2	F_2	6230.259	−1.179
4	3	1	F_1	6228.881	−0.110
4	3	1	F_2	6230.927	−1.044
4	4	1	F_1	6389.273	−0.829
4	4	1	F_2	6392.409	−1.218
4	4	0	F_1	6389.303	−0.819
4	4	0	F_2	6392.437	−1.211

Observed minus calculated table (000) of $\tilde{A}\,^2A_1$

J	K_a	K_c	$F_{1,2}$	Obs.	O−C
0	0	0	F_1	11122.349	−0.021
1	0	1	F_1	11139.922	0.068
1	0	1	F_2	11139.875	0.021
1	1	1	F_1	11329.550	−0.411
1	1	1	F_2	11322.367	2.200
1	1	0	F_1	11329.084	−2.775
1	1	0	F_2	11321.778	−0.317
2	0	2	F_1	11175.118	0.305
2	0	2	F_2	11174.946	0.192
2	1	2	F_1	11366.047	1.235
2	1	2	F_2	11362.872	7.840
2	1	1	F_1	11364.507	−6.007
2	1	1	F_2	11361.229	0.394
2	2	1	F_1	11695.305	−0.328
2	2	1	F_2	11686.892	1.279
2	2	0	F_1	11695.257	−0.391
2	2	0	F_2	11686.841	1.207
3	0	3	F_1	11227.630	0.425
3	0	3	F_2	11227.492	0.397
3	1	3	F_1	11421.347	4.418
3	1	3	F_2	11419.279	12.091
3	1	2	F_1	11418.159	−10.184
3	1	2	F_2	11415.931	−2.911
3	2	2	F_1	11749.351	−1.270
3	2	2	F_2	11743.953	3.276
3	2	1	F_1	11749.159	−1.534
3	2	1	F_2	11743.715	2.929
3	3	1	F_1	12156.677	0.522
3	3	1	F_2	12147.746	1.755
3	3	0	F_1	12156.679	5.445
3	3	0	F_2	12147.842	1.848
4	0	4	F_1	11297.852	−0.617
4	0	4	F_2	11297.550	−2.887
4	1	4	F_1	11495.098	8.908
4	1	4	F_2	11493.653	17.135
4	1	3	F_1	11489.625	−15.597
4	1	3	F_2	11487.929	−8.101
4	2	3	F_1	11821.999	−1.732
4	2	3	F_2	11818.069	4.157
4	2	2	F_1	11821.455	−2.481
4	2	2	F_2	11817.407	3.163
4	3	2	F_1	12228.004	−1.380
4	3	2	F_2	12222.359	3.055
4	3	1	F_1	12228.534	−0.870
4	3	1	F_2	12222.328	2.994
4	4	1	F_1	12692.571	14.735*
4	4	1	F_2	12683.410	34.910*
4	4	0	F_1	12692.571	46.434*
4	4	0	F_2	12683.439	34.868*

Results of Analysis I

Large residuals arise for high-lying levels

---

[1] Jungen & Merer, *Molec. Phys.* **40** (1980) 1

[2] Jensen, Brumm, Kraemer, & Bunker, *J. Molec. Spec.* **171** (1995) 31

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Large residuals arise for high-lying levels

Since the effects of the RT-coupling are the largest for such levels, it is suspected that the Renner interaction should be refined[1,2]

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$$\langle {}^{e}A_1 | L_z | {}^{e}B_1 \rangle = i[\Lambda - \sum_{i=1}^{4} \mathcal{L}^i (1+t)^i]$$

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Analysis of the ground and (010) states

Unlike in the previous vibrational states, the effects of the Renner interaction are very small for the ground and (010) states which can be treated as isolated states

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Recent measurements[1] carried out up to $K_a = 13$ showed that an anomalous centrifugal distortion takes place in these two states

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[1] Martin-Drumel, Pirali, and Vervloet, *J. Phys. Chem. A* **118** (2014) 1331

[2] Coudert, *J. Mol. Spectrosc.* **154** (1992) 427; and Coudert, *ibid.* **165** (1994) 406

Analysis of the ground and (010) states

Unlike in the previous vibrational states, the effects of the Renner interaction are very small for the ground and (010) states which can be treated as isolated states

Recent measurements[1] carried out up to $K_a = 13$ showed that an anomalous centrifugal distortion takes place in these two states

The Bending-rotation approach[2] previously used to treat the anomalous centrifugal distortion of the water molecule is applied to the fitting of data pertaining to these two states

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[1] Martin-Drumel, Pirali, and Vervloet, *J. Phys. Chem. A* **118** (2014) 1331

[2] Coudert, *J. Mol. Spectrosc.* **154** (1992) 427; and Coudert, *ibid.* **165** (1994) 406

Effective Hamiltonian

Bending-rotation Hamiltonian[1]

$$H_{\mathrm{b-r}} = B_e P_t (1 - t^2) P_t + B_e \left[\frac{N_x^2}{2(1-t)} + \frac{N_y^2}{4} + \frac{N_z^2}{2(1+t)} \right] + V(t) + \cdots$$

where B_e is a constant, $t = \cos\tilde{\theta}$, and $V(t)$ is the bending potential.

---

[1] Coudert, *J. Mol. Spectrosc.* **165** (1994) 406

[2] Brown & Sears, *J. Mol. Spectrosc.* **75** (1979) 111

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where B_e is a constant, $t = \cos\tilde{\theta}$, and $V(t)$ is the bending potential.
Spin-rotation coupling accounted for using[2]

$$H_{\mathrm{s-r}} = \sum_{\alpha\beta = x,y,z} \epsilon_{\alpha,\beta}(t)\, N_\alpha S_\beta + \cdots$$

where $\epsilon(t)$ is the spin-rotation tensor depending on t.

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[1] Coudert, *J. Mol. Spectrosc.* **165** (1994) 406

[2] Brown & Sears, *J. Mol. Spectrosc.* **75** (1979) 111

Basis set functions

The bending wavefunctions are expanded using[1]

$$\phi_{v_2}^{NkSJ}(t) = (1-t)^{\frac{\alpha}{2}}(1+t)^{\frac{\beta}{2}} \sum_{n=0} a_n^{v_2,NkSJ} P_n^{(\alpha,\beta)}(t)$$

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Singularity for the linear configuration taken into account if

$$\alpha = \sqrt{[N(N+1)-k^2]} \quad \text{and} \quad \beta = |k|$$

---

[1] Coudert, *J. Mol. Spectrosc.* **154** (1992) 427; and Coudert, *ibid.* **165** (1994) 406

Data set

				Max.	
Data	State	Reference	N	J	K_a
FIR	Ground	Morino & Kawaguchi[1]	266	13	8
IR	ν_2	Burkholder *et al.*[2]	331	10	5
CD	Ground	Dixon *et al.*[3]	64	18	18
FIR	Ground	Martin-Drumel *et al.*[4]	872	25	13
FIR	(010)	Martin-Drumel *et al.*[4]	164	19	4
FIR	Ground	*This work*	210	25	11
All			1907	25	18

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[1] Morino & Kawaguchi, *J. Mol. Spec.* **182** (1997) 428

[2] Burkholder, Howard & McKellar, *J. Mol. Spec.* **127** (1988) 415

[3] Dixon, Irving, Nightingale & Vervloet, *J. Chem. Soc. Faraday Trans.* **87** (1991) 2121

[4] Martin-Drumel, Pirali & Vervloet, *J. Phys. Chem. A* **118** (2014) 1331

Results

Varying 85 parameters the unitless standard deviation was 1.3

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[1] Morino & Kawaguchi, *J. Mol. Spec.* **182** (1997) 428
[2] Burkholder, Howard & McKellar, *J. Mol. Spec.* **127** (1988) 415
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[4] Martin-Drumel, Pirali & Vervloet, *J. Phys. Chem. A* **118** (2014) 1331

Results

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			This work		Ref. [4]	
Data	State	Reference	N	σ	N	σ
FIR	Ground	Morino & Kawaguchi[1]	266	1.1	269	1.1
IR	ν_2	Burkholder *et al.*[2]	331	1.2	332	0.9
CD	Ground	Dixon *et al.*[3]	64	1.2	52	1.3
FIR	Ground	Martin-Drumel *et al.*[4]	872	1.0	835	1.0
FIR	(010)	Martin-Drumel *et al.*[4]	164	1.9	165	1.0
FIR	Ground	*This work*	210	1.7		

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[1] Morino & Kawaguchi, *J. Mol. Spec.* **182** (1997) 428

[2] Burkholder, Howard & McKellar, *J. Mol. Spec.* **127** (1988) 415

[3] Dixon, Irving, Nightingale & Vervloet, *J. Chem. Soc. Faraday Trans.* **87** (1991) 2121

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High order parameters

	Value		
Param	*This work*	Ref. [1]	Operator
L_K^0	$+3.0(4) \times 10^{-9}$	-355.7×10^{-9}	N_z^8
L_K^2	$-142.6(170) \times 10^{-9}$		$N_z^8(t - t_e)^2$
M_K^0		$+1.5 \times 10^{-9}$	N_z^{10}
N_K^0		-6.9×10^{-12}	N_z^{12}
O_K^0		$+24.6 \times 10^{-15}$	N_z^{14}
P_K^0		-52.7×10^{-18}	N_z^{16}
Q_K^0		$+49.7 \times 10^{-21}$	N_z^{18}

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[1] Martin-Drumel, Pirali & Vervloet, *J. Phys. Chem. A* **118** (2014) 1331

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The anomalous centrifugal distortion is accounted for

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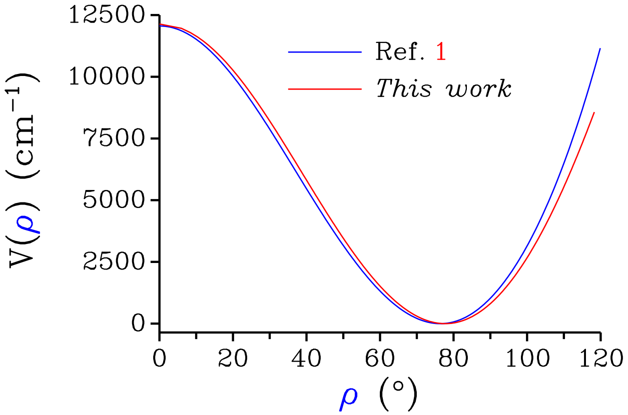
[1] Martin-Drumel, Pirali & Vervloet, *J. Phys. Chem. A* **118** (2014) 1331

$X\,^2B_1$ bending potential comparison



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[1] Jensen, Kraemer, & Bunker, *Molec. Phys* **101** (2003) 613

Thank You