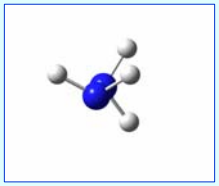

Reanalysis of the Symmetric Amino Wagging Band of Hydrazine

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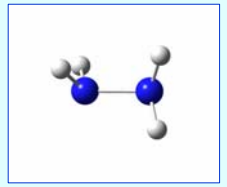

Motivation

The aim of this work was to reassign the experimental data of two states of hydrazine being in a strong **Fermi resonance**, the symmetric , ν_6, and the third excited torsional, $3\nu_7$, using the LWW (Loomis Wood for Windows; http://www.lww.amu.edu.pl; *poster J25*) software, and next to fit these states simultaneously. The band centers for these bands are located at 795 cm^{-1} and 860 cm^{-1}, respectively. The program written to deal with the perturbation is based on an effective rotational Hamiltonian described earlier (I. Gulaczyk et al. / *J.Mol.Spectrosc. 241* (2007) 75-89).

Phenomenological Effective Operator for a coupling between wagging-torsion-rotation states

$$\hat{W} = \sum_{n=1,2,3,4,5,7} wh_n + wf_n\left(J_+^2 + J_-^2\right) + wg_n\left[i\left(J_+^2 - J_-^2\right)\right] + wq_n J_z + wd_n\left(J_+^4 + J_-^4\right) + wp_n\left[i\left(J_+^4 - J_-^4\right)\right] + \left[wr_{n^+} J_+ + wr_{n^-} J_-\right] + \left[ws_{n^+}\left(J_z J_+ + J_+ J_z\right) + ws_{n^-}\left(J_z J_- + J_- J_z\right)\right]$$

- n = 1 Parameters involving no tunneling, i.e. ordinary asymmetric rotor parameters.
- n = 2 Parameters involving inversion transition of both NH_2 groups.
- n = 3 Parameters involving internal rotation tunneling through the trans barrier.
- n = 4 Parameters involving internal rotation and inversion of both NH_2 groups.
- n = 5 Parameters involving inversion of one NH_2 group.
- n = 7 Parameters involving internal rotation and inversion of one NH_2 group.

Matrix elements for Fermi resonance between vibrational states

$$\left\langle \Gamma'; v'; K'; J \middle| \hat{W} \middle| \Gamma''; v''; K''; J \right\rangle$$

$\Delta K = 0$ operators containing: wh_n , wq_n
for K=1 operators containing: wf_n
for K=2 operators containing: wd_n
$\Delta K = 2$ operators containing: wf_n , wg_n
$\Delta K = 4$ operators containing: wd_n , wp_n
$\Delta K = 1$ operators containing: wr_{n^+} , wr_{n^-}, ws_{n^+} , ws_{n^-}.
Γ- symmetry of the wagging-torsion-rotation state
v' - symmetric amino-wagging state (ν_6)
v'' - third excited torsional state ($3\nu_7$)

Experimental data

The Fourier transform high-resolution infrared spectrum of hydrazine has been recorded at the University of Paris. The spectrum has been recorded in the range from 729 cm^{-1} to 1198 cm^{-1} at a pressure of 0.5 Torr with a 10-m-pathlength white cell at a temperature of 20ºC. The resolution of the spectrum is about 0.002 cm^{-1} and the relative wavenumber precision is one order of magnitude better.

Analysis of the symmetric inversion band of hydrazine (ν_6)

1. **Fermi Resonance**
   The ν_6 band is strongly perturbed through a Fermi resonance with the third excited torsional state, $3\nu_7$ (**Fig. 1**). Generally, the $3\nu_7$ is too weak to be directly observed. However, because of the resonance some intensity could be borrowed from the ν_6 inversion band. Indeed the series of the B←A symmetry of the $3\nu_7$ band (K= 3 to 9 and J=<25) were found. The E←E series could not be seen. The A←B series are not involved in the Fermi resonance and none of the series of these symmetry could be observed in the $3\nu_7$ state.
2. **Estimation of the parameters for $3\nu_7$**
   From the inversion - torsional potential function (W. Łodyga, M. Kręglewski and J. Makarewicz, *J.Mol.Spectrosc.* **183**, 374-387 (1997)) the energy and torsional and inversion splittings for the $3\nu_7$ state were calculated. These values and extrapolated parameters from the ν_7 and $2\nu_7$ were then used for the initial estimation of the parameters for $3\nu_7$ in the effective Hamiltonian.
3. **Reassignment of the symmetric state using a Loomis-Wood for Windows software (LWW program)**
   The LWW program (**Fig. 2**) has been used for the first time for the LAV molecule The individual rotational lines of the band previously labeled by the Loomis-Wood program from Giessen have been reassigned. Some new lines were added to the series and the assignment was confirmed through the ground state combination differences.
4. **Global fit**
   The global fit for all K' values (from 0 to 10 for the symmetric wagging and from 3 to 9 for the third torsional) gave the standard deviation of 0.019 cm^{-1}, and the results are shown in **Table 1**.
5. **Local fits**
   Satisfactory fits for individual K' values (from 3 to 8 for both states) were carried out. In **Table 2** obtained effective parameters are given for each K' value separately.

Final conclusions

There are two possible explanations of the significant difference between global and individual fits (**Fig. 3**). Firstly, the ν_6 band can be perturbed by other „dark" states. Secondly, there might be problems with the effective Hamiltonian.
Anyway, about 5200 transitions of the ν_6 (for all symmetry species) and $3\nu_7$ (only A and E') have been analyzed and they are presented in **Fig. 4**.
The LWW program appeared extremely useful, particularly through automation of the GSCD procedure and easy transfer of data.

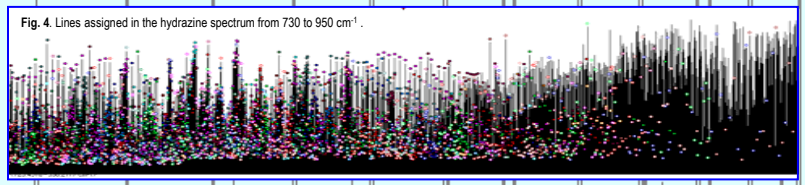

Fig. 4. Lines assigned in the hydrazine spectrum from 730 to 950 cm^{-1} .

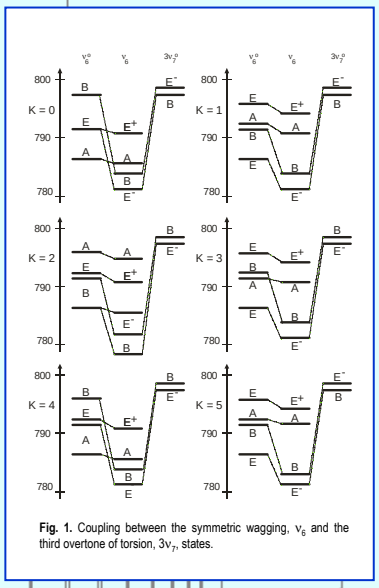

Fig. 1. Coupling between the symmetric wagging, ν_6 and the third overtone of torsion, $3\nu_7$, states.

Fig. 2. Part of the hydrazine spectrum and two LW diagrams showing mainly the structure of the $^RQ_2(A)$ branch where the lower state species of the observed doublets are A_{1U}^- or A_{2U}^+.

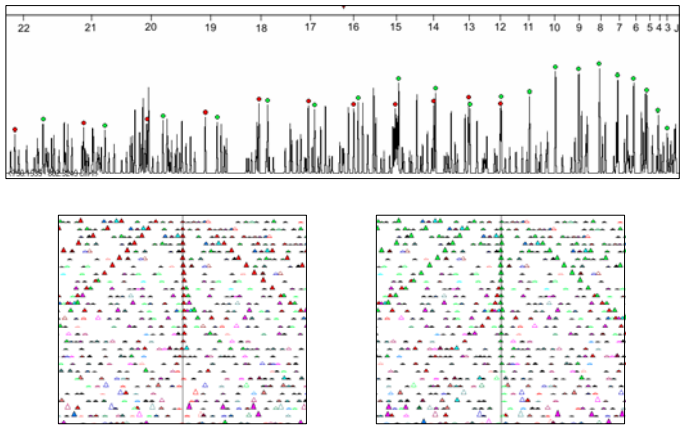

Table 2. Effective parameters of N_2H_4 for the symmetric wagging band and the third torsional band (J≤25).

	K					
	3	4	5	6	7	8
B (MHz)	23978.7(13)	23971.0(11)	24002.4(12)	23979.1(15)	24054.5(23)	23999.53(46)
B-C (MHz)	160.8(79)		-1335(10)	-1464(25)	-1579(92)	
D_J (MHz)	0.049753(91)	0.05767(18)	0.09412(46)	0.06391(12)	0.177(10)	0.0917(14)
H_{2V} (MHz)	-16155(1100)		698(2)			
H_{2J} (MHz)	6.01(45)					
H_{3TV} (MHz)	21589(1700)	-7267(560)	-91069(13)	-69639(16)	-85744(75)	-187062(690)
H_{3TJ} (MHz)	1.26(58)	3.6(16)	25.35(56)	16.02(33)	71.3(12)	1014(11)
H_{5TV} (MHz)	-82581(740)	-64622(1300)	-54944.4(73)	-71238.3(37)	-59430(81)	-124190(360)
H_{5TJ} (MHz)	1.75(60)	7.19(78)			-10.23(37)	
H_{5JJ} (kHz)	-0.7690(49)	0.134(11)				
ν_K (cm^{-1})	795.821(44)	794.91(04)	795.42852(10)	795.53611(14)	795.47848(42)	795.5212(21)
Q_5 (MHz)					-436.1(38)	
B (MHz)	23459.4(50)	23643(19)	23842.3(17)	23860.6(21)	23793.1(42)	23848.0(17)
B-C (MHz)			684(18)			
D_J (MHz)	0.0588(15)	0.071(10)	-0.0269(11)	0.0556(13)		
H_{2V} (MHz)	95357(5500)					
H_{2J} (MHz)	-164.2(58)					
WH_1 (MHz)	-627632(1600)	-591586(1900)	-663618(25)	-663885(514)	-664770(75)	-662945(34)
WH_{1J} (MHz)	11.6(17)	-11.6(16)	-53.14(98)	-39.1(14)	-44.9(17)	-20.65(35)
#lines	529	632	545	367	173	128
σ_K (cm^{-1})	0.00087	0.00102	0.00083	0.00089	0.00172	0.00128

Fig. 3. $^RR_0(A)$ series in the LW diagram using the energy scheme from the global fit (a) and from the local fit for K'=5 (b).

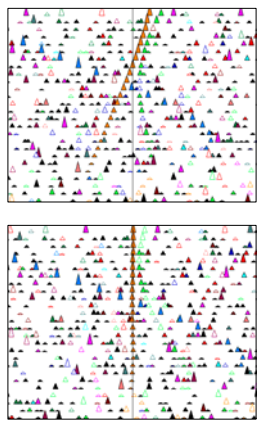

Table 1. Molecular parameters from the global fit (K' from 0 to 10, J ≤20).

A (MHz)	143779.0(21)
B (MHz)	23964.08(54)
B-C (MHz)	90.9(13)
D_J (MHz)	0.0590(14)
D_{JK} (MHz)	0.4440(85)
H_{3TV} (MHz)	-7645(39)
H_{5TV} (MHz)	-66431(29)
ν_K (cm^{-1})	795.137(47)
A (MHz)	139937.7(30)
B (MHz)	23624.09(53)
B-C (MHz)	1137.1(44)
H_{3TV} (MHz)	-1318497(190)
H_{5TV} (MHz)	-3082(46)
WH_1 (MHz)	-598833(1300)
WH_{1J} (MHz)	1.06(78)
WH_{1K} (MHz)	293.7(80)
WH_5 (MHz)	-4999(150)
WH_{5J} (MHz)	1.48(15)
#lines	3683
σ (cm^{-1})	0.019