

Non-covalent interactions and internal dynamics in pyridine-ammonia: A combined quantum-chemical and microwave spectroscopy study

Lorenzo Spada,^{*[b]} Nicola Tasinato,^[b] Fanny Vazart,^[b] Vincenzo Barone,^[b] Walther Caminati^{*[a]} and Cristina Puzzarini^{*[a]}

Abstract: The 1:1 complex of ammonia with pyridine has been characterized by using state-of-the-art quantum-chemical computations combined with pulsed-jet Fourier-Transform microwave spectroscopy. The computed potential energy landscape pointed out the formation of a stable σ -type complex, which has been confirmed experimentally: the analysis of the rotational spectrum showed the presence of only one 1:1 pyridine – ammonia adduct. Each rotational transition is split into several components due to the internal rotation of NH_3 around its C_3 axis and to the hyperfine structure of both ^{14}N quadrupolar nuclei, thus providing the unequivocal proof that the two molecules form a σ -type complex involving both a $\text{N-H}\cdots\text{N}$ and a $\text{C-H}\cdots\text{N}$ hydrogen bond. The dissociation energy (BSSE and ZPE corrected) has been estimated to be $11.5\text{ kJ}\cdot\text{mol}^{-1}$. This work represents the first application of an accurate, yet efficient computational scheme, designed for the investigation of small biomolecules, to a molecular cluster.

Introduction

Pyridine (PYR) is a prototype heterocyclic aromatic molecule, of great importance in organic and industrial chemistry. The simultaneous presence of n and π orbitals makes the molecule particularly suitable for forming non-covalent linkages, and for this reason many of its molecular adducts have been investigated. A detailed knowledge of the typology and strength of these non-bonding interactions has been obtained using high-resolution spectroscopy. For example, PYR is the only molecule whose 1:1 adducts with all stable rare gases (from He to $\text{Xe}^{[1]}$) and with all fluorine containing freons derived from methane ($\text{CH}_n\text{F}_{4-n}$, $n = 0$ to 4 ^[2]) have been investigated by means of rotational spectroscopy. The results for these two families are graphically summarized in Figure 1. One can note that either π - or σ -type complexes are formed, depending on the type of the dominant interaction, dispersive or specific. Figure 1 shows that complexes with rare gases and methane belong to the first class, whereas those with freons, which can form weak hydrogen or halogen bonds, belong to the second class. Figure 1 also

collects the dissociation energies, which range between 0.5 and $5\text{ kJ}\cdot\text{mol}^{-1}$ for the π -type complexes. We also note that the π -interaction is generally weaker than the hydrogen or halogen bond (PYR- CF_4), which ranges between 10 and $16\text{ kJ}\cdot\text{mol}^{-1}$ (see Figure 1), with PYR acting as donor. Furthermore, σ -type arrangements have been found in molecular adducts of PYR with other partners, such as CO , CO_2 , SO_2 , SO_3 and acetylene. All of them are linked to the n non-bonding orbital of PYR through formal $\text{C}\cdots\text{N}$ or $\text{S}\cdots\text{N}$ or $\text{C-H}\cdots\text{N}$ contacts.^[3] In particular, we mention that PYR- SO_3 is a charge transfer complex, where PYR donates its pair of electrons to SO_3 . The resulting S-N bond is thus a covalent one, with a corresponding bonding energy as large as $\sim 120\text{ kJ}\cdot\text{mol}^{-1}$.^[3d]

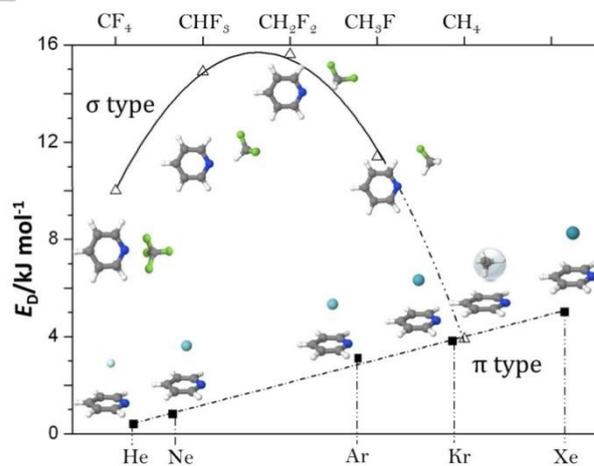


Figure 1. PYR forms π -type complexes with rare gases and methane, and σ -type complexes with all the remaining molecules so far investigated. (Reproduced from Ref. [2e] with permission from the PCCP Owner Societies).

Moving to other types of complexes, ZEKE spectroscopy has been used to investigate PYR-Metal (metal=Li, Ca, and Sc) complexes, produced using laser-vaporization techniques. Both π - and σ -bonds are formed: it was found that Li and Ca complexes favour σ bonding, whereas Sc prefers a π coordination, with binding energies of 27.0 , 49.1 and $110.6\text{ kJ}\cdot\text{mol}^{-1}$, respectively.^[4]

Despite the fact that such a large variety of molecular adducts involving PYR has been studied, the complexes with two very simple and important molecules, namely, water and ammonia, have not been investigated yet. For this reason, we have decided to investigate the electronic structure and rotational spectrum of PYR- NH_3 . This study aims at answering to the following key questions: does ammonia interact with the n or the π electronic system? Is more than one type of conformer stable?

[a] Prof. Dr. W. Caminati, Prof. Dr. C. Puzzarini
Dipartimento di Chimica "G. Ciamician" dell'Università
Via Selmi 2, 40126 Bologna (Italy)
E-mail: walther.caminati@unibo.it, cristina.puzzarini@unibo.it

[b] Dr. L. Spada, Dr. N. Tasinato, Ms. F. Vazart, Prof. Dr. V. Barone
Scuola Normale Superiore
Piazza dei Cavalieri 7, I-56126 Pisa (Italy)
E-mail: lorenzo.spada@sns.it

Supporting information for this article is given via a link at the end of the document.

What is the strength of this interaction? How much is the PYR molecular structure affected by this interaction? Does NH₃ freely rotate around its symmetry axis in the complex?

The importance of this investigation lies also on the fact that molecular complexes involving hydrogen bonding between nitrogen-containing systems can be considered as prototypes for studying the (N-H...N) interaction in biological systems.

To elucidate the structure of the PYR-NH₃ complex and the type of interaction occurring, we have undertaken a combined theoretical-experimental investigation. Guided by state-of-the-art quantum-chemical calculations, the rotational spectrum of the molecular complex (further complicated by the quadrupolar interactions of the two ¹⁴N nuclei with the overall rotation) has been recorded and analysed. The results are presented and discussed in the following section.

Results and Discussion

Quantum-chemical Calculations

The exploration of the potential energy surface (PES) of the pyridine...ammonia complex has been carried out by employing density functional theory (DFT). Although standard DFT can handle large molecular systems and its accuracy has been validated for several molecular properties, the majority of density functional approximations fail to correctly describe the long range London dispersion interactions, particularly the correct $-R^{-6}$ dependence of the interaction energy on the intermolecular separation R .^[5] As a consequence, dispersion correlation effects have been taken into account by the DFT-D3 correction scheme,^[6] which combines reliability and computational effectiveness. Up to now, the DFT-D3 model has been successfully applied to thousands of different systems, including dimers, large supra-molecular complexes and reaction energies/barriers, as well as surface processes (e.g. see [7] and references therein). Within the DFT-D3 approach, Becke-Johnson damping has been used and the exploration of the pyridine...ammonia PES has been carried out using the B3LYP functional^[8] in conjunction with the SNSD basis set.^[9,10] These calculations have led to the identification of three distinct minima (M1, M2 and M3 in Figure 2), featuring hydrogen bonds between ammonia and pyridine. All of these minima show a σ -type arrangement, with the M1 isomer being the most stable because of the double interaction.

A more thorough characterization of the PES, also including the saddle points (TS1, TS2 and TS3) connecting the stable structures, has been carried out by using the double-hybrid B2PLYP-D3 functional^[11] in conjunction with the triple- ζ m-aug-cc-pVTZ basis set^[12] in which d functions on hydrogen atoms have been removed (referred to in the following as maug-cc-pVTZ-dH). Figure 2 provides the graphical representation of the stationary points found on the PES at the B2PLYP-D3/m-aug-cc-pVTZ-dH level.

An isomer with a π -type arrangement has also been searched on the PES. While an energy minimum has been found at the B3LYP-D3 level, this has not been confirmed by the more

reliable B2PLYP-D3/m-aug-cc-pVTZ-dH calculations. Therefore, we have not further considered π -type arrangements.

According to the relative energies reported in Figure 2, the M1 isomer is the best candidate to be observed in the rotational spectrum and, thus, to be characterized. Experimental observations and spectral analysis can be profitably guided by accurate predictions of the rotational constants, which, in turn require a highly accurate determination of the complex structure. To fulfil the required accuracy, the equilibrium geometry has been determined by means of a composite scheme that accounts simultaneously for basis-set and electron-correlation effects.^[13] In particular, we employed the so-called "cheap" geometry scheme.^[14] The starting point is a geometry optimization at the CCSD(T)^[15] level (within the frozen-core approximation): as a matter of fact, the coupled-cluster approach including single and double excitations (CCSD) with a perturbative treatment of triple excitations ((T)) is nowadays the method of choice when accurate results are sought. For a large system as that under consideration, to include the most relevant contributions in the electronic structure treatment without losing computational efficiency, second-order Møller-Plesset perturbation theory (MP2)^[16] geometry optimizations are used. In particular, the extrapolation to the complete basis set limit (CBS) has been performed by means of the consolidated n^{-3} extrapolation equation^[17] applied to MP2 optimized geometries obtained with triple- and quadruple-zeta quality basis sets. The contribution of core-valence electron correlation has been included by means of the corresponding correction, $\Delta r(\text{CV})$, and the effect of diffuse functions in the **basis** set ($\Delta r(\text{aug})$) has also been taken into account. On the whole, the best-estimated equilibrium structure has been determined as:

$$r(\text{best}) = r(\text{CCSD(T)/VTZ}) + \Delta r(\text{CBS}) + \Delta r(\text{CV}) + \Delta r(\text{aug}) \quad (1)$$

In the computational section, at the end of this manuscript, the so-called "cheap" geometry scheme is described in more detail. Starting from the equilibrium rotational constants, B_e^i , corresponding to the computed equilibrium geometry, best-estimated ground-state rotational constants B_0^j have been obtained by adding the vibrational corrections, ΔB_{vib} , evaluated at the B2PLYP-D3/m-aug-cc-pVTZ-dH level:

$$B_0^j = B_e^j + \Delta B_{\text{vib}}^j \quad (2)$$

where i denotes the principal inertial axis. The vibrational corrections have been computed by means of second-order vibrational perturbation theory (VPT2) applied to the molecular r_0 -vibrational Hamiltonian expressed in normal coordinates (see e.g. Ref. [18] and references therein), which requires the calculation of semi-diagonal cubic force constants (once again, more details are provided in the computational section). Computation of the anharmonic force field (performed at the B2PLYP-D3/m-aug-cc-pVTZ-dH level) also provided the quartic centrifugal-distortion constants, for which the symmetric-top reduction (Watson's S reduction) has been considered.^[19]

A composite scheme analogous to that used for the structural determination has been employed for accurately predicting equilibrium nuclear quadrupole-coupling constants of both

nitrogen atoms (one belonging to PYR and one to NH₃).^[14,20] Subsequently, the ground-state quadrupole-coupling constants have been obtained by correcting the best-estimated equilibrium values through vibrational contributions evaluated at the **B2PLYP-D3/m-aug-cc-pVTZ-dH level**.^[21]

The computed spectroscopic results are summarized in Table 1, while selected geometrical parameters are given in Table 2 (the whole set of best-estimated bond distances and angles is provided in the Supporting Information).

Rotational spectrum

Guided by the quantum-chemical calculations described above, the rotational spectrum recording started with the search of the most intense μ_a -type rotational transitions of the most stable isomer (M1). Two separated lines, showing a complex hyperfine structure pattern due to the presence of two ¹⁴N nuclei (that possess nuclear spin $I=1$), have been found around 7504.85 and 7505.85 MHz. They have been assigned to the $J_{K_a, K_c} = 3_{0,3} \leftarrow 2_{0,2}$ transition of the *E* and *A* states, respectively, underlying the internal rotation of the NH₃ group around its *C*₃ axis. Later on, several μ_a -type lines up to $J = 7$ and $K_a = 2$ and some weaker μ_b -type transitions have been assigned and fitted using Pickett's SPFIT program,^[22] within the *I'*-representation of Watson's *S* reduction.^[19] To account for the nuclear spin of the two nitrogen atoms, the coupling schemes $F_1 = I_1 + J$ and $F = I_2 + F_1$ have been employed for both *A* and *E* states, where I_1 and I_2 are the quantum number of the ¹⁴N nuclear spin in pyridine and NH₃, respectively. An example of such a doubling is provided by Figure 3, for the $J_{K_a, K_c} = 6_{0,6} \leftarrow 5_{0,5}$ rotational transition. The measured transition frequencies are collected in the Supporting Information.

The results of the fit are reported in Table 1 together with those obtained by fitting the centre frequencies of each transition (corrected for the nuclear hyperfine structure) using the XIAM program,^[23] which provides directly the V_3 internal rotation barrier. It is worth mentioning that the **rotational constants** obtained by the XIAM approach correspond to the **limiting case** of an infinite barrier, thus leading to intermediate values between the *A* and *E* cases, as dealt by the SPFIT code. Note that, for the *E* state, in the SPFIT fit it was also necessary to include terms of the type $D_a P_a$ and $D_b P_b$ in order to take into account the torsion-rotation interaction.

Finally, it should be noted that no lines belonging to the other isomers have been observed.

In addition to the intrinsic importance of the accurate determination of the spectroscopic parameters of the most stable PYR-NH₃ isomer, Table 1 shows a very good agreement between experiment and theory. This is a particularly important result because the present study provides the first opportunity to test the reliability and accuracy of the "cheap" geometry scheme also for molecular complexes. While several investigations have demonstrated that this composite approach is able to determine accurate molecular and spectroscopic properties of semi-rigid as well as flexible systems,^[14,24] the present application to the PYR-NH₃ complex suggests that the same accuracy is also obtainable for molecular adducts. This means that, for instance, the bond distances determined in this study are expected to be accurate within 0.001-0.002 Å. As evident in Table 1, the best-estimated equilibrium rotational constants augmented by vibrational corrections agree with the experimental ground-state rotational constants well within 0.1%.

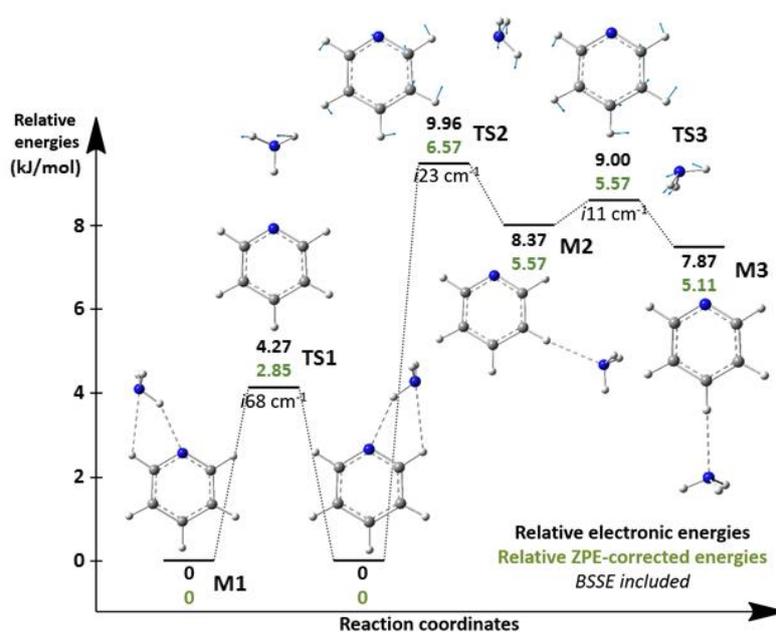


Figure 2. Schematic representation of PES for PYR-NH₃: three different minima (M1, M2, and M3) and the connecting transition state structures (TS1, TS2, and TS3) are shown together with the corresponding relative energies (including the correction for the basis set superposition error, BSSE [25]), as obtained at the B2PLYP-D3/m-aug-cc-pVTZ-dH level.

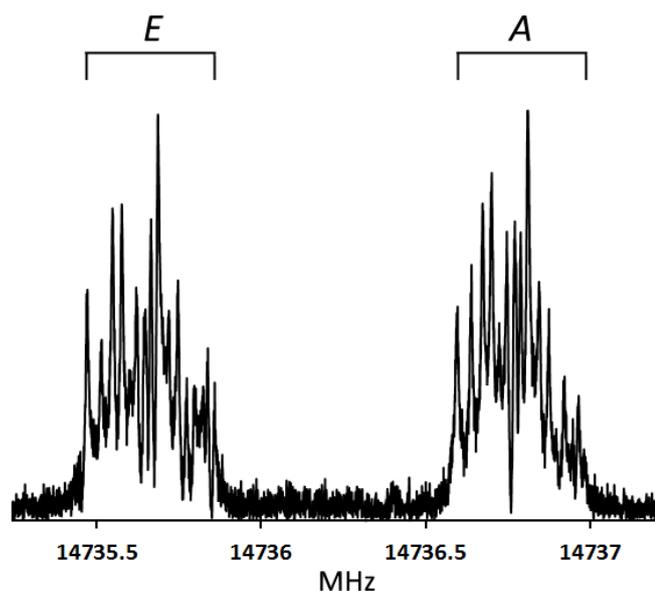


Figure 3. The $J = 6_{0,6} \leftarrow 5_{0,5}$ rotational transition for the observed isomer of pyridine-ammonia showing, for both E and A states, the hyperfine structure due to the presence of two ^{14}N nuclei (the component values can be found in the Supporting Information) and the doubling due to Doppler effect.

$(^{14}\text{N PYR})$		$(^{14}\text{N NH}_3)$	
χ_{aa} [MHz]	1.42	1.437(5)	
$\chi_{bb} - \chi_{cc}$ [MHz]	-4.49	-4.792(8)	
χ_{ab} [MHz]	-0.51	[-0.51] ^[b]	
$\angle(i,a)$ [°] ^[c]			80.51(2)
I_a [$\text{u}\cdot\text{\AA}^2$] ^[d]			2.551(7)
V_3 [cm^{-1}]	238		319.8(7)
N^{e}		28	28
σ^{f} [kHz]		3.0	2.6

[a] Errors in parentheses are expressed in units of the last digit. [b] Fixed at the best-estimated equilibrium value augmented by vibrational corrections. [c] $\angle(i,b)$ is the complement to 90° with respect to $\angle(i,a)$ ($\angle(i,c)$ is 90° because of the C_s symmetry of the M1 complex), where i is the NH_3 internal rotation axis. [d] Moment of inertia of NH_3 around its C_3 axis (a). [e] Number transition frequencies included in the fit. [f] Standard deviation of the fit.

Table 1. Computed and experimental^[a] (using SPFIT and XIAM programs) spectroscopic parameters of the M1 PYR- NH_3 complex.

	THEORY	SPFIT	XIAM	
		"A"	"E"	
A [MHz]	5875.20	5872.300(1)	5872.136(1)	5872.203(2)
B [MHz]	1386.28	1387.6497(2)	1387.3647(2)	1387.4676(3)
C [MHz]	1127.93	1128.7913(1)	1128.7818(1)	1128.7904(3)
D_a [MHz]	-	-	-15.575(2)	
D_b [MHz]	-	-	-22.23(3)	
$D_{\text{pi}2J}$ [kHz]				
D_J [kHz]	0.459	0.5364(6)		
D_{JK} [kHz]	7.929	7.95(1)		
D_K [kHz]	-7.147			
d_1 [kHz]	-0.105	-0.1192(9)		
d_2 [kHz]	-0.0348	-0.0357(4)		
χ_{aa} [MHz]	-3.92	-3.747(5)		
$\chi_{bb} - \chi_{cc}$ [MHz]	-2.86	-2.860(8)		
χ_{ab} [MHz]	2.23	1.6(2)		

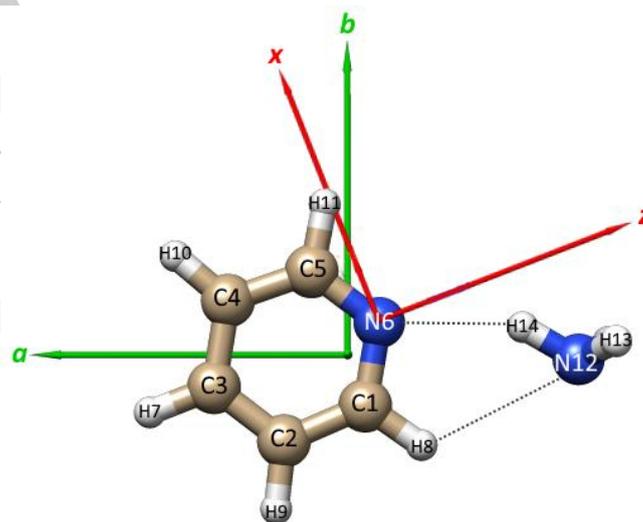


Figure 4. Orientation of the pyridine-ammonia cluster with respect to the principal axes of inertia a, b, c (the c axis is perpendicular to the figure plane), also showing the atom numbering and the N-H...N and C-H...N hydrogen bonds. The principal quadrupole axes x, y, z are also depicted, with y being parallel to c .

In addition to the accurate calculation of the equilibrium structure of the M1 isomer, from the analysis of the experimental data a partial effective structure has been derived by fitting the N12-N6-C5 angle of Figure 4 ($\angle\text{N12N6C5}$ in Table 2), while keeping the other parameters fixed at the vibrationally-averaged B2PLYP/m-aug-cc-pVTZ- d H values (the complete geometry is available as Supporting information). The results, reproducing the experimental rotational constants with a maximum discrepancy on A within 0.1%, together with the hydrogen bond parameters and a selection of the best-estimated structural values, are reported in Table 2. It should be noted that, while it is straightforward to

derive rotational constants from the geometrical structure, the inviolable. In a zeroth approximation, this energy barrier provides an problem, i.e., the derivation of the structure from the rotational constant indication of the strength of the hydrogen bond. The value obtained, is not solvable. Only the availability of the rotational constants for several isotopic species would allow such determination. In order to support dynamics of the cluster. One could argue that the maximum of the analysis in terms of an effective structure, the vibrationally averaged potential energy function for the internal rotation of NH₃ has a bifurcated geometry, evaluated at the B2PLYP/m-aug-cc-pVTZ-dH level, has both NH₂...N hydrogen bond, but in the present case the N-H bonds of ammonia are not along the symmetry axis of the n-orbital of the pyridinic nitrogen. Furthermore, the value obtained is in line with literature results. To give an example, in the 1,4-difluorobenzene – ammonia complex, the V₃ barrier has been estimated to be 60 cm⁻¹ (0.7 kJ mol⁻¹).^[27] In that case the internal rotation of NH₃ breaks a N-H...F hydrogen bond, which is rather weaker than the N-H...N one.

Table 2. Effective r_0 and best-estimated equilibrium r_e structural parameters^{a]}

	r_0	r_e
\angle N12N6C5	157.5(1) ^[b]	154.6
Derived Hydrogen Bond Parameters		
r_{N6H14}	2.326	2.208
r_{N12H8}	2.710	2.742
\angle N12H14N6	150.5	150.8
\angle C1H8N12	119.9	116.2
r_{N6C1}	1.344	1.337
r_{N6C5}	1.339	1.336
r_{C1C2}	1.394	1.391
r_{C4C5}	1.393	1.390
r_{C2C3}	1.392	1.388
r_{C3C4}	1.394	1.389

[a] Distances in Å, angles in degrees. [b] Error in parentheses is expressed in units of the last digit.

As already mentioned, the XIAM program directly provides the internal rotation barrier V_3 . The value obtained, 319.8(7) cm⁻¹, is reported in Table 1. However, a second approach can be used to determine from our data the V_3 barrier. In fact, the D_a and D_b terms of Table 1 are related to the first-order perturbation sum relative to the E state, W , according to the following equation:^[25,26]

$$D_a = \frac{F}{2} \left(1 - \sum_a \frac{\lambda_a^2}{I_a} \right) \quad (3)$$

where

$$F = \frac{h^2}{I_a \left(1 - \sum_a \frac{\lambda_a^2}{I_a} \right)} \quad ; \quad \rho_g = \frac{\lambda_g I_g}{I_a}$$

with λ_g denoting the direction cosines between the internal rotation axis of NH₃ and the principal axis g (with $g=a,b$) of the complex, and I_a is the NH₃ moment of inertia. The value of $W_E^{(1)}$ (derived from D_a and D_b) of the ground torsional level $v=0$ depends on the reduced barrier value s , which is related to both the V_3 potential energy barrier and the reduced mass of the motion. In particular, the V_3 barrier (in kcal mol⁻¹) calculated via the following expression:^[25]

$$V_3 = 0.2146 \cdot F \cdot s \quad (4)$$

Using D_a and D_b of Table 1, we obtain the values $V_3^{(a)} = 321$ cm⁻¹ and $V_3^{(b)} = 343$ cm⁻¹, respectively. These agree with the XIAM fitted V_3 value of Table 1 and are also in reasonably good agreement with the result obtained at the B2PLYP-D3/m-aug-cc-pVTZ-dH level including ZPE and BSSE corrections, $V_3 = 238$ cm⁻¹.

We note that the V_3 barrier corresponds to the energy difference between the global minimum structure, characterized by the N-H...N hydrogen bond, and the conformation in which this hydrogen bond is

broken. The value obtained is in line with literature results. To give an example, in the 1,4-difluorobenzene – ammonia complex, the V_3 barrier has been estimated to be 60 cm⁻¹ (0.7 kJ mol⁻¹).^[27] In that case the internal rotation of NH₃ breaks a N-H...F hydrogen bond, which is rather weaker than the N-H...N one.

Important chemical information can be derived from the quadrupole-coupling analysis thanks to the availability of the full nuclear quadrupole-coupling tensor (in the principal inertia axes) for the ¹⁴N nucleus of pyridine (see Table 1). From the diagonalization of this tensor (by means of the QDIAG program^[28]), the quadrupole-coupling constants in the quadrupole principal coordinate system are obtained. For the nitrogen atom belonging to the ammonia unit, the experimental data have been complemented by the computed off-diagonal term, thus allowing the determination of the corresponding principal quadrupole tensor. However, this prevents a reliable estimate of the experimental uncertainties affecting the constants obtained from the diagonalization. In Table 3, for comparison purposes, the quadrupole-coupling constants of the pyridine and ammonia monomers are collected. Concerning the nitrogen atom of the pyridine unit, we note that the small decrease (up to a maximum of 0.6 MHz, see Table 3) of their values accompanying the formation of the PYR-NH₃ complex is a clear diagnostic of a small degree of N-H...N proton transfer, as also suggested by the length of the N12H14 distance which is about 30 mÅ longer than the N12H13 or N12H15 ones (see r_0 values of Table S4 in the Supporting Information).

Upon inspection of Table 3, it can be noted that the vibrational motions have small effect on the χ_{zz} values for free ammonia and pyridine. Conversely, upon clustering, the quadrupole coupling constant of ammonia moves from -3.69 MHz at the equilibrium to -3.01 MHz at the 0°K while pyridine values vary of about 0.1 MHz at most. The large variation shown by ammonia in the complex with respect to the free molecule may be ascribed to the effects of molecular oscillations and internal motions contribute.

Further structural information can be derived from the rotation angles, obtained from the matrix diagonalization mentioned above. These are $\theta_{za} = 19(2)^\circ$ and $\theta_{xa} = 71(2)^\circ$ ($\theta_{ya} = 90^\circ$ for symmetry reasons), and provide useful information on the orientation of ammonia in the molecular complex.

Finally, it is worthwhile noting that the agreement between experiment and theory for the quadrupole-coupling constants is less good than what has been observed for rotational constants. This should be mainly ascribed to the vibrational corrections. In this respect, the VPT2 approach shows strong limitation in dealing with the large amplitude motions (see, for example, Ref. [20]).

Table 3. Experimental (Exp)^[a], computed (Theory) vibrationally averaged (Vib.Ave.) and equilibrium (Equil)^[c] principal quadrupole tensor of ¹⁴N in the complex as well as the pyridine and ammonia monomers. Values in MHz.

Pyridine-Ammonia						
	¹⁴ N(PYR)			¹⁴ N(NH ₃)		
	Exp	Theory Vib.Ave.	Equil	Exp ^[d]	Theory Vib.Ave.	Equil
χ_{zz}	-4.3(1)	-4.84	-4.97	-3.17	-3.01	-3.69
χ_{xx}	1.0(1)	1.48	1.47	1.68	1.54	2.09
χ_{yy}	3.304(5)	3.41	3.50	1.49	1.48	1.60
η ^[e]	0.53(3)	0.40	0.41	-0.06	-0.02	-0.13
Monomers						
	¹⁴ N(PYR)			¹⁴ N(NH ₃)		
	Exp ^[f]	Theory Vib.Ave.	Equil	Exp ^[g]	Theory Vib.Ave.	Equil
χ_{zz}	-4.908(3)	-4.99	-5.04	-4.08983 (2)	-3.79	-3.74
χ_{xx}	1.434(3)	1.47	1.46			
χ_{yy}	3.474(3)	3.52	3.58			
η ^[e]	0.416(9)	0.41	0.42			

[a] Errors in parentheses are expressed in units of the last digit.

[b] Best-estimated equilibrium values augmented by vibrational corrections at the B2PLYP/m-aug-cc-pVTZ-dH (see text).

[c] Best-estimated equilibrium values (composite scheme, see text).

[d] Obtained by using the χ_{ab} calculated value of Table 1.

[e] Quadrupole asymmetry parameter: $\eta = (\chi_{xx} - \chi_{yy}) / \chi_{zz}$.

[f] Ref. [29].

[g] Ref. [30].

Dissociation Energy

From the partial effective structure determination, it is furthermore possible to evaluate the distance between the effective centres of mass of pyridine and ammonia, R_{CM} , which turned out to be 4.48 Å. By assuming a pseudo-diatomic approximation, the force constant (k_s) for the intermolecular stretching along the axis connecting the two centres of mass, which is to a rough approximation the a inertial axis, can be estimated as:^[31]

$$k_s = \frac{16\pi^4 (\mu R_{CM})^2 [4B^4 + 4C^4 - (B-C)^2(B+C)^2]}{hD_J} \quad (6)$$

where μ is the pseudo-diatomic reduced mass. By using the B , C and D_J values from Table 1, and R_{CM} derived from the data of Table 2, a value of 10 N·m⁻¹ has been obtained for k_s , which corresponds to a harmonic fundamental frequency of 110 cm⁻¹. Subsequently, k_s and R_{CM} can be used, within a Lennard-Jones type potential, to determine the dissociation energy (E_D):^[32]

$$E_D = \frac{1}{72} k_s (R_{CM})^2 \quad (7)$$

thus leading to a value of 16.7 kJ mol⁻¹.

A more rigorous determination of the dissociation energy can be obtained via quantum chemistry. To accurately compute E_D , single-point energy calculations at the best-estimated equilibrium geometry of the complex and of the isolated non-interacting fragments, have been carried out by means of a composite scheme similar to that employed for geometry (see the Computational section). Then, the best-estimated dissociation energy has been evaluated as the difference between the electronic energy of the PYR-NH₃ complex and those of the isolated monomers, with the BSSE taken into account via the counterpoise correction (CP) procedure, proposed by Boys and Bernardi.^[33] The composite approach has led to a value of 16.7 kJ mol⁻¹, with an estimated uncertainty around 1-2 kJ mol⁻¹.^[14c,20] It is noteworthy that, despite the limitations of the pseudo-diatomic approximation, the dissociation energy obtained at this level is in remarkable agreement with the quantum-chemical result. Subsequently, electronic energies have been corrected for the anharmonic ZPE contribution calculated at the B2PLYP-D3/m-aug-cc-pVTZ-dH level by adopting the resonance-free perturbative approach within the hybrid degeneracy corrected second-order perturbation theory (HDCPT2).^[21] ZPE energy turns out to reduce the dissociation energy by 5.2 kJ mol⁻¹, thus leading to a ZPE-corrected value for the dissociation energy of 11.5 kJ mol⁻¹.

Conclusions

The joint experimental-computational investigation reported in this manuscript provides incontrovertible evidence that the PYR-NH₃ complex shows a σ -type bonding structure in which ammonia interacts via two hydrogen bonds within the plane of the pyridine ring, with a small degree of proton transfer from ammonia to pyridine. No evidence was obtained that supports the formation of a stable π -bound adduct.

For the first time, the so-called "cheap" composite scheme, purposely set up for accurately describing the electronic structure and spectroscopic properties of small biomolecules, has been applied to a weakly bonded molecular complex and its accuracy and reliability tested by means of a high-resolution MW spectroscopic study. The results reported demonstrated the suitability of this approach also for accurately studying molecular complexes. In detail, the molecular structure has been determined by means of a computational approach able to provide structural parameters with an estimated accuracy of about 0.001-0.002 Å for bond distances and of about 0.1° for angles.

The binding energy has also been determined by means of a composite scheme analogous to that employed for the evaluation of equilibrium geometry. Our best-estimated, ZPE and BSSE corrected, dissociation energy is 11.5 kJ mol⁻¹ and can be considered a reliable reference value, undoubtedly fulfilling chemical accuracy requirements. This value is perfectly in line with those previously derived for σ -type pyridine - CH_nF_{4-n} freons complexes shown in Figure 1.

Experimental Section

A 1% mixture of anhydrous NH_3 (>99.99 %, commercial sample) in Helium at stagnation pressure of 0.2 MPa has been streamed over a sample of pyridine (>99.8%, commercial sample) kept at room temperature, and expanded through the solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry-Pérot-type cavity. The rotational spectrum in the 6.5 – 18.5 GHz range has been recorded by means of a COBRA-type^[34] pulsed-jet Fourier-transform microwave (FTMW) spectrometer,^[35] described elsewhere.^[36]

Rest frequencies have been obtained as the arithmetic mean of the frequencies of the two Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz, and the resolution is better than 7 kHz.

Computational Section

a) Composite approach

As described in [13], the “cheap” geometry scheme is a composite scheme where the various contributions are evaluated separately and then combined to obtain the best theoretical estimates. The MP2 method has been used in conjunction with the cc-pVnZ basis sets ($n = \text{T, Q}$), the triple- ζ basis set augmented by diffuse functions, aug-cc-pVTZ, as well as the core-valence correlation consistent cc-pCVTZ basis set.^[37] To account for triple excitations, the CCSD(T)/cc-pVTZ geometry optimization is used as starting point of this approach. As mentioned in the text, the best estimate for a generic structural parameter r is given by equation (1).^[13] In detail, the terms of equation (1) are:

$$\Delta r(\text{CBS}) = \frac{n^2 r(n) - (n-1)^2 r(n-1)}{n^3 - (n-1)^3} - r(n-1) \quad (1a)$$

where $n=4$ (thus corresponding to the cc-pVQZ basis set), $r(n)$ is the geometrical parameter optimized at the MP2/cc-pVQZ level and $r(n-1)$ that at the MP2/cc-pVTZ level;

(1b)

with $r(\text{CVTZ,all})$ and $r(\text{CVTZ,fc})$ being the MP2/cc-pCVTZ optimized parameter correlating all electrons and within the frozen core (fc) approximation, respectively.

(1c)

where $r(\text{augVTZ,fc})$ and $r(\text{VTZ})$ are the structural parameters optimized at the MP2 level within the fc approximation by using the aug-cc-pVTZ and cc-pVTZ basis sets, respectively. The correction due to the inclusion of diffuse functions in the basis set ($\Delta r(\text{aug})$) has been introduced to recover on an empirical basis the limitations affecting extrapolation procedures carried out with small- to medium-sized basis sets.

The same composite approach has also been worked out for the equilibrium nitrogen quadrupole-coupling constants, χ_{ij} , in order to determine best-estimated values.^[14,20] Actually, the additivity scheme has been applied to the electric-field gradient components.^[14,20] Then, ground-state quadrupole-coupling constants have been obtained by correcting the best-estimated equilibrium values through vibrational contributions evaluated at the B2PLYP-D3/ m-aug-cc-pVTZ-dH level.^[20]

b) Force field

As mentioned in the text, B3LYP-D3 and B2PLYP-D3 density functionals have been used in conjunction with either the SNSD or m-aug-cc-pVTZ-dH basis set. For both functionals, geometry optimizations

have been carried out first, and then, at the optimized geometry, harmonic frequencies have been computed by using analytic second derivatives.^[38] Anharmonic force fields have been obtained by numerical differentiations of the analytic force constants.^[37]

All HF, MP2 and DFT computations have been performed with the Gaussian 09 software,^[39] while the CFOUR program package^[40] has been employed for CCSD(T) calculations.

Acknowledgements

This work was supported by Italian MIUR (PRIN 2012 “STAR: Spectroscopic and computational Techniques for Astrophysical and atmospheric Research”) and by the University of Bologna (RFO funds) and Scuola Normale Superiore (funds for project “COSMO: Combined experimental and computational spectroscopic modeling for astrochemical applications”). The support of the COST CMTS-Action CM1405 (MOLIM: MOLEcules In Motion) is acknowledged. Support from the Italian MIUR (FIRB 2013 “Futuro in ricerca” Project “Advanced nanostructured materials for eco-sustainable cements: investigation of the structural properties and innovative strategies for their improvement” Protocollo: RBFR132WSM) is acknowledged. The SMART@SNS Laboratory (<http://dreams.sns.it>) is acknowledged for providing high performance computer facilities.

Keywords: Hydrogen bonding • pyridine-ammonia complex • rotational spectroscopy • Quantum chemistry • Equilibrium structure

- [1] a) C. Tanjaroan, W. Jäger, *J. Chem. Phys.*, **2007**, *127*, 034302; b) A. Maris, W. Caminati, P. G. Favero, *Chem. Commun.*, **1998**, 2625-2626; c) B. Velino, W. Caminati, *J. Mol. Spectrosc.*, **2008**, *251*, 176-179; d) T. D. Klots, T. Emilsson, R. S. Ruoff, H. S. Gutowsky, *J. Phys. Chem.*, **1989**, *93*, 1255-1261; e) R. M. Spycher, D. Petitprez, F. L. Bettens, A. Bauder, *J. Phys. Chem.*, **1994**, *98*, 11863-11869; f) S. Melandri, G. Maccaferri, A. Maris, A. Millemaggi, W. Caminati, P. G. Favero, *Chem. Phys. Lett.*, **1996**, *261*, 267-271; g) S. Tang, L. Evangelisti, B. Velino, and W. Caminati, *J. Chem. Phys.*, **2008**, *129*, 144301.
- [2] a) A. Maris, L. B. Favero, B. Velino, W. Caminati, *J. Phys. Chem. A*, **2013**, *117*, 11289-11292; b) L. B. Favero, B. M. Giuliano, A. Maris, S. Melandri, P. Ottaviani, B. Velino, W. Caminati, *Chem. Eur. J.*, **2010**, *16*, 1761-1764; c) L. Spada, Q. Gou, M. Vallejo-López, A. Lesarri, E. J. Cocinero, W. Caminati, *Phys. Chem. Chem. Phys.*, **2014**, *16*, 2149-2153; d) M. Vallejo-López, L. Spada, Q. Gou, A. Lesarri, E. J. Cocinero, W. Caminati, *Chem. Phys. Lett.*, **2014**, *591*, 216-219; e) Q. Gou, L. Spada, M. Vallejo-López, A. Lesarri, E. J. Cocinero, W. Caminati, *Phys. Chem. Chem. Phys.*, **2014**, *16*, 13041-13046.
- [3] a) R. P. A. Bettens, A. Bauder, *J. Chem. Phys.*, **1995**, *102*, 1501; b) J. L. Doran, B. Hon, and K. R. Leopold, *J. Mol. Struct.*, **2012**, *1019*, 191-195; c) M. S. Labarge, J.-J. Oh, K. W. Hillig II, R. L. Kuczkowski, *Chem. Phys. Lett.*, **1989**, *159*, 559-562; d) S. W. Hunt, and K. R. Leopold, *J. Phys. Chem. A*, **2001**, *105*, 5498-5506; e) R. B. Mackenzie, C. T. Dewberry, E. Coulston, G. C. Cole, A. C. Legon, D. P. Tew, K. R. Leopold, *J. Chem. Phys.*, **2015**, *143*, 104309.
- [4] S. A. Krasnokutski, D.-S. Yang, *J. Chem. Phys.*, **2009**, *130*, 134313.
- [5] S. Grimme, *WIREs Comput. Mol. Sci.* **2011**, *1*, 211-228.
- [6] S. Grimme, J. Anthony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [7] a) L. Goerigk, S. Grimme, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670-6688; b) S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955-9964; c) M. Delle Piane, M. Corno, P. Ugliengo, *J. Chem. Theor. Comput.* **2013**, *9*, 2404-2415; d) M. Delle Piane, S. Vaccari, M. Corno, P. Ugliengo, J.

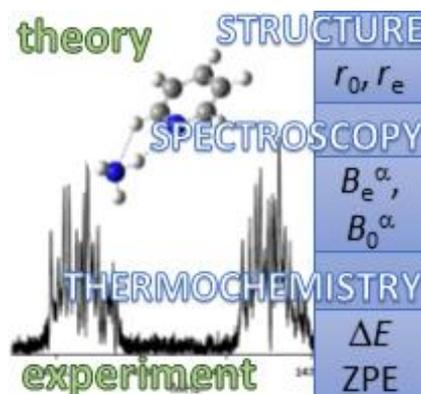
- Phys. Chem. A* **2014**, *118*, 5801-5807; e) N. Tassinato, S. Grimme, *Phys. Chem. Chem. Phys.* **2015**, *17*, 5659-5669; f) R. Sure, S. Grimme, *J. Chem. Theor. Comput.* **2015**, *11*, 3785-3801; g) N. Tassinato, D. Moro, S. Stoppa, A. Pietropoli Charmet P. Toninello, S. Giorgianni, *Appl. Surf. Sci.* **2015**, *353*, 986-994.
- [8] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- [9] I. Carnimeo, C. Puzzarini, N. Tassinato, P. Stoppa, A. Pietropoli Charmet, M. Biczysko, C. Cappelli, V. Barone, *J. Chem. Phys.* **2013**, *139*, 074310.
- [10] <http://dreamslab.sns.it/>.
- [11] S. Grimme, *J. Chem. Phys.* **2006**, *124*, 034108.
- [12] E. Papajak, H. R. Leverentz, J. Zheng, D. G. Truhlar, *J. Chem. Theory Comput.* **2009**, *5*, 1197-1202.
- [13] C. Puzzarini, *Int. J. Quantum. Chem.* **2016**, *116*, 1513-1519.
- [14] a) C. Puzzarini, V. Barone, *Phys. Chem. Chem. Phys.* **2011**, *13*, 7158-7166; b) C. Puzzarini, M. Biczysko, V. Barone, I. Peña, C. Cabezas, J. L. Alonso, *Phys. Chem. Chem. Phys.* **2013**, *15*, 16965-16975; c) C. Puzzarini, M. Biczysko, *J. Phys. Chem. A* **2015**, *119*, 5386-5395.
- [15] a) G. D. Purvis III, R. J. Bartlett, *J. Chem. Phys.* **1982**, *76*, 1910-1918; b) K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479-483.
- [16] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618-622.
- [17] T. Helgaker, W. Klopper, H. Koch, J. Noga, *J. Chem. Phys.* **1997**, *106*, 9639-9646.
- [18] E. Penocchio, M. Mendolicchio, N. Tassinato, V. Barone, *Can. J. Chem.* **2016**, *94*, 1065-1076.
- [19] J. K. G. Watson, In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: New York/Amsterdam, **1977**; Vol. 6, pp 1-89.
- [20] C. Puzzarini, M. Biczysko, V. Barone, L. Largo, I. Peña, C. Cabezas, J. L. Alonso, *J. Phys. Chem. Lett.* **2014**, *5*, 534-540.
- [21] a) J. Bloino, M. Biczysko, V. Barone, *J. Chem. Theory Comput.* **2012**, *8*, 1015-1036; b) A. Pietropoli Charmet, P. Stoppa, N. Tassinato, S. Giorgianni, V. Barone, M. Biczysko, J. Bloino, C. Cappelli, I. Carnimeo, C. Puzzarini, *J. Chem. Phys.* **2013**, *139*, 164302.
- [22] H. M. Pickett, *J. Mol. Spectrosc.* **1991**, *148*, 371-377.
- [23] H. Hartwig, H. Dreizler, *Z. Naturforsch., A: Phys. Sci.*, **1996**, *51*, 923-932.
- [24] a) V. Barone, M. Biczysko, J. Bloino, C. Puzzarini, *Phys. Chem. Chem. Phys.* **2013**, *15*, 10094-10111; b) V. Barone, M. Biczysko, J. Bloino, P. Cimino, E. Penocchio, C. Puzzarini, *J. Chem. Theory Comput.* **2015**, *11*, 4342-4363.
- [25] W. Gordy, R. L. Cook, *Microwave molecular spectra*, in: A. Weissberger (Ed.), *Techniques of Chemistry*, Wiley, New York, **1984**.
- [26] D. Gerhard, A. Hellweg, I. Merke, W. Stahl, M. Baudelet, D. Petitprez, G. Wlodarczak, *J. Mol. Spectrosc.*, **2003**, *220*, 234-241.
- [27] B. M. Giuliano, L. Evangelisti, A. Maris, W. Caminati, *Chem. Phys. Lett.* **2010**, *485*, 36-39
- [28] a) Z. Kisiel, E. Bialkowska-Jaworska, L. Pszczolkowski, *J. Chem. Phys.* **1998**, *109*, 10263 - 10272; b) Z. Kisiel in *Spectroscopy from Space* (Eds.: J. Demaison, K. Sarka, E. A. Cohen), Kluwer Academic Publishers, Dordrecht, **2001**, pp. 91 - 106; c) Z. Kisiel, PROSPE - Programs for ROTational SPEctroscopy, available at <http://www.ifpan.edu.pl/~kisiel/prospe.htm>.
- [29] N. Heineking, H. Dreizler, R. Schwarz, *Z. Naturforsch.* **1986**, *41a*, 1210-1213.
- [30] G. Cazzoli, L. Dore, C. Puzzarini, *Astron. Astrophys.* **2009**, *507*, 1707-1710.
- [31] D. J. Millen, *Can. J. Chem.*, **1985**, *63*, 1477-1479.
- [32] S. E. Novick, S. J. Harris, K. C. Janda, and W. Klemperer, *Can. J. Phys.*, **1975**, *53*, 2007-2015.
- [33] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553-566.
- [34] J.-U. Grabow, W. Stahl, H. Dreizler, *Rev. Sci. Instrum.* **1996**, *67*, 4072-4084.
- [35] T. J. Balle, W. H. Flygare, *Rev. Sci. Instrum.* **1981**, *52*, 33-45.
- [36] W. Caminati, L. Evangelisti, G. Feng, B. M. Giuliano, Q. Gou, S. Melandri, J.-U. Grabow, *Phys. Chem. Chem. Phys.* **2016**, *18*, 17851-17855.
- [37] a) T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007-1023; b) R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 67966806; c) K. A. Peterson, T. H. Dunning, Jr., *J. Chem. Phys.* **2002**, *117*, 10548-10560.
- [38] M. Biczysko, P. Panek, G. Scalmani, J. Bloino, V. Barone, *J. Chem. Theory Comput.* **2010**, *6*, 2115-2125.
- [39] *Gaussian Development Version*, revision I.04+, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
- [40] CFOUR, a quantum chemical program package written by J.F. Stanton, J. Gauss, M.E. Harding, P.G. Szalay with contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W.J. Lauderdale, F. Lipparini, D.A. Matthews, T. Metzroth, L.A. Mück, D.P. O'Neill, D.R.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

In this combined theoretical and experimental investigation of the 1:1 pyridine – ammonia adduct it has been pointed out that, contrary to the 1:1 pyridine – methane complex, only the σ -type interaction leads to a stable system. We have demonstrated the validity and accuracy of the so-called “cheap” computational scheme also for molecular adducts as well as we have obtained important chemical information on the N-H...N prototypic interaction.



Lorenzo* Spada, Nicola Tasinato, Fanny Vazart, Vincenzo Barone, Walther Caminati*, Cristina Puzzarini*

Page No. – Page No.

Non-covalent interactions and internal dynamics in pyridine-ammonia: A combined quantum-chemical and microwave spectroscopy study