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Interactions between alkanes and aromatic molecules: a rotational study of pyridine – methane

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The rotational spectrum of the adduct pyridine – methane shows that methane links to an aromatic molecule apparently through a C-H···π weak hydrogen bond. The shape and the internal dynamics behaviour of this complex are very similar to that of the van der Waals complexes involving aromatic molecules with rare gases.

Introduction

As the simplest carbon hydride, and a potent greenhouse gas, the methane (CH_4) chemistry has been an attractive subject in recent years.[1] Understanding how CH_4 interacts with the various kinds of molecules helps to figure out its role in the chemical processes in which it is involved and its effects on the atmospheric reactions.

For decades, high resolution spectroscopy, especially Fourier transform microwave (FTMW), has proved to be an ideal tool for probing experimentally the structures, energetics and dynamics of molecular systems or weakly-bound clusters in the unperturbed environments of the gas phase or a supersonic jet. The spectral investigations yield an accurate description of the intrinsic factors governing the structure and the relative magnitude of the different intermolecular interactions.

However, methane binding is elusive. Till now, only a few rotationally resolved investigations are reported on complexes of CH_4, with very simple molecules such as water,[2] halogen hydrides,[3] OCS[4] and O_3.[5] All the spectra of these complexes displayed several vibrational sublevels, due to the high symmetry of the CH_4 subunit, and hence a large number of equivalent minima.

Pyridine (PYR) is the best-known heterocyclic aromatic molecule, used extensively in coordination[6] and surface chemistry.[7] For this reason many of its molecular adducts have been investigated using high resolution spectroscopy. Depending on the chemical nature of the partner species both π or σ type complexes have been observed. These interactions activate either the π system of the aromatic ring, or the non-bonding orbital (*n*) at the nitrogen atom. PYR-Metal (metal=Li, Ca, and Sc) complexes, produced with laser-vaporization, have been studied by ZEKE spectroscopy.[8] It has been found that Li and Ca complexes prefer σ bonding, whereas the Sc complex favors a π mode, with binding energies of 27.0, 49.1 and 110.6 kJ mol^{-1}, respectively.

Plenty of information on the typology and strength of the non-bonding interactions of PYR with its partners have been obtained also by rotational spectroscopy.[9-13] Interestingly, PYR is the only aromatic molecule for which, thanks to its permanent dipole moment, the rotational spectra of all complexes with rare gases (RG, except radon) have been reported, providing experimental evidences of the magnitude and geometry of the dispersive interactions. In all complexes, a T-shape π-type structure is observed,[9] even for complexes with two RG atoms, which exhibit a "double π" arrangement with one atom above and one atom below the ring.[9e, 10] The interaction energies are in the range 0.5-5 kJ mol^{-1}, may be weaker than weak hydrogen bonds (WHB).

Conversely, MW studies of molecular adducts of PYR with any other partners revealed always, to our knowledge, a σ-type arrangement. Four investigations are available describing this kind of interaction, including PYR complexes with simple molecules such as CO, CO_2, SO_2 and SO_3. All of them are linked to the *n* orbital of PYR, through formal C···N or S···N contacts.[11] In the adduct with SO_3, PYR acts as a Lewis base, donating its pair of electrons to the sulphur trioxide Lewis acid. The S-N bond becomes in this case a covalent bond, with unusually high bonding energy (about 120 kJ mol^{-1}).[11d]

Complexes of PYR with freons also have a σ-type arrangement. In the case of PYR-CF_4, where the two subunits are held together by a CF_3···N halogen bond, the top undergoes a free rotation with respect to PYR.[12] In PYR-CHF_3, PYR-CH_3F and CH_2F_2 two kinds of WHBs, C-H···N and C-H···F, have been found to connect the two constituent units.[13] The barriers to internal rotation of the CHF_3 and of the CH_3F groups have been determined from the *A*-*E* tunnelling splittings of the rotational transitions.

Which one will be the absolute minimum conformation of the complex of PYR with CH_4? The methane hydrogen atoms are much less acidic than the freon's hydrogens. Will they interact with the *n* or with the π electronic system? Will the high symmetry of methane still generate internal rotation splittings of the rotational transitions also in a complex so heavy as PYR-CH_4? This would be the first rotational characterization of a molecular complex constituted of an alkane (the simplest one, methane) and an aromatic ring.

Experimental section

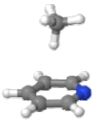
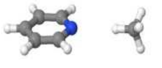
Molecular clusters were generated in a supersonic expansion, under conditions optimized for the complex formation. Details of the Fourier transform MW[14] spectrometer (COBRA-type[15]), which covers the range 6.5-18.5 GHz, have been described previously[16].

A gas mixture of ca. 5% of CH_4 in Helium at a stagnation pressure of ~ 0.6 MPa was passed over a sample of pyridine (cooled to 0 °C) and expanded through a solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry-Pérot cavity. The spectral line positions were determined after Fourier transformation of the time-domain signal with 8k data points, recorded with 100 ns sample intervals. Each rotational transition appears as doublets due to Doppler Effect. The line position is calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of the frequency measurements is better than 3 kHz. Lines separated by more than 7 kHz are resolvable.

Theoretical calculation

One can assume, by chemical intuition, a stable conformer of PYR-CH_4 to be based on a C-H···π or on a C-H···*n* link. Full *ab initio* geometry optimization (MP2/6-311++G(d,p) calculations), performed by using the Gaussian03 program package[17] confirmed this hypothesis. The obtained relative energies (ΔE) and spectroscopic parameters are collected in Table 1. We also calculated the zero-point corrected energies (ΔE_0 are the relative values reported in Table1) and, in order to have a better estimation of the relative energy of the two conformers, all intermolecular binding energy values were counterpoise corrected (ΔE_{BSSE}) for basis set superposition error (BSSE).[18] The vibrational frequency calculations resulted in two negative frequencies for species II, which is probably a transition state for the motion which transfers CH_4 from one side to the opposite one of the ring. According to the obtained results, the C-H···π interaction is predicted slightly stronger than the C-H···*n* one.

Table 1 MP2/6-311++G(d,p) shapes and spectroscopic parameters of the two forms predicted to be the most stable of PYR-CH_4. These structures are stabilized by a C-H···π (form **I**) or a C-H···N (form **II**) weak hydrogen bond.

	I	**II**
		
$A/B/C$/MHz	2901/1895/1873	5793/1128/950
$\chi_{aa}/\chi_{bb}-\chi_{cc}$/MHz	3.29/-6.28	-4.86/-1.95
$\mu_a/\mu_b/\mu_c$/D	0.4/2.3/0.0	2.7/0.2/0.0
$\Delta E/\Delta E_0/\Delta E_{BSSE}$/cm^{-1}	0/0/0[a]	346/65/19

[a] Absolute energies: -287.992494 E_h, -287.858116 E_h and -287.990053 E_h for the three cases, respectively.

Rotational spectra

Since μ_b is the largest dipole moment component of the π-complex, we started our search in the frequency region of the most intense μ_b–type transitions. We could assign three transitions of the *R*-branch family $(J+1)_{1,J+1}\leftarrow J_{0,J}$, with J = 1 to 3. Then, several more μ_b–transitions and some very weak m_a-transitions have been also measured. Each transition (see, for example, the $2_{12}\leftarrow 1_{01}$ transition illustrated in Figure 1) appeared as a multiplet of lines due to the ^{14}N quadrupolar coupling effects.

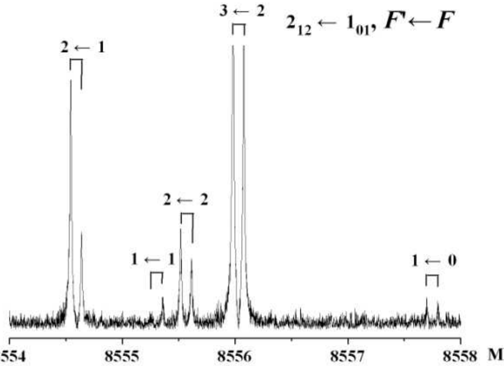


Figure 1 Recorded $2_{12}\leftarrow 1_{01}$ rotational transition of the observed conformer of PYR–CH_4 showing the ^{14}N hyperfine structure. Each component line exhibits the instrumental Doppler doubling.

The transition frequencies were fitted with Pickett's SPFIT computer program,[19] according to the following Hamiltonian:

$$H = H_R + H_{CD} + H_Q \quad (1)$$

where H_R represents the rigid rotational parts of the Hamiltonian. The centrifugal distortion contributions (analyzed using the *S* reduction and I^r representation)[20] are represented by H_{CD}. H_Q is the operator associated with the ^{14}N (I = 1) quadrupolar interaction. The experimental spectroscopic parameters resulted from a non-linear least-squares fit[17] and are reported in the first column of Table 2.

Table 2 Spectroscopic constants of the two measured isotopologues of PYR–CH_4

	[^{14}N]PYR-CH_4	[^{15}N]PYR-CH_4
A/MHz	2995.7148(9)[a]	2961.1510(6)
B/MHz	1873.3363(6)	1872.2691(6)
C/MHz	1853.4941(6)	1838.9538(5)
D_J/kHz	5.46(1)	5.33(2)
D_{JK}/kHz	53.70(6)	[53.70][b]
D_K/kHz	-56.59(8)	[-56.59]
d_1/kHz	-0.23(2)	[-0.23]
χ_{aa}/MHz	3.251(5)	-
$\chi_{bb}-\chi_{cc}$/MHz	-6.137(7)	-
N[c]	55	18
σ/kHz[d]	2.6	2.2

[a] Uncertainties (in parentheses) are expressed in units of the last digit. [b] Fixed to the values of the normal species. [c] Number of transitions in the fit. [d] Standard deviation of the fit.

The rotational spectrum of the ^{15}N isotopologue was searched and assigned after empirical scaling of the rotational constants of the parent species. The unsplit (I = 1/2) transition frequencies were fitted as described above, and the spectroscopic parameters are shown in the right column of Table 2. All experimental transitions are given as Supporting Information.

Clearly, a comparison of the experimental values of the rotational and quadrupole coupling constants (Table 2) to the theoretical values (Table 1) gives an acceptable match only for conformer I (the *ab initio* geometries are available as

Supporting Information). The large values of D_{JK} and D_K indicate a rather flat potential energy function of the bending motions of methane with respect to the aromatic ring, a feature often encountered in rotational analysis of the spectra of aromatic ring with RGs.[21]

In previous investigations of adducts of CH_4 with very small molecules (H_2O, HCl, HF, HCN), many of the microwave transitions appeared as triplets, according to its three nuclear-spin modifications, denoted as *A*, *F*, and *E*.[2,3] In the complexes with slightly heavier molecules, such as OCS and ozone, only doublets were observed, and the splittings among the observed *A* and *F* component lines were quite smaller.[4,5] For PYR-CH_4, we observed only a single spin line for each transition. We think that for such a heavy complex, all nuclear spin components are overlapped with each other.

Further spectral searching has been dedicated to the second conformer of Table 1, but without success. Probably this form is relaxing to the most stable conformer upon supersonic expansion.[22]

Molecular structure

The determination of the structure of PYR-CH_4 was not straightforward, as the molecular cluster is considerably floppy. By combining the rotational constants of the two isotopologues, we could calculate the substitution coordinates[23] of the N atom. The obtained values are shown in Table 3 in the principal axes system of the parent species. The *c* coordinate would have had a slightly imaginary value, but, by symmetry, we fixed it to zero to obtain the *a* and *b* coordinates of Table 3.

Table 3 r_s coordinates (Å) of the N atom in the principal axes system of the parent species. c has been fixed to zero by symmetry.

	a	*b*
Exptl.	±0.411(4)[a]	±1.424(1)
Calc.	-0.441	1.427

[a]Uncertainties (in parentheses) are expressed in units of the last digit.

Motions of methane with respect to pyridine

Upon formation of the complex, the three translational motions of the isolated spherical top CH_4 are replaced by three low energy vibrational modes. The low energy and large amplitude of these motions bring Coriolis coupling contributions to the moments of inertia, rendering defective the usual methods for rigid structure determinations. In consequence we used a procedure accounting for these effects successfully applied in the van der Waals complexes of PYR with Ne, Ar and Xe.[9] One of the large amplitude motions can be described as the stretching between the two centres of mass (CM) of the two constituent molecules, while the remaining ones can be thought as two bending motions of CH_4 around PYR.

a) Stretching motion and dissociation energy

The stretching motion can be, in a first approximation, isolated from the other motions. For such a kind of asymmetric top complex in which the stretching motion between the two subunits is almost parallel to the *a*-axis of the complex, the stretching force constant (k_s) can be roughly estimated to be 2.73 N/m, corresponding to the harmonic stretching fundamental ν_s = 59.0 cm^{-1}, within pseudo-diatomic approximation through the equation:[24]

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

where μ is the pseudo diatomic reduced mass, R_{CM} (3.664 Å from *ab initio* calculation) is the distance between the CMs of the two subunits, and *B*, *C* and D_J are the experimental spectroscopic parameters of Table 2.

A one-dimensional flexible model[25] has been used to calculate the rotational and vibrational energy levels to adjust the values of dissociation energy E_D and equilibrium distance between the two CMs of the two moieties R_e within a Lennard-Jones type potential, in such a way to reproduce ν_s and $(B+C)_0$. Figure 2 shows the Lennard-Jones potential energy curves for PYR-CH_4. The values of E_D = 3.9(1) kJ mol^{-1} and *R* = 3.642(1) Å have been obtained. The calculations have been resolved into 41 mesh points[25] in the range from -2.0 to +2.0 Å with respect to the minimum of the potential energy function.

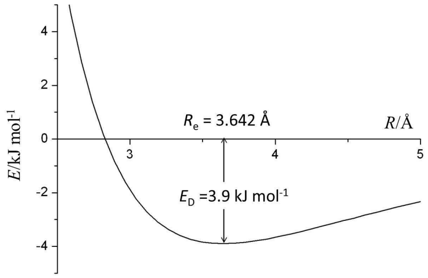


Figure 2 Lennard-Jones potential energy diagrams for the dissociation of PYR-CH_4.

b) Bending motions

The planar moments of inertia are defined and related to the moments of inertia through:

$$M_{aa} = \Sigma_i m_i a_i^2 = 1/2\ (-I_a+I_b+I_c), \text{ etc.} \qquad (3)$$

They represent the mass extension along each principal axis. In going from isolated PYR to PYR-CH_4, the principal axes are switched as shown in Figure 3, but we consider the *x*, *y*, *z* directions to be almost the same for the monomer and the complex. The corresponding changes of the planar moments of inertia are listed in Table 3. The negative values of ΔM_{xx} and ΔM_{yy} are surprising at the first sight. Similar changes in going from pyrimidine to pyrimidine-Ar, have been interpreted as a combination of mass dispersion and vibrational Coriolis coupling associated with the two bendings.[21]

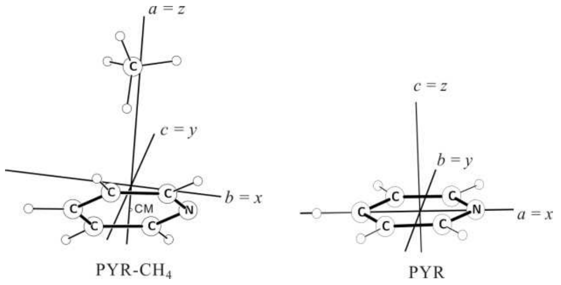


Figure 3 Geometry and principal axis system in PYR-CH4 and PYR. CM is the centre of mass of PYR.

In PYR-CH_4 the problem is slightly different, because CH_4 is not an atom and the four hydrogen atoms contribute to the I_g (g = a, b, c) values. However, assuming a free rotation of CH_4 with respect to PYR, in the $m = 0$ torsional ground state, it will not contribute to the I_a value, while its contributions to I_b and I_c are about the same. As a consequence, the M_{bb} and M_{cc} values do not include the contributions of the four hydrogen atoms. We can apply then the same method used for pyrimidine-Ar to evaluate the force constants of the bending motions of CH_4 with respect to PYR. The two motions are considered local harmonic oscillations, on one side of the aromatic plane, by a model that describes—notation according to the C_s symmetry of the complex—the A' type mode in the xz plane by the displacement X and the A'' type displacement in the y direction by Y,

$$V(X, Y) = (1/2)[k_x Y^2 + k_y (X-X_e)^2] \qquad (4)$$

where X_e is the displacement, within the symmetry plane, of the CM of CH_4 from the z-axis of PYR at equilibrium. The calculation has been done within two-dimensional flexible model, resolving the range (-2.0 Å, +2.0 Å) into 21 mesh points for each of the X and Y displacements.

Since only two experimental data (ΔM_{xx} and ΔM_{yy}) are available, only two of the three parameters X_e, k_x and k_y can be estimated. Thus we assumed $k_x = k_y$, a condition nearly fulfilled for the van der Waals complexes with the same shape as PYR-CH_4. At the meantime, ΔM_{zz} was used to estimate the z-coordinate of the CM of CH_4, Z_0. The best agreement with the experimental data was obtained for the coordinates and listed in Table 3. The result indicates that, at equilibrium position, the CM of CH_4 is 3.544 Å above the ring, and tilted about 6.0° from the CM of PYR towards the nitrogen atom.

Table 3 The values of M_{gg} of PYR and PYR-CH_4 and ΔM_{gg} upon complexion, and the flexible model results corresponding to the parameters determined

(a) Experimetal and calculated data

	M_{gg}(uÅ)		ΔM_{gg}(uÅ)	
	PYR	PYR-CH_4	Exptl.	Calc.
x	87.738(M_{aa})	85.794(M_{bb})	-1.944	-1.944
y	83.974(M_{bb})	82.906(M_{cc})	-1.068	-1.069
z	0(M_{cc})	186.888(M_{aa})	186.888	186.842

(b) Determined parameters

$k_x = k_y = 0.36(1)$ N m^{-1} $X_e = 0.375(1)$ Å $Z_0 = 3.544(1)$ Å

Conclusions

The rotational spectrum of PYR-CH_4 represents an unprecedented investigation of a complex of an alkane with an aromatic molecule. The obtained results point out that CH_4 prefers to locate above the ring and link to PYR through a C-H···π WHB, rather than C-H···n interaction. This behaviour, typical of complexes of PYR with RGs, would suggest classifying CH_4, in relation to his ability to form molecular complexes with aromatic molecules, as a pseudo rare gas. In this sense, and taking into account the dissociation energy of PYR-CH_4, the "rare gas" methane is very similar to Kr, as shown in Figure 4.

We report in Figure 4 the dissociation energies of the complexes of PYR with two families of partners, fluoromethanes (CF_nH_{4-n}, n = 0 to 4) and rare gases (He to Xe). The intermediate members of the CF_nH_{4-n} group (n = 1-3) are linked to PYR through C-H···N and C-H···F WHBs and have higher interaction energies than the members at the extremes. CF_4 (n = 4) is linked through a halogen bond to the N atom, while CH_4 (n = 0), similarly to a rare gas displays the lowest interaction energy of the group. It is also interesting to note a sort of linearity in the dissociation energy of the complexes of RG with the increase of the atomic number: actually such a linearity was found for a plot of the dissociation (E_D) against the RG polarizabilities, as described in Ref. [9g]. Kr and CH_4 have, indeed, very similar polarizabilities (2.448 and 2.465 Å^3, respectively), and this is plausibly the reason of the similar E_D values of their complexes with PYR.

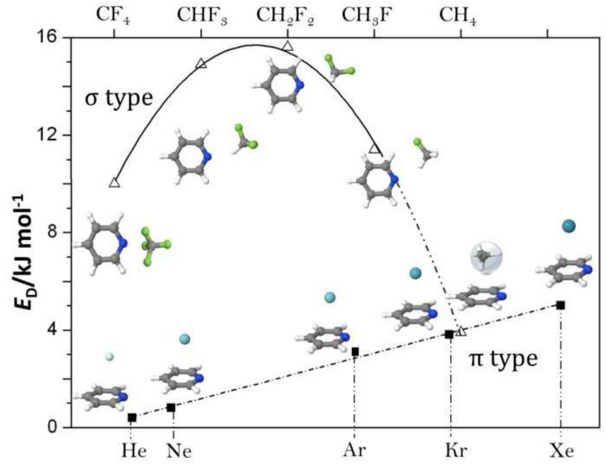


Figure 4 The dissociation energies and the typologies of the complexes that the CF_nH_{4-n} family (n = 0 to 4) and the full set of RGs form with PYR are graphically shown. The member CH_4 behaves similarly to Kr, and it can be considered like a pseudo rare gas.

Despite the low interaction energy, ab initio calculations suggest the directionality of methane towards the π system of PYR in such a way to form a weak hydrogen bond, probably representing a limit case between dispersion and electrostatic forces. CH_4 seems to be "one-leg" connected to the π system of PYR, and to freely rotate around it, as suggested by the rotational constants A, which is larger than the rotational constant C of isolated PYR (2995.715 against 2959.21 MHz).

It seems, in addition, that in such a large complex, a coalescing of the CH_4 spin states takes place.

The internal dynamics in PYR-CH_4 is comparable to that of the van der Waals complexes involving aromatic molecules with RGs. The effects of the CH_4's large amplitude motions on the rotational spectrum have been used to obtain the equilibrium location of the CH_4 moiety and the potential energy surface describing its dynamics.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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