



Interactions between freons and aromatic molecules: The rotational spectrum of pyridine–difluoromethane



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ABSTRACT

The pulsed jet Fourier transform microwave spectrum of the molecular adduct pyridine–difluoromethane shows that the two subunits are linked to each other through a bifurcated CH₂...N and a CH...F weak hydrogen bond. Energies and structural information of these links are given.

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1. Introduction

Probably, after benzene, the prototype aromatic system, pyridine is the best-known heterocyclic aromatic molecule. It has many industrial and pharmaceutical applications and it is a ligand extensively used in coordination [1,2] and surface chemistry [3].

From a spectroscopic point of view, its simple structure has allowed the study of several adducts with several partner atoms or molecules. Depending on the nature of the chemical species linked to pyridine (Py from now on), π or σ type complexes have been observed, in relation to the Py interaction sites, that is the π system of the aromatic ring, or the n orbital of the nitrogen atom.

Py–Metal (metal = Li, Ca, and Sc) complexes have been produced in laser-vaporization molecular beams and studied by ZEKE spectroscopy and theoretical calculations [4]. It has been found that Li and Ca complexes prefer a σ bonding mode, whereas the Sc complex favors a π mode, with bond energies of 27.0, 49.1 and 110.6 kJ mol⁻¹, respectively.

Plenty of information on the typology and strengths of the non-bonding interactions of Py with its partners have been obtained also by rotational spectroscopy [5–20].

Py is the only aromatic molecule for which, thanks to its permanent dipole moment, the rotational spectra of all complexes with rare gases (except radon) have been reported. In all cases, a π -type complex has been observed [5–20], even for complexes with two rare gas atoms, which have a 'double' π arrangement, with one atom above and one below the ring [9,12,13]. The interaction energies are in the range 0.5–5 kJ mol⁻¹.

The molecular adducts of Py with other partners, apart from rare gases, studied by microwave (MW) spectroscopy displayed,

to our knowledge, a σ -type arrangement. Four investigations are available, describing this kind of interaction, on the complexes of Py with simple molecules, such as CO [14], CO₂ [15], SO₂ [16] and SO₃ [17]. All of them are linked to the n orbital of Py, through formal C...N or S...N contacts. In the adduct with SO₃, Py acts as a Lewis base, donating its lone pair to the sulfur trioxide Lewis acid. The S–N bond becomes in this case a covalent bond, with a bond energy of about 120 kJ mol⁻¹.

Also complexes of Py with freons have a σ -type arrangement. This is the case of Py–CF₄, where the two subunits are held together by a CF₃...N halogen bond, with the top undergoing a free rotation with respect to Py [18]. In Py–CHF₃, and Py–CH₃F two weak hydrogen bonds (WHB), C–H...N and C–H...F, are observed [19,20]. The barriers to internal rotation of the CHF₃ and of the CH₃F groups have been determined from the A – E splittings of the rotational transitions.

Unlike CF₄ (spherical top) and CHF₃ or CH₃F (symmetric tops), CH₂F₂ is an asymmetric top freon. We considered interesting to investigate the rotational spectrum of the Py–CH₂F₂ molecular adduct, for which multiple WHB interactions are possible between the constituent monomers. The obtained results are presented below.

2. Experimental

The rotational spectra of the complex were observed in a FTMW spectrometer [21] with a COBRA (Coaxial Oriented Beam and Resonator Axes) configuration [22] in the frequency range 6–18 GHz which has been described previously [23]. Briefly, the experimental detection is made up by three stages. The first step is the creation of the molecular pulse by opening the injection valve allowing the adiabatic expansion of our gas sample in the cavity. The macroscopic polarization of the molecular beam is the next stage. It

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is generated by applying a microwave pulse into the Fabry–Perot resonator where the sample was previously introduced. Finally the following spontaneous molecular emission is digitalized in the time-domain and Fourier transformed in order to obtain the frequency of the rotational transitions of the system under study. Additionally, the coaxial arrangement in the cavity causes the splitting of the molecular signals into two different components due to the Doppler effect. Transitions separated by more than 7 kHz are resolvable with an estimated accuracy above 0.5 kHz.

A mixture of 2% CH₂F₂ in He was flown through commercial samples of Py or ¹⁵N–Py (Aldrich) cooled at 0 °C, at pressures of ca. 0.3 MPa, and it is guided to a pulsed valve where the supersonic jet was created.

3. Computational methods

To explore the conformational landscape of our complex, molecular mechanics calculations were carried out using the Merck Molecular Force Field (MMFFs) [24] implemented in the program MacroModel 9.2 [25]. 62 different structures were identified within a window energy of 50 kJ mol⁻¹, and the provided geometries were later fully optimized with *ab initio* methods at MP2 level in order to get more reliable data for the plausible conformers. Frequency calculations were also performed, to check the nature of the stationary points and to estimate additional spectroscopic parameters, such as centrifugal distortion constants. After the re-optimization, only three conformers with relative energies below 5 kJ mol⁻¹ were found (see Table 1), susceptible to be detected experimentally in the jet. All the calculations were performed with GAUSSIAN 09 [26] suite of programs and using the Pople triple- ζ 6-311++G(d,p) basis set.

To evaluate the dissociation energy of the complex, the geometries of the monomers were optimized and the respective energies, zero point corrected, were calculated. The obtained dissociation energy has finally been corrected for the Basis Set Superposition Error (BSSE) [27]. All obtained energies and spectroscopic parameters of the three most stable conformations are shown in Table 1.

4. Results

According to the theoretical predictions, the most stable conformer (see Table 1) is a near prolate top with a Ray's asymmetry parameter $\kappa \sim -0.97$ with two active selection rules: μ_a and μ_b . As long as the dipole moment is much stronger along the *a*-axis, μ_a -type R bands have been searched first. They are groups of lines evenly separated in frequency by a *B* + *C* value. Two of these bands (*J*: 7–6 and 8–7) are shown in Figure 1. The experimental transi-

tion frequencies have been fitted using Pickett's SPFIT program [28] within semirigid Watson's Hamiltonian [29] in the symmetric reduction and *I'* representation. An additional correction takes into account the quadrupole coupling effect [30] due to the non-spherical charge distribution in the ¹⁴N nucleus. As a consequence of that hyperfine effect, each transition is split into several component lines, as it can be seen in Figure 2.

All obtained spectroscopic parameters are reported in Table 2. The experimental rotational constants are in good agreement with the theoretical values of conformer 1, showing that the conformer identified in the jet corresponds to the most stable species predicted by the theory. From the rotational constants, the inertial defect, Δ_c , has been calculated to be -4.59 uÅ². This value, although slightly higher than that expected for two methylenic hydrogens out of the plane, confirms the conformational assignment. The calculated values of Δ_c are, indeed, -3.75 , -39.64 and -176.20 uÅ² for conformers 1, 2 and 3, respectively. Part of the unassigned transitions recorded in the spectrum could be identified with lines of Py–H₂O [31] or of the (CH₂F₂)_n aggregates (with *n* = 2, 3 and 4) [32–34]. No other conformers were detected in the spectrum, despite the small energy gap between the other predicted structures stabilized by only two hydrogen bonds.

After the spectrum of the parent species, the one of the quadrupole-less complex with ¹⁵N–Py was easily assigned. The obtained spectroscopic parameters are also shown in Table 2.

All measured transitions are available in the Supplementary Material.

When the intermolecular stretching motion leading to dissociation is almost parallel to the *a*-axis of the complex, it is plausible to derive the corresponding force constant within the pseudo diatomic approximation, through the equation [35]:

$$k_s = 16\pi^4(\mu R_{CM})^2[4B^4 + 4C^4 - (B - C)^2(B + C)^2]/(hD_j) \quad (1)$$

μ is the pseudo diatomic reduced mass, R_{CM} is the distance between the centers of the mass of the two subunits, and D_j is the centrifugal distortion constant. Moreover, assuming a Lennard–Jones type potential, the zero point dissociation energy of the complex can be derived applying the approximate expression [36]:

$$E_D = 1/72k_sR_{CM}^2 \quad (2)$$

Hence, the dissociation energy of the complex was found to be 15.6 kJ mol⁻¹, relatively in good agreement with the *ab initio* value. In Table 3, we compare the dissociation energies of the complexes of Py with other freons. There we give the number and kind of interactions linking the freon molecules to Py. One can note that the lower dissociation energy is for Py–CF₄, where the interaction can be classified as halogen bond. The partially hydrogenated

Table 1
Spectroscopic parameters and relative energies of the three most stable conformations of Py–CH₂F₂.

	Conformer 1	Conformer 2	Conformer 3
A/B/C/MHz	4407/587/520	3799/590/532	2383/891/838
$\chi_{aa}/\chi_{bb}/\chi_{cc}$ /MHz	-4.34/1.00/3.34	-3.65/0.67/2.99	3.07/1.51/-4.58
$\mu_a/\mu_b/\mu_c$ /D	-4.24/-0.72/0.0	-3.44/-0.43/-0.91	2.60/-0.38/-1.52
$D_j/D_{jk}/D_k$ /kHz	0.11/1.38/4.60	0.62/-2.39/59.3	0.67/1.83/-0.25
d_1/d_2 /Hz	-12.6/-1.91	48.0/-7.48	-9.77/16.5
$\Delta E_{ZPE}^a/E_d^b$ /kJ mol ⁻¹	0.0 ^c /11.8	1.6/10.5	4.7/3.8

^a Zero point relative energies.

^b Dissociation energy.

^c Absolute energy is $-486.151117 E_h$.

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