Bond energy of complexes of neon with aromatic molecules: rotational spectrum and dynamics of pyridine–neon

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The equilibrium configuration of the very weakly bonded pyridine···Ne complex has been deduced from its free jet millimeter-wave spectrum; the three van der Waals motions have approximated fundamentals in the range 19–31 cm^{-1} and the dissociation energy has been estimated to be 1.1 kJ mol^{-1}.

At very low pressures and temperatures, conditions similar to those of interstellar space, rare gases (RG) form stable adducts with various molecules.[1] It can be questionable if these processes are real chemistry, but we will see that the difference with respect to 'normal' chemistry is quantitative rather than qualitative. The combination of supersonic expansion with spectroscopic techniques[2] has allowed an extensive investigation of the chemistry of these adducts.

Jet cooled rotationally resolved spectra supply the most detailed information on the dynamics (and thus on the binding energy) of the van der Waals motions: the measured distortion from a rigid rotor behaviour is in fact mainly due to the van der Waals vibrations (see for example refs. 3–6).

Taking into account the van der Waals complexes between a RG atom and an aromatic ring molecule investigated with such techniques, about twenty complexes involve an Ar atom while only one (benzene–Ne[7]) involves a Ne atom.[1] This is likely to be due to the lower interaction energy of Ne.

Most of these studies have generally been performed with pulsed molecular beam microwave Fourier transform, as for example benzene–RG[7,8] (RG = Ne, Ar, Kr, Xe) and pyridine–RG[9,10] (RG = Ar, Kr). Recently a direct absorption technique, free jet millimeter-wave absorption spectroscopy, has also been applied to the investigation of such complexes, as, for example, pyrimidine–Ar[6] and pyridazine–Ar.[11]

Here we report the rotational spectrum of pyridine–neon (PYR-Ne), investigated with the latter technique. Fig. 1 shows PYR–Ne, PYR, the switching of the principal axes upon formation of the adduct, and the van der Waals structural parameters.

The Stark and pulse modulated free jet absorption millimeter-wave spectrometer used in this study has already been described elsewhere.[12] The complex was formed by flowing neon at a pressure of *ca.* 1.5 bar over the sample at room temperature, and expanding the mixture through a pulsed nozzle (repetition rate 5 Hz) with a diameter of 0.35 mm, reaching an estimated 'rotational' temperature of *ca.* 7–8 K. Neon (99.995%) was supplied by Linde, and pyridine by Aldrich. The accuracy of the frequency measurements is about 0.05 MHz.

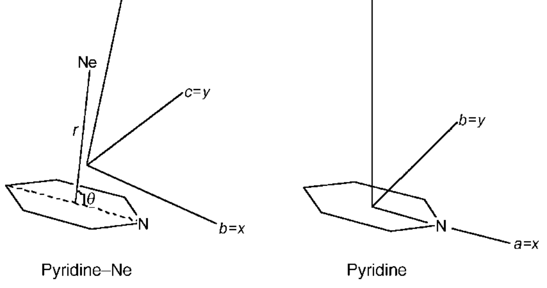

Fig. 1 Geometry and principal axes system in PYR···Ne and PYR.

The first estimate of the rotational constants of PYR–Ne has been based on a model similar to that of Fig. 1, with Ne positioned 3.4 Å above the PYR plane, along the perpendicular to the center of mass (c.m.), and with the r_0 geometry of PYR as in the isolated molecule.[13] The spectrum has been assigned and the 43 measured transitions (available upon the authors) have been fitted with Watson's 'S' reduced Hamiltonian (I^r representation).[14] Quartic and sextic centrifugal distortion parameters where required to fit the spectrum, in accord with the large amplitude inherent in the Ne motions. Only μ_b-type transitions have been observed. Owing to the low value of the μ_a-dipole component and to the high J values involved, μ_a-type transitions were too much weak to be detected with our spectrometer. Table 1 collects the determined parameters.

The three translational motions of the isolated Ne are replaced by three low energy vibrational modes upon formation of the complex. Because of the low energy and large amplitude of these van der Waals motions, which bring Coriolis coupling contributes to the moments of inertia, usual methods for structure determination supply poor results. Here we will apply a method which takes into account these effects. One of the van der Waals motions can be considered the stretching between the two centers of mass of the two constituent molecules, while the remaining ones can be thought of as two internal rotations of Ne around PYR.

The stretching (radial part of the Ne motions) can be, in a first approximation, isolated from the other motions. For asymmetric top complexes in which the stretching coordinate is near-parallel to the inertial a-axis the stretching force constant (k_s) can be estimated by approximating the complex to a molecule made of two rigid parts, by using equations of the type:[3]

$$k_s = 16\,\pi^4\,(\mu_D\,R_{CM})^2\,[4B_D^4 + 4C_D^4 - (B_D - C_D)^2(B_D + C_D)^2]/(hD_J) \qquad (1)$$

The subscript D denotes a dimer quantity, μ_D is the pseudo diatomic reduced mass, R_{CM} is the distance between the centers of mass of the monomers (3.386 Å for PYR–Ne), and D_J is the centrifugal distortion constant. k_s, the corresponding harmonic stretching fundamental (ν_s), the dissociation energy (E_B) and the equilibrium distance of Ne (r_e) from the center of mass of PRM are reported in Table 2, and compared to the correspond-

Table 1 Spectroscopic constants of pyridine–Ne (S-reduction, I^r-representation)

A/MHz	3011.42(7)[a]	d_1/kHz	−0.55(1)
B/MHz	1876.40(7)	d_2/kHz	−0.029(2)
C/MHz	1858.03(7)	H_J/Hz	−1.8(3)
D_J/kHz	20.3(2)	H_{JK}/Hz	−20.3(9)
D_{JK}/kHz	90.7(6)	H_{KJ}/Hz	62(1)
D_K/kHz	−105.2(2)	H_K/Hz	−38.9(4)
N^b	43	σ^c/MHz	0.11

[a] Errors in parenthesis are expressed in units of the last digit. [b] Number of transitions in the fit. [c] Standard deviation of the fit.

Table 2 Parameters describing the van der Waals motions, geometry and dissociation energy for PYR–Ne and PYR–Ar

	PYR–Ne	PYR–Ar[a]		PYR–Ne	PYR–Ar[a]
k_s/N m^{-1}	0.92	3.05	ν_Y/cm^{-1}	19.9	34.5
k_X/N m^{-1}	0.12	0.39	X_e[b]/Å	0.245	0.298
k_Y/N m^{-1}	0.12	0.38	r_e[b]/Å	3.316	3.485
ν_s/cm^{-1}	31.1	44.2	ϕ_e[b]/°	4.2	4.9
ν_X/cm^{-1}	19.6	34.1	E_B/cm^{-1}	90	259

[a] From ref. 4. [b] The equilibrium position of the noble gas is shifted in the direction from the center of mass of the ring towards the nitrogen atom, forming an angle ϕ_e (= 90 − θ of Fig. 1) with the perpendicular to the ring.

ing values for the related complex PYR–Ar.[4] E_B and r_e have been adjusted within a Lennard-Jones type potential in such a way to reproduce ν_s and $(B + C)_0$. A one-dimensional flexible model[15] has been used to calculate rotational and vibrational energy levels. Fig. 2 shows the Lennard-Jones potential energy curves for PYR–Ne and PYR–Ar.

As to the two Ne internal rotations their effects are reflected either in the anomalous high values of the Δ_{JK} and Δ_K centrifugal distortion parameters, as outlined in several of the complexes of aromatic molecules with rare gases (see, *e.g.* refs. 4, 5, 11), and in the negative changes of the planar moments of inertia M_{xx} and M_{yy} (Fig. 1) in going from isolated PYR to PYR–Ne. The procedure to extract the bends van der Waals potential energy parameters from centrifugal distortion is rather complex for low symmetry complexes as PYR–Ne. For this reason we extracted this information for the C_s symmetry PYR–Ne complex from the ΔM_{xx} and ΔM_{yy} values of Table 3. The planar moments of inertia are defined and related to the rotational constants through eqn (2):

$$M_{aa} = \Sigma_i m_i a_i^2 = h/(16\pi^2)\,(-1/A + 1/B + 1/C),\ etc. \qquad (2)$$

They represent the mass extension along the principal axes. Their shifts on going from the isolated molecule to the complex (Fig. 1) are shown in Table 3 for the PYR/PYR–Ne and PYR/PYR–Ar systems. Owing to the axis switching upon formation of the complexes the more consistent quantities ΔM_{xx}, ΔM_{yy} and ΔM_{zz} (Fig. 1) are reported there. The smaller value of ΔM_{zz} for PYR–Ne is in accord with the fact that Ne is lighter than Ar, and closer to the ring center of mass. By contrast, it is difficult, at first sight, to understand the negative value of ΔM_{yy}, and why this value for PYR–Ne is more negative than that of PYR–Ar. A rather simple interpretation of this effect has been given for pyrimidine–Ar,[6] in terms of mass dispersion and vibrational Coriolis couplings associated with the two bendings. The two motions are considered local harmonic oscillations on one side of the ring, by a model that describes the A′ type mode in the *xz* plane by the displacement *X* and the A″ type displacement in the *y* direction by *Y*:

$$V(X,Y) = (1/2)\,[k_x (X - X_e)^2 + k_y Y^2] \qquad (3)$$

where X_e is the displacement, within the symmetry plane, of the neon atom from the *z* axis at equilibrium. The calculations were made by using the two-dimensional version of the above mentioned flexible model,[15] resolving the range (−2.0 Å, +2.0 Å) into 21 mesh points for each of the *X* and *Y* displacements. X_e, k_x, and k_y have been adjusted in order to reproduce ΔM_{xx} and ΔM_{yy}. Since the two pieces of data do not allow one to estimate more than two of the three parameters, we assumed $k_x = k_y$, a condition nearly fulfilled for this kind of complexes.[4] The results are shown in Table 2. Although $X_e = \pm 0.245$ Å was obtained, a comparison with other complexes[4,6] suggests the minus rather than the plus sign and yields $X_e = -0.245$ Å, which means that the vertical on the ring plane passing through the equilibrium position of the neon atom, at 3.316 Å above the ring plane, is tilted by about 4.2° from the center of mass of the ring towards the nitrogen atom. The 'equilibrium' values discussed above refer to the limit situation without van der Waals vibrations, but with half a quantum of each ring vibrations. Despite the fact that Ne is much lighter than Ar, the bend vibrational fundamental frequencies of 19.6 and 19.9 cm^{-1}, are considerably lower than the values of 34.1 and 34.5 cm^{-1} for PYR–Ar,[4] indicating that PYR–Ne is much floppier than PYR–Ar (see Table 2 for a comprehensive comparison).

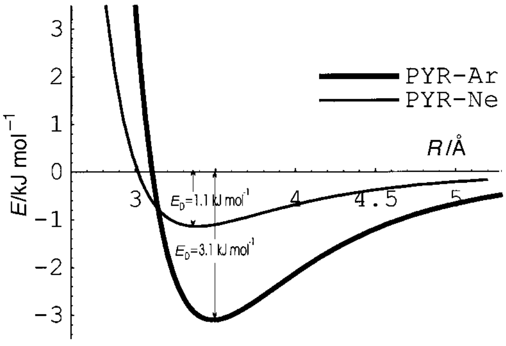

Fig. 2 Lennard-Jones potential energy diagrams for the dissociation of PYR···Ne and PYR···Ar.

Table 3 Shifts of planar moments of inertia (in uÅ^2) in going from the isolated molecule to the complex for PYR–Ne and PYR–Ar

	PYR→PYR–Ne	PYR→PYR–Ar[a]
ΔM_{xx}	−1.838	−1.081
ΔM_{yy}	−1.123	−0.697
ΔM_{zz}	186.775	335.404

[a] From data of refs. 12 and 13.

As a conclusion we can remark that Ne has a binding energy to aromatic molecules which is about 1/3 of that of Ar, and about two–three orders of magnitude smaller of that of normal chemical bonds.

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