Chemistry at Low Pressure and Low Temperature: Rotational Spectrum and Dynamics of Pyrimidine – Neon

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Abstract: The equilibrium configuration, dynamics, and dissociation energy of the very weakly bonded pyrimidine ··· Ne complex have been deduced from its free jet millimeter wave spectrum. The equilibrium distance of Ne with respect to the center of mass of the molecule is 3.27 Å, with Ne tilted 5.1° from the perpendicular to the center of mass of the ring toward the mid-point of the two nitrogen atoms. The dissociation energy is estimated, from the centrifugal distortion constant D_J, to be about 1.3 kJ mol^{-1}.

Keywords: molecular dynamics · rotational spectroscopy · Van der Waals complexes

Introduction

The combination of supersonic expansion with spectroscopic techniques[1] has allowed an extensive investigation of the chemistry of the rare gases, that is the formation of stable adducts of rare gas atoms with various molecules. These adducts do not normally exist on the earth because they are stable only at very low pressure and temperature values, that is in conditions similar to those in interstellar space, where, however, adducts of this form have not been identified so far. Laboratory data would be essential for their search if they would exist there. These adducts can be formed in laboratory by adiabatic expansion; correspondingly the origin of the interstellar space is related to the adiabatic explosion which brought about the formation of the universe.

The dynamics of the Van der Waals motions and the dissociation energies of the rare gas atom can be estimated to an extent which depends on the spectroscopic resolving power and on the symmetry of the rare gas partner molecule.[2] Jet-cooled rotationally resolved spectra supply the most detailed information, since they display the measured distortion from rigid rotor behavior mainly due to the Van der Waals vibrations.[3–7]

Several of the Van der Waals complexes investigated in this way are between a rare gas atom and a molecule with an aromatic ring, probably because of the high number of interaction centers at an almost equivalent distance from the rare gas atom. Most of these complexes (about ten) involve an Ar atom, while only one or two involve a Ne, Kr, or Xe atom,[8] presumably due to the high cost of Kr and Xe, and to the low interaction energy of Ne. It is in fact known that the value of the binding energy is proportional to the atomic number of the rare gas.[9, 10]

These studies have generally been performed with pulsed molecular beam microwave Fourier transform (MBMWFT) spectrometers. Let us consider, for the sake of simplicity, only complexes with aromatic unsubstituted rings. Only adducts with Ar have been studied with MBMWFT for the three prototype five-membered aromatic compounds, furan (furan-Ar[11] was the first observed adduct of a rare gas with a cyclic molecule), pyrrole,[12] and thiophene,[13] and for some other five-membered molecules with two heteroatoms.[14–16] Complexes with six-membered rings have been reported for two molecules, but with several rare gases: benzene – rare gas (rare gas = Ne, Ar, Kr, Xe[10, 17]) and pyridine-rare gas (rare gas = Ar, Kr[18, 19]). Recently we applied a direct absorption technique—free jet millimeter-wave absorption spectroscopy (FJMMWA)—to the investigation of such a kind of complex, and reported the results for some complexes of Ar with aromatic molecules.[7, 20–23] However, due to the weak linkage, we could only recently observe the rotational spectrum of an adduct with Ne, pyrimidine – neon (PRM – Ne). Figure 1 shows PRM – Ne, PRM, the switching of the principal axes upon formation of the adduct, and the Van der Waals structural parameters.

Benzene – Ne is a symmetric top and has a weak but simple spectrum, interpreted in terms of one rotational, and two first-order centrifugal distortion constants.[10] From these data a dissociation energy of 151 cm^{-1} has been calculated.[10] The investigation of an asymmetric top complex such as PRM – Ne would supply more experimental data (three rotational and five first-order centrifugal distortion constants), and possibly give more information on the structure and dynamics of the complex.

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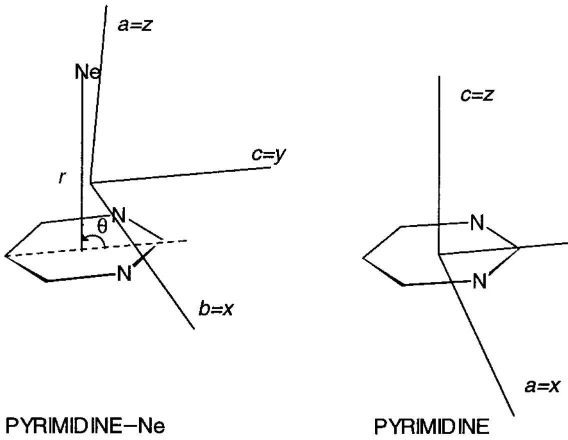

Figure 1. Geometry and principal axes system in PRM···Ne.

Results and Discussion

Rotational spectrum

The first estimate of the rotational constants of PRM–Ne was based on a model similar to that given in Figure 1, with Ne positioned 3.4 Å above the PRM plane, along the perpendicular to the center of mass, and with the r_0 geometry of PRM as in the isolated molecule.[24]

The experimental spectrum showed several high J high K_a μ_c-R-type lines, doubly overlapped due to the K_a near prolate degeneracy of the involved levels. Subsequently, the weaker lines with lower K_a values, resolved in asymmetry doublets, were also been measured. The measured transition frequencies are reported in Table 1. They have been fitted with Watson's S reduced Hamiltonian (I^r representation).[25] Quartic and sextic centrifugal distortion parameters were required to fit the spectrum, in accord with the large amplitude inherent in the Ne motions. The parameters determined are collected in Table 2.

Table 1. Experimental transition frequencies (ν [MHz]) of PRM–Ne.

Doubly overlapped transitions[a] $J'_{K'_a} \leftarrow J''_{K''_a}$	ν	Non overlapped transitions $J'_{K'_a,K'_c} \leftarrow J''_{K''_a,K''_c}$	ν
11(8)–10(7)	60355.24	13(5,9)–12(4,9)	60737.96
12(8)–11(7)	64141.39	13(5,8)–12(4,8)	60737.58
13(8)–12(7)	67917.18	14(5,10)–13(4,10)	64525.33
11(9)–10(8)	62791.86	14(5,9)–13(4,9)	64524.44
12(9)–11(8)	66570.74	15(5,11)–14(4,11)	68302.00
10(10)–9(9)	61465.90	15(5,10)–14(4,10)	68300.45
11(10)–10(9)	65247.55	14(4,11)–13(3,11)	62162.69
12(10)–11(9)	69019.00	14(4,10)–13(3,10)	62129.48
11(11)–10(10)	67724.51	15(4,12)–14(3,12)	65950.44
12(11)–11(10)	71488.58	15(4,11)–14(3,11)	65899.50
13(11)–12(10)	75241.18	16(4,13)–15(3,13)	69728.99
12(12)–11(11)	73981.42	16(4,12)–15(3,12)	69653.27
13(12)–12(11)	77726.49	15(3,13)–14(2,13)	63824.97
12(7)–11(6)	61728.57	15(3,12)–14(2,12)	63209.61
13(7)–12(6)	65512.12	16(3,14)–15(2,14)	67670.45
14(7)–13(6)	69285.09	16(3,13)–15(2,13)	66903.87
13(6)–12(5)	63120.25		
14(6)–13(5)	66900.79		
15(6)–14(5)	70670.51		

[a] Due to the K_a asymmetry degeneracy of levels, only K_a is given.

Table 2. Spectroscopic constants of PRM–Ne (I^r representation, S reduction).

A [MHz]	3136.18(6)[a]	d_1 [kHz]	–0.13(3)
B [MHz]	1946.53(12)	d_2 [kHz]	[0]
C [MHz]	1920.33(16)	H_J [kHz]	–3.5(5)
D_J [kHz]	19.2(4)	H_{JK} [kHz]	–23.0(11)
D_{JK}[kHz]	104.2(6)	H_{KJ} [Hz]	75.2(17)
D_K [kHz]	–118.3(5)	H_K [Hz]	–46.5(6)
N[b]	35	σ [MHz]	0.079

[a] Standard errors are given in parenthesis in units of last digit. [b] Number of transitions in the fit.

Table 3. r_0 and r_s Van der Waals geometry for PRM–Ne.

	Van der Waals parameters ([Å] and [°]) r_0[a]	r_s
r_{CM}	3.338(7)[b]	3.337
θ	82(1)	74.3
	Ne r_s coordinates [Å][c] experimental	calculated[d]
$\lvert x \rvert$	0.340(2)	0.0
$\lvert y \rvert$	0.296(2)	0.465
$\lvert z \rvert$	3.3066(2)	3.3055

[a] From the fit of rotational constants. [b] Error (in parentheses) is expressed in units of the last digit. [c] Coordinates in the principal axes system of PRM. [d] Calculated with the r_0 parameters above.

Geometry

Due to the effects of the Ne motions (see below) only an approximate, but significant, Van der Waals geometry can be obtained with usual methods. We report in Table 3 an r_0 structure, obtained from a fit of the three rotational constants to the two (r and θ) Van der Waals parameters (the geometry of PRM has been fixed to that of the isolated molecule). Alternatively the substitution coordinates were obtained by applying Kraitchmann's equations[26] to the rotational constants of isolated pyrimidine and PRM–Ne, supposing a dummy atom of zero mass to be substituted by an Ne atom. These coordinates are also reported in Table 3, and give more indications on the structure of the complex. The small nonzero values of $|x|$ are attributed to large amplitude motions that underlie this kind of molecular complex,[7] and therefore are compatible with zero equilibrium values. The values obtained are affected by the Coriolis contributions to the moments of inertia, are thus implicitly approximated values. Additional information on the structure and dynamics of the complex can be obtained from the shifts of planar

Abstract in Italian: *Dallo spettro millimetrico in assorbimento del complesso debolmente legato pirimidina···Ne si sono ottenute informazioni sulla configurazione di equilibrio, sulla dinamica e sull' energia di dissociazione. La distanza di equilibrio di Ne rispetto al centro di massa della molecula e' 3.27 Å, con Ne piegato di 5.1° dalla perpendicolare al centro di massa dell' anello verso il punto intermedio della congiungente i due atomi di azoto. L' energia di dissociazione e' stata stimata in ca. 1.3 kJ mol^{-1} dalla costante di distorsione centrifuga D_J.*

moments of inertia on going from the monomer to the complex. The planar moments of inertia are defined and related to the rotational constants through Equation (1).

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

They represent the mass extension along the principal axes. Their shifts on going from the isolated molecule to the complex (see Figure 1) are shown in Table 4 for the PRM/PRM–Ne and PRM/PRM–Ar systems. Since the axis switches upon formation of the complexes, the more consistent quantities ΔM_{xx}, ΔM_{yy}, and ΔM_{zz} (see Figure 1) are reported there. The smaller value of ΔM_{zz} for PRM–Ne is in accord with the fact that Ne is lighter than Ar, and closer to the ring center of mass. Similarly, it is difficult, at a first sight, to understand the negative values of ΔM_{xx} and ΔM_{yy}, and why these values are even more negative for PRM–Ne. A rather simple interpretation of this effect has been given for PRM–Ar, in terms of mass dispersion and vibrational Coriolis couplings.[7]

Table 4. Shifts of planar moments of inertia (in uÅ^2) in going from the isolated molecule to the complex for PRM–Ne and PRM–Ar.

	PRM →PRM–Ne	PRM →PRM–Ar[7]
ΔM_{xx}	−0.971	−0.615
ΔM_{yy}	−1.731	−1.052
ΔM_{zz}	180.830	330.145

Van der Waals motions

The three translational motions of the isolated Ne atom are replaced upon formation of the complex by three low-energy vibrational modes. One of these motions can be considered as the stretching between the two centers of mass of the two constituent molecules, while the remaining ones can be considered as two internal rotations of Ne around PRM.

The radial part of the Ne motions (stretching) 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 expressions such as Equation (2), in which 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 (3.337 Å for PRM-Ne), and D_J is the centrifugal distortion constant.[3, 27]

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

For PRM-Ne k_s, the corresponding harmonic stretching fundamental (ν_s), and the dissociation energy (E_B), obtained assuming a Lennard-Jones type potential, are reported in Table 5, and compared to the corresponding values for the related complexes PRM-A [7] and PRM-water.[28] Figure 2 shows the three Lennard-Jones potential curves.

Table 5. Parameters describing the Van der Waals motions for PRM–Ne and PRM–Ar.

	PRM–Ne	PRM-Ar[7]
k_s[Nm^{-1}]	1.08	2.94
k_X [Nm^{-1}]	0.22	0.52
k_Y [Nm^{-1}]	0.22	0.52
ν [cm^{-1}]	33.8	43.3
ν_X [cm^{-1}]	26.8	39.6
ν_Y [cm^{-1}]	26.7	39.6
Y_e[Å][a]	0.29	0.27
r_e [Å][a]	3.27	3.47
θ_e [°][b]	5.1	4.4
E_B [cm^{-1}]	109	305

[a] The equilibrium position of Ar is shifted in the direction from the center of mass of the ring towards the nitrogen atoms.

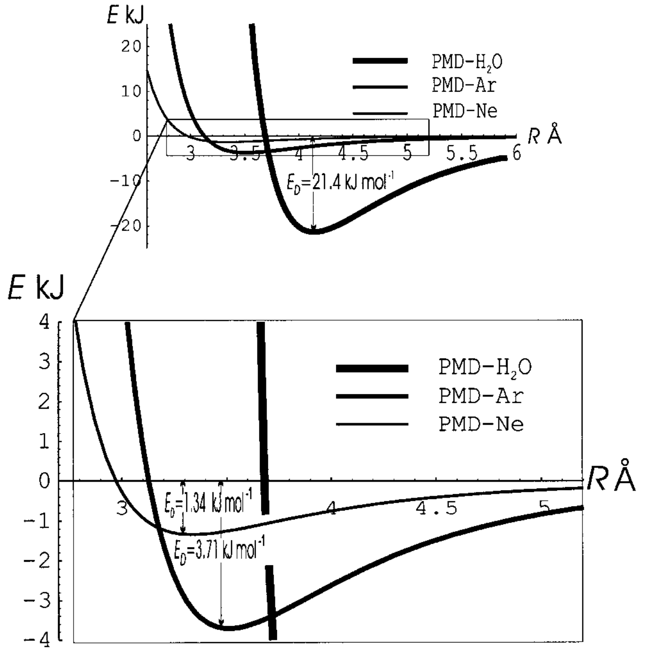

Figure 2. Lennard-Jones potential energy diagrams for the dissociation of PRM ··· Ne, PRM ··· Ar, and PRM ··· water (the last one appears only in the upper graphics). The dissociation energy for a normal bond, that is O–H of water, is 459 kJ mol^{-1}.

As to the two Ne internal rotations their effects are reflected in their contribution to the negative values of ΔM_{xx} and ΔM_{yy}, as mentioned above, and to 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.[4,5,22] The procedure to extract the bends Van der Waals potential energy parameters from centrifugal distortion is rather complex for low-symmetry complexes such as PRM-Ne; thus, we extracted this information for the C_s-symmetric PRM-Ne complex from the ΔM_{xx} and ΔM_{yy} values given in Table 4. 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* [Eq. (3); in which Y_e is the displacement, within the symmetry plane, of the neon atom from the *z* axis at equilibrium].

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

The calculations were made by using the two-dimensional flexible model approach,[29] resolving the range (-2.0 Å, $+2.0$ Å) into 21 mesh points for each of the X and Y displacements.

Since the two pieces of data, ΔM_{xx} and ΔM_{yy} do not allow one to estimate more than two of the three parameters Y_e, k_x, and k_y, we assumed $k_x = k_y$, a condition nearly fulfilled for this kind of complex.[4] The results are shown in Table 5. Although a value of $Y_e = \pm 0.293$ Å was obtained, a comparison with other complexes[4, 7, 18] suggests the minus rather than the plus sign and yields $Y_e = -0.293$ Å, which means that the vertical on the ring plane passing through the equilibrium position of the argon atom, at 3.302 Å above the ring plane, is tilted by about 5.1° from the center of mass of the ring towards the midpoint between the two nitrogen atoms. In spite of the fact that Ne is much lighter than Ar, the bend vibrational fundamental frequencies 26.8 cm^{-1} and 26.7 cm^{-1} are considerably lower than the values of 39.6 cm^{-1} for PRM–Ar,[7] indicating that PRM–Ne is much floppier than PRM–Ar.

Conclusions

It can be questionable if adducts of aromatic molecules with rare gas atoms are real chemical compounds, but in light of the results depicted in Figure 2 and Table 5, it seems that the difference with respect to normal chemical compounds is quantitative rather than qualitative. It can be argued that this kind of study is molecular physics rather than chemistry, but this would be the chemistry of a world with very low standard pressure and temperature. The observed configuration of PRM–Ne is certainly the most stable one; less stable conformers, although not excluded, would relax during the supersonic expansion to the observed one.[31]

Experimental Section

The Stark- and pulse-modulated free jet absorption millimeter-wave spectrometer used in this study has already been described elsewhere.[20, 30] The complex was formed by flowing neon at a pressure of about 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 about 7 K. Neon 99.995 % was supplied by Linde, and pyrimidine by Aldrich. The accuracy of the frequency measurements is about 0.05 MHz.

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