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Free Jet Absorption Millimeter Wave Spectrum and van der Waals Potential Energy Surface of the Pyridazine−Argon Adduct

Walther Caminati,* Aldo Millemaggi, and Paolo G. Favero

Dipartimento di Chimica "G.Ciamician" dell'Università, Via Selmi 2, I-40126 Bologna, Italy

Jan Makarewicz

Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, PL-60780 Poznan, Poland

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The free jet millimeter wave spectrum of the pyridazine−argon molecular complex has been investigated in the 60−78 GHz frequency range. From the information contained in the rotational spectrum the equilibrium position of the argon atom with respect to the center of mass of pyridazine ($x_e = -0.368$, $y_e = 0.0$ and $z_e = 3.427$ Å, respectively) and the two bending and stretching force constants ($f_{xx} = 0.211$, $f_{yy} = 0.214$, $f_{xx} = 2.052$ N m^{-1}, respectively) have been obtained.

Introduction

Molecular complexes between aromatic molecules and rare gas atoms are relatively stable in free jet conditions, and the rotational spectra of several of them have been obtained by molecular beam Fourier transform microwave spectroscopy (MBFTMW).[1−16] Within the six-membered ring aromatics, besides the prototype molecule benzene[10−13] and benzene derivatives,[14−16] only the dimers of argon with pyridine[5,8] have been investigated. Recently, a simple technique, supersonic jet, millimeter-wave absorption spectroscopy, has been applied to the study of this kind of molecular complex. In addition to the investigation of pyridine−Ar in the millimeter-wave range,[17] the spectrum of pyrimidine−Ar has been observed and assigned for the first time.[18] Owing to the "rigidity" and to the high symmetry of the aromatic moiety, it has generally been possible to obtain information on the potential energy surface of the van der Waals motions, whose effects on the rotational energy levels dominate those of the remaining vibrations.

The presence of electronegative interaction centers, such as nitrogen atoms, in the six-membered aromatic ring increases the stability of the complex.[18,19] To further study this effect, we investigated the millimeter-wave absorption free jet spectrum of pyridazine−argon (PRD−Ar; see Figure 1). However, PRD does not have enough vapor pressure at room temperature for our experiments and the heating of the sample raised some technical difficulties. Here, we present the results of our approach to these problems.

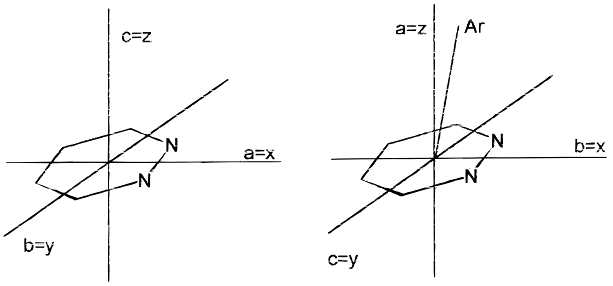
Experimental Part

The Stark and pulse-modulated free jet absorption millimeter-wave spectrometer used in this study has been described elsewhere.[17,20]

A sample of PRD was purchased from Aldrich and used without further purification. The sample seeded in argon at a stagnation pressure of ca. 100 kPa at 60 °C was expanded to about 5 mPa through a pulsed nozzle (repetition rate of 5 Hz) with a 0.35 mm diameter. The accuracy of the frequency measurements is about 0.05 MHz

Rotational Spectrum

The first estimates of the rotational constants of the complex were obtained by attaching an argon atom perpendicular to the ring and across the center of mass of PRD at a distance of 3.5 Å, as suggested for similar molecular aggregates. The r_s geometry of PRD[21] has been assumed to be unaltered in the complex. In going from the molecule to the adduct, an inversion of the principal axis of inertia takes place with respect to the ring skeleton (see Figure 1) so that the predominant μ_a-type spectrum of pyridazine is converted to a predominant μ_b-type spectrum in the adduct. The μ_a value generated by the Ar-ring linkage, even if small, is very important for our technique, which is based on Stark modulation.



a) PYRIDAZINE b) PYRIDAZINE-Ar

Figure 1. (a) Principal axes system in PRD; (b) principal axes system in PRD−Ar.

Several high J, high K_a μ_b-R-type lines doubly overlapped owing to the K_a near-prolate behavior, were assigned first. Later, the weaker lines with lower K_a's with resolved asymmetry doublets have been measured. The measured transitions are listed in Table 1.

All transitions have been fitted with Watson's Hamiltonian.[22] Since PRD−Ar is an almost prolate symmetric top, the S reduction and the I^r representation have been chosen. The spectroscopic constants obtained are reported in the first column of Table 2 together with some statistical parameters of the fits. Three quartic and three sextic centrifugal distortion constants have been determined.

van der Waals Vibrations

The three translational degrees of freedom of the isolated argon atom are replaced by three van der Waals vibrational modes upon formation of the complex. These motions are generally represented as a stretching and two bendings. Information on the force constants for these motions are rather straightforward from the rotational spectrum when the complex is a symmetric top; Legon and Lister for argon−1,3,5-trioxane[23]

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* To whom correspondence should be addressed. Email: CAMINATI@CIAM.UNIBO.IT. Fax: +39-51-259456. Phone: +39-51-259480.

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TABLE 1: Experimental Transition Frequencies of PRD−Ar (MHz)

$J'(K'_aK'_c)-J''(K''_aK''_c)$[a]	ν	$J'(K'_aK'_c)$-$J''(K''_aK'_c)$[a]	ν
10(10)−9(9)[a]	59 995.85	17(8)−16(7)[a]	69 500.11
11(10)−10(9)[a]	62 426.91	17(10)−16(9)[a]	76 972.47
11(11)−10(10)[a]	66 179.88	18(5)−17(4)[a]	60 735.71
12(9)−11(8)[a]	61 108.93	18(7)−17(6)[a]	68 190.93
12(10)−11(9)[a]	64 856.18	18(8)−17(7)[a]	71 920.96
12(11)−11(10)[a]	68 607.29	19(5)−18(4)[a]	63 160.08
13(8)−12(7)[a]	59 796.00	19(7)−18(6)[a]	70 611.61
13(9)−12(8)[a]	63 538.00	20(4,17)−19(3,16)	61 854.23
13(10)−12(9)[a]	67 283.46	20(4,16)−19(3,17)	61 858.33
13(11)−12(10)[a]	71 033.00	20(5)−19(4)[a]	65 582.21
13(12)−12(11)[a]	74 786.75	20(6)−19(5)[a]	69 305.80
14(8)−13(7)[a]	62 224.98	20(7)−19(6)	73 029.78
14(9)−13(8)[a]	65 965.29	21(3,19)−20(2,18)	60 434.49
14(11)−13(10)[a]	73 456.56	21(3,18)−20(2,19)	60 632.23
14(12)−13(11)[a]	77 208.52	21(4,18)−20(3,17)	64 274.25
15(7)−14(6)[a]	60 916.34	21(4,17)−20(3,18)	64 280.07
15(8)−14(7)[a]	64 651.89	21(5)−20(4)[a]	68 002.04
15(9)−14(8)[a]	68 390.52	21(6)−20(5)[a]	71 723.73
15(10)−14(9)[a]	72 132.41	22(3,20)−21(2,19)	62 829.67
15(11)−14(10)[a]	75 878.03	22(3,19)−21(2,20)	63 068.47
16(6)−15(5)[a]	59 611.43	22(4,19)−21(3,18)	66 692.00
16(7)−15(6)[a]	63 343.11	22(4,18)−21(3,19)	66 699.29
16(8)−15(7)[a]	67 077.11	23(4,20)−22(3,19)	69 106.60
16(9)−15(8)[a]	70 813.66	23(4,19)−22(3,20)	69 116.18
16(10)−15(9)[a]	74 553.57	24(4,21)−23(3,20)	71 518.02
17(6)−16(5)[a]	62 038.12	24(4,20)−23(3,21)	71 530.88
17(7)−16(6)[a]	65 768.08		

[a] Transitions are doubly overlapped owing to the near-prolate degeneracy of the involved levels. Only K_a is given ($K_c = J - K_a$ or $J + 1 - K_a$ for the levels of the two component lines, respectively).

TABLE 2: Spectroscopic Constants (I^r Representation, *S* Reduction) Derived from the Observed Spectra and from the Fitted PES of PRD−Ar

	expt	PES
A(MHz)	3094.020(36)[a]	3094.008(5)
B(MHz)	1227.924(12)	1227.944(3)
C(MHz)	1219.798(12)	1219.815(3)
D_J(kHz)	3.666(11)	3.689(3)
D_{JK}(kHz)	20.56(17)	20.57(2)
D_K(kHz)	−22.27(21)	−22.39(4)
H_{JK}(Hz)	−0.84(21)	−0.66(4)
H_{KJ}(Hz)	2.84(44)	2.32(7)
H_K(Hz)	−2.24(47)	−1.99(8)
σ(kHz)	77	10[b]
N[c]	53	45

[a] Errors in parentheses are expressed in units of the last digit. [b] The value of σ for the fit of the Watsonian to the transition frequencies calculated from the PES. [c] Number of fitted transitions.

and Brupbacher et al.[11] for argon−benzene used D_J and D_{JK} centrifugal distortion parameters to estimate the force constants of the stretching and bending motions. For molecular complexes with C_s symmetry the procedure is more complicated. Bettens et al. developed a model obtaining the harmonic local force field from quartic force constants for a series of complexes of C_s symmetry,[24] among them pyridine−Ar, which is somewhat related to PRD−Ar. Alternatively, the direct inversion of the rotational spectrum to the interaction potential parameters has been pursued for benzene−Ar,[11] pyridine−Ar,[19] and 2,5-dihydrofuran−Ar.[25]

Determination of the Potential Energy Surface for Intermolecular van der Waals Vibrations

The complex of the Ar atom with a planar monomer can have two equivalent equilibrium structures with Ar located above or below the monomer plane. These two structures correspond to two local minima in the potential energy surface (PES) of the complex. The Ar atom can move from one minimum to the other one if the potential barrier separating the minima is not too high.

We did not observe in the spectra any evidence for such a tunneling motion of Ar, so we can conclude that the potential barrier is very high. For this reason, we can consider only one structure with Ar located above the monomer plane.

To fit the PES directly to the observed rotational transition frequencies, an analytic representation of this PES and also a dynamical model of the complex have to be specified. Then its rovibrational energy levels have to be calculated by solving the rovibrational Schrödinger equation for the postulated model.

In the proposed model, only the three low-frequency van der Waals vibrations of Ar in the complex were taken into account. The high-frequency harmonic vibrations of the monomer in the complex were neglected because they weakly interact with the van der Waals modes. However, their effect on the structure of the monomer was partly accounted for using an average effective structure of the PRD monomer, instead of its reference structure. Two structural parameters a_x and a_y were chosen to modify the PRD substitution structure,[21] according to a simple rule

$$x_{\mathrm{eff,k}} = a_x x_{\mathrm{e},k} \quad \text{and} \quad y_{\mathrm{eff},k} = a_y y_{\mathrm{e,k}} \tag{1}$$

where $x_{\mathrm{eff},k}$ ($x_{\mathrm{e},k}$) is the effective (equilibrium) x coordinate of the kth nucleus of the PRD monomer. However, both the parameters a_x and a_y could not be simultaneously fitted, owing to a strong correlation, so a_x was fixed to 1.

The contribution of the small amplitude vibrations of the monomer to the rotational energy levels of the complex was accounted for in the Hamiltonian by adding the term $\tau_{zzzz}\, J_z^2$, which is dominant among the other centrifugal distortion terms generated by the monomer vibrations.[24]

In the dynamical model of the complex, three Cartesian coordinates of the position vector $\vec{r}$ of Ar, measured with respect to the principal axis system (PAS) of the monomer, were treated as vibrational coordinates. Additionally, three standard Euler angles were used to describe the rotational motion of the complex. The resulting model was solved by employing the variational method described in ref 19. For the fit of the PES parameters, the rotational transitions up to $J = 21$ were taken into account. The calculation of the energy levels with higher J was unfeasible, owing to the diagonalization of too large Hamiltonian matrices.

The simplest model of the PES can be constructed from pair interactions between Ar and monomer atoms. Such a model is a consequence of the assumption that Ar interacts with the electron cloud of the monomer, which can approximately be partitioned into the electron densities of the atoms forming the monomer. To describe more accurately the electron density, which is high in the regions of multiple bonds and lone electron pairs, we assumed that the Ar atom interacts with some effective interaction centers placed in the monomer. These centers could be shifted from the monomer atoms. For simplicity, the hydrogen atoms as interaction centers were neglected in our PES model, since they do not contribute significantly to the total electron density of the monomer.

The model of pair interactions was improved by including in the potential energy three-body interactions. As a consequence, this potential energy was expressed in the Lennard-Jones form[1]

$$V(\vec{r}) = \sum_i W^2(r_i) + w\sum_{i>j} W(r_i)W(r_j) \tag{2}$$

with two-body interaction term $W(r_i) = V_e(1 - (R_e/r_i)^6)$.

TABLE 3: Structural and Potential Energy Parameters of PDR−Ar, Fitted to Its Rotational Transition Frequencies with $J \leq 21^c$

potential parameters		equilibrium structure		average structure	
V/cm^{-1}	94.86 (4)^a	x_e/Å	−0.368	$\bar{x}$/Å	−0.349
w	−0.0821(5)	z_e/Å	3.427	$\bar{z}$/Å	3.480
R_e/Å	3.68858(8)	r_e/Å	3.447	$\bar{r}$/Å	3.527
ΔX/Å	−0.38868(8)	$\theta_e{}^b$/deg	6.12	$\bar{\theta}$/deg	9.35

[a] Errors in parentheses are expressed in units of the last digit. [b] $\theta = \arccos(z_e/r_e)$ is the angle between the equilibrium position vector of Ar, $\vec{r}_e$, and the z axis of the monomer. [c] Average structure parameters are defined by $\bar{x} = \langle x^2\rangle^{1/2}$ and $\bar{z} = \langle z^2\rangle^{1/2}$.

The Lennard-Jones parameter V_e is the binding energy for the pair interaction potential and R_e is the equilibrium distance at which this potential approaches a minimum; $r_i = |\vec{r} - R_i|$ is the instantaneous distance between the Ar atom and the ith interaction center located at $\vec{R}_i$. All vectors are measured with respect to the PAS of the monomer. Let us note that R_e is different from the equilibrium distance r_e between the Ar atom and the center of mass of the monomer. r_e depends on all two- and three-body interactions and has to be determined numerically after the fitting of the potential parameters.

The interaction centers were assumed to be shifted from the ring atoms of the monomer located at $\vec{A}_i$, so $\vec{R}_i = \vec{A}_i + \vec{R}_i$. All components ΔX_i were assumed to be the same for all ring atoms. ΔY_i and ΔZ_i were taken as zero owing to the symmetry of the PRD monomer. The set of four potential parameters, V, w, R_e, and ΔX, which was selected in preliminary fits, was sufficient to determine adequately the shape of the PES near its minimum.

The standard error of the fit of the above parameters to 45 observed transitions with $J \leq 21$ was 73 kHz. The parameter a_y was determined to be 1.003835(±2), and $a_x = 1$ was fixed. The value of a_y, which is close to 1, indicates that the effective structure of the PRD monomer is only slightly affected by the complexation with the Ar atom.

The influence of the monomer vibrations on the dynamics of the complex, measured by the parameter τ_{zzzz}, is not large. Its value of −0.34(±2) kHz, obtained from the fit, is similar to that of pyridine−Ar (−0.45 kHz).[24]

The values of the PES parameters obtained from the fit are presented in Table 3. The components of the equilibrium position vector of Ar, x_e, y_e, and z_e calculated from the PES, are compared with the corresponding values of $\langle\xi\rangle^{1/2}$ for $\xi = x$ and z, where $\langle\xi^2\rangle$ is the quantum mechanical expectation value of ξ^2 calculated for the ground vibrational state of the complex. The quantities $\langle\xi^2\rangle$ are closely related to an average structure of the complex. Argon average coordinates are very close to r_s coordinates, obtained by applying Kraitchman equations[25] to the rotational constants of isolated PRD and of PRD−Ar. This corresponds to the substitution of a hypothetical atom of zero mass with an argon atom. The so-obtained r_s values are $|z| = 3.4742(1)$, $|x| = 0.473(1)$, $|y| = 0.207(5)$, and $|r| = 3.5124(1)$. In our model, the Ar atom appeared to be shifted from the center of mass of the monomer toward the nitrogen atoms. Such a structure is analogous to the similar complex of pyridine with Ar[19] and of pyrimidine with Ar.[18]

TABLE 4: Fundamental Frequencies, v_ξ (cm^{-1}), Diagonal Force Constants $f_{\xi\xi}$ (N m^{-1}), and Amplitudes $\Delta\xi \equiv (\langle\xi^2\rangle - \langle\xi\rangle^2)^{1/2}$ (Å) of the Three van der Waals Vibrations along $\xi = x, y$, and z, Derived from the PES of PRD−Ar

ξ	ν	f	$\Delta\xi$
x	30.6	0.211	0.308
y	32.2	0.214	0.312
z	43.4	2.052	0.117

From the determined PES, the fundamental frequencies of the van der Waals vibrational modes were calculated. They are presented, together with the mean vibrational amplitudes $\Delta\xi \equiv (\langle\xi^2\rangle - \langle\xi\rangle^2)^{1/2}$, in Table 4. The calculated quantities are very close to those determined previously for pyridine−Ar [19] but the stretching frequency is slightly higher in PRD−Ar. The force field calculated from the PES indicates that the interaction between the van der Waals modes in the ground vibrational state is weak because the off-diagonal constant f_{xz} (0.017 N m^{-1}) is much smaller than the diagonal constants $f_{\alpha\alpha}$, collected in Table 4.

To compare the fitting procedures based on the PES and on the standard Watson's effective rotational Hamiltonian, we derived the *theoretical* rotational constants and centrifugal distortion constants from the obtained PES. For this purpose, the rotational transition frequencies, calculated from the determined PES, were fitted using the Watson's rotational Hamiltonian. The obtained theoretical spectroscopic constants are compared to the corresponding experimental constants in Table 2. The two sets of constants are in a good agreement with each other. Thus, we can conclude that the determined PES correctly reproduces the information on the structure and on the PES of the complex contained in the observed rotational spectra.

Conclusions

The rotational spectrum of the PRD−Ar complex has been measured and assigned using free jet millimeter-wave absorption spectroscopy. The three-dimensional potential energy surface of argon van der Waals vibrations has been determined from the information contained in the rotational spectrum. Since only ground-state measurements are available, the description of the van der Waals motions has been limited to the range near its minimum. The direct observation of van der Waals vibrational satellites would provide precious data to improve the present model.

We measured lines up to $J = 24$ with rotational energy up to 25 cm^{-1}. We did not observe any interaction in the observed spectrum. This fact supports our estimation of the van der Waals vibrational frequencies, which are larger than 25 cm^{-1}.

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References and Notes

(1) Kukolich, S. G.; Shea, J. A. *J. Chem. Phys.* **1982**, *77*, 5242.

(2) Kukolich, S. G.; Aldrich, P. D.; Read, W. G.; Campbell, E. J. *Chem. Phys. Lett.* **1982**, *90*, 329.

(3) Kukolich, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 2207.

(4) Kukolich, S. G.; Campbell, E. J. *Chem. Phys. Lett.* **1983**, *94*, 73.

(5) Klots, T. D.; Emilsson, T.; Ruoff, R. S; Gutowsky, H. S. *J. Phys. Chem.* **1989**, *93*, 1255.

(6) Bohn, R. K.; Hillig, K. W. D., II; Kuczkowski, R. L. *J. Chem. Phys.* **1989**, *93*, 3456.

(7) Spycher, R. M.; Hausser-Primo, L.; Grassi, G.; Bauder, A. *J. Mol. Struct.* **1995**, *351*, 7.

(8) Spycher, R. M.; Petiprez, D.; Bettens, F. L., Bauder, A. *J. Phys. Chem.* **1994**, *98*, 11863.

(9) Oh, J. J.; D.Hillig, K. W., II; Kuczkowski, R. L.; Bohn, R. K. *J. Chem. Phys.* **1990**, *94*, 4453.

(10) Brupbacher, Th.; Bauder, A. *Chem. Phys. Lett.* **1990**, *173*, 435.

(11) Brupbacher, Th.; Makarewicz, J.; Bauder, A. *J. Chem. Phys.* **1994**, *101*, 9736.

(12) Klots, T. D.; Emilsson, T.; Gutowsky, H. S. *J. Chem. Phys.* **1992**, *97*, 5335.

(13) Arunan, E.; Emilsson, T.; Gutowsky, H. S. *J. Chem. Phys.* **1993**, *99*, 6208.

(14) Jochims, E.; Grabow, J.-U.; Stahl, W. *Z. Naturforsch.* **1992**, *A47*, 681.

(15) Stahl, W.; Grabow, J.-U. *J. Mol. Spectrosc*. **1993**, *158*, 278.

(16) Jochims, E.; Mäder, H.; Stahl, W. *J. Mol. Spectrosc*. **1996**, *180*, 116.

(17) Melandri, S.; Maccaferri, G.; Maris, A.; Millemaggi, A.; Caminati, W.; Favero, P. G. *Chem. Phys. Lett.* **1996**, *261*, 267.

(18) Caminati, W.; Melandri, S.; Favero, P. G.; Meyer, R. *Chem. Phys. Lett.* **1997**, *268*, 393.

(19) Makarewicz, J.; Bauder, A. *Mol. Phys*. **1995**, *84*, 853.

(20) Melandri, S.; Caminati, W.; Favero, L. B.; Millemaggi, A.; Favero, P. G. *J. Mol. Struct*. **1995**, *352/353*, 253.

(21) Werner, W.; Dreizler, H.; Rudolph, H. D. *Z. Naturforsch.* **1967**, *22A*, 532.

(22) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: New York, Amsterdam, 1977; Vol. 6, p 1.

(23) Legon, A. C.; Lister, D. G. *Chem. Phys. Lett.* **1993**, *204*, 139.

(24) Bettens, R. P. A.; Spycher, R. M.; Bauder, A. *Mol. Phys*. **1995**, *86*, 487.

(25) Caminati, W.; Melandri, S.; Favero, P. G.; Makarewicz, J. *Mol. Phys.* **1997**, *91*, 663.

(26) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17.