Intermolecular dynamics of NH₃-rare gas complexes in the ν_2 umbrella region of NH₃ investigated by rovibrational laser jet-cooled spectroscopy and *ab initio* calculations

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Abstract

High resolution jet-cooled spectroscopy experiments have been realized to investigate the intermolecular dynamics of van der Waals (vdW) heterodimers between NH₃ and rare gas (Rg) atoms in the ν_2 umbrella mode region of NH₃. With respect to a previous study dedicated to NH₃-Ar [Asselin et al. Mol. Phys. **116**, 3642 (2018)], the sensitivity and spectral resolution of our laser spectrometer coupled to a pulsed supersonic jet have been significantly improved to derive more accurate excited state spectroscopic parameters from rovibrational analyses. In addition, we calculated the ground and ν_2 excited vibration-rotation-tunneling (VRT) states of these complexes on the four-dimensional *ab initio* potential energy surfaces from Loreau et al. [J. Chem. Phys. **141**, 224303(2014), *ibid.* **143**, 184303 (2015).] Transition frequencies and intensities of the allowed $\nu_2 = 1 \leftarrow 0$ transitions obtained from the calculated energy levels and wave functions agree well with the experimental data and are helpful in their analysis. By means of a pseudodiatom model with the assumption of weak Coriolis coupling, the rovibrational analysis of both the $\Pi_{e/f}(j=1, k=0) \leftarrow \Sigma_f(j=1, k=0)$ and $\Sigma_f(j=1, k=0) \leftarrow \Sigma_f(j=0, k=0)$ transitions in ortho NH₃-Rg (Rg= Ne, Ar, Kr, Xe) complexes enabled us to determine reliable excited state parameters and derive accurate values of the effective vdW bond length R_{eff} , force constant k_s , and vdW stretching frequency ν_s . Comparison between the experimental structural parameters and those from the *ab initio* calculated VRT levels shows good agreement for NH₃-Ne, NH₃-Ar and NH₃-Kr, and a similar variation of R_{eff} , k_s , and ν_s with the polarizability of Rg in the ground and ν_2 excited states. Anomalously small values of ν_s et k_s derived for NH₃-Xe in the $\Pi_{e/f}(j=1, k=0)$ state suggest that the applied model is not valid in this case, due to the presence of another state coupling to the perturbed Π_f state. Such a state could not be found, however.

Introduction

Over the three last decades, a large number of spectroscopic and theoretical studies of NH₃-containing van der Waals (vdW) complexes have been undertaken, leading to a better understanding of weak interactions involving NH₃.¹⁻¹⁰ Among them, binary complexes consisting of a rare gas (Rg) atom bound to NH₃ offer the possibility to build advanced theoretical models to describe such interactions since

the Rg atom behaves as a structureless probe. However, past experimental and theoretical results highlighted that the internal rotation and inversion degrees of freedom of the NH₃ subunit within the complex make it quite challenging to characterize such systems. Nevertheless, NH₃-Rg complexes are good prototypes to investigate in detail inter- and intramolecular dynamics. In particular, the inversion-tunneling splitting in NH₃ represents a valuable probe of the asymmetry in the intermolecular potential energy surface (IPES) and in the vibration-rotation-tunneling (VRT) states of NH₃ complexes along the inversion coordinate. In many previous high resolution spectroscopic studies of NH₃-containing complexes^{11,12,13}, it was shown that NH₃ acts as a hydrogen acceptor upon complexation, which leads to a large asymmetry in the NH₃ inversion potential that quenches the tunneling. The NH₃-Rg complexes form an exception to this case.

NH₃-Ar was the first vdW complex of the series to be extensively studied both in the microwave^{3,4} and far-infrared⁷ regions. Besides assigned pure rotational transitions, many other transitions due to the non-rigidity of the complex were observed and attributed to inversion-tunneling transitions, which showed that ammonia behaves as a nearly free rotor in the complex.^{5,6,7,8,9} This large collection of results provided further evidence for the free-rotor picture from the precise knowledge of the bound states of the complex with approximate quantum numbers j and k that correlate to the $j_k = 0_0, 1_0$ and 1_1 levels of free NH₃. Also, vibrational excitations in the vdW ν_s stretch coordinate were identified in these states. Early *ab initio* studies combined with these in-depth far-infrared measurements and considering the interplay of anisotropy in the well depth, Coriolis interactions, NH₃ inversion tunneling and degenerate NH₃ states led to a semi-empirical IPES.¹⁰ Recently, more sophisticated IPESs have been developed to improve the understanding of spectroscopic data, such as the four-dimensional one computed by Loreau et al.¹⁴ that includes explicitly the ν_2 umbrella motion of NH₃ and ND₃, which will be used in the present study (see Section I). Further insight into the internal-rotation dynamics of the complex could be obtained from a direct comparison between the bound states of both NH₃-Ar and ND₃-Ar calculated for total angular momentum values up to $J = 10$ with the inclusion of Coriolis interactions, and all spectroscopic data collected in both the microwave and far-infrared regions for both complexes.

Advanced microwave studies of three other members of the NH₃-Rg family were reported by Jäger et al.^{15,16,17}, including the study of several isotopologues (up to ten for the NH₃-Kr complex) and the support of *ab initio* calculations. Ground state spectroscopic constants were used to derive molecular parameters from a pseudodiatom model. The observation of two inversion components for each deuterated isotopologue provided evidence of inversion tunneling in the ground internal rotor state. As expected, the *ab initio* potential energy surfaces display deeper wells for Xe compared to Ne-, Ar- and Kr-, while the observed rotational spectra indicate nearly free internal rotation of NH₃ unit within the complex whatever the Rg atom.

Mid-^{18,19} and near-infrared²⁰ data on NH₃-Rg remain scarce due to the lack of broadband laser sources in both regions. Using a microwave-sideband CO₂ laser

optothermal spectrometer, Fraser et al.¹⁸ observed in the ν_2 inversion mode region an ortho $\Pi_{e/f}(j=1, k=0) \leftarrow \Sigma_i(j=1, k=0)$ -type transition (where the subscripts ‘e’ and ‘f’ designate symmetric and antisymmetric NH_3 inversion wave functions, respectively) and derived spectroscopic constants containing information about the ν_2 dependence of the NH_3 interaction. Previously, Fraser et al.³ had detected a laser coincidence at 938.6893 cm^{-1} assigned to the P(5) line of the para $\Pi(j=1, k=1) \leftarrow \Sigma(j=1, k=1)$ transition while Bizzari et al.¹⁹ found two more located at about 32 and 36 cm^{-1} above this frequency. These results were taken as further evidence that the NH_3 inversion frequency is essentially unchanged upon complexation, since the tunneling splitting in the $\nu_2=1$ state of free NH_3 is about 36 cm^{-1} .

More recently, high resolution infrared laser jet-cooled measurements were realized in the ν_2 umbrella mode region of $\text{NH}_3\text{-Ar}$ using a pulsed supersonic jet coupled to a laser spectrometer (named SPIRALES) implemented at the MONARIS laboratory.²¹ Two bands in ortho- $\text{NH}_3\text{-Ar}$ and three bands in para- $\text{NH}_3\text{-Ar}$ were unambiguously assigned in the $936\text{-}975 \text{ cm}^{-1}$ region based on a rovibrational analysis for the ortho ones, and by comparison with *ab initio* VRT levels from the 4D IPES of Loreau et al.¹⁴ for the para ones. The *ab initio* results for both the ortho and para species turned out to be very predictive in terms of band centers, upper state rotational constants, and relative weight of Coriolis couplings in the ground and excited ν_2 states.

The present study aims to investigate more in detail the intense ortho bands of the $\text{NH}_3\text{-Rg}$ family with $\text{Rg} = \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$ using the SPIRALES set-up taking advantage of recent improvements of the set-up’s performances in terms of line widths and absorption. The upper vibrational states investigated, above 900 cm^{-1} , are well above the dissociation limits inferred from quantum dynamics calculations on *ab initio* potentials. This raises the interesting issue of investigating vibrational predissociation dynamics within the $\text{NH}_3\text{-Rg}$ series to prove the existence of ultra-long lived vibrational Feshbach resonances in atom-molecule systems. Unfortunately, our experimental line widths are dominated by residual static and dynamic Doppler contributions at the slit jet temperature, and are on the order of about 60 MHz, which precludes a vibrational dynamics study. In the following, we will treat the excited vibrational states of $\text{NH}_3\text{-Rg}$ as quasi-bound states. This assumption is justified by the study of Fraser et al.¹⁸ who measured linewidths up to 3 MHz (compared to 0.5 MHz for free NH_3) for many transitions of the ν_2 inversion mode of $\text{NH}_3\text{-Ar}$, which establishes a lower bound to the vibrational predissociation lifetime of about 50 ns. This result might be compared to measurements on ground state $\text{NH}_3\text{-Ar}$ in the far-infrared range, where linewidths as low as 600 KHz were obtained from hyperfine analyses,⁶ which confirms the predissociation broadening of the ν_2 excited levels.

On the other hand, the substantial gain in absorption in our experiments makes it possible to derive accurate excited state rotational and quartic distortion parameters from rovibrational analyses of the ortho $\Pi_{e/f}(j=1, k=0) \leftarrow \Sigma_i(j=1, k=0)$ transition as well as the doubling constant q which contains indirect information about the relative positions of the $\Pi_{e/f}$ states of different parity, and about the position of

the neighboring Σ_f state perturbing the Π_f state. The precise position of the Σ_f state could be directly determined from the analysis of the ortho $\Sigma_f(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$ transition. Using a pseudodiatomic model, molecular parameters of the $\text{NH}_3\text{-Rg}$ family are estimated from the set of experimental spectroscopic constants, which enabled us to follow their evolution with the polarizability of the Rg atom. These experimental molecular parameters are compared with those derived from *ab initio* VRT levels, transition frequencies and line strengths based on 4D IPESs that explicitly include the NH_3 umbrella inversion motion. The predictive character of the *ab initio* VRT levels enabled us to explain the unexpected molecular parameter values for $\text{NH}_3\text{-Xe}$, which do not show the good agreement between spectroscopic constants and derived molecular parameters obtained for the three other $\text{NH}_3\text{-Rg}$ complexes. Based on the energy difference between both the $\Pi_{e/f}(j=1,k=0)$ states and the $\Sigma_f(j=1,k=0)$ states of $\text{NH}_3\text{-Rg}$ complexes, the possibility of a perturbation has been examined.

I Theory: rovibrational state calculations

The bound states of the $\text{NH}_3\text{-Rg}$ complexes have been computed on the global 4D IPES reported in Refs. [14,22], for the most abundant isotope of neon and argon and for the standard atomic weight in the case of krypton and xenon. The IPES depends on four coordinates: the length R of the vector $\mathbf{R}$ pointing from the center of mass of the ammonia molecule to the rare gas atom, two spherical angles θ and φ that define the orientation of this vector $\mathbf{R}$, and the NH_3 umbrella inversion coordinate ρ . The N-H bond length r was fixed at its vibrationally averaged value, $r_0 = 1.9204 a_0$ derived from a submillimeter and far-infrared spectroscopic study of the ground state of NH_3 ²³.

The IPESs were constructed through calculations with the coupled-cluster method with single, double, and perturbative triple excitations [CCSD(T)] with the aug-cc-pVQZ basis set for all atoms, supplemented by a set of mid-bond functions. In addition, the 10 and 28 core electrons of Kr and Xe, respectively, were described by relativistic pseudopotentials.²⁴ The IPESs were fitted based on 10472 unique geometries for $\text{NH}_3\text{-Ne}$, 6820 points for $\text{NH}_3\text{-Ar}$ and $\text{NH}_3\text{-Kr}$, and 6160 points for $\text{NH}_3\text{-Xe}$. The IPESs show similar characteristics along the rare gas series; further details of the calculation of the IPESs and their features can be found in Ref. [22]. The minimum of the IPES always occurs for $\varphi = 60^\circ$, i.e., when the rare gas atom is located in the plane that contains the C_3 axis and passes midway between the two hydrogen atoms.

The equilibrium value of θ decreases from 87.5° for $\text{NH}_3\text{-Ne}$ to 79.9° for $\text{NH}_3\text{-Xe}$, while the equilibrium distance R_e increases from $6.23 a_0$ for $\text{NH}_3\text{-Ne}$ to $7.35 a_0$ for $\text{NH}_3\text{-Xe}$. There are three saddle points at $\varphi = 0^\circ$ (with values of θ decreasing from 77.2° for Ne to 46.3° for Xe), $\theta = 0^\circ$, and $\theta = 180^\circ$; the corresponding energy barriers hinder the rotation of NH_3 in the complex. The accuracy of the IPES has already been

established for NH₃-Ar by comparison with spectroscopic^{14,21} and scattering experiments^{25,26}, while for Ne, Kr, and Xe the present work represents the first test of the IPESs. The calculation of the bound states of the complexes with NH₃ either in the $v_2 = 0$ state or in the $v_2 = 1$ state has been performed following the approach detailed in our previous work.²¹ Briefly, the Hamiltonian of the complex is

$$H = H_{\text{NH}_3} - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{1}{2\mu R^2} (J^2 + j^2 - 2\mathbf{j} \cdot \mathbf{J}) + V(R, \theta, \varphi, \rho) \quad (1)$$

where μ is the reduced mass of the system and H_{NH_3} is the Hamiltonian of the NH₃ monomer that depends explicitly on the umbrella coordinate ρ . We obtained the bound states energies and wave functions of the complex by means of a variational approach²⁷ with the basis

$$|j, k, \Omega, J, M, n, v\rangle = \left[\frac{(2j+1)(2J+1)}{32\pi^3} \right]^{1/2} D_{Kk}^{(j)*}(0, \theta, \varphi)^* D_{MK}^{(J)*}(\alpha, \beta, \gamma)^* \frac{\chi_n(R)}{R} \phi_v^\pm(\rho) \quad (2)$$

where j and k are the rotational quantum numbers of NH₃, J is the total angular momentum, K is its projection on the intermolecular bond axis, M is its projection on the space-fixed z-axis, D denotes the Wigner functions, and (α, β, γ) are the overall rotation angles of the complex. $\phi_v^\pm(\rho)$ are eigenfunctions of the umbrella motion in free NH₃, with the superscript $\pm$ labeling the symmetric and antisymmetric umbrella tunneling components of each v . In this work we considered the first four wave functions corresponding to $v_2 = 0$ (ϕ_0^+ and ϕ_0^-) and $v_2 = 1$ (ϕ_1^+ and ϕ_1^-), which are obtained by solving the one-dimensional Schrödinger equation for the umbrella motion.²⁸ Finally, $\chi_n(R)$ is a set of radial basis functions. These functions are obtained using an effective radial potential of the form $V_{\text{eff}}(R) = \alpha [V_0(R) + \zeta R]$, where $V_0(R)$ is a radial cut through the minimum of the 4D PES. The parameters α and ζ were optimized by minimizing the energy of the lowest rovibrational state of the complexes. The optimized values are given in Table 1. The basis contained angular functions with $j_{\text{max}} = 10$ and 20 radial functions $\chi_n(R)$ calculated on an equidistant radial grid of n_R points between R_{min} and R_{max} . The grid parameters are also given in Table 1. For each irreducible representation of the full molecular symmetry group $D_{3h}(M)$, we calculated the lowest 20 eigenvalues of the Hamiltonian for J ranging from 0 to 10 by means of the iterative Davidson algorithm.²⁹

As in Ref. [21], the intensities of all allowed transitions between the VRT states were calculated for each complex in order to generate a theoretical spectrum corresponding to the $v_2 = 0 \rightarrow 1$ transition. The line strengths of the transitions were computed from the wave functions of the bound states and the dipole moment function corresponding to the $v_2 = 0 \rightarrow 1$ transition in the complex. The spectra are

obtained from the line strengths assuming a Boltzmann distribution of the lower states.

The ground state of all ortho-NH₃-Rg complexes is a Σ state with the approximate quantum number $K = 0$, with dissociation energies D_0 that range from 30.35 cm⁻¹ for NH₃-Ne to 144.36 cm⁻¹ for NH₃-Xe. In Table 2 these values of D_0 are compared with the binding energies D_e . We observe that the zero-point energy accounts for about 55% of the binding energy for NH₃-Ne, while this decreases along the rare gas series to 27% for NH₃-Xe. By comparison with the results presented in Table II of Ref. [22] we observe that the energy of the ground state of all the complexes is above the two saddle points of the PES that appear respectively at $\varphi = 0^\circ$ (and values of θ that depend on the Rg atom) and $\theta = 0^\circ$, while it is above the saddle point at $\theta = 180^\circ$ only for NH₃-Ne.

II- Experimental

The rovibrational spectra recorded in the region of the ν_2 umbrella mode of NH₃-Rg (Rg = Ne, Ar, Kr, Xe) have been obtained using the SPIRALES set-up, a jet-cooled laser spectrometer which couples an external-cavity quantum cascade laser (EC-QCL) and a pulsed free supersonic jet to probe by direct absorption the molecular complexes cooled down in the adiabatic expansion. SPIRALES has already been described in detail in recent papers^{30,31} and only the main characteristics and most recent developments will be presented hereafter.

The light source is a continuous-wave room-temperature mode hop-free EC-QCL with a spectral width of about 10 MHz, which covers the 930–990 cm⁻¹ range (Daylight Solutions). Less than 10% of the total light is sent through two additional laser channels for relative and absolute frequency calibrations reaching a precision of about 0.0005 cm⁻¹, while the main part is sent through a multipass optical cavity mounted in the jet chamber and composed of two 1.5" astigmatic mirrors (R = 99.2%, AMAC-36, Aerodyne Research) aligned according to a 182-pass configuration.

The molecular jet is produced from a pulsed nozzle (General Valve Series 9) by fitting a 0.9 mm diameter pin hole nozzle with two modified industrial blades, forming a 30 mm length x 150 μ m width slit opening, and serving as the molecular expansion source. With respect to the first version of pulsed slit nozzle²¹ two major changes were made: (i) Due to the very short distance ($\sim$ 1 mm) between the pin hole and the blades forming the slit, a strongly inhomogeneous distribution of the gas between the center and both ends of the slit is expected leading to a nearly axially symmetric behavior and consequently to residual Doppler line broadenings and reduced absorption pass. To overcome this a six-way distribution gas channel already used by the Calgary group³² is implemented between the pinhole and the slit zones. Experimental full-width-at-half-maximum (FWHM) line widths of rovibrational lines measured in the present work reach typically 40 MHz, (ii) Owing to the delicate parallelism adjustment of blades initially spaced by 50 μ m, the slit width is enlarged

by a factor 3 to minimize width change effects. With this new slit version, the gain in intensity in similar experimental conditions is a factor of 5.

To reach a better precision of spectroscopic parameters derived from the rovibrational analyses for all $\text{NH}_3\text{-Rg}$ complexes, the dilution conditions of the ternary mixture $\text{NH}_3/\text{Rg}/\text{He}$ have been systematically explored to get the highest absorption signal. Compared to the previous $\text{NH}_3\text{-Ar}$ study, larger Rg/NH_3 ratios and higher total backing pressures up to 8 bar have been used. Rovibrationally cooled complexes were probed by the infrared laser light at axial distances not larger than 3 mm from the nozzle exit to keep a sufficient density of van der Waals complexes to be probed in the slit jet expansion.

III- Jet-cooled laser spectra results

In the following, we present two series of rovibrational bands of ortho $\text{NH}_3\text{-Rg}$ observed in the region of the $\nu_2 = 1 \leftarrow 0$ NH_3 monomer band. Both transitions involve the same initial level in the ground state, i.e. $\nu_2 = 0$, $K=0$ (Σ state) and two different levels in the $\nu_2 = 1$ excited state, $K = 0$ (Σ state) and $K = 1$ (Π state). In the following, these transitions will be labeled $\Pi_{e/f}(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$ and $\Sigma_f(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$. Guided by the results of previous infrared experiments on $\text{NH}_3\text{-Ar}$, gas mixture and backing pressure conditions could be optimized on the intense ortho $\Pi_{e/f}(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$ transition of this complex before recording the much weaker bands such as for $\text{NH}_3\text{-Ne}$ and $\text{NH}_3\text{-Xe}$. In spite of the use of large helium backing pressures to observe the ortho bands of $\text{NH}_3\text{-Rg}$, no absorption signal of $\text{NH}_3\text{-He}$ (expected around 950 cm^{-1} for the $\Pi_{e/f}(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$ transition) could be detected, probably due to the very small binding energy of this complex.

Fig. 1 displays the four EC-QCL jet-cooled spectra of $\text{NH}_3\text{-Rg}$ for $\text{Rg} = \text{Ne}, \text{Ar}, \text{Kr},$ and Xe observed in the $947\text{-}957\text{ cm}^{-1}$ range. The spectra are locally blurred around 948.222 and 951.778 cm^{-1} by intense absorptions of the NH_3 monomer but no overlap has been observed with rovibrational lines of the vdW complexes. The rovibrational band contour is typical of a $\Pi \leftarrow \Sigma$ -type vibrational band of a linear molecule with characteristic features such as a strong Q branch, the presence of a $R(0)$ line and the absence of a $P(1)$ line evidenced by the simulations shown below. As seen in Fig. 1, the Q branch is fully resolved in J for each of the $\text{NH}_3\text{-Rg}$ complexes, as a consequence of the improved gas homogeneity provided by the multichannel distribution along the slit nozzle which strongly reduces the Doppler broadening. The spectrum of $\text{NH}_3\text{-Kr}$ in natural abundance, as used in the present study, displays a characteristic $P(J)$ and $R(J)$ line structure which evidences the presence of four main isotopes: ^{82}Kr (11.3%), ^{83}Kr (11.5%), ^{84}Kr (57.0%) and ^{86}Kr (17.3%) (see a zoom of the $P(7)$ line of the $\text{NH}_3\text{-Kr}$ spectrum in Fig. 1). In the following, our rovibrational analyses will be focused on the dominant isotope of each rare gas while those concerning the different Kr isotopes are presented in the ESI.

It is noteworthy that P(J), Q(J) and R(J) lines with high values of J (up to 15 for Ne, larger than 24 for Ar, Kr, Xe) are still sufficiently intense to be observed, which means that the rotational temperature of the vdW complexes is higher than in our previous study. Finally, Fig.1 (left) clearly illustrates that the asymmetry of the Q branch changes notably with the Rg atom, first degraded to the high-frequency side for Ne and then more and more degraded to the low-frequency side, from Ar to Xe.

For the ortho $\Pi_{e/f}(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$ transition, we should consider the Coriolis coupling between $\Pi_f(j=1,k=0)$ and $\Sigma_f(j=1,k=0)$, two states spaced by about 10 cm^{-1} with the same j and J and the same parity f , but with different K values. The doubling constant q , which represents the energy splitting $\Delta E_{\Pi} = E_{\Pi_e} - E_{\Pi_f}$ between the unperturbed e and perturbed f components of the Π state, occurs in the energy expression of the P, Q and R transitions

$$E(\pm, J, K) = \nu_0 + B[J(J+1) - K^2] - D_J[J(J+1) - K^2]^2 + H_J[J(J+1) - K^2]^3 \pm (q/2)J(J+1) \pm (q_D/2)J(J+1)^2 \pm (q_H/2)J(J+1)^3 \quad (3)$$

where ν_0 , B , D_J , H_J , q , q_D and q_H are fit parameters for the excited state. The + sign is taken for the upper state in the Q-branch transition and the – sign is taken for the upper state in the P- and R-branch transitions of the K -doubled pair in the excited $\Pi(j=1,k=0)$ state. This expression has been applied in the rovibrational analysis of all transitions in ortho $\text{NH}_3\text{-Rg}$, but it is not applicable to transitions in para $\text{NH}_3\text{-Rg}$, due to the larger density of interacting states.²¹ We use a model dealing with the interacting Σ_f and Π_f excited states in which the energy spacing $\Delta E_{\Sigma-\Pi}$ enabled us to evaluate the strength of the Coriolis coupling. When $\Delta E_{\Sigma-\Pi} \gg B^2/q$ the density of interacting states is considered to be negligible.

To check the reliability of our jet-cooled EC-QCL spectra we start the rovibrational analysis with the ortho $\Pi_{e/f}(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$ transition of $\text{NH}_3\text{-Ar}$ which can be compared with the study of Fraser et al.¹⁸ who used a sub-Doppler Lamb-dip technique and the recent study by our group with the same but a less advanced SPIRALES setup as in the present study.²¹ All the simulations of the $\Pi_{e/f}(j=1,k=0)$ and $\Sigma_f(j=1,k=0)$ states were performed with the PGOPHER software which contains the spectroscopic parameters derived from the experimental analyses. For all $\text{NH}_3\text{-Rg}$ complexes we estimate that the accuracy of the ground state parameters (B'' , D_J'') derived from jet-cooled microwave experiments^{15,16,17} is sufficiently high to keep them fixed in the simulations, which enabled us to better determine the eight adjustable excited state parameters. Table 3 lists the excited state molecular parameters derived for the $\Pi_{e/f}(j=1,k=0)$ state from the simulation of the rovibrational band contours of four $\text{NH}_3\text{-Rg}$ complexes, as well as the parameter values extracted from a fit to the VRT levels that we calculated for total angular

momentum values up to $J = 8$. Table S1 (ESI) lists the experimental and *ab initio* calculated (up to $J = 10$) transitions for the two bands of four ortho $\text{NH}_3\text{-Rg}$ complexes. Table S2 lists the experimental transitions for the three less abundant $\text{NH}_3\text{-Kr}$ isotopologues with ^{82}Kr , ^{83}Kr and ^{86}Kr . Table S3 contains the corresponding excited state molecular parameters for the $\Pi_{\text{eff}}(j=1, k=0)$ state. Fig. 2 displays the comparison between jet-cooled laser and simulated spectra of the $\Pi_{\text{eff}}(j=1, k=0) \leftarrow \Sigma_{\text{f}}(j=0, k=0)$ transition for the series of $\text{NH}_3\text{-Rg}$ complexes. In all cases, the asymmetry of the Q branch is fairly reproduced to the low frequency side for Ar, Kr and Xe, indicating that the effective rotational constant in the excited state, $B_{\text{eff}} = B + (q/2) + 2q_{\text{D}}$, is smaller than in the ground state, while the opposite holds for the Ne complex.

The rotational temperatures (T_R) of $\text{NH}_3\text{-Rg}$ derived from the simulations suggest several comments: first, the evolution of T_R (from 6.5 K for Ne to 15 K for Xe) as a function of the seeded rare gas agrees well with the thermodynamic properties of the supersonic expansion, namely that the translational temperature varies inversely with the average mass of the gas mixture. This dependence is transferable to the rotational temperature because of similar translational and rotational relaxation achieved in the high collision regime of pulsed jets with large backing pressures. Secondly, the much higher T_R value obtained from the $\text{NH}_3\text{-Ar}$ spectrum with respect to our first study (10 K versus 3 K) is mainly due to the planar expansion behavior of the multichannel slit nozzle. The increase of the slit width probably also affects the warming of the pulsed jet, but we did not investigate further to what extent.

The jet-cooled spectra of the ortho $\Sigma_{\text{f}}(j=1, k=0) \leftarrow \Sigma_{\text{f}}(j=0, k=0)$ transition of $\text{NH}_3\text{-Ne}$, -Ar and -Kr provide reliable information about the location of the $\Sigma_{\text{f}}(j=1, k=0)$ neighboring state perturbing the $\Pi_{\text{eff}}(j=1, k=0)$ state. Fig. 3 displays the comparison between jet-cooled laser and simulated spectra of the ortho $\Sigma_{\text{f}}(j=1, k=0) \leftarrow \Sigma_{\text{f}}(j=0, k=0)$ transition for the three lightest $\text{NH}_3\text{-Rg}$ complexes. The excited state parameters of the $\Sigma_{\text{f}}(j=1, k=0)$ state are collected in Table 3. The band center of $\text{NH}_3\text{-Xe}$ that could not be detected is estimated from the available frequency shifts between observed and *ab initio* calculated frequencies. From the list of observed and *ab initio* frequencies reported in Table S1, frequency shifts equal to $-0.283(3)$, $+0.044(8)$, $+0.460(8)$ and $+1.364(21)$ cm^{-1} from Ne to Xe should be applied to the *ab initio* frequencies to match the observed values for the $\Pi_{\text{eff}}(j=1, k=0) \leftarrow \Sigma_{\text{f}}(j=0, k=0)$ transition. These shifts amount to $-0.323(20)$, $-0.723(14)$ and $-0.226(12)$ cm^{-1} from Ne to Kr for the $\Sigma_{\text{f}}(j=1, k=0) \leftarrow \Sigma_{\text{f}}(j=0, k=0)$ transition. Taking into account that the variation of the frequency shifts of the three lightest $\text{NH}_3\text{-Rg}$ complexes between both transitions ranged between -0.04 (Ne) and -0.769 cm^{-1} (Kr), we assumed that the experimental band center of the ortho $\Sigma_{\text{f}}(j=1, k=0) \leftarrow \Sigma_{\text{f}}(j=0, k=0)$ transition of $\text{NH}_3\text{-Xe}$ is shifted from the *ab initio* one by a value ranging from 0.60 to 1.32 cm^{-1} (Table 3). These small shifts probably originate from the 4D PESs: in the case of $\text{NH}_3\text{-Ar}$ in the ground state, a difference of $0.01\text{-}0.5$ cm^{-1} between the origins of experimental and theoretical bands was observed.¹⁴

Also the lines corresponding to the transition frequencies and line strengths obtained from the *ab initio* calculated energy levels and wave functions up to $J = 8$ are shown in Figs. 2 and 3. The highly predictive level of the *ab initio* VRT calculations is illustrated in Table 4 which collects measured and *ab initio* band origins and e/f splittings of the $\Pi_{e/f}(j=1,k=0)$ levels for both ortho bands of $\text{NH}_3\text{-Rg}$ complexes. The agreement between experiment and theory is excellent with average band origins shifts of $0.5(4) \text{ cm}^{-1}$ and very small deviations of the q values between 3 and 7 % for $\text{NH}_3\text{-Ne}$, -Ar and -Kr .

IV- Discussion

Validity of the pure-precession model

By assuming that $\Sigma_f(j=1,k=0)$ is the only state Coriolis perturbing the $\Pi_{e/f}(j=1,k=0)$ state we can use the pure-precession model of van Vleck³³ to estimate the energy difference $\Delta E_{\Sigma-\Pi}$ to be $4B^2/q$. Its positive sign confirms that the $\Sigma_f(j=1,k=0)$ level is above the $\Pi_{e/f}(j=1,k=0)$ level. The $\text{NH}_3\text{-Ar}$ complex already investigated in our previous study has demonstrated that the pure-precession model overestimates the value of q by about 17 %.²¹

Spectroscopic constants derived from rovibrational analyses of the $\text{NH}_3\text{-Rg}$ series (Table 3) have been exploited to evaluate the error level of the pure-precession model from the comparison between the energy difference of interacting $\Sigma_f(j=1,k=0)$ and $\Pi_f(j=1,k=0)$ states measured experimentally and calculated from the relation of van Vleck.³³ The pure-precession model systematically overestimates the energy difference by 8%, 17% and 25 % for $\text{NH}_3\text{-Ne}$, $\text{NH}_3\text{-Ar}$ and $\text{NH}_3\text{-Kr}$, and in the 6-16 % range for $\text{NH}_3\text{-Xe}$ by extrapolating the *ab initio* band center of the $\Sigma_f(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$ transition as explained in Section III.

Comparison between experimental and theoretical structural parameters

From the spectroscopic constants that we obtained from fits of the spectra, as well as from fits of the *ab initio* calculated VRT levels, we extracted a set of molecular parameters with the use of a pseudodiatomic model. First, we defined effective rotational and distortion constants for the upper state, namely $B_{\text{eff}} = B + q/2 + 2q_D$ and $D_{J,\text{eff}} = D_J - q_D$. Then we used the following pseudodiatomic relationships³⁴ $B_{\text{eff}} = h/8\pi^2 c \mu R_{\text{eff}}^2$, $\nu_s = (4B_{\text{eff}}^3/D_{J,\text{eff}})^{1/2}$ and $k_s = 4\pi^2 c^2 \nu_s^2 \mu$, where μ is the reduced mass, to obtain an effective R -value R_{eff} , a force constant k_s and a vdW stretching frequency ν_s for each isotopologue. Table 5 compares the molecular parameters of the $\text{NH}_3\text{-Rg}$ complexes, all derived from the pseudodiatomic model : in the ground state from microwave measurements^{15,16,17}, in both the $\Pi_{e/f}(j=1,k=0)$ and

$\Sigma_f(j=1,k=0)$ states from the present experimental study and from *ab initio* calculated VRT levels.¹⁴ Table S3 displays the very small variations of R_e and ν_s (about 0.1 %) between the different NH₃-Kr isotopologues.

In the ortho $\nu_2=1$, $\Pi_{e/f}(j=1,k=0)$ state, the same tendencies are observed for the NH₃-Rg complexes as in the lowest $\nu_2=0$, $\Sigma_f(j=0,k=0)$ state: from Ne to Xe, the experimental vdW bond length R_{eff} increases by 9% in the $\Sigma_f(j=0,k=0)$ ground state and by 11% in the $\Pi_{e/f}(j=1,k=0)$ state, the force constant k_s increases by 400% and 200%, while the experimental vdW stretching frequency ν_s increases by 57% and 21 % (87% and 61% from the *ab initio* levels) in both ground and ν_2 states. These results clearly show that the vdW bond is more rigid when the polarizability of the Rg atom increases. However, the values of ν_s and k_s derived experimentally for the $\Pi_{e/f}(j=1,k=0)$ state of NH₃-Xe are surprisingly lower than for the NH₃-Ar and -Kr complexes. Moreover, the experimental value of ν_s is lower than the *ab initio* value, while very good agreement (~2.5-7 %) between experiment and theory is obtained for the three other NH₃-Rg complexes. Lastly, the *ab initio* calculations display the same frequency variation in the $\nu_2=1$ state as in the ground state, which suggests an anomaly in the results derived from the NH₃-Xe spectra.

Two possible causes are examined hereafter:

- the small number of P(J) lines (only 2) assigned in the band contour fitting of the $\Pi_{e/f}(j=1,k=0)$ spectrum. To evaluate the consequences of a rovibrational analysis with only two rotational branches, the NH₃-Ne, NH₃-Ar and NH₃-Kr jet-cooled spectra have been reanalyzed without the P(J) lines. The set of molecular parameters thus obtained is very close to the values reported in Table 3, which discards this hypothesis.
- an unreliable determination of the energy splitting ΔE_{ff} . The RMS error obtained for the NH₃-Xe spectrum analysis (two times larger compared to other NH₃-Rg spectra) supports this assumption. Table S4 reports, for the four NH₃-Rg complexes the energy splitting ΔE_{ff} extracted for each rotational level (up to $J = 8$) from the *ab initio* calculated VRT states. As already mentioned above, the differences between the experimental q values derived from the fits and the values of the *ab initio* *e/f* energy differences do not exceed 7% for the three lightest NH₃-Rg complexes but are as high as 23% in the case of NH₃-Xe. This error in the determination of q is partly compensated by the D_J distortion constant, which causes a notable error in this parameter: the comparison between experimental and *ab initio* D_J values (Table 3) shows differences ranging from 6 to 17% from Ne to Kr and higher than 100% for Xe, which confirms our assumption. Therefore, it is not surprising that the vdW stretching frequency of NH₃-Xe is too large when the effective distortion constant $D_{J,eff}$ is underestimated by a factor close to 2. In conclusion, the fit of the NH₃-Xe spectrum seems not to be predictive for the f perturbed state.

An additional argument is provided by analyzing only the Q(J) lines of the ortho $\Pi_{e/f}(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$ transition to derive molecular constants and structural parameters for the unperturbed *e* symmetry component of the $\Pi_e(j=1,k=0)$ state

(Table 6). The rotational constants B derived from the fit of the Q(J) lines are very close ($\sim 0.1\%$) to the effective values B_{eff} reported in Table 3 for the whole series of NH₃-Rg complexes. The difference between the distortion constants D_J and the effective values $D_{J,\text{eff}}$ varies between 5 and 20% for Rg=Ne, Ar, Kr but reaches 90 % for Xe. Structural parameters obtained for the NH₃-Rg series in the $\Pi_e(j=1, k=0)$ state are consistent with those in the ground state, namely similar values of the stretching vdW frequency and an increase of ν_s with the polarizability of the Rg atom. These results clearly show that the discrepancy originates from the perturbed Π_f state.

Finally, the model of weak Coriolis coupling which determines the rotational energy in the excited vibrational states through Eqn (3) can be used to evaluate the doubling constant q as a function of experimental transition frequencies of the R and Q branches (by neglecting distortion) and of the J rotational quantum number :

$$q = \frac{R(J) - Q(J) - 2B(J+1)}{(J+1)^2} \quad (4)$$

While the $(E_{\Pi_e} - E_{\Pi_f})$ *ab initio* energy differences reported in Table S4 vary very little as J increases for all NH₃-Rg complexes, Fig. 4 compares the evolution of the *ab initio* q value and that derived experimentally from Eqn (4) as a function of J . For NH₃-Ne, NH₃-Ar and NH₃-Kr complexes, both $(E_{\Pi_e} - E_{\Pi_f})$ and the experimental q values are found to be nearly independent of J (relative variations not larger than 1-3% for NH₃-Ne), showing that the quasi-constant behavior of q corresponding to the weak Coriolis coupling case is well reproduced. On the other hand, the experimental value of q for NH₃-Xe increases by about 10 % for $J=1-12$ and differs from the *ab initio* one by 26 % in average.

All these additional analyses support the hypothesis that the Coriolis perturbations involving the Π_f state are so strong in the case of NH₃-Xe that the weak Coriolis coupling model is unsuitable. Given that the rotational study of Wen et al.¹⁷ clearly proved that there was no sign of a tunneling component and a Coriolis perturbation for the lowest ortho state $\Sigma_f(j=0, k=0)$ of NH₃-Xe, the most probable explanation is the presence of Coriolis coupling between the $\nu_2=1$, $\Pi_f(j=1, k=0)$ state and another vibrational state. The energy difference between the $\Sigma_f(j=1, k=0)$ and $\Pi_f(j=1, k=0)$ states of NH₃-Xe, predicted to be around 7 cm⁻¹ is very close to that of NH₃-Ne (6.991 cm⁻¹) for which the weak coupling model holds. Consequently, we have no proof of a Coriolis perturbation involving the $\Sigma_f(j=1, k=0)$ state.

Conclusion

The present work reports a high resolution IR spectroscopic study of NH₃-Rg (Rg= Ne, Ar, Kr, Xe) heterodimers in the region of the umbrella ν_2 band of the NH₃ monomer. Recent instrumental improvements on our infrared tunable quantum

cascade laser spectrometer coupled to a pulsed supersonic jet enabled us to largely increase the collection of spectroscopic data derived from a preliminary study of NH₃-Ar, by extending it to the whole rare gas series. Thus we could investigate the intermolecular dynamics from both ortho $\Pi_{eff}(j=1,k=0) \leftarrow \Sigma_f(j=1,k=0)$ and $\Sigma_f(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$ transitions with the aid of a pseudodiatom model applied to a weak Coriolis coupling case.

Accurate vdW bond lengths R_{eff} , force constants k_s , and intermolecular stretching frequencies ν_s in the ν_2 state have been derived from rovibrational analyses for NH₃-Ne, -Ar and -Kr. They compare well with ground state structural parameters and with *ab initio* calculations based on a 4D IPES that explicitly takes into account the umbrella motion of NH₃. However, strong deviations are observed for ν_s et k_s in the $\Pi_{eff}(j=1,k=0)$ state in the case of NH₃-Xe, which suggests that the applied model is not predictive in this case. The presence of another state coupling to the perturbed Π_f state has been suggested, but no evidence has been found that weak Coriolis coupling between Π_f and Σ_f states could be responsible for these anomalous NH₃-Xe results.

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Figure 1 EC-QCL jet-cooled spectra of $\text{NH}_3\text{-Rg}$ of the ortho $\Pi_{e/f}(j=1, k=0) \leftarrow \Sigma_f(j=0, k=0)$ transition recorded in the $947\text{-}957\text{ cm}^{-1}$ range with 2 % NH_3 seeded in 4 bar Rg and 4 bar Helium for Rg = Ar, Kr, Xe, in 8 bar Ne for $\text{NH}_3\text{-Ne}$ (right). Expanded view of the Q branch fully resolved in rotation, which displays the asymmetry change between Ne and the heaviest Rg atoms (left). The spectra of $\text{NH}_3\text{-Ne}$ and $\text{NH}_3\text{-Xe}$ have been magnified by a factor of 7 and 18, respectively, to obtain a maximum absorption similar to that of $\text{NH}_3\text{-Ar}$ or $\text{NH}_3\text{-Kr}$. An expanded view of the P(7) line of the $\text{NH}_3\text{-Kr}$ spectrum highlights the rich isotopic structure of krypton with ^{82}Kr , ^{83}Kr , ^{84}Kr and ^{86}Kr . Ten rotational lines marked with an asterisk belong to the ν_2 band of $^{14}\text{NH}_3$ monomer. The rotational line marked with a cross corresponds to the transition $\nu_2=1(e) \leftarrow 0(f)$, $^{\text{Q}}\text{R}(0,0)$ of $^{15}\text{NH}_3$ at 947.79221 cm^{-1} line, according to the notation $^{\Delta K}\Delta J(J'', K'')$. [35]

Figure 2: Rovibrational band contour simulations at T_R equal to 6.5, 10, 12.5 and 13 K, respectively for Ne, Ar, Kr and Xe (top) compared to EC-QCL jet-cooled slit spectra of both ortho $\Pi_{\text{eff}}(j=1, k=0) \leftarrow \Sigma_f(j=0, k=0)$ transitions of four $\text{NH}_3\text{-Rg}$ heterodimers (middle) and *ab initio* frequencies derived from VRT states calculated (up to $J=8$) on the IPES of Loreau et al. (bottom). The P, Q and R branches of *ab initio* spectra have been shifted by $-0.283(3)$, $+0.044(8)$, $+0.460(8)$ and $+1.364(21)$ cm^{-1} for Ne, Ar, Kr and Xe, respectively.

Figure 3: Rovibrational band contour simulations at T_R equal to 6.5, 10, 12.5 K, respectively for Ne, Ar and Kr (top) compared to EC-QCL jet-cooled slit spectra of the ortho Σ_f ($j=1, k=0$) $\leftarrow$ Σ_f ($j=0, k=0$) transition of NH_3 -Rg heterodimers (middle), and *ab initio* frequencies derived from VRT states calculated on the IPES of Loreau et al.¹⁴ (bottom). The P and R branches of *ab initio* spectra have been shifted by -0.323(20), -0.723(14) and -0.226(12) cm^{-1} , for Ne, Ar and Kr, respectively.

Figure 4: Evolution of the *ab initio* energy difference ($E_{\Pi_e} - E_{\Pi_f}$) as a function of the rotational quantum number J compared to the experimental K -type doubling constant q derived from Eqn.(4) for the complexes $\text{NH}_3\text{-Rg}$ with $\text{Rg}=\text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$.

	$R_{min}(a_0)$	$R_{max}(a_0)$	n_R	α	$\zeta(E_h a_0^{-1})$
NH ₃ -Ne	4.7	25	120	0.7	5×10^{-4}
NH ₃ -Ar	4.5	20	110	1.0	1×10^{-3}
NH ₃ -Kr	4.0	25	163	1.2	1×10^{-3}
NH ₃ -Xe	6.0	30	192	0.8	1×10^{-3}

Table 1: Parameters used in the bound state calculations. The first three columns contain the radial grid parameters. The last two columns contain the parameters of the effective potential used to optimize the radial basis functions.

	D_e (cm ⁻¹)	D_0 (cm ⁻¹)
NH ₃ -Ne	66.81	30.35
NH ₃ -Ar	147.6	94.22
NH ₃ -Kr	173.6	119.78
NH ₃ -Xe	197.7	144.36

Table 2: Binding energy and dissociation energy of the ortho-NH₃-Rg complexes.

	²⁰ Ne	⁴⁰ Ar	⁸⁴ Kr	¹³² Xe
		$\Sigma_f (j=0, k=0)$		
B''	3965.8506(20) ^a	2876.84901(79) ^b	2321.1770(1) ^c	2026.5134(3) ^d
D_J''	0.5164(1) ^a	0.088695(98) ^b	0.0454(1) ^c	0.02785(4) ^d
		$\Pi_{eff} (j=1, k=0)$		
		This work		
		<i>Calculated</i>		
ν_0	950.25492(9)	950.38809(8)	951.55658(6)	954.34849(5)
B	3862.37(13)	2827.160(51)	2273.984(33)	1958.471(67)
	3729.2	2772.4	2225.2	1901.9
B_{eff}	4003.22(29)	2872.55(12)	2307.048(76)	2000.43(16)
D_J	0.397(2)	0.07853(3)	0.03765(14)	0.00589(27)
	0.366	0.074	0.032	0.012
$D_{J,eff}$	0.591(4)	0.0919(4)	0.0498(3)	0.0504(7)
$H_J(10^6)$	-76.4(47)	-1.06(38)	-1.69(18)	-3.53(30)
q	282.08(16)	90.845(67)	66.177(43)	84.104(89)
q_D	-0.194(2)	-0.0134(4)	-0.0122(2)	-0.0445(4)
$q_H(10^6)$	261(8)	6.0(7)	4.2(3)	22.9(5)
# lines	34	56	65	51
RMS error	5.7	6.9	6.3	12
		$\Sigma_f (j=1, k=0)$		
		This work		
		<i>Calculated</i>		
ν_0	957.2462(1)	960.73361(5)	960.13595(64)	960.98-961.70 ^a 960.38
B	4055.90(11)	2922.83(5)	2366.44(10)	-
	4037.78(2.76)	2913.0(80)	2364.61(8.44)	2087.50(11.66)
D_J	0.67675(75)	0.11470(33)	0.063856(38)	-
	0.78(4)	0.22(12)	0.19(12)	0.26(17)
# lines	13	23	22	-
RMS error	3.2	5.0	7.8	-

^aEstimated band center frequency range

Table 3: Spectroscopic constants (expressed in MHz, except for the band centers in cm⁻¹) for the transitions $\nu_2=1 \leftarrow 0$ $\Pi_{eff}(j=1, k=0) \leftarrow \Sigma_f(j, k=0)$ and $\Sigma_f(j=1, k=0) \leftarrow \Sigma_f(j, k=0)$ bands of ortho NH₃-Rg with Rg =Ne, Ar, Kr and Xe. The molecular parameters of the $\Sigma_f(j, k=0)$ state are given by Nelson et al.² for NH₃-Ar, by Van Wijngaarden et al.^{15,16} for NH₃-Ne and NH₃-Kr and by Wen et al.¹⁷ for NH₃-Xe. The parameters “*calculated*” in italics are obtained from fits to the VRT levels calculated for J values up to 10. The

observed band center of the $\Sigma_f(j=1,k=0) \leftarrow \Sigma_f(j,k=0)$ transition in $\text{NH}_3\text{-Xe}$ has been estimated by comparison of the observed and *ab initio* band centers of the three other $\text{NH}_3\text{-Rg}$ complexes (see text).

	NH ₃ -Ne		NH ₃ -Ar		NH ₃ -Kr		NH ₃ -Xe	
	Exp	<i>Ab initio</i>	Exp	<i>Ab initio</i>	Exp	<i>Ab initio</i>	Exp	<i>Ab initio</i>
$\Pi_{e/f}(j=1,k=0) \leftarrow \Sigma_f(j=1,k=0)$								
ν_0 (cm⁻¹)	950.25492(9)	950.534	950.38809(8)	950.336	951.55658(6)	951.091	954.34849(5)	952.966
q	282.08(16)	273.9(48)	90.845(67)	85.20(21)	66.177(43)	61.96(21)	84.104(89)	65.44(56)
$\Sigma_f(j=1,k=0) \leftarrow \Sigma_f(j=0,k=0)$								
ν_0 (cm⁻¹)	957.2462(1)	957.591	960.73361(5)	961.470	960.13595(64)	960.370	-	959.011

Table 4: Comparison between experimental and *ab initio* band origins and q doubling constants of ortho $\Pi_{e/f}(j=1,k=0)$ and $\Sigma_f(j=1,k=0)$ states of NH₃-Rg complexes. The errors between parentheses of the *ab initio* q values correspond to the standard deviation for $J = 1-8$ (see Table 6).

		²⁰ Ne-NH ₃	⁴⁰ Ar-NH ₃	⁸⁴ Kr-NH ₃	¹³² Xe-NH ₃
		$\Sigma_f (j=0, k=0)$			
$R_{\text{eff}} (\text{\AA})$	Exp	3.7227 ^a	3.8358 ^b	3.9220 ^c	4.067 ^d
	<i>Ab initio</i>	3.71	3.86	3.95	4.09
$\nu_s (\text{cm}^{-1})$	Exp.	23.2 ^a	34.6(1) ^b	35.0 ^c	36.5 ^d
	<i>Ab initio</i>	19.3	33.6	34.6	36.1
$k_s (\text{N/m})$		0.291 ^a	0.840 ^b	1.02 ^c	1.18 ^d
		$\Pi_{\text{eff}} (j=1, k=0)$			
$R_{\text{eff}} (\text{\AA})$	Exp	3.70487(4)	3.83839(2)	3.93434(6)	4.09369(4)
	<i>Ab initio</i>	3.77	3.87	3.97	4.16
$\nu_s (\text{cm}^{-1})$	Exp	22.0(1)	33.9(1)	33.1(1)	26.6(2)
	<i>Ab initio</i>	20.4	32.0	32.3	32.8
$k_s (\text{N/m})$		0.26	0.81	0.91	0.63
		^a from Van Wijngaarden et al. ^b from Nelson et al. ^c from Van Wijngaarden et al. ^d from Wen et al.			

Table 5: Experimental and *ab initio* molecular parameters of the four NH₃-Rg complexes for the $\Pi_{\text{eff}} (j=1, k=0)$ state determined using the expressions of the pseudodiatom model applied to either the experimental or the *ab initio* calculated transition frequencies. Using the same approach, molecular parameters of the $\Sigma_f(j=0, k=0)$ ground state obtained from microwave experiments are compared to our *ab initio* 4D PES results.

	²⁰ Ne	Ar	⁸⁴ Kr	¹³² Xe
	$\Pi_e (j=1, k=0)$			
<i>B</i> (MHz)	4003.134(50)	2872.313(339)	2307.083(22)	2000.316(17)
<i>D_J</i> (MHz)	0.49127(61)	0.0876(27)	0.04387(15)	0.02675(22)
<i>H_J</i> (10 ⁵ MHz)	4.77(10)	1.59(63)	0.05(2)	-0.081(36)
# lines	15	18	28	20
RMS (MHz)	1.2	6.9	1.4	2.6
<i>R_{eff}</i> (Å)	3.705	3.838	3.934	4.094
<i>ν_s</i> (cm ⁻¹)	24.0	34.6	35.2	36.4

Table 6: Spectroscopic constants and molecular parameters of the four NH₃-Rg complexes for the $\Pi_e (j=1, k=0)$ state derived from the band contour fitting of the Q(J) lines of the $\nu_2=1 \leftarrow 0 \Pi_e(j=1, k=0) \leftarrow \Sigma_f(j, k=0)$ transition.

References

- ¹F. Pirani, L. Roncaratti, L. Belpassi, F. Tarantelli, and D. Cappelletti, *J. Chem. Phys.* **135**, 194301 (2011).
- ²D. D. Nelson, Jr., G. T. Fraser, and W. Klemperer, *Science* **238**, 1670 (1987).
- ³G. Fraser, D. Nelson, Jr., A. Charo, and W. Klemperer, *J. Chem. Phys.* **82**, 2535 (1985).
- ⁴D. Nelson, Jr., G. Fraser, K. I. Peterson, K. Zhao, and W. Klemperer, *J. Chem. Phys.* **85**, 5512 (1986).
- ⁵E. Zwart and W. Meerts, *Chem. Phys.* **151**, 407 (1991).
- ⁶C. Schmuttenmaer, R. Cohen, J. Loeser, and R. Saykally, *J. Chem. Phys.* **95**, 9 (1991).
- ⁷C. Schmuttenmaer, J. Loeser, and R. Saykally, *J. Chem. Phys.* **101**, 139 (1994).
- ⁸E. Zwart, H. Linnartz, W. Meerts, G. Fraser, D. Nelson, Jr., and W. Klemperer, *J. Chem. Phys.* **95**, 793 (1991).
- ⁹A. Grushow, W. Burns, S. Reeve, M. Dvorak, and K. Leopold, *J. Chem. Phys.* **100**, 2413 (1994).
- ¹⁰C. A. Schmuttenmaer, R. C. Cohen, and R. J. Saykally, *J. Chem. Phys.* **101**, 146 (1994).
- ¹¹P. Herbine and T. R. Dyke, *J. Chem. Phys.* **83**, 3768 (1985).
- ¹²G. T. Fraser, D. D. Nelson, Jr, G. J. Gerfen and W. Klemperer, *J. Chem. Phys.* **83**, 5442 (1985).
- ¹³D. D. Nelson, Jr, G. T. Fraser and W. Klemperer, *J. Chem. Phys.* **83**, 6201 (1985).
- ¹⁴J. Loreau, J. Liévin, Y. Scribano and A. van der Avoird, *J. Chem. Phys.* **141**, 224303(2014).
- ¹⁵J. van Wijngaarden, W. Jäger, *J. Chem. Phys.* **115**, 6504 (2001).
- ¹⁶J. Van Wijngaarden, W. Jäger, *Mol. Phys.* **99**, 1215 (2001).
- ¹⁷Q. Wen, W. Jäger, *J. Chem. Phys.* **128** 204309 (2008).
- ¹⁸G. T. Fraser, A. S. Pine, and W. A. Kreiner, *J. Chem. Phys.* **94**, 7061(1991).
- ¹⁹A. Bizzari, B. Heijman, S. Stolte, and J. Reuss, *Z. Phys. D* **10**, 291 (1988).
- ²⁰K. Didriche, T. Földes, T. Vanfleteren, and M. Herman, *J. Chem. Phys.* **138**, 181101 (2013).
- ²¹P. Asselin, Y. Belkhodja, A. Jabri, A. Potapov, J. Loreau, A. van der Avoird, *Mol. Phys.* **116**, 3642 (2018).
- ²²J. Loreau and A. van der Avoird, *J. Chem. Phys.* **143**, 184303 (2015).
- ²³S. Yu, J. C. Pearson, B. J. Drouin, K. Sung, O. Pirali, M. Vervloet, M-A. Martin-Drumel, C. P. Endres, T. Shiraishi, K. Kobayashi and F. Matsushima, *J. Chem. Phys.* **133**, 174317 (2010).
- ²⁴K. A. Peterson, D. Figgen, E. Goll, H. Stoll and M. Dolg, *J. Chem. Phys.* **119**, 11113 (2003).
- ²⁵O. Tkac, A. K. Saha, J. Loreau, D. H. Parker, A. van der Avoird, and A. J. Orr-Ewing, *J. Phys. Chem. A* **119**, 5979 (2015).
- ²⁶A. P. P. van der Poel, P. C. Zieger, S. Y. T. van de Meerakker, J. Loreau, A. van der Avoird, and H. L. Bethlem, *Phys. Rev. Lett.* **120**, 033402 (2018).
- ²⁷G. C. Groenenboom, P. E. S. Wormer, A. van der Avoird, E. M. Mas, R. Bukowski, and K. Szalewicz, *J. Chem. Phys.* **113**, 6702 (2000).
- ²⁸J. van Bladel, A. van der Avoird, and P. Wormer, *Chem. Phys.* **165**, 47 (1992).
- ²⁹E. Davidson, *J. Comput. Phys.* **17**, 87 (1975).
- ³⁰P. Asselin, Y. Berger, T. R. Huet, R. Motiyenko, L. Margulès, R. J. Hendricks, M. R. Tarbutt, S. Tokunaga, B. Darquié, *Phys. Chem. Chem. Phys.* **19**, 4576 (2017).
- ³¹P. Asselin, A. Potapov, A. C. Turner, V. Boudon, L. Bruel, M-A. Gaveau, M. Mons, *Phys. Chem. Chem. Phys.* **19**, 17224 (2017).
- ³²M. Delghany, M. Afshari, Z. Abusara, C. Van Eck, N. Moazzen-Ahmadi, *J. Mol. Spectr.* **247**, 123 (2008).
- ³³J. H. Van Vleck, *Phys. Rev.* **33**, 467 (1929).
- ³⁴W. Gordy and R. L. Cook, *Microwave Molecular spectra*, 3rd ed. (Wiley, London, 1984).

³⁵ E. Cané, G. Di Lonardo, L. Fusina, F. Tamassia and A. Predoi-Cross, J. Chem. Phys. **150**, 194301 (2019).