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Rotational Spectroscopy of the NH₃–H₂ Molecular Complex

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Abstract

We report the first high resolution spectroscopic study of the NH₃–H₂ van der Waals molecular complex. Three different experimental techniques, a molecular beam Fourier transform microwave spectrometer, a millimeter-wave intracavity jet OROTRON spectrometer, and a submillimeter-wave jet spectrometer with multipass cell, were used to detect pure rotational transitions of NH₃–H₂ in the wide frequency range from 39 to 230 GHz. Two nuclear spin species, (ο)-NH₃–(ο)-H₂ and (ρ)-NH₃–(ο)-H₂, have been assigned as carriers of the observed lines on the basis of accompanying rovibrational calculations performed using the ab initio intermolecular potential energy surface (PES) of Maret et al. The experimental spectra were compared with the theoretical bound state results, thus providing a critical test of the quality of the NH₃–H₂ PES, which is a key issue for reliable computations of the collisional excitation and de-excitation of ammonia in the dense interstellar medium.

Key words: ISM: molecules – methods: laboratory: molecular – molecular data – molecular processes – techniques: spectroscopic

1. Introduction

The ammonia molecule is the most commonly used tracer of the temperature in a variety of interstellar environments, ranging from pre-stellar cores and molecular clouds to external galaxies (Ho & Townes 1983; Walmsley & Ungerechts 1983; Mauersberger et al. 2003; Mangum et al. 2013). These interstellar environments are usually far from thermodynamic equilibrium, and rotational excitation and de-excitation of the NH₃ molecules in collisions with H₂, the dominant colliding partner in most of the molecular regions, are of crucial importance for the observed ammonia population distributions and the interpretation of its spectra. Collisional state-to-state rates are difficult to measure experimentally, and as a result such information often relies on theoretical estimates based on potential energy surfaces (PESs). Laboratory measurements are important to establish the predictive abilities of these PESs. One of the most efficient tools for a reliable elucidation of intermolecular forces is high resolution spectroscopy of van der Waals complexes, because their (quasi)-bound states are very sensitive to the interaction potential (Wormer & van der Avoird 2000).

For NH₃–H₂, however, very little is known about its bound states. The high resolution infrared (IR) and microwave (MW) spectra of the related and isoelectronic HF–H₂ and H₂O–H₂ in the gas phase have been observed (Hunt et al. 2003; Weida & Nesbitt 1999; Harada et al. 2014), but no such data exist for ammonia. The available experimental studies of the NH₃–H₂ complex are limited to the observation of the ν₁HH vibration (which is dipole forbidden in free H₂) in argon and neon matrices (Moroz et al. 1990; Jacox & Thompson 2006). In addition, ab initio calculations were performed in the latter work, which yielded a coaxial C₃ᵥ minimum energy arrangement and electronic dissociation energies of 215 and 237 cm⁻¹ at the MP2 and CCSD(T) levels, respectively.

Not long ago, two high-accuracy ab initio five-dimensional PESs, including the anisotropy of H₂, were obtained for the NH₃–H₂ system using the coupled-cluster CCSD(T) method (Mladenović et al. 2008; Maret et al. 2009). In both studies the equilibrium structure of NH₃–H₂ was found to be axial, with molecular hydrogen collinear with the C₃ᵥ symmetry axis of ammonia. The H₂ monomer approaches NH₃ from the nitrogen side. This global minimum is bound by D₀ = 253 cm⁻¹ according to Mladenović et al. (2008) and 267 cm⁻¹ according to Maret et al. (2009). The potential rises steeply for other H₂ orientations, indicating hindered internal rotation. The bond-dissociation energy D₀ was expected to be only a small fraction of D₀.

In the present paper, all bound rovibrational levels of the weakly bound NH₃–H₂ complex have been calculated for total angular momentum J = 0...6 on the intermolecular potential surface reported by Maret et al. (2009). The energy levels were obtained for four different nuclear spin states of NH₃–H₂ arising from combinations of (para)-H₂ and (ortho)-H₂ with (ortho)-NH₃ and (para)-NH₃. The (ρ)-H₂ and (ο)-H₂ complexes and the (ο)-NH₃ and (ρ)-NH₃ complexes behave as different molecules, because they do not interconvert at the timescale of the experiment, due to the different nuclear spin statistics.

The pure rotational (end-over-end rotation) spectra of two nuclear spin species—namely, (ο)-NH₃–(ο)-H₂ and (ρ)-NH₃–(ο)-H₂—were detected in the frequency range of 39–230 GHz guided by the bound state calculations. The experimental data on the rotational levels are in good agreement with the theoretical results, which indicates the high quality of the PES used in this study.

2. Theory

2.1. Details on the Potential Surface

In our bound state calculations we applied the five-dimensional PES calculated ab initio by Maret et al. (2009).
This potential depends only on the intermolecular coordinates, while the NH$_3$ and H$_2$ monomers were both kept rigid at their ground state vibrationally averaged geometries. Maret et al. constructed this PES by starting with a reference potential based on 89,000 data points from CCSD(T) calculations with Dunning’s correlation consistent aug-cc-pVTZ basis set. In the next step, this reference PES was calibrated using a complete basis set extrapolation procedure on a smaller set of 29,000 data points from CCSD(T)/aug-cc-pVTZ calculations. The global minimum in the final potential deduced from an analytical fit to all data points has a depth $D_c$ of 267 cm$^{-1}$ and corresponds to a structure with intermolecular center-of-mass distance $R = 3.23$ Å and H$_2$ collinear with the C$_3v$ axis of ammonia at the nitrogen end (see Figure 1). This PES has been employed in studies of collision dynamics of NH$_3$ with H$_2$ (Maret et al. 2009; Wiesenfeld et al. 2011; Pirani et al. 2013; Daniel et al. 2014; Ma et al. 2015; Tkáč et al. 2015).

2.2. Bound State Calculations

The rovibrational levels of NH$_3$--H$_2$ were calculated by a method similar to the coupled-channels method used in scattering calculations; it is described by van der Avoird and Nesbitt (2011). We used the ground state experimental values for the rotational constants of NH$_3$: $A_0 = B_0 = 9.9402$ cm$^{-1}$ (298,000 MHz) and $C_0 = 6.3044$ cm$^{-1}$ (189,001 MHz), given by Danby et al. (1986), and H$_2$: $B_0 = 59.3398$ cm$^{-1}$ (1,778,962 MHz), given by Tkáč et al. (2015). The atomic masses are 1.007825 u for H and 14.003074 u for $^{14}$N. For the intermolecular center-of-mass distance $R$, we used a discrete variable representation (DVR) with a grid of 95 equidistant points ranging from $R = 4$ to $26 a_0$. This DVR basis was contracted into a radial basis of 20 functions constructed in the same way as in van der Avoird and Nesbitt (2011). To represent the hindered rotations of NH$_3$ and H$_2$ in the complex, we used a basis of symmetric rotor functions and spherical harmonics, respectively, which was truncated to internal rotor quantum numbers $j_{\text{NH}_3}$ $\leq$ 10 and $j_{\text{H}_2}$ $\leq$ 6. Wigner D-functions are used in the basis for the overall rotation of the dimer. With this basis, the bound levels of the complex are converged to better than 0.0001 cm$^{-1}$; the energies of transitions between the levels are converged even more accurately.

In order to explain the observed spectrum of NH$_3$--H$_2$, we must also include umbrella inversion tunneling of the NH$_3$ monomer in our calculations. The ground state inversion levels are split by 0.7934 cm$^{-1}$ in the free monomer. Since the potential of Maret et al. (2009) does not depend on the umbrella inversion coordinate, we used a two-state model tested in previous work on NH$_3$--He (Gubbels et al. 2012) and NH$_3$--Ar (Loreau et al. 2014). It is assumed in this model that the NH$_3$ molecule tunnels between two structures, umbrella up and umbrella down, with an umbrella angle given by the equilibrium value in free ammonia. Maret et al. (2009) calculated their potential only for one of these structures; a symmetry relation (Gubbels et al. 2012) obeyed by the expansion coefficients of the potential yields its value for the umbrella-inverted structure. The basis for the rovibrational states of the complex is multiplied with two NH$_3$ inversion tunneling states, which according to the two-state model are the plus and minus combinations of the two localized umbrella states. NH$_3$ tunneling is partly quenched by the interaction with H$_2$ in the complex, and the tunneling states become more or less localized. The symmetry group used in the calculations is the permutation-inversion group $G_{24}$.

Due to the nuclear spin statistics of H$_2$, (p)-H$_2$ complexes with total nuclear spin $I_h = 0$ have their lowest internal rotor state with $j_{\text{H}_2} = 0$, while (o)-H$_2$ complexes with $I_h = 1$ have their lowest internal rotor state with $j_{\text{H}_2} = 1$, where $j_{\text{H}_2}$ denotes the rotational angular momentum of H$_2$. The NH$_3$ part has also two nuclear spin states, (o)-NH$_3$ and (p)-NH$_3$, with the corresponding lowest rotational levels $(j_{\text{NH}_3}, k_{\text{NH}_3}) = (0, 0)$ and $(j_{\text{NH}_3}, k_{\text{NH}_3}) = (1, 1)$, where $j_{\text{NH}_3}$ and $k_{\text{NH}_3}$ denote the angular momentum of NH$_3$, and its projection on the symmetry axis.

Exact quantum numbers are the total angular momentum $J$ of the complex and the parity $\pi = \pm 1$ under inversion $E^\prime$. It is conventional in spectroscopy to use the spectroscopic parity $\varepsilon$ that is related to the inversion parity by $\pi = \varepsilon (1-\varepsilon)^0$. We follow this convention and label states of even/odd spectroscopic parity by e/f. An approximate quantum number that is important to understand the nature of the rovibrational states is the projection $K$ of the total angular momentum $J$ on the intermolecular axis. We also follow the convention to use the absolute value of $K$ as a label, and distinguish the pairs of states with $K > 0$ by their parity $e/f$. States with $K = 0$ are called $\Sigma$ states, those with $K = 1$ are $\Pi$ states, and those with $K = 2$ are $\Delta$ states. Four different nuclear spin species occur in the complex: (o)-NH$_3$--(p)-H$_2$, (p)-NH$_3$--(p)-H$_2$, (o)-NH$_3$--(o)-H$_2$, and (p)-NH$_3$--(o)-H$_2$. For each of these species, we computed all bound rovibrational levels with total angular momentum $J = 0$–6 and both parities.

The rotational energy levels of NH$_3$--H$_2$ with $K = 0$ ($\Sigma$) and 1 ($\Pi$) are shown in Figure 2 for (p)-H$_2$ (left diagram) and (o)-H$_2$.
levels of free NH$_3$. Circles mean that rotations is large. The levels that belong to the ground states of the complexes. The relative position of the NH$_3$-H$_2$ and NH$_3$-H$_2$ energy scales is 91.33 cm$^{-1}$, as determined by the zero-point levels from the bound state calculations. (j, k) are quantum numbers of the correlating states.

![Diagram](image)

**Figure 2.** Calculated energy levels with $K = 0$ (left) and $K = 1$ (right) for NH$_3$-(p)-H$_2$ (left) and NH$_3$-(o)-H$_2$ (right), up to 25 cm$^{-1}$. The relative position of the NH$_3$-(o)-H$_2$ and NH$_3$-(p)-H$_2$ energy scales is 91.33 cm$^{-1}$, as determined by the zero-point levels of the complexes with (o)-H$_2$ and (p)-H$_2$ obtained from the bound state calculations.

Each level shown in Figure 2 involves a number of *end-over-end* rotational levels. The levels that belong to Σ states ($K = 0$) start at $J = 0$; levels that belong to Π states ($K = 1$) start at $J = 1$. The (p)-NH$_3$ dimers have a Π ground state with $J = 1$, and (p)-NH$_3$ dimers have a Σ ground state with $J = 0$.

The bound state calculations yield different dissociation energies $D_0$ for the four nuclear spin species of the complex: 32.43, 34.25, 59.78, and 66.00 cm$^{-1}$ for (o)-NH$_3$-(p)-H$_2$, (p)-NH$_3$-(p)-H$_2$, (o)-NH$_3$-(p)-H$_2$, and (p)-NH$_3$-(o)-H$_2$, respectively. Hence the dissociation energy $D_0$ is substantially larger for the (p)-H$_2$ dimers than for the (p)-H$_2$ dimers, while it is only slightly larger for the (p)-NH$_3$ dimers than for the (o)-NH$_3$ dimers. Similar stability differences among the (p)-H$_2$O-(p)-H$_2$, (o)-H$_2$O-(p)-H$_2$, (p)-H$_2$O-(o)-H$_2$, and (o)-H$_2$O-(o)-H$_2$ species were found for H$_2$O–H$_2$ by van der Avoird and Nesbitt (2011). It is also remarkable that $D_0$ is much smaller than the binding energy $D_s = 267$ cm$^{-1}$ in the potential of Maret et al. (2009), which implies that the zero-point energy associated with the intermolecular vibrations and hindered rotations is large.

### 3. Experimental

Three different instruments, an intracavity OROTRON MMW spectrometer, a supersonic jet spectrometer for terahertz applications (SuJeSTa), and a Fourier transform microwave (FTMW) spectrometer were used to record the pure rotational spectrum of NH$_3$–H$_2$ in a jet expansion. Both OROTRON and FTMW spectrometers use an open Fabry–Perot cavity as a sample cell, and SuJeSTa uses a multipass cell, thus providing very high sensitivity, which is important for the detection of weakly bound van der Waals species. For most measurements, a gas mixture of 0.5%–1% of NH$_3$ in normal H$_2$ at a backing pressure of 4–6 bar was used to generate the NH$_3$–H$_2$ complexes in the molecular jet. In a few of the experiments, we used also neon or helium as a carrier gas. In all cases, the gas mixture adiabatically expanded into the cavity or multipass cell. The pulsed pinhole nozzle (General Valve, Series 9) of a 1 mm diameter operated at a repetition rate of 10–30 Hz. The accuracy of the measurements is about 100 kHz for MMW spectra and 2 kHz for FTMW spectra.

#### 3.1. OROTRON Experiment

MMW spectra in the frequency range of 112–139 GHz were measured using the intracavity OROTRON spectrometer combined with a molecular jet expansion. This is a well-known technique (Surin et al. 2001) that has been used for more than 15 years for the observation of weakly bound complexes.

Briefly, the MMW generator OROTRON together with a pulsed supersonic jet is placed in a vacuum chamber. The free jet with a pulse duration of 500 µs enters the OROTRON resonant cavity perpendicularly to its axis. The high quality of the cavity ($Q \approx 10^5$) results in nearly 100 effective passes of the MMW radiation through the jet. Molecular absorption causes changes of the electron current in the OROTRON collector circuit and is detected by measuring these current changes. The radiation frequency of the OROTRON generator is modulated at 25 kHz, and phase sensitive detection of the absorption signal is achieved by a lock-in amplifier operated in 2f-mode. In addition, an on–off modulation of the jet is used for
baseline subtraction through a pair of gated integrators. Data averaging occurs within a time window of 1 ms. The double modulation technique substantially improves the signal-to-noise ratio. A small fraction of the OROTRON radiation is taken out from the cavity through coupling slits in the center of spherical mirror and mixed on a Schottky diode with the radiation of a MW synthesizer for frequency determination. The range of operation of the OROTRON tube used is 112–155 GHz, with a few small gaps. The double resonance method was applied for measurements at 75–80 GHz, outside the OROTRON frequency range. A MW synthesizer (Rohde & Schwarz, SMF100A) followed by wide-band amplifier and tripler (Virginia Diodes, Inc., AMC-S179/180) was used as a pump radiation source, giving relatively high output power (up to 10 mW).

3.2. SuJeSTA Experiment

The supersonic jet spectrometer for terahertz applications (SuJeSTA; Caris et al. 2009) has been applied for measurements of the NH$_3$–(o)-H$_2$ transitions at frequencies from 150 to 230 GHz. To obtain this frequency range, the 8–14 GHz output frequency of a synthesizer (Agilent 83650 B) is multiplied by a commercial multiplier chain (Virginia Diodes, Inc.). The resulting millimeter-wave radiation crosses a pulsed molecular jet approximately 5 cm downstream in a perpendicular position. Multipass optics (10 paths) is used to increase the signal-to-noise ratio. The absorption of radiation in the jet is detected by a low-noise liquid-He cooled InSb hot electron bolometer. The frequency of the synthesizer is modulated with a sine wave of 40 kHz, and phase sensitive detection of the signal is achieved by a lock-in amplifier operated in 2f-mode. Similar to the experiments with the OROTRON spectrometer, we used in addition to the frequency modulation of the radiation source an on–off modulation of the jet for baseline subtraction through a pair of gated integrators. Apart from substantially improving the signal-to-noise ratio, the double modulation technique suppresses standing wave etalon effects.

3.3. FTMW Experiment

The $J = 1$–0 line of (o)-NH$_3$–(o)-H$_2$ ($\Sigma_g^+$) near 39 GHz was measured at very high spectral resolution (0.1 ppm) with a high-$Q$ FTMW spectrometer, the details of which are available elsewhere (McCarthy et al. 1997). The sample gas is injected through a pulsed pinhole nozzle into an evacuated Fabry–Perot resonator via a small hole in one of the cavity mirrors. A near resonant $\pi/2$ microwave pulse creates a macroscopic polarization of the molecular ensemble, and the resulting coherent emission signal is recorded as a function of time. Subsequently, Fourier transformation yields the frequency spectrum. Because the IF bandwidth of this spectrometer is very narrow, about 0.5 MHz, wide spectral searches are undertaken by synchronously changing the applied frequency and mirror separation under computer control. The (o)-NH$_3$–(o)-H$_2$ spectra at each setting of the cavity were averaged over 500 cycles at the 6 Hz repetition rate of the nozzle, using a gas sample consisting of about 0.5% NH$_3$ in 3–6 bar of normal H$_2$.

All observed transitions are Doppler-doubled, since the molecular beam travels parallel to the resonator axis. The full width at half-height for each line is 15 kHz, and the uncertainty in the line center frequencies is estimated to be $\approx 2$ kHz.

At the extremely high resolution of the FTMW spectrometer, hyperfine structure due to the nuclear spin-spin and spin-rotation interactions of the H$_2$ part of the complexes is well resolved. The double resonance experiment was also performed to measure the $J = 2$–1 line of (o)-NH$_3$–(o)-H$_2$ ($\Sigma_e^+$) near 78 GHz, albeit with somewhat lower accuracy (20–50 kHz).

4. Observed Rotational Spectrum and Analysis

According to the bound states calculations (Section 2), the complexes of ammonia with (o)-H$_2$ are more strongly bound than those with (p)-H$_2$, and the formation of the NH$_3$–(o)-H$_2$ species in the molecular jet is more favorable. The initial search for rotational transitions was performed with the OROTRON spectrometer in the 115–118 GHz range, where the R(2) line of (o)-NH$_3$–(o)-H$_2$ in the ground $\Sigma_g^+$ state was predicted. One line was found at 117,789 MHz that is 1.3 GHz higher than the expected value. Then, the R(1) transition was successfully detected at 78,836 MHz (about 900 MHz higher than the theoretical value) by the double resonance technique using the supposed R(2) transition as a probe, thus confirming the assignment of both lines. The illustration of the double resonance recording is shown in Figure 3. In the same manner, two R(2) transitions at 112 GHz and two R(1) transitions at 75 GHz were detected and assigned for another spin modification, (p)-NH$_3$–(o)-H$_2$, in the $\Pi_e/\Pi_e$ state.

These initial observations allowed a more accurate prediction of the higher-$J$ transitions for the measurements with the SuJeSTA, in the frequency range from 150 to 230 GHz. The R(3), R(4), R(5) transitions were detected for (o)-NH$_3$–(o)-H$_2$ in the ground $\Sigma_g^+$ state, and the R(3), R(4) transitions for (p)-NH$_3$–(o)-H$_2$ in the $\Pi_e/\Pi_e$ state.

Finally, the lowest $J = 1$–0 transition of (o)-NH$_3$–(o)-H$_2$ in the ground $\Sigma_g^+$ state was measured near 39 GHz with the FTMW spectrometer. The observed line of (o)-NH$_3$–(o)-H$_2$ is split by the quadrupole interaction of the nitrogen nucleus ($I_N = 1$) into three hyperfine components, $F_1 = 1$–1, 2–1, and 0–0, and each component, except for $F_1 = 0$–0, is split further into three components due to the magnetic nuclear spin interaction of the H nuclei ($I_{H_2} = 1$), where $F_1$ and $F$ denote the angular momenta $F_1 = J + I_N$ and $F = F_1 + I_{H_2}$, respectively. Applying the double resonance technique to the detected R(0) transition, the R(1) line of (o)-NH$_3$–(o)-H$_2$ near 78 GHz was also observed. Six $^{14}$N hyperfine components $F_1 = 2$–2, 1–0, 2–1, 3–2, 1–2, and 1–1 were resolved, which complements the initial measurement of the same rotational transition in the double resonance OROTRON experiment. All measured microwave and millimeter-wave transitions of the (o)-NH$_3$–(o)-H$_2$ and (p)-NH$_3$–(o)-H$_2$ complexes are listed in Table 1.

To analyze the observed spectra, we used an empirical energy expression for symmetric top molecules, in which the rotational energy including centrifugal distortion terms for each $K$-stack of levels were represented by a power series in $[J(J + 1) - K^2]$

$$E = B[J(J + 1) - K^2] - D[J(J + 1) - K^2]^2 + H[J(J + 1) - K^2]^3 + L[J(J + 1) - K^2]^4,$$

where $K = 0$ for the $\Sigma$ states and $K = 1$ for the $\Pi$ states. The quadrupole hyperfine interaction due to the N nucleus ($I_N = 1$) is given by

$$H_{eqQ} = (1/4)eqQ(3I_{H_2}^2 - I_N^2),$$
where $I_N$ and $I_{N2}$ represent the nuclear spin of N and its projection on the intermolecular axis.

The hyperfine interaction of the H$_2$ unit (for (α)-H$_2$ species) originates from two sources, $H_{siH} = H_{siH} + H_{slH}$ (Kellogg et al. 1939, 1940). The first term $H_{siH}$ denotes the interaction between the H nuclear spins and the rotation of the complex,

$$H_{siH} = -4I_{H2} \cdot J,$$

where $I_{H2}$ is the resultant nuclear spin of H$_2$ and c is the nuclear spin-rotation interaction constant. The second term $H_{slH}$ denotes the nuclear spin magnetic dipole–dipole interaction,

$$H_{slH} = -\frac{5d}{(2J-1)(2J+3)} \left[3(I_{H2} \cdot J)^2 + (3/2)I_{H2} \cdot J - I_{H2} \cdot J^2\right],$$

where $d$ is the nuclear spin-spin interaction constant for NH$_3$–(α)-H$_2$.

The transitions of NH$_3$–H$_2$ assigned in this work were fitted using the PGOPHER program, which is open to the public (Western 2016). According to the corresponding measurement accuracies, the frequencies of the MMW and FTMW transitions were given weights of 1:50 in the fitting procedure. The double resonance frequencies measured with the FTMW spectrometer were included with a weight of 10. The results of the fit for NH$_3$–(α)-H$_2$ are given in Table 2, together with the rotational constants and hyperfine coupling constants determined from the theoretical energy levels and wave functions. The weighted value of the root mean squared deviation $\sigma_{fit} = 106$ kHz is close to our experimental uncertainty for the MMW data.

5. Discussion

The calculated positions of the lower states (≤25 cm$^{-1}$) with $K = 0$ and 1 of the NH$_3$–H$_2$ complex that involve pure rotational transitions detected in the present work are shown in Figure 2. It was established in the bound state calculations and confirmed by the experiment that (α)-NH$_3$–(α)-H$_2$ has a ground state with $K = 0$ ($\Sigma$), while the ground state of (p)-NH$_3$–(α)-H$_2$ is a $K = 1$ (Π) state. The levels in Figure 2 are designated also by free internal rotor quantum numbers ($J_{NH3}$, $K_{NH3}$). Such a free internal rotor interpretation is of limited validity for NH$_3$–(α)-H$_2$, however, since analysis of the calculated wave functions shows that the $J_{NH3}$ values are strongly mixed by the anisotropic interaction potential. Thus the contributions of the ($J_{NH3}$, $K_{NH3}$) = (0, 0) and (1, 0) wave functions to the ground $K = 0$ ($\Sigma$) state of (α)-NH$_3$–(α)-H$_2$ are 51% and 43%. For the ground $K = 1$ (Π) state of (p)-NH$_3$–(α)-H$_2$, the contributions of the ($J_{NH3}$, $K_{NH3}$) = (1, 1) and (2, 1) wave functions are 86% and 13%.

The inversion tunneling motion of ammonia is nearly quenched for all states ($\Sigma$ and Π levels) in (p)-NH$_3$–(α)-H$_2$. For the (p)-NH$_3$–(p)-H$_2$ species, the situation is somewhat different. The calculated splitting of the $\Sigma$ levels is about 0.765 cm$^{-1}$, which is comparable with the value of the inversion splitting in free NH$_3$ (0.7934 cm$^{-1}$). Qualitatively, this picture is the same as observed and calculated for the NH$_3$–Ar complex (Zwart et al. 1991; Loreau et al. 2014), where the inversion motion of ammonia is hardly affected in the $\Sigma = 0$ states, while it is nearly quenched in the Π states. The reason that the inversion splittings are much smaller in NH$_3$–(α)-H$_2$ than in NH$_3$–(p)-H$_2$ is that the anisotropy of the intermolecular potential with respect to the orientation of H$_2$ is reflected by the interaction of NH$_3$ with (α)-H$_2$, whereas it is largely averaged out when NH$_3$ interacts with (p)-H$_2$.

In Tables 1 and 2 the measured transition frequencies and determined molecular parameters of (α)-NH$_3$–(α)-H$_2$ and (p)-NH$_3$–(α)-H$_2$ are compared with the results of bound state calculations. The theory predicts accurately the pure rotational transitions for the observed $K$-stacks, as can be seen by comparison, but the (Obs.–Calc.) deviations grow rapidly with increasing total angular momentum and amount to about +0.09 cm$^{-1}$ at the maximum calculated value of $J = 6$. This indicates that the end-over-end rotational constant $B$ from the calculations is too small by about 1%, which corresponds to the average distance $R$ being too large by about 0.5%. A possible reason could be that the minimum in the intermolecular potential occurs slightly too far outward, because our calculations use the rigid monomer model, which may be somewhat inaccurate.

The average center-of-mass distances $\langle R \rangle$ are calculated to be 3.77 and 3.86 Å for (α)-NH$_3$–(α)-H$_2$ and (p)-NH$_3$–(α)-H$_2$, respectively, from the observed rotational constants, using the pseudo-diatomic approximation. The force constants for the vdW stretch vibration derived from the $D_0$ values are $k = 0.48$ and 0.61 N m$^{-1}$, while the vdW stretch frequencies are calculated to be 67.4 and 75.9 cm$^{-1}$ for (α)-NH$_3$–(α)-H$_2$ and (p)-NH$_3$–(α)-H$_2$, respectively.

Dynamical information about the orientation of the ammonia unit within the van der Waals complex can be obtained from the determined quadrupole coupling constants using the expression $eqQ = eqQ_0 \langle P_2(\cos \theta_{NH3}) \rangle$, where $eqQ_0$ is the quadrupole coupling constant for the free NH$_3$ molecule, −4.0898 MHz (Marshall & Muentzer 1981), and $\theta_{NH3}$ is the angle between the $C_3$ axis of NH$_3$ and the intermolecular axis. The expression assumes that complexation with the H$_2$ molecule has little effect on the electron distribution around the $^{14}$N nucleus, and the angular brackets represent averaging over the internal motions of ammonia in the complex. Solving this expression for $\theta_{NH3}$ yields two possible angles 42°9’/137°1 for the $\Sigma_f$ state of (α)-NH$_3$–(α)-H$_2$. The ab initio equilibrium structure value of $\theta_{NH3} = 0^\circ$ is closer to the first number. Such
is the angle between the $H_2$ bond and the

The Legendre polynomial factor $\langle P_2(\cos \vartheta_{\text{NH}_3}) \rangle$ in the previous equation will be zero if the ammonia subunit undergoes free internal rotation. For (o)-NH$_3$-(o)-H$_2$, it is 0.306, a value that is remarkably large in comparison to $-0.066$ for the Ne-(o)-NH$_3$ (van Wijngaarden & Jäger 2001) and $-0.086$ for Ar-(o)-NH$_3$ (Nelson et al. 1986) complexes. This suggests a more hindered internal motion of NH$_3$ in the (o)-NH$_3$-(o)-H$_2$ complex. The different sign of $\langle P_2(\cos \vartheta_{\text{NH}_3}) \rangle$ for (o)-NH$_3$-(o)-H$_2$ assumes an “on average” more parallel orientation of NH$_3$ to the intermolecular axis, in contrast to more perpendicular in case of Ar– and Ne–(o)-NH$_3$. The theoretical $\langle P_2(\cos \vartheta_{\text{NH}_3}) \rangle$ factor (0.268) obtained from the calculated ground $\Sigma_f$ state wave functions of (o)-NH$_3$-(o)-H$_2$ and the corresponding angle (44°3) agree well with experiment (0.306; 42°6).

The magnetic nuclear spin interaction parameters of the H nuclei in o-H$_2$ provide information about the average orientation of the hydrogen molecule with the complex. The hyperfine coupling constant $d$ determined for (o)-NH$_3$-(o)-H$_2$ is 24.29 kHz, while the $d_{\text{H}}$ value for the free H$_2$ molecule is reported to be 57.671 kHz from molecular beam experiments (Harrick et al. 1953). The equation $d = d_{\text{H}} \langle P_2(\cos \vartheta_{\text{H}}) \rangle$, where $\vartheta_{\text{H}}$ is the angle between the H$_2$ bond and the intermolecular axis, can be used to estimate the average value $\langle P_2(\cos \vartheta_{\text{H}}) \rangle$, which is sensitive to the internal rotation state of H$_2$. The derived $\langle P_2(\cos \vartheta_{\text{H}}) \rangle$ value of 0.42 for (o)-NH$_3$-(o)-H$_2$ is almost equal to 0.4 expected for uniaxial free rotation (Yu et al. 2005; Harada et al. 2014). It is also worth noting that the hyperfine coupling constant inferred from our study ($d = 24.29$ kHz) is very close to the value of 24.68 kHz determined earlier for the (p)-H$_2$O-(o)-H$_2$ molecular complex (Harada et al. 2014). The theoretical $\langle P_2(\cos \vartheta_{\text{H}}) \rangle$ factor (0.39) obtained from the calculated ground $\Sigma_f$ state wave functions of (o)-NH$_3$-(o)-H$_2$ agrees well with experiment (0.42).
Unfortunately, we were unable in the present study to detect the pure rotational transitions in the \( \Sigma \) and \( \Pi \) states of the \((p)\text{-}H_2\) nuclear spin species (shown in Figure 2, left). This is not surprising with the use of normal hydrogen, because NH\(_3\) complexes containing \((o)\text{-}H_2\) bind significantly stronger than those with \((p)\text{-}H_2\). Also, in H\(_2\text{O}\)–H\(_2\) spectra reported by van der Avoird & Nesbitt (2011), the \((p)\text{-}H_2\) complexes could not be observed, and a similar stability difference between the complexes of H\(_2\text{O}\) with \((p)\text{-}H_2\) and \((o)\text{-}H_2\) was explained in this paper in more detail by a kinetic mechanism. Moreover, for the \((p)\text{-}H_2\) complex, the dipole moment may be averaged out to a larger extent because of a more nearly free rotation of NH\(_3\) in the complex. It seems that an enriched sample of \((p)\text{-}H_2\) is necessary for the production and observation of the \((o)\text{-}NH_3\text{–}(p)\text{-}H_2\) and \((p)\text{-}NH_3\text{–}(o)\text{-}H_2\) complexes.

6. Conclusions

This paper describes the first observation of the pure rotational spectrum of the NH\(_3\)–H\(_2\) complex and a calculation of the rovibrational bound states on a 5D intermolecular potential surface obtained through high-level ab initio calculations. The observed transitions were assigned to two nuclear spin species, \((o)\text{-}NH_3\text{–}(o)\text{-}H_2\) and \((p)\text{-}NH_3\text{–}(o)\text{-}H_2\). These data were included in a fit to determine a set of empirical molecular parameters for both \((o)\text{-}NH_3\text{–}(o)\text{-}H_2\) and \((p)\text{-}NH_3\text{–}(o)\text{-}H_2\). All bound rovibrational levels of the four nuclear spin species were computed for total angular momentum \(J = 0\text{–}6\).

A significant fraction of the NH\(_3\)–H\(_2\) binding energy goes into the zero-point energy associated with the intermolecular vibrations and internal rotations: the dissociation energies \(D_0\) are 32.43, 34.25, 59.78, and 66.00 cm\(^{-1}\) for \((o)\text{-}NH_3\text{–}(p)\text{-}H_2\), \((p)\text{-}NH_3\text{–}(p)\text{-}H_2\), \((o)\text{-}NH_3\text{–}(o)\text{-}H_2\), and \((p)\text{-}NH_3\text{–}(o)\text{-}H_2\), respectively. The computed energy levels were compared with the rotational spectra measured in the present work. We found good agreement with the experiment for all detected stacks, although we noted a systematic increase of the rotational energy differences with increasing \(J\), which indicates that the calculated end-over-end rotational constant of the complex is too small by about 1\%. The reason for the latter deviation may be the use of a rigid monomer model.

Finally, we conclude that the present results provide a considerable amount of new information, both experimental and theoretical, which elucidates the intermolecular interactions and dynamics in the astrophysically relevant NH\(_3\)–H\(_2\) system.

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