The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/16140

Please be advised that this information was generated on 2017-09-04 and may be subject to change.
The NH$_3$ umbrella motion in the Ar–NH$_3$ dimer

J.W.I. van Bladel, A. van der Avoird and P.E.S. Wormer
Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Received 2 March 1992

In the calculation of the van der Waals states of Ar–NH$_3$ we have explicitly included the umbrella coordinate which corresponds with the $v_2$ vibration and the inversion tunneling of the NH$_3$ monomer in the complex. We have calculated the rovibrational states of the complex derived from the monomer vibration inversion ($v = \pm 1$) states with $v = 0$ and 1. As expected, we find very little interaction between the $v = 0$ and the $v = 1$ states and good agreement with our earlier approximate model for the $0^+$ and $0^-$ states, which was compared with experimental far-infrared spectra. The $1^+$ and $1^-$ states are coupled more strongly with the intermolecular motions, however. Comparison with a recently observed $v = 0 \rightarrow 1$ infrared band of Ar–NH$_3$ shows that the umbrella coordinate dependence of the ab initio intermolecular potential might still be improved.

1. Introduction

The Ar–NH$_3$ complex has been subject to detailed spectroscopic studies in the microwave, far-infrared and mid-infrared regions [1–9]. In two articles [6,8] an effective angular Ar–NH$_3$ potential has been fitted to these spectra. Very recently, Schmuttenmaer [9] has even obtained a complete (three-dimensional) intermolecular potential surface, in which the long range part was mostly fixed by ab initio calculations [10], while some parameters that determine the short range repulsion and the van der Waals well, have been fitted to the microwave and far-infrared spectra. In our own work we have used a complete ab initio potential [10] to calculate the bound rovibrational levels and the spectra of Ar–NH$_3$. In our first paper [11] we computed the intermolecular vibrations for $J = 0, 1, 2$ and 3; the umbrella vibration ($v_2$) and inversion of NH$_3$ were neglected in this study. The agreement between the experimental data known at that time and our calculations was good. When later new transitions were found, it appeared that not all our predictions were correct, which we attribute to deficiencies in our potential.

In our second paper [12], we scaled one term in the angular expansion of the ab initio potential to regain agreement with experiment. Furthermore, we calculated all the rovibrational levels up to $J = 15$ and the effect of the NH$_3$ umbrella inversion on these levels. A complete theoretical far infrared spectrum was generated by calculating the intensities of all the allowed transitions from a dipole function. The umbrella inversion splitting was computed via a simple model. This model assumes that the inversion tunneling of the NH$_3$ monomer can be adiabatically separated from the van der Waals motions and that the inversion splitting is considerably smaller than the van der Waals transition frequencies. For the $v_2$ ground state of NH$_3$, this splitting is indeed small. The same model was used by Schmuttenmaer [9] in his fitting of the three-dimensional Ar–NH$_3$ potential to the far-infrared spectra. However, for the $v_2$ first excited state, which is observed in the mid infrared spectra [1,3,7], the inversion tunneling splitting becomes comparable to the typical van der Waals transition frequencies and the model is expected to fail.

In the present paper we calculate, again from the (scaled) ab initio potential, the rotation–vibration inversion levels for both the ground and $v_2$ first excited states of Ar–NH$_3$, taking the inversion coordinate explicitly into account. Hence, we include the full coupling between the umbrella motions of NH$_3$. 

Correspondence to: A. van der Avoird, Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

0301-0104/92/$05.00 © 1992 Elsevier Science Publishers B.V. All rights reserved.
and the van der Waals motions of the Ar–NH₃ complex. The test of our simple model [12] for the inversion splitting in the Ar–NH₃ complex which is thus obtained, is also of interest for the empirical fit of the potential in ref. [9], which uses the same model. The ab initio potential of Bulski et al. [10] was already calculated for four different umbrella angles. In our earlier papers we only used the data for the equilibrium angle, but in this work we need all four umbrella angles. Our calculations will be compared especially to the mid-infrared spectra [1,3,7] that probe the \( \nu_2 \) first excited state. Calculations of the state-to-state scattering cross sections for Ar and NH₃ with the same potential are in progress [13]. With the \( \nu_2 \) first excited states obtained in this paper and the calculated scattering states we will also be able to calculate the line widths of the observed transitions.

The use of an ab initio potential - rather than a model potential fitted to the spectra - can be justified by several arguments. In the first place, the ab initio potential contains explicitly the coupling between the umbrella angle and the van der Waals coordinates in this complex, which the current model potentials do not give. Secondly, it is important to investigate the strengths and weaknesses of ab initio potentials, since they are relatively easy to generate and in principle contain a wealth of information. The infrared spectroscopy of van der Waals molecules offers a beautiful testing ground for this investigation.

2. Theory

The coordinate system for the Ar–NH₃ dimer is discussed in detail in the appendix of a previous paper [12]. The distance between the center of mass of NH₃ and the argon atom is denoted by \( R \). The angles \( \beta \) and \( \alpha \) are the polar angles of the dimer bond axis relative to a space-fixed frame. Thus, the coordinates \( \alpha \) and \( \beta \) define the dimer frame. The principal axes frame of NH₃ has the Euler angles \( \gamma \), \( \phi \) and \( \varphi \), relative to this dimer frame. In ref. [12] we defined the inversion coordinate \( \rho \) as the distance between the center of mass of NH₃ and the nitrogen nucleus. In this work we find it more convenient to define this coordinate as the angle between the \( C_3 \) axis of NH₃ and one of the N–H bonds.

The Hamiltonian for the nuclear motions of the dimer can be separated into the following terms:

\[
\hat{H} = \hat{H}_{\text{umb}}(\rho) + \hat{H}_{\text{rad}}(R) + \hat{H}_{\text{ang}}(R, \beta, \varphi, \gamma, \beta, \alpha, \rho) .
\] (1)

This separation of the Hamiltonian \( \hat{H} \) does not imply an approximation. In fact, the term \( \hat{H}_{\text{ang}} \) contains all coupling terms between radial, angular and umbrella motions. We only apply the separation in order to generate a convenient basis for diagonalizing \( \hat{H} \).

The umbrella Hamiltonian \( \hat{H}_{\text{umb}} \) is associated with the umbrella motion of free NH₃. The Hamiltonian \( \hat{H}_{\text{rad}} \) describes the van der Waals stretching motion. Before attempting to diagonalize the full Hamiltonian we consider the first two terms separately.

In describing the umbrella motion of NH₃ we have introduced two constraints. We fixed the N–H distance at \( r_0 \) and kept the three-fold symmetry. The umbrella Hamiltonian \( \hat{H}_{\text{umb}} \) describes both the fast umbrella vibration (\( \nu_2 \)) and the slow inversion tunneling as a combined motion in the inversion coordinate \( \rho \). This Hamiltonian can be derived [14] along the same lines as described by Papoušek and Aliev [15]. The umbrella Hamiltonian can be written as

\[
\hat{H}_{\text{umb}}(\rho) = -\frac{\hbar^2}{2} g(\rho)^{-1/2} \frac{\partial}{\partial \rho} I_{pp}^{-1}(\rho) g(\rho)^{1/2} \frac{\partial}{\partial \rho}
+ V_{\text{umb}}(\rho) ,
\] (2)

where

\[
g(\rho) = I_{xx}, I_{yy}, I_{zz}, I_{pp} , \tag{3a}
\]

\[
I_{xx}(\rho) = I_{yy}(\rho) = 3m_H r_0^2 \left( \frac{1}{2} \sin^2 \rho + \zeta \cos^2 \rho \right) , \tag{3b}
\]

\[
I_{zz}(\rho) = 3m_N r_0^2 \sin^2 \rho , \tag{3c}
\]

\[
I_{pp}(\rho) = 3m_H r_0^2 \cos^2 \rho + \zeta \sin^2 \rho , \tag{3d}
\]

\[
\zeta = m_N / (3m_H + m_N) . \tag{3e}
\]

Here \( m_H \) and \( m_N \) are the masses of the hydrogen and nitrogen nuclei, respectively. The first term is the kinetic energy expressed as a part of the Laplace operator in a curvi-linear coordinate system with metric tensor \( g = \text{diag}(I_{xx}, I_{yy}, I_{zz}, I_{pp}) \). The determinant of \( g \) is denoted by \( g(\rho) \). The quantities \( I_{xx}, I_{yy} \) and \( I_{zz} \) are the moments of inertia of NH₃, which depend on the inversion coordinate \( \rho \). The generalized moment of inertia \( I_{pp} \) is associated with the umbrella motion and depends also on the inversion coordinate. The second term \( V_{\text{umb}}(\rho) \) is the double-well potential. We
have chosen to represent this potential by a harmonic force field augmented by a Gaussian
\[ V_{\text{umb}}(\rho) = \frac{1}{2} k (\rho - \frac{1}{2} \pi)^2 + a \exp \left[ -b (\rho - \frac{1}{2} \pi)^2 \right]. \] (4)

The parameters \(a\) and \(b\) are related to two other parameters: the angle \(\rho_0\) at which the double-well potential has its minimum and the height of the barrier \(V_{\text{barrier}} = V_{\text{umb}}(\frac{1}{2} \pi) - V_{\text{umb}}(\rho_0)\). The symmetry of the problem (molecular symmetry group \(D_3h\), see ref. [12]) can be used to block the Hamiltonian matrix of \(H_{\text{umb}}\) into a positive and negative parity part (under the operation \(E\), which transforms \(\rho\) into \(\pi - \rho\)). The Hamiltonian \(H_{\text{umb}}\) is diagonalized in the basis
\[ \sin(m \rho), \]
\[ m = 1, 3, ..., 99, \text{ for positive parity}, \]
\[ m = 2, 4, ..., 100, \text{ for negative parity}. \]

Since the volume element corresponding to the \(\rho\) coordinate is \(g(\rho)^{1/2} d\rho\), this basis is not orthogonal and a generalized eigenvalue problem was solved. In this manner we obtained 100 umbrella eigenstates \(\varphi_{\rho}^{\text{umb}}(\rho)\).

Next we diagonalize \(H_{\text{rad}}\), which is defined by
\[ H_{\text{rad}}(R) = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial \rho^2} R + V_{\text{rad}}(R), \] (5a)
\[ V_{\text{rad}}(R) = (4\pi)^{-1/2} v_{00}(R, \rho = \frac{1}{2} \pi). \] (5b)

This Hamiltonian describes the van der Waals stretch motion in the radial coordinate \(R\). The first term represents the kinetic energy; for the potential \(V_{\text{rad}}(R)\) we choose the isotropic part of the intermolecular potential for the flat \(NH_3\) configuration. The intermolecular potential has been taken from Bulski et al. [10]. They performed ab initio calculations for 360 points on the potential surface and expanded this potential in spherical harmonics. The coefficients in this expansion depend on both \(R\) and \(\rho\). The analytical representation of the \(\rho\) dependence is given in section 3. As found in our earlier paper [12], in which we included the inversion tunneling via a model, the ab initio potential has to be scaled to give good agreement with experiment. This scaling consists of multiplying the short range parameter \(F_{33}\) in the expansion coefficient \(v_{33}(R, \rho)\), see eq. (6) below, by a factor of 1.43. In this work we applied the same scaling, irrespective of the value of the inversion coordinate \(\rho\). In order to diagonalize \(H_{\text{rad}}\), we have used the orthogonal Morse type basis functions \(R^{-1} \chi_n(R)\) \((n = 0, ..., 5)\). The functions \(\chi_n(R)\) [16] are characterized by three parameters: \(D_{\text{Morse}}, R_{\text{Morse}}\) and \(\omega_{\text{Morse}}\). These parameters were optimized to give the lowest energy for the ground state of the radial problem. In this manner we obtained six radial eigenstates \(\varphi_{s}^{\text{rad}}(R)\).

The angular Hamiltonian \(H_{\text{ang}}\), which contains also the coupling between radial, angular and umbrella motions, is defined by
\[ H_{\text{ang}}(R, \theta, \varphi, \gamma, \beta, \alpha, \rho) = \frac{1}{2} \sum_{m,n} I_{mn}^{(2)}(\rho) \frac{1}{2} \mu R^2 \left( \beta^2 + \gamma^2 - 2 \beta \gamma J \right) \]
\[ - V_{\text{rad}}(R) + \sum_{l,m} (-1)^m v_{lm}(R, \rho) S_{lm}(\theta, \phi), \] (6)

where \(S_{lm}\) denotes a normalized tesseral harmonic (real spherical harmonic). The first term is the rotational Hamiltonian of \(NH_3\), in which the rotational constants depend on the inversion coordinate \(\rho\). Note that this is the remaining part of the Laplace operator in the curvi-linear coordinate system with metric tensor \(g\) mentioned above. It would have been possible to include this term into \(H_{\text{umb}}\). The only difference with the present treatment would have been that the functions \(\varphi_{\rho}^{\text{umb}}(\rho)\) would have become \(j, k\) dependent in that case. This is expected to yield only a very slight improvement, whereas the computations would have been considerably more complex. The second term in eq. (6) describes the overall rotation of the dimer and the Coriolis coupling between internal and overall rotation. The last two terms form the intermolecular potential, from which the isotropic potential \(V_{\text{rad}}(R)\) has to be subtracted, because it is already included in eq. (5).

Having \(\varphi_{\rho}^{\text{umb}}(\rho)(u = 0^+, 0^-, 1^+ \text{ and } 1^-)\) and \(\varphi_{s}^{\text{rad}}(R)(s = 0, ..., 5)\) at our disposal we diagonalize the full Hamiltonian \(\tilde{H}\) defined in eq. (1), in the orthonormal basis
\[ \left( \frac{(2j+1)(2J+1)}{32\pi^3} \right)^{1/2} D_{jJ}^{(2)}(\alpha, \beta, \gamma) \varphi_{\rho}^{\text{umb}}(\rho) \varphi_{s}^{\text{rad}}(R), \] (7)
where the first two functions are Wigner rotation functions describing the monomer internal rotations and dimer overall rotations, respectively. We will follow the same procedure as in ref. [12] to diagonalize $\hat{H}$. First we neglect the small off-diagonal Coriolis interaction, contained in the term $\hat{J} \cdot \hat{J}/\mu R^2$, which makes the helicity $\Omega$ a good quantum number. For fixed $J$, we take the lowest $\ell_{max}$ eigenfunctions for different helicities ($\vert \Omega \vert \leq J$) as basis functions to solve the eigenvalue problem of the Hamiltonian $\hat{H}$, including the off-diagonal Coriolis interaction. The resulting eigenfunctions will be specified by $\vert J M \ell \rangle$, where $i$ labels the different van der Waals states.

In order to describe the splitting of the rovibrational energies caused by the interaction with the quadrupole of the $^{14}$N ($I=1$) nucleus, we use the first non-vanishing term of the spherical multipole expansion

$$\hat{H}_Q = q^{(2)} \cdot Q^{(2)} .$$

Here $2q^{(2)}$ is the gradient of the field at the position of the nitrogen nucleus. This field, which is due to the electrons and the other nuclei, interacts with the quadrupole tensor $2Q^{(2)}$. Note that the factor 2 in front of $Q^{(2)}$ is necessary to adhere to the convention commonly used in the description of the quadrupole splitting.

Coupling the total angular momentum $J$ and the $^{14}$N nuclear spin $I$ to a resulting $F$, we must evaluate in first-order perturbation theory

$$E_Q = \langle (JI)FM_F \vert \hat{H}_Q \vert (JI)FM_F \rangle .$$

Doing this along the lines described in ref. [17], we find

$$E_Q = eQqJ \cdot \frac{2J+3}{J} Y(J, I, F) ,$$

where

$$Y(J, I, F) = \frac{\frac{3}{2}C(C+1) - I(I+1)J(J+1)}{2(2J-1)(2J+3)I(I-1)} ,$$

$$C = F(F+1) - J(J+1) - I(I+1) ,$$

$$Q = 2\langle II \vert \hat{Q}^{(2)} \vert II \rangle ,$$

$$q_J = 2\langle JJi \vert \hat{q}_J^{(2)} \rangle \langle \theta, \beta, \gamma \rangle \vert JJi \rangle .$$

The operators $\hat{Q}^{(2)}$ and $\hat{q}_J^{(2)}$ are with respect to the space-fixed frame.

In the NH$_3$ monomer frame the field gradient is axial and has only one component $q = 2q_0^{(2)}$. Here we assume that the field gradient is not changed by the weak interactions with the argon atom and we do not explicitly include its $\rho$ dependence. The operator $\hat{q}_J^{(2)}$ is related to $\hat{q}_0^{(2)}$ by [12]

$$\hat{q}_0^{(2)}(\theta, \beta, \gamma) = \sum_{\mu} q_0^{(2)} D_{\mu 0}^{(2)}(0, \theta, \phi) D_{\mu 0}^{(2)*}(\alpha, \beta, \gamma)$$

$$= q_0^{(2)} \sum_{\mu} (-1)^{\mu} C_{\mu}^{(2)}(\theta, \gamma) C_{\mu}^{(2)}(\beta, 0) ,$$

where $C_{\mu}^{(2)}$ is a spherical harmonic normalized to $4\pi/(2\mu+1)$. It is easy to calculate the matrix elements of this operator between the basis functions of eq. (7) and, thus, to evaluate eqs. (11c) and (10).

It is of interest to observe that for most of the van der Waals states in Ar-NH$_3$ the helicity decoupling approximation is nearly valid. If it were exactly valid, $\Omega$ would be a good quantum number and the only contribution to $eQq_J$ for states with $\Omega = 0$ (also called $I$ states [6,8]) would arise from the term in eq. (12) with $\mu = 0$. In that case, the quadrupole splitting would be proportional to $\langle C_{\mu}^{(2)}(\theta, \gamma) \rangle = \langle P_2(\cos \theta) \rangle$. Our calculations do not make the helicity decoupling approximation, however, i.e. we account for the mixing of states with different $\Omega$, in the manner explained above.

### 3. Results and discussion

In tables 1–4 we show the parameters used and the results obtained for the diagonalization of $\hat{H}_{\text{umb}}$. The parameters $k$, $\rho_0$ and $V_{\text{barrier}}$ are fitted such that the measured inversion tunneling splitting in the $v_2$ ground state (23786 MHz [18]) and both transition

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Parameters used for the NH$_3$ umbrella Hamiltonian</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_{\text{NH}}$ = 1.0078 amu</td>
<td>$m_{\text{NH}}$ = 14.0031 amu</td>
</tr>
<tr>
<td>$n_0$ = 1.0124 Å</td>
<td>$k_0$ = 1.809 mdyn Å</td>
</tr>
<tr>
<td>$\rho_0$ = 112.434$^a$</td>
<td>$V_{\text{barrier}}$ = 2024.0 cm$^{-1}$</td>
</tr>
</tbody>
</table>

$^a$Ref. [21].

$^b$Ref. [22].
Table 2
Calculated levels in cm⁻¹

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>512.7670 a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>513.5604 a)</td>
<td></td>
</tr>
<tr>
<td>1+</td>
<td>1445.4135</td>
<td></td>
</tr>
<tr>
<td>1-</td>
<td>1480.6318</td>
<td></td>
</tr>
</tbody>
</table>

a) ν₂ zero point energy 513.1637.

Table 3
Transitions

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Experiment, refs. [18,19]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0+→0−</td>
<td>23786.5 MHz</td>
<td>23786 MHz</td>
</tr>
<tr>
<td>0+→1−</td>
<td>967.86 cm⁻¹</td>
<td>968.08 cm⁻¹</td>
</tr>
<tr>
<td>0−→1+</td>
<td>931.85 cm⁻¹</td>
<td>931.66 cm⁻¹</td>
</tr>
</tbody>
</table>

Table 4
Rotational constants in cm⁻¹

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Experiment, ref. [20]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axx</td>
<td>Azz</td>
<td>Axx</td>
</tr>
<tr>
<td>0+</td>
<td>10.000</td>
<td>6.337</td>
</tr>
<tr>
<td>1+</td>
<td>10.189</td>
<td>6.182</td>
</tr>
</tbody>
</table>

frequencies to the ν₂ first excited state (931.66 and 968.08 cm⁻¹ [19]) are reproduced with minimum deviation. As can be seen in table 3, the microwave and infrared transitions used in the fit are indeed reproduced very well. Table 4 gives the calculated rotational constants (Axx=Ayy and Azz) for a given umbrella inversion state u, as defined by

\[ A_\lambda = \frac{1}{2} \int_0^\pi g^{1/2}(\rho) \, d\rho \, I_\lambda^{-1}(\rho) \, |\phi^{\text{umb}}_u(\rho)|^2 \]

and the experimental values of Bunker et al. [20]. In fig. 1 a graphical representation is given of the potential \(V_{\text{umb}}(\rho)\) and the four lowest eigenfunctions obtained from diagonalizing \(H_{\text{umb}}\). Note that the wavefunctions only have appreciable amplitude between 45° and 135°.

The parameters used in the Morse type basis for the Hamiltonian \(H_{\text{rad}}\) are: \(D_{\text{Morse}}=134.274\ \text{cm}^{-1}\), \(R_{\text{Morse}}=3.884\ \text{Å}\) and \(\omega_{\text{Morse}}=32.636\ \text{cm}^{-1}\). The reduced mass of the complex is \(\mu=11.9396\ \text{amu}\), when we take the masses from table 1 and \(m_{\text{Ar}}=39.9627\ \text{amu}\) for the mass of argon [21].

Fig. 2 shows the dependence of the dominant expansion coefficients \(v_{lm}(R, \rho)\) on the umbrella coordinate \(\rho\) for a fixed value \(R=3.69\ \text{Å}\), near the equilibrium distance. The ab initio calculated points are marked with asterisks. The analytical representation of the curves is a sixth-order polynomial in \(\rho-\frac{1}{2}\pi\), containing even/odd terms depending on whether \(l+m\) is even/odd. These polynomials are used to calculate matrix elements of \(v_{lm}(R, \rho)\) between different inversion states \(\phi_{\text{umb}}^u(\rho)\). After the rightmost ab initio points some sharp increases or decreases arise in the curves. These are artifacts of the fit and it has been checked that they do not have an effect on the calculated integrals over \(v_{lm}(R, \rho)\), because the amplitude of the wavefunctions \(\phi_{\text{umb}}^u(\rho)\) is very small in this region (see fig. 1).

First we performed calculations of the rovibrational levels for the ν₂ ground state with the basis of
Fig. 2. The dominant expansion coefficients of the anisotropic potential (with scaling in $v^3$) for $R = 3.69\ \text{Å}$.

Eq. (7), including the two umbrella states $u = 0^+$ and $0^-$. The calculations including the off-diagonal Coriolis interactions were performed with $v_{\text{max}} = 50$. The results of these calculations are given in table 5, for the lowest allowed rotational levels ($J = 0$ or $J = 1$) of different van der Waals states $i$. The convergence of the energies ranges from $2 \times 10^{-4}$ to $4 \times 10^{-2}\ \text{cm}^{-1}$, for the lowest and highest state shown, respectively. The energies given in table 5 include the off-diagonal Coriolis interaction, as well as the shift due to the inversion tunneling of the NH$_3$ monomer. These shifts, as given explicitly in the next column of table 5, have been deduced from the two tunneling components calculated. Note that for ortho-NH$_3$--Ar only one of these components is Pauli allowed (see ref. [12]). In addition the expectation values of the dimer bond length $\langle R \rangle$, of the rotational constant $B = \langle \hbar^2 / 2\mu R^2 \rangle$ and of the second Legendre polynomial $\langle P_2(\cos \theta) \rangle$ are given for each van der Waals state calculated. If no external field is applied, the expectation value of the first Legendre polynomial $\langle P_1(\cos \theta) \rangle$ will be zero due to the symmetry $\Pi(D_{3h})$. In order to compare with experimental data we define the effective quadrupole coupling constant as

$$eQ_{\text{eff}} = \frac{2J + 3}{J} eQ_{\nu^2}.$$

The values calculated for this constant can also be found in table 5. The quadrupole coupling constant for the $\nu_2$ ground state of free NH$_3$ has been taken as $eQ_{\nu^2} = -4.08983\ \text{MHz}$ [23], for both the $0^+$ and $0^-$ states. Our results are generally in good agreement with the experimental data given in table 5. Note that for states with $|\Omega| \approx 1$ (also called $\Pi$ states [6,8]) the effective quadrupole coupling constants are not given by $-eQ_{\nu^2} \langle P_2(\cos \theta) \rangle$, because terms other than $\mu = 0$ in eq. (14) are important. The model used in ref. [12] to calculate the effect of the NH$_3$ inversion motion on the van der Waals states relied on the fact that the inversion tunneling splitting in the free monomer is much smaller than the van der Waals transition frequencies. If we compare the inversion tunneling shifts found in this work to those found in ref. [12] (see table 5), we may conclude that this model indeed works well for the $\nu_2$ ground state.

Because the energy difference between the ground and $\nu_2$ first excited states is large ($\approx 950\ \text{cm}^{-1}$) compared to the van der Waals frequencies, the inclusion of the $1^+$, $1^-$ states is expected to have little influence on the energies presented in table 5. To check this we performed some calculations including four umbrella states ($u = 0^+, 0^-, 1^+ \text{ and } 1^-$) in the basis. These calculations are much more expensive than those presented above. It was found that the influence on the energies was approximately $10^{-2}\ \text{cm}^{-1}$ and on the inversion tunneling shifts approximately $10^{-4}\ \text{cm}^{-1}$, which proves our assertion.

Next we calculated the rovibrational levels for the $\nu_2$ first excited state, including the two umbrella states $u = 1^+$ and $1^-$ in the basis of eq. (7). The calculations including the off-diagonal Coriolis couplings were performed with $v_{\text{max}} = 35$. The convergence of the energies is the same as for the $\nu_2$ ground state. The results of the calculations are compiled in table 6.

We used the same labeling as for the $\nu_2$ ground state, augmented with a prime, to facilitate comparison. The inversion tunneling splitting in the NH$_3$, monomer in its $\nu_2$ first excited state ($35.6\ \text{cm}^{-1}$) is comparable to the van der Waals transition frequencies. Therefore, we expect the coupling between the umbrella
Table 5

Energies, inversion tunneling shifts and expectation values of the dimer bond length \( \langle R \rangle \), of the rotational constant \( B = \langle h^2/2\mu R^2 \rangle \) and of the second Legendre polynomial \( \langle P_2(\cos \theta) \rangle \) for the lowest \( J \) level in each rotational ladder in the \( v_2 \) ground state of Ar-NH\(_3\). The approximate quantum number \( |\Omega| \) is equal to the \( J \) value given in parentheses (so, \( J = 0 \) and \( J = 1 \) indicate the \( \Sigma \) and \( \Pi \) states of refs. [4-9]). Also given are the effective quadrupole coupling constants \( eQ_{\text{eff}} \). For levels with \( J = 0 \), the latter constants are listed for the next level in the rotational ladder (\( J = 1 \)).

<table>
<thead>
<tr>
<th>vDW state / Symmetry</th>
<th>Energy (cm(^{-1}))</th>
<th>Inversion shifts (cm(^{-1}))</th>
<th>( \langle R \rangle ) (Å)</th>
<th>( B ) (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>this work</td>
<td>model (^a)</td>
<td>experiment (^b)</td>
</tr>
<tr>
<td>ortho</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 ( \text{A}_2^\pi(J=0) )</td>
<td>-86.88983</td>
<td>0.30885</td>
<td>0.30392</td>
<td>3.792</td>
</tr>
<tr>
<td>1a ( \text{A}_2^\pi(J=1) )</td>
<td>-70.10364</td>
<td>0.34950</td>
<td>0.34728</td>
<td>3.752</td>
</tr>
<tr>
<td>1b ( \text{A}_2^\pi(J=1) )</td>
<td>-70.10035</td>
<td>0.34960</td>
<td>0.34737</td>
<td>3.752</td>
</tr>
<tr>
<td>2 ( \text{A}_2^\pi(J=0) )</td>
<td>-60.53940</td>
<td>0.30437</td>
<td>0.31263</td>
<td>3.986</td>
</tr>
<tr>
<td>3 ( \text{A}_2^\pi(J=0) )</td>
<td>-55.90431</td>
<td>-0.24658</td>
<td>-0.25881</td>
<td>3.922</td>
</tr>
<tr>
<td>para</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0a ( \text{E}'(J=0) )</td>
<td>-77.38287</td>
<td>-0.35517</td>
<td>-0.35090</td>
<td>-0.38989</td>
</tr>
<tr>
<td>0b ( \text{E}^+(J=0) )</td>
<td>-76.67523</td>
<td>0.35517</td>
<td>0.35090</td>
<td>0.38989</td>
</tr>
<tr>
<td>1a ( \text{E}'(J=1) )</td>
<td>-75.68856</td>
<td>0.00333</td>
<td>0.00409</td>
<td>0.00708</td>
</tr>
<tr>
<td>1b ( \text{E}'(J=1) )</td>
<td>-75.68191</td>
<td>0.00333</td>
<td>0.00409</td>
<td>0.00708</td>
</tr>
<tr>
<td>2a ( \text{E}^+(J=1) )</td>
<td>-66.88853</td>
<td>0.00004</td>
<td>0.00003</td>
<td>0.00080</td>
</tr>
<tr>
<td>2b ( \text{E}^+(J=1) )</td>
<td>-66.88845</td>
<td>0.00004</td>
<td>0.00003</td>
<td>0.00080</td>
</tr>
</tbody>
</table>

\( \langle P_2(\cos \theta) \rangle \) values are given in parentheses (\( \text{MH} \_z \))

- Ref. [12] with \( 2|J| = 0.8 \text{ cm}^{-1} \).
- Refs. [2,4,5].
- Refs. [2,5,6].

motion and the van der Waals modes to be stronger. Indeed, if we look at the eigenfunctions we observe a much stronger mixing in the \( v_2 \) first excited state than in the \( v_2 \) ground state. Especially the levels 0' and 3' of ortho-NH\(_3\)–Ar are mixtures of the basis functions \( \gamma = 0, \alpha = 0, \) \( s = 0 \) and \( j = 1, \alpha = 1, \gamma = 0, \) \( s = 0 \).

The level 0' contains approximately 44% of the former and 34% of the latter state. For the level 3' these percentages are 19% and 63%, respectively. This mixing is very sensitive to the energy differences between the levels involved and, thus, to the anisotropy of the potential surface.

Fraser et al. [7] have found a transition at 950.482165(3) cm\(^{-1}\) (band origin) and assigned this to the 0→1a'/1b' transition in ortho-NH\(_3\)–Ar. This transition is red shifted by approximately 1.3 cm\(^{-1}\)
Table 6

Energies, inversion tunneling shifts and expectation values of the dimer bond length \( \langle R \rangle \), of the rotation constant \( B = \langle h^2/2\mu R^2 \rangle \) and of the second Legendre polynomial \( \langle P_2(\cos \theta) \rangle \) for the lowest \( j \) level in each rotational ladder in the \( v_2 \) first excited state of Ar-NH\(_3\). The approximate quantum number \( |\Omega| \) is equal to the \( j \) value given in parentheses \((J=0 \text{ and } J=1 \text{ indicate the } \Sigma \text{ and } \Pi \text{ states of refs. } [4-9])\).

<table>
<thead>
<tr>
<th>VdW state ( i )</th>
<th>Symmetry</th>
<th>Energy ( (\text{cm}^{-1}) )</th>
<th>Inversion shifts ( (\text{cm}^{-1}) )</th>
<th>( \langle R \rangle ) ( (\text{Å}) )</th>
<th>( B ) ( (\text{GHz}) )</th>
<th>( \langle P_2(\cos \theta) \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho 1a'</td>
<td>A(^2_2) ( (J=1) )</td>
<td>865.34277</td>
<td>-15.56876</td>
<td>-15.54861</td>
<td>3.773</td>
<td>3.004 (^b)</td>
</tr>
<tr>
<td></td>
<td>B(^2_2) ( (J=1) )</td>
<td>865.34943</td>
<td>-15.57126</td>
<td>-15.55216</td>
<td>3.773</td>
<td>3.004 (^b)</td>
</tr>
<tr>
<td></td>
<td>A(^2_0) ( (J=0) )</td>
<td>871.63906</td>
<td></td>
<td>19.31064</td>
<td>13.76727</td>
<td>3.921</td>
</tr>
<tr>
<td></td>
<td>A(^2_1) ( (J=1) )</td>
<td>891.72554</td>
<td></td>
<td>3.969</td>
<td>2.765</td>
<td>-0.240</td>
</tr>
<tr>
<td></td>
<td>A(^2_0) ( (J=1) )</td>
<td>891.72593</td>
<td></td>
<td>3.969</td>
<td>2.765</td>
<td>-0.240</td>
</tr>
<tr>
<td></td>
<td>B(^2_0) ( (J=0) )</td>
<td>902.47299</td>
<td>14.11710</td>
<td>13.64964</td>
<td>4.041</td>
<td>2.656</td>
</tr>
<tr>
<td>para 0a'</td>
<td>E(^0_0) ( (J=0) )</td>
<td>857.65263</td>
<td>-15.88079</td>
<td>-15.79142</td>
<td>3.742</td>
<td>3.052</td>
</tr>
<tr>
<td></td>
<td>E(^1_1) ( (J=1) )</td>
<td>863.50028</td>
<td>-0.00066</td>
<td>-0.12385</td>
<td>3.791</td>
<td>2.976</td>
</tr>
<tr>
<td></td>
<td>E(^0_1) ( (J=1) )</td>
<td>863.50160</td>
<td>0.00066</td>
<td>0.12385</td>
<td>3.791</td>
<td>2.976</td>
</tr>
<tr>
<td></td>
<td>E(^0_0) ( (J=0) )</td>
<td>885.18257</td>
<td></td>
<td>3.967</td>
<td>2.763</td>
<td>-0.239</td>
</tr>
<tr>
<td></td>
<td>E(^1_1) ( (J=1) )</td>
<td>885.26885</td>
<td>-0.03007</td>
<td>-0.00178</td>
<td>3.920</td>
<td>2.821</td>
</tr>
<tr>
<td></td>
<td>E(^0_1) ( (J=1) )</td>
<td>885.32899</td>
<td>0.03007</td>
<td>0.00178</td>
<td>3.935</td>
<td>2.801</td>
</tr>
<tr>
<td></td>
<td>E(^0_0) ( (J=0) )</td>
<td>889.41420</td>
<td>15.88079</td>
<td>15.79142</td>
<td>3.722</td>
<td>3.085</td>
</tr>
</tbody>
</table>

\(^a\) Ref. [12] with \( 2|\Delta| = 35.6 \text{ cm}^{-1} \).

\(^b\) Experiment [7]: \( \beta = 2.82691 \text{ (1 GHz) } \).

with respect to the \( j=0, k=0, u=0 \rightarrow j=1, k=0, u=1 \) transition at 951.8 \text{ cm}^{-1} in free NH\(_3\). We calculate a blue shift of 0.2 \text{ cm}^{-1}. As found in ref. [12], the position of the 1a'/1b' states is very sensitive to the scaling of the short range parameter \( F_3 \) in the anisotropic term \( v_3 = R, p \) of the intermolecular potential. This parameter was optimized for the \( v_2 \) ground state. Also the upper levels 1a'/1b' involved in the above transition will depend sensitively on this scaling. We conclude that the scaling applied is in fact too simple to give correct van der Waals energies for both the ground and \( v_2 \) first excited states. Because the upper state has a positive \( \Lambda \)-type doubling constant, Fraser et al. assert that the 1a'/1b' states are below the 0' state. As can be seen in table 3 we confirm this finding.

Earlier, Fraser et al. [1] and Bizzarri et al. [3] found three single lines which were attributed to Ar-NH\(_3\), but not assigned. The positions of these photodissociation lines are 938.6893(2), 970.5498(4) and 974.6248(4) \text{ cm}^{-1}. Fraser et al. [7] assign the line at 938.69 cm\(^{-1}\) to a rotational transition in the 0a/0b->1a'/1b' band of para-NH\(_3\)-Ar. We calculate the band origin of this transition at approximately 940 \text{ cm}^{-1}, which is consistent with the above assignment. Furthermore, the two lines near 970 cm\(^{-1}\) can be assigned to rotational transitions in the 0a/0b--3a', the 0a/0b->2a'/2b' or the 0a--0b' band of para-NH\(_3\)-Ar.

In table 6 we list values for the same quantities as in table 5, except for the effective quadrupole coupling constants which probably cannot be measured in the \( v_2 \) first excited state. The inversion splitting predicted by the model of ref. [12] is obtained by replacing the NH\(_3\) monomer splitting for the \( v_2 \) ground state, \( 2|\Delta| = 0.8 \text{ cm}^{-1} \), by the splitting for the \( v_2 \) first excited state, \( 2|\Delta| = 35.6 \text{ cm}^{-1} \). For some states the inversion tunneling splitting calculated deviates substantially from that obtained from the model, as expected. Unfortunately, the experimental data available are still scarce. We can only compare the rotational constant of the 1a'/1b' states. Fraser et al. [7] have found \( B = 2.82691 \text{ (1 GHz) } \), while we find \( B = 3.004 \text{ GHz} \).

We conclude that the modified ab initio potential
is still not perfect. Although the results for the $\nu_2$ ground state are generally in good agreement with experiment, the results for the $\nu_2$ first excited state are still open to improvement. We can in fact improve the potential by using more sophisticated ab initio methods. However, such an improved ab initio potential can only be tested when further experimental data for the $\nu_2$ first excited state become available. From the line width and the time of flight Fraser et al. [7] have deduced that the lower and upper limits for the vibrational predissociation lifetime of the states $1a'/1b'$ are approximately 1 $\mu$s and 1 ms, respectively. By combining the $\nu_2$ first excited states from the present work with the scattering states also calculated in our group [13], we will be able to calculate vibrational predissociation lifetimes, as well as product distributions.

Acknowledgement

We thank Dr. W. Leo Meerts for stimulating discussions and Edgar Olthof for his calculation of the NH$_3$ monomer tunneling states. Part of this work has been performed as an IBM Academic Information Systems (ACIS) project.

References