Fragmentation dynamics of the vibrationally excited ammonia–argon van der Waals complex

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Quantum mechanical calculations have been performed to study the fragmentation dynamics of the Ar–NH$_3$ van der Waals complex excited in the $v_2$ ("umbrella") vibrational level with $v_2=1$. Vibrational predissociation has been investigated for different initial quasibound states, corresponding to excitation in the stretching or bending van der Waals levels or in the tunneling motion of the NH$_3$ umbrella inversion, for both ortho and para varieties of NH$_3$, and for three values of the total angular momentum $J$ and its projection $\Omega$ onto the intermolecular axis, $(J,\Omega)=(0,0)$, $(1,0)$, and $(1,\pm 1)$. The calculations were performed for two different intermolecular potential energy surfaces, one determined $ab\ initio$ by Bulski et al. [J. Chem. Phys. 94, 491 (1991)], and the other where the $ab\ initio$ potential has been scaled to fit spectroscopic data of Ar–NH$_3$, proposed by van Bladel et al. [J. Phys. Chem. 95, 5414 (1991)]. The lifetime obtained from the $ab\ initio$ potential lies within the limits set by experiment for the lowest ortho $\Pi$ (i.e., $|\Omega|=1$) level with $J=1$, while the scaled potential gives too short a lifetime. The results also show that excitation of the van der Waals stretching mode accelerates the predissociation but does not affect the NH$_3$ final state rotational distribution very much. On the other hand, bending or tunneling excitation does lead to a very different final rotational state distribution. Ortho states have very similar final state distributions for $\Sigma_3(|\Omega|=0)$ and $\Pi_1(|\Omega|=1)$ states, but this is not true for para states. Finally, comparing the $ab\ initio$ and scaled potentials, no systematic trend emerges for the amount of even $(\pm)$ and odd $(-)$ symmetry of the final states, but the scaling of the potential shortens the lifetimes, gives a wider final state rotational distribution, and provides more excitation in the $k$ quantum number (the projection of the NH$_3$ rotational angular momentum on its $C_3$ axis). © 1995 American Institute of Physics.

I. INTRODUCTION

van der Waals complexes provide important model problems for understanding energy transfer and relaxation.$^1$ van der Waals complexes have also attracted interest because they provide a direct probe of intermolecular forces.$^{2,3}$

In recent years, the argon–ammonia system has been the subject of intense experimental and theoretical investigation. Some of the reasons for this are the soft internal inversion (umbrella) mode of NH$_3$, which can couple to the intermolecular vibrational modes, and the ability of the NH$_3$ subunit to undergo nearly free internal rotation within the complex. From an experimental point of view, a variety of spectroscopic techniques has been used; microwave,$^{4,5}$ millimeter wave,$^6$ and far infrared$^{7,8,6}$ to examine the internal rotor levels of the complex derived from the lowest few rotation–inversion states. Fraser et al.$^9$ have established limits to the $v_2$ excited state lifetime from a measurement of infrared spectral linewidths. Recently, Grushow et al.$^{10}$ reported a study of the states of Ar–NH$_3$ derived primarily from the $j=2, k=\pm 1$ states of free ammonia, improving the determination of the angular Ar–NH$_3$ interaction potential. And, finally, Schmuttenmaer et al.$^{11}$ have observed eight more intermolecular vibrational states of Ar–NH$_3$ by tunable far infrared spectroscopy, and determined the complete three-dimensional intermolecular potential energy surface. Two relevant nonspectroscopic studies of Ar–NH$_3$ have been reported as well. Schleipen et al.$^{12}$ have measured the state-to-state cross sections for rotational excitation of ortho and para NH$_3$ by Ar, which are very sensitive to the anisotropy in the repulsive part of the intermolecular potential energy surface. And Schramm et al.$^{13}$ have measured the second virial coefficients which relate to the well depth.

From the theoretical point of view, Bulski et al.$^{14}$ have determined an $ab\ initio$ potential energy surface for the interaction of Ar with NH$_3$. Using this potential energy surface, van Bladel et al.$^{15}$ have determined the van der Waals rovibrational states of the Ar–NH$_3$ dimer for a total angular momentum $J=0–3$, not including inversion tunneling. They found that, as inferred from experiment, the NH$_3$ monomer exhibits nearly free internal rotations within the complex. However, the van der Waals vibrations show characteristic differences from free internal rotations. In particular, there is a strong mixing between the fundamental stretch vibration of the dimer and the lowest bending mode. Using these results, they were able to assign the only band in the far infrared...
region that had been observed at the time to the lowest, primarily bending, mode, and to predict further transitions in the far infrared region. In a following publication,\textsuperscript{16} Van Bladel et al. introduced the tunneling inversion of the NH\textsubscript{3} monomer by means of a simple model, based on the separation of the inversion tunneling motion (frequency =0.8 cm\textsuperscript{-1}) and the van der Waals modes (frequencies\textsuperscript{20} =20 cm\textsuperscript{-1}), to generate the vibration-rotation-inversion spectrum of Ar-NH\textsubscript{3} (up to \(J=15\)). They observed that the \(v_{10}(R)\) and \(v_{13}(R)\) terms in the anisotropic expansion of the potential were especially important and proposed scaling the \(v_{3}\) term to obtain a good agreement between the computed and measured far-infrared and microwave frequencies of ortho and \(p\) Ar-NH\textsubscript{3}. Finally, the same authors\textsuperscript{17} have explicitly included the umbrella coordinate which corresponds to the \(v_{2}\) vibration and the inversion tunneling of the NH\textsubscript{3} monomer in the calculation of the van der Waals states of Ar-NH\textsubscript{3} derived from the monomer vibration-inversion \(|p_{2}\pm\rangle\) states with \(v_{2}=0,1\), where \(v_{2}\) denotes the number of quanta in the \(v_{2}\) vibration. As expected, they found very little interaction between the \(v_{2}=0\) and \(v_{2}=1\) states, and good agreement with their earlier approximate model for the \(|0\rangle\) and \(|0\rangle\) states. However, since for \(v_{2}=1\) the tunneling frequency is of the order of 35 cm\textsuperscript{-1}, the \(|1\rangle\) and \(|1\rangle\) states are more strongly coupled to the intermolecular motions. Comparing with the experimentally measured\textsuperscript{9} \(v_{2}=1 \leftrightarrow 0\) infrared band of Ar-NH\textsubscript{3}, they concluded that the umbrella coordinate dependence of the \textit{ab initio} intermolecular potential might still be improved. van der Sanden et al.\textsuperscript{18} have used both the \textit{ab initio} and the scaled potentials to study rotational excitation and inversion of NH\textsubscript{3} by collisions with Ar. They found that the scaled potential gave better agreement with the experimental data of Ref. 12 than the \textit{ab initio} potential, implying that the anisotropy of the \textit{ab initio} potential was too small.

Apart from the potential from Bulski et al. used in the previously described studies, other calculations have been performed to investigate the Ar-NH\textsubscript{3} potential energy surface. Chalasinski et al.\textsuperscript{19} determined two cuts through the potential surface from \textit{ab initio} calculations in 1989. Tao and Klemperer\textsuperscript{21} also carried out an \textit{ab initio} study and calculated a large number of points on the surface using M\textsuperscript{3}ller-Plesset perturbation theory up to 4th order (MP4). However, the only other complete analytical potential energy surface available up to now has been determined recently by Schmuttenmaer et al.\textsuperscript{20} from a least-square fit to 61 far infrared and microwave vibration-rotation-tunneling measurements and temperature-dependent second virial coefficients. Since the latter potential does not depend on the NH\textsubscript{3} \(v_{2}\) vibration coordinate we have used the potential of Bulski et al. and the scaled variation proposed by Van Bladel et al.

In this work, we are interested in the vibrational predissociation of the Ar-NH\textsubscript{3} dimer excited to the \(v_{2}=1\) vibrational level of NH\textsubscript{3} in the ground electronic state. We test the predictions of both the \textit{ab initio} and the scaled potentials for the experimentally measured linewidth (for the lowest \textit{ortho} \(J=1, \Omega=1\) quasibound state). We also study the vibrational predissociation from the \(J=0\) and from the \(J=1, \Omega=0, \pm 1\), \textit{ortho} and \textit{para} complex in different van der Waals states with \(v_{2}=1\), for both potentials. For this we solve the quantum mechanical problem including both even (+) and odd (−) tunneling functions explicitly, the \(v_{2}\) vibration of NH\textsubscript{3} within the framework of the Golden Rule, and the rotation of NH\textsubscript{3}. For the \(J=1\) level we apply the Coriolis decoupling approximation, after testing for its validity. We obtain the linewidths of the initial quasibound states, and the final NH\textsubscript{3} \(|0\pm j,k\rangle\) tunneling-rotational distribution. We discuss the results as a function of the nature of the initial quasibound states, and examine the influence of overall rotation and the role of the potential. The method is presented in Sec. II, with computational details in Sec. III. Section IV is devoted to the results and Sec. V to the discussion. Finally, the conclusions of this study are given in Sec. VI.

II. METHODOLOGY

In the calculation of the vibrational predissociation of van der Waals complexes, the Golden Rule approximation has proved to be very accurate.\textsuperscript{22} The main reasons for the validity of this approximation are the following. Due to the large difference between the frequencies of the intra and intermolecular modes, the NH\textsubscript{3} vibration can be separated at first order from the other degrees of freedom. Another consequence of this frequency mismatch between the NH\textsubscript{3} and the van der Waals modes is that vibrational predissociation is relatively inefficient. Hence this process can be described as the decay of a quasibound state where NH\textsubscript{3} has one quantum of vibration and the van der Waals modes are in a given level \(n\), to a continuum state at the same total energy where the vibrational energy of NH\textsubscript{3} has been transferred to the van der Waals degrees of freedom, causing the dissociation

\[
\text{Ar-NH}_3(v_2 = 0) \rightarrow \text{Ar} + \text{NH}_3(v_2 = 1, n)
\]

\[
\rightarrow \text{Ar} + \text{NH}_3(v_2 = 0, j, k, \pm). \tag{1}
\]

In the framework of the Golden Rule approximation, the partial width associated with vibrational predissociation from an initial quasibound state \(|\psi_0\rangle\) to a final dissociative continuum channel with rotational quantum numbers \((j, k)\) and tunneling symmetry \((\pm)\) for NH\textsubscript{3}, \(|\psi_{jk \pm}\rangle\), is given by

\[
\Gamma_{hjk \pm} = \pi |\langle \psi_0 | W | \psi_{jk \pm} \rangle|^2, \tag{2}
\]

where \(W\) is the operator which couples the quasibound state with \(v_2=1\) to the continuum channels with \(v_2=0\), and the continuum functions are energy-normalized.

We have studied the vibrational predissociation of the ground, first and second excited van der Waals levels for \(J=0\), and of the ground and first excited van der Waals levels for \(J=1\) (\(J\) being the total angular momentum of the system). The quasibound states of Ar-NH\textsubscript{3} have been calculated as in Ref. 17, except that Coriolis coupling was neglected for the \(J=1\) states. We use the \textit{ab initio} potential of Bulski et al.,\textsuperscript{14} and a modification proposed by van Bladel et al. to get better agreement with the experimental infrared and microwave spectra.\textsuperscript{16} We calculate the final continuum wave functions by integrating the coupled channel equations.

We used three coordinate frames. The vector \(R\), pointing from the center of mass of NH\textsubscript{3} to the argon atom, is refer-
enced by its polar angles $\beta$ and $\alpha$ in the space-fixed frame. The orientation of $R$ defines the $z$-axis of the body-fixed frame (dimer frame). Rotating the body fixed (dimer) frame by the Euler angles $\varphi$, $\theta$, and $\gamma$, we obtain the NH$_3$ frame. The $z$-axis of this frame lies along the $C_3$ axis of NH$_3$ and one of the hydrogen atoms is in the $xz$ plane, along the positive $x$ direction. The monomer umbrella inversion coordinate $\rho$ is defined as the angle between the $C_3$ axis of NH$_3$ and one of the N--H bonds.

After separation of the center-of-mass motion, the Hamilton operator of the Ar--NH$_3$ complex can be written as

$$
\hat{H} = \hat{H}_{\text{umb}}(\rho) + \hat{H}_{\text{vod}}(\gamma, \varphi, \rho, R, \beta, \alpha, \rho),
$$

where $\hat{H}_{\text{umb}}$ is the Hamiltonian for the umbrella motion of ammonia which depends on the coordinate $\rho$. This Hamilton operator describes both the fast $\nu_2$ umbrella vibration and the slow inversion tunneling. The tunneling states of NH$_3$ are labeled by the parity of their wave function under inversion with respect to the symmetry plane with $\rho=(\pi/2)$. This notation is combined with that of the $\nu_2$ vibration, which corresponds to the “umbrella” vibrational mode. For instance, $|0+\rangle$ designates the tunneling state with parity $+$ and $\nu_2=0$ (no excitation in the $\nu_2$ umbrella vibration). In NH$_3$, the height and width of the barrier are such that the $|0+\rangle$ and $|0-\rangle$ states are very close in energy (relative to the bottom of the double well potential 512.7670 cm$^{-1}$ and 513.5604 cm$^{-1}$, respectively) whereas $|1+\rangle$ and $|1-\rangle$ are more separated (1445.4135 cm$^{-1}$ and 1480.6318 cm$^{-1}$, respectively).

The van der Waals Hamiltonian can be written as

$$
\hat{H}_{\text{vod}} = \sum_{\lambda} A_{\lambda}(\rho) j_\lambda^2 + \frac{1}{2\mu R^2} \left( j^2 - 2j \cdot \mathbf{J} \right)
+ \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + V_{\text{int}}(R, \theta, \varphi, \rho).
$$

In Eq. (4) the first term is the rotor Hamiltonian for NH$_3$ (symmetric top Hamiltonian) with rotational constants $A_\lambda (\lambda = x, y, z)$ that depend on the umbrella coordinate $\rho$, and $j_\lambda$ are the components of the NH$_3$ angular momentum in the NH$_3$ frame. The second term describes the overall rotation of the complex (including Coriolis coupling), $\mu$ being the reduced mass of the complex, and $\mathbf{J}$ the total angular momentum operator of the complex. The third term is the kinetic energy for the intermolecular coordinate $R$. The last term, $V_{\text{int}}(R, \theta, \varphi, \rho)$, is the intermolecular potential calculated $ab$ initio by Bulski et al. or its scaled variation. We use its expansion in normalized tesseral harmonics (real spherical harmonics) $S_{lm}$, with $m$ non-negative because the potential is an even function of $\varphi$.

$$
V_{\text{int}}(R, \theta, \varphi, \rho) = \sum_{l,m} (-1)^m v_{lm}(R, \rho) S_{lm}(\theta, \varphi),
$$

where $S_{lm}$ is defined as

$$
S_{lm}(\theta, \varphi) = \left\{ \begin{array}{ll}
Y_{lm}(\theta, \varphi) & \text{if } m = 0 \\
\frac{1}{\sqrt{2}} \left[ (-1)^m Y_{lm}(\theta, \varphi) + Y_{l,-m}(\theta, \varphi) \right] & \text{if } m > 0.
\end{array} \right.
$$

Due to the threefold symmetry of the ammonia, only terms with $m=0,3,6,...$ are present in the expansion of the interaction potential in Eq. (5). The coefficients $v_{lm}(R, \rho)$ were calculated at different points of a grid in $R$ in Ref. and cubic-spline interpolated for our calculations.

We used the same angular basis set as van Bladel et al. in their bound state calculation

$$
\langle \theta \varphi \alpha \beta | J M \Omega | j \rangle = \frac{(2j+1)(2J+1)}{2\pi^3} \sum_{\lambda\mu\nu} D_{\lambda\mu}^* (\alpha, \beta, \gamma) D_{\mu\nu}^* (0, \theta, \varphi),
$$

where $D$ are Wigner rotation functions, $\Omega$ is the quantum number associated with the projection of the total angular momentum $J$ onto the body fixed (dimer) frame $z$-axis, $k$ is the quantum number associated with the projection of $J$ onto the NH$_3$ frame $z$-axis and $M$ is the quantum number associated with the projection of $J$ onto the space-fixed frame $z$-axis. Both $J$ and $M$ are good quantum numbers for the complex. If we neglect Coriolis coupling interaction, $\Omega$ is also a good quantum number.

The molecular symmetry group for Ar--NH$_3$ described by the Hamiltonian in Eq. (3) is the permutation-inversion group PI ($D_{3h}$). The states of the complex are either ortho (with $A'_2$ or $A''_2$ symmetry and a spin statistical weight of 12) or para (with $E'$ or $E''$ symmetry and a spin statistical weight of 6).

The matrix elements of the van der Waals Hamiltonian [Eq. (4)] in the angular basis set [Eq. (6)] are

$$
\langle J'M'\Omega' j'k'|\hat{H}|J M \Omega j\rangle = \left[ \begin{array}{c}
\{ A_\lambda(\rho) j(j+1) + [A_\lambda(\rho) - A_\lambda(\rho)] k^2 \} \delta_{JJ'} \delta_{kk'} \delta_{\Omega\Omega'} + \frac{\hbar^2}{2\mu R^2} \left[ (J(J+1) \\
+ j(j+1) - 2\Omega^2) \delta_{\Omega\Omega'} - C_{\Omega'\Omega}^{+} C_{\Omega'\Omega}^{+} \delta_{\Omega',\Omega' - 1} - C_{\Omega'\Omega}^{+} C_{\Omega'\Omega}^{+} \delta_{\Omega',\Omega' + 1} \right] \delta_{jj'} \delta_{kk'} - \frac{\hbar^2}{2\mu R} B_{J\Omega'} \delta_{jj'} \delta_{kk'} \delta_{\Omega\Omega'} + C_{J'\Omega}^{+} \right] \delta_{J'J} \delta_{M'M'}
\end{array} \right].
$$

\text{(7)}
TABLE I. NH₃ rotational constants (cm⁻¹) and vibration-inversion tunneling state energies. (The reference energy E₀ is the average energy of the NH₃ |0⁺⟩ and |0⁻⟩ states).

<table>
<thead>
<tr>
<th></th>
<th>λ=x,y</th>
<th>λ=z</th>
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<tbody>
<tr>
<td>(0⁺</td>
<td>A₀</td>
<td>0⁺)</td>
</tr>
<tr>
<td>(1⁺</td>
<td>A₀</td>
<td>0⁺)</td>
</tr>
<tr>
<td>(0⁻</td>
<td>A₀</td>
<td>0⁻)</td>
</tr>
<tr>
<td>(1⁻</td>
<td>A₀</td>
<td>0⁻)</td>
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<tr>
<td>(0⁺</td>
<td>A₀</td>
<td>1⁺)</td>
</tr>
<tr>
<td>(1⁺</td>
<td>A₀</td>
<td>1⁺)</td>
</tr>
</tbody>
</table>

Energy (cm⁻¹) (E₀=513.1637 cm⁻¹)

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<tbody>
<tr>
<td></td>
<td>0⁺)</td>
</tr>
<tr>
<td></td>
<td>0⁻)</td>
</tr>
<tr>
<td></td>
<td>1⁺)</td>
</tr>
<tr>
<td></td>
<td>1⁻)</td>
</tr>
</tbody>
</table>

where

\[ C_{jm} = [j(j+1) - \Omega(\Omega \pm 1)]^{1/2}, \]  

(8)

and

\[ g_{jm}(j',j'k',k',\Omega) = (-1)^{n-k'} m \left( \frac{(2j'+1)(2j+1)(2l+1)}{8\pi(1+\delta_{m0})} \right)^{1/2} \]

\[ \times \left( \begin{array}{c} j' \\ \Omega \\ -j' \end{array} \right) \left( \begin{array}{c} l \\ 0 \\ j \end{array} \right) \left( \begin{array}{c} j' \\ -k' \\ m \\ k \end{array} \right) \]

(9)

The last terms in parentheses in Eq. (9) are Wigner 3j symbols. ²⁴

The tunneling basis functions are only coupled by the intermolecular potential and by Aₖ(ρ). As in the study of the NH₃ umbrella motion in the Ar–NH₃ dimer by van Bladel et al., ¹⁷ the inversion coordinate was explicitly taken into account with the basis \( \langle p|v₂\rangle \) of eigenstates of \( \hat{H}_{umb}(\rho) \). The matrix elements of Aₖ(ρ) between basis functions with \( v₂=0 \) and \( v₂=1 \) are small (see Table I) and the energy gap between these states is very large (∼950 cm⁻¹); hence we may neglect these off-diagonal matrix elements. ¹⁷ Because of symmetry properties with respect to inversion, the matrix elements of the intermolecular potential in this basis set obey

\[ \{v₂±|v₂\rangle \langle v₂±\} = 0 \quad \text{for } l+m \; \text{odd}, \]  

(10a)

\[ \{v₂±|v₂\rangle \langle v₂±\} = 0 \quad \text{for } l+m \; \text{even}. \]  

(10b)

Because the coupling between the initial quasibound state and the final dissociative states in Eq. (2) is weak, we applied the Golden Rule approximation to obtain the vibrational predissociation lifetime and the final rotational state distribution of the NH₃ fragment. ²⁶ In the framework of the Golden Rule approximation, the partial width associated with vibrational predissociation from an initial quasibound state \( \psi_b \) to a final dissociative continuum channel with NH₃ rotational quantum numbers \( j, k, \) and tunneling parity \( ±, \) is given by Eq. (2), where the final continuum wave function is to be calculated at the same total energy as the initial quasibound state. Due to the high frequency of the \( v₂ \) vibrational mode, the wave function \( \psi_b \) for the initial quasibound state \( \text{Ar}–\text{NH}_₃ (v₂=1) \) and the energy-normalized wave function \( |\psi_{jk±}\rangle \) for the final continuum state \( \text{Ar}+\text{NH}_₃ (v₂=0, j, k, ±) \) are eigenfunctions of

\[ H_{v₂} = \sum_{p=±} \{ |v₂p\rangle \langle v₂p'| \hat{H}|v₂p\rangle \langle v₂p'| \}, \]  

(11)

with \( v₂=1 \) for the quasibound state and \( v₂=0 \) for the continuum wave function. As mentioned above, the continuum wave functions were expanded in the angular basis set of Eq. (6). The resulting coupled equations were solved by the De Vogelaere integrator. ²⁸ Finally, the coupling \( W \) responsible for vibrational predissociation is

\[ W = \sum_{p=±} |1p\rangle \langle 1p' |\hat{H}|0p\rangle \langle 0p'|. \]  

(12)

The partial widths \( \Gamma_{bjk±} \) in Eq. (2) are proportional to the probability of the quasibound state of Ar–NH₃ decomposing to yield a particular final state \( (0±j,k) \) of the NH₃ monomer. The total width is given by the sum

\[ \Gamma = \sum_{bjk±} \Gamma_{bjk±} = \pi \sum_{jk±} |\langle \psi_b|W|\psi_{jk±}\rangle|^2 \]  

(13)

from which the vibrational predissociation lifetime of the quasibound state is deduced

\[ \tau = \frac{\hbar}{2\Gamma}. \]  

(14)

and the final rotational-tunneling state distribution of the NH₃ fragment is given by

\[ P_{jk±} = \frac{\Gamma_{jk±}}{\Gamma}. \]  

(15)

In Eq. (7), the off-diagonal terms in \( \Omega \) are due to Coriolis coupling (off-diagonal terms due to \( \lambda \)). In the bound state calculations of van Bladel et al., ¹⁵ this coupling has been shown to give corrections to the energy of the \( J>0 \) quasibound states (for \( J=1 \) the largest one is 0.03 cm⁻¹) which are very small with respect to the kinetic energy in the continuum channels. The amount of mixing between \( \Omega=0 \) and \( \Omega=±1 \) is sufficient to perturb the intensities of the \( \text{para} \) \( |1\rangle=1 \rightarrow 1 \) transitions, but this is because the \( |\Omega|=1 \rightarrow 1 \) transition is much weaker than that from \( |\Omega|=0 \rightarrow 1 \). ¹⁶ The percentage of mixing remains very small in the quasibound states. On the other hand, neglecting this coupling in the collisional excitation of NH₃ with Ar led to significant errors. ¹⁸ However, in a photodissociation event the number of \( J \) populated is much smaller than in a collision, especially if the experiment is performed in a supersonic expansion. In order to check to what extent Coriolis coupling affects the results of the vibrational predissociation, we have performed two calculations, one including and the other neglecting off-diagonal Coriolis coupling in Eq. (7). In the first case, only \( J \)
TABLE II. Vibrational predissociation lifetimes and widths (HWHM) of the Ar···NH$_3$ ($v_2=1$) quasibound states calculated with the \textit{ab initio} (ab) and scaled (sc) potentials, and assignment. For the nature of the quasibound states, see Table IV. For the $\Omega$ states we have listed the inversion symmetry of the $\Omega$=1 component; for the $\Omega$=0 component it is reversed. $\Gamma$ (MHz) were calculated as $\Gamma$ (MHz)=$c\Gamma$ (cm$^{-1}$).

<table>
<thead>
<tr>
<th>$J$</th>
<th>State</th>
<th>Energy (cm$^{-1}$)</th>
<th>$\tau_{ab}$ (ns)</th>
<th>$\Gamma_{ab}$ (MHz)</th>
<th>Energy (cm$^{-1}$)</th>
<th>$\tau_{sc}$ (ns)</th>
<th>$\Gamma_{sc}$ (MHz)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho</td>
<td>$\Sigma(1^1_L, v_j=0) (A_\Delta^2)$</td>
<td>873.993 51</td>
<td>372.9</td>
<td>0.213</td>
<td>871.639 06</td>
<td>124.8</td>
<td>0.638</td>
<td>3'</td>
</tr>
<tr>
<td>1</td>
<td>$\Sigma(1^1_L, v_j=0) (A_\Delta^2)$</td>
<td>874.180 05</td>
<td>373.3</td>
<td>0.213</td>
<td>871.831 09</td>
<td>126.3</td>
<td>0.630</td>
<td>3'</td>
</tr>
<tr>
<td>0</td>
<td>$\Sigma(0^1_L, v_j=0) (A_\Delta^2)$</td>
<td>892.343 23</td>
<td>319.1</td>
<td>0.249</td>
<td>887.273 67</td>
<td>54.04</td>
<td>1.473</td>
<td>0'</td>
</tr>
<tr>
<td>1</td>
<td>$\Sigma(0^1_L, v_j=0) (A_\Delta^2)$</td>
<td>892.521 51</td>
<td>319.2</td>
<td>0.249</td>
<td>887.459 91</td>
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<td>1.877</td>
<td>902.472 99</td>
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</tr>
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<td>3.408</td>
<td>2'</td>
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<tr>
<td>para</td>
<td>$\Pi(1^0_M, v_j=0) (A_\Delta^2,A_\Sigma^2)$</td>
<td>875.174 74</td>
<td>212.9</td>
<td>0.374</td>
<td>865.350 37</td>
<td>14.94</td>
<td>5.326</td>
<td>1$a'$,1$b'$</td>
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<tr>
<td>1</td>
<td>$\Pi(1^0_M, v_j=1) (A_\Delta^2,A_\Sigma^2)$</td>
<td>893.059 66</td>
<td>19.36</td>
<td>4.110</td>
<td>891.726 27</td>
<td>6.07</td>
<td>13.11</td>
<td>4$a'$,4$b'$</td>
</tr>
</tbody>
</table>

and $M$ are good quantum numbers. In the second case (helicity decoupling approximation),$^{22,29}$ $\Omega$ is also a good quantum number since the only coupling between channels with different $\Omega$ values was due to the Coriolis terms.

III. COMPUTATIONAL ASPECTS

The following masses were used in the calculations: $m_{Ar}$=39.9627 amu, $m_{N}$=14.0031 amu, and $m_{H}$=1.0078 amu. The matrix elements of the rotational constants of NH$_3$ over the eigenfunctions of $\tilde{H}_{\text{orb}}(p)$ are displayed in Table I, as well as the energies of the $\left|v_2\pm\right|$ levels (from Ref. 17).

The continuum wave functions were determined by integrating the coupled channel equations from $R$=3 Å to $R$=10 Å by steps of 0.011 Å, and were asymptotically matched to sine/cosine functions.

The expansion of the interaction potential in Eq. (5) was given in Ref. 14 with 15 terms ($l\leq7$ and $m\leq6$). The coefficients $\langle v_2^p \mid v_j \mid v_2^p \rangle$ ($v_j=0$ or 1, $p=\pm$) are calculated$^4$ at 33 grid points in $R$ (from 2 to 16 Å) and cubic-spline interpolated. According to Ref. 16 the \textit{ab initio} potential has to be scaled to give good agreement with spectroscopic data for the bound Ar···NH$_3$ complex. This scaling consists in multiplying the short range parameter $v_{33}$ in Eq. (5) by a factor of 1.43. In order to check the sensitivity of the results to the potential, we performed our calculations both for the original \textit{ab initio} potential and for the modified ("scaled") potential.

To check the effect of Coriolis coupling, we performed calculations including the off-diagonal terms for the \textit{ortho} states with $J=1$. For a converged calculation ($j_{\text{max}}=16$) neglecting Coriolis coupling gives an error of less than 0.09 for the percentage of the individual final state population and of 0.01 ns for the lifetime. We concluded that Coriolis correction can be neglected in our case ($J=0$ or 1).

We conducted Coriolis-decoupled calculations for $J=0$ and 1, for both the \textit{ortho} and \textit{para} species. We investigated the vibrational predissociation of the three lowest van der Waals states with $J=0$, $\Omega=0$ and $J=1$, $\Omega=0$, and of the two lowest van der Waals states with $J=1$ and $\Omega=\pm1$. Convergence in the solution of the coupled equations was obtained with $j_{\text{max}}=17$. The maximum number of coupled channels used was 194 for states with $J=0$ (97 coupled channels per parity block) and 192 channels for states with $J=1$ (96 coupled channels per parity block). The programs were executed on the CRAY C98 of IDRIS. A converged calculation took 9 min of cpu time.

IV. RESULTS

In Table II we present the vibrational predissociation lifetimes and linewidths for all the $J=0$, $\Omega=0$ and $J=1$, $\Omega=\pm1$ levels studied, calculated with the \textit{ab initio} and the scaled potentials. In Tables II–V we label states with $|\Omega|=0$ and 1, by $\Sigma$ and $\Pi$, respectively, in accordance with Fraser \textit{et al.}.$^9$ To indicate which angular basis function $j_{\Delta}$ corresponds to the even (+) and odd (−) inversion tunneling functions, gives the largest contribution to the eigenstate, we include in parentheses, together with the quantum number $v_j$ to denote the number of quanta in the van der Waals stretch. This means that we designate the states, for instance, by $\Sigma(1^1_L, v_j=0)$.

The lifetimes are very different, ranging from 6 ns to 380 ns. They change with the nature of the quasibound state (\textit{ortho} or \textit{para}, van der Waals excitation), and with $\Omega$, but not with $J$. They do not change with the sign of $\Omega$ since Coriolis decoupling is valid, hence we only give one entry for $\Omega\neq0$. They are also sensitive to the potential, the lifetimes for the scaled potential being shorter than those corresponding to the \textit{ab initio} potential which is less anisotropic.
Table III gives the average rotational energy of the NH₃ fragment after dissociation for each parity of the final tunneling state. Like the lifetimes in Table II, they are very sensitive to the nature of the quasibound state, to the value of \( \Omega \) and to the potential, but not to the value of \( J \). In addition, the average rotational energy is not the same for the + and the − tunneling states of NH₃, and the relative magnitude of these two energies also varies.

Table IV presents the characterization of the initial quasibound states, and Table V gives the percentage of + and − parity of the NH₃ tunneling states before and after dissociation. Since the \( \Sigma \) states with \( J=1 \) have the same characterization as the \( \Sigma \) states with \( J=0 \), and give the same final proportion of + and − tunneling states, we omitted the corresponding entries in Tables IV and V. Except for the ortho \( \Sigma \) states, and for the \( \Sigma \) para states which have mainly an odd inversion tunneling character, the quasibound states have a well-defined parity with respect to inversion of NH₃. However, this character tends to be lost during the dissociation, as can be seen in Table V where the proportions of +/− final states are almost all between 40% and 60%, with many levels leading to near equipartition. Some levels that were originally almost purely one given parity can even give a larger proportion of the opposite parity in the final states [e.g., the \( \Omega(1^+_o, v_4=0) \) ortho state].

In Tables VI and VII we present the final rotational state distributions for the NH₃ fragment from all the initial ortho and para states, respectively. Some selected state distributions are displayed in Figs. 1-4. Figures 1 and 2 correspond to the ortho \( \Omega(1^+_o, v_4=0) \) state, for which the lifetime has been experimentally studied. Figures 3 and 4 present the NH₃ rotational state distribution for the para \( \Sigma(1^+_p, v_4=0) \), which is remarkably selective. Some selection rules appear for the quasibound \( \Sigma \) states and will be given in next section devoted to the discussion of the results. In this section, we also show that some trends can still be found, and the comparison with the experimentally determined lifetimes will be discussed.

V. DISCUSSION

A. Quasibound states

One of the important parameters in the analysis of the results is the nature of the initial quasibound state. In Ar–NH₃, only a few free internal rotor states are mixed. However, for \( v_4=1 \), the tunneling frequency is of the order of the van der Waals frequencies so that the states of the complex can have mixing of the + and − components of the inversion states. As stated above, our state labeling indicates the free rotor state \( j_{25} \) of NH₃ which has the most important contribution to the quasibound state, and which consequently determines the amount of bending excitation, while \( v_4 \) is the quantum number for the van der Waals stretching mode. To indicate the importance of the contributions from the other zero-order states \( j_{25} \) to the quasibound state, we list the main contributions in Table IV.

<table>
<thead>
<tr>
<th>( J )</th>
<th>State</th>
<th>( \pm ) ( j_{25} )</th>
<th>( \pm ) ( j_{25} )</th>
<th>( \pm ) ( j_{25} )</th>
<th>( \pm ) ( j_{25} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \Sigma(1^+_o, v_4=0) )</td>
<td>82.6%</td>
<td>55.5%</td>
<td>71.0%</td>
<td>59.8%</td>
</tr>
<tr>
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<td>( \Sigma(0^+_o, v_4=0) )</td>
<td>74.3%</td>
<td>59.9%</td>
<td>62.5%</td>
<td>56.4%</td>
</tr>
<tr>
<td>1</td>
<td>( \Pi(1^+_o, v_4=0) )</td>
<td>74.8%</td>
<td>53.3%</td>
<td>53.7%</td>
<td>67.7%</td>
</tr>
<tr>
<td>1</td>
<td>( \Pi(1^+_o, v_4=0) )</td>
<td>98.4%</td>
<td>62.0%</td>
<td>98.3%</td>
<td>52.1%</td>
</tr>
<tr>
<td>1</td>
<td>( \Pi(1^+_o, v_4=0) )</td>
<td>98.1%</td>
<td>53.9%</td>
<td>99.5%</td>
<td>51.4%</td>
</tr>
<tr>
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<td>( \Sigma(1^+_o, v_4=0) )</td>
<td>98.4%</td>
<td>68.8%</td>
<td>98.4%</td>
<td>55.5%</td>
</tr>
<tr>
<td>0</td>
<td>( \Sigma(1^+_p, v_4=0) )</td>
<td>99.1%</td>
<td>59.2%</td>
<td>99.5%</td>
<td>58.5%</td>
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<td>( \Sigma(1^+_p, v_4=0) )</td>
<td>74.7%</td>
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<td>96.9%</td>
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<td>( \Pi(1^+_o, v_4=0) )</td>
<td>97.9%</td>
<td>53.7%</td>
<td>94.4%</td>
<td>55.1%</td>
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</table>
TABLE VI. Final Jf rotational state distribution of the NH3 fragment following vibrational predissociation of Ar–NH3 (v3=1) in the ortho states calculated with the ab initio and the scaled potentials. f stands for forbidden channels and c for closed channels.

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<th>4Π+</th>
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<th>6Π+</th>
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B. Lifetimes

As can be seen in Table II, the lifetimes for vibrational predissociation of Ar–NH3 can vary within two orders of magnitude. There are several origins for these variations. The lifetimes are very sensitive to excitation in the van der Waals degrees of freedom. In Ar–NH3, van der Waals excitation leads to shorter lifetimes. The effect is stronger for the states that we assigned as stretching excited levels. For instance, the Σ(1Σ, v3=1) ortho level for the ab initio potential has a lifetime of 373 ns. Also, the lifetimes are very sensitive to excitation in the van der Waals potential. However, the differences in lifetime, caused by the use of different potentials, show large variations depending on the initial state considered. The lifetime of the Σ(1Σ, v3=1) ortho state varies by about a factor of 2 between the ab initio (42 ns) and scaled (23 ns) potentials, while the Π(1Π, v3=0) para state lifetime varies by a factor of 20 (380 ns for the ab initio and 19 ns for the scaled potential). Another factor that could influence the lifetimes is the ortho/para nature of the initial quasibound state. There is no clear effect here. If we compare the van der Waals states with the same assignment, the para Σ states

(12)]
<table>
<thead>
<tr>
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<th>$\Omega_2$</th>
<th>$\Omega_3$</th>
<th>$\Omega_4$</th>
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</table>

**TABLE VII.** Final $f^2$ rotational state distribution of the NH$_3$ fragment following vibrational predissociation of Ar–NH$_3$($v_2=1$) in the para states calculated with the *ab initio* and the scaled potentials. *f* stands for forbidden channels and *c* for closed channels.
have shorter lifetimes but the tendency is reversed for the Π states. No clear effect of the parity of the initial quasibound state could be deduced either, because most of the states studied have parity +, and the others are a mixture of + and −.

The only state for which there is experimental information on the predissociation linewidth is the ortho state Π(10+, νs=0). Fraser et al. give 2Γ = 1.5 – 3 MHz [note that the Γ listed in our tables are half-widths at half-maximum (HWHM) while Fraser et al. give full widths (FWHM)] from infrared linewidth measurements and τ = 0.9 ms from the transit time between the IR excitation and bolometer detector.
regions. This would correspond to a lifetime 50–100 ns < τ < 0.9 ms. The result we obtain with the \textit{ab initio} potential (213 ns) falls within this range, while the scaled potential gives a lifetime which lies just outside the lower limit (15 ns). It should be noted that the scaling was intended to give a better agreement with spectroscopic data (bound states), and was not intended to include also a \( \rho \)-dependence (which affects the lifetime). A third potential could be tested, in which only the \( v_{33}(R,\rho_x) \) term would be scaled and the \( \rho \)-dependent terms would not. However, these kind of adjustments need more experimental data to have a chance of succeeding.

C. Final state distribution

Additional selection rules apply for the \( \Omega = 0 \) case, both for \textit{ortho} and \textit{para} NH\(_3\). For the \textit{ortho} states they are the same as for collisional excitation of NH\(_3\) with Ar when NH\(_3\) is initially in the \( j_z = 0 \) (hence \( \Sigma \)) state and the coupled states approximation is used in the scattering calculations.\(^{18}\) In scattering there are no such rules for the \textit{para} states of NH\(_3\), because these start at \( j_z = 1 \) and their collisions with Ar involve both \( \Omega = 0 \) and \( \pm 1 \). These rules (deduced with the help of Refs. 15 and 16 for instance) are the following. For the \textit{ortho} states with \( A' \) symmetry or \textit{para} states with \( E' \) symmetry in the \( \Pi(D_{3h}) \) group, the coefficients of the quasibound state wave function and of the final continuum wave function \( \Psi'' \) obey

\[
\langle +JM\Omega = 0|Jk|\Psi'' \rangle = 0 \text{ if } J + j + k \text{ even,}
\]

\[
\langle -JM\Omega = 0|Jk|\Psi'' \rangle = 0 \text{ if } J + j + k \text{ odd. (16)}
\]

For the \textit{ortho} \( A'_2 \) and \textit{para} \( E' \) states these rules are reversed. The coefficients of the wave functions cannot depend on the sign of \( k \) since the Hamiltonian in Eq. (4) only depends on \( j_z^2 \). Hence when presenting the final state distributions, the populations in \( k \) and \( -k \) are summed for the \textit{ortho} states (the \textit{para} states only involve \( k \) or \( -k \)). In addition, the results do not depend on the sign of \( \Omega \) since within the Coriolis decoupling approximation the Hamiltonian only depends on \( \Omega^2 \) (only the noninertia coupling forces depend on which direction the whole system is rotating about the intermolecular axis). It should be realized that these selection rules hold only when Coriolis coupling is neglected, so that \( \Omega \) is a good quantum number. In reality they will not be strictly obeyed, but since the effects of Coriolis coupling are negligible (see above), they will be observable as propensity rules.

The final rotational state distributions can be characterized by the average rotational energy of the NH\(_3\) product, as presented in Table III. About one third of the available energy goes into NH\(_3\) rotation. Depending on the initial quasibound state considered, this fraction can vary from 10\% [the \( \Sigma(1^+_1, v_z = 1) \) \textit{ortho} state for the \textit{ab initio} potential] to 55\% [the \( \Sigma(1^+_1, v_z = 0) \) \textit{para} state for the \textit{ab initio} potential, for the \( |+\rangle \) final states]. However, some trends still emerge if one considers at the same time the nature of the initial quasibound states given in Table IV. For instance, the states involving excitation in the van der Waals stretching mode clearly give lower final rotational excitation. One could expect an effect from scaling the potential since the scaling increased the anisotropy [by multiplying the \( v_{33} \) coefficient in the expansion (5) of the potential by 1.43]. But the average rotational energy of the NH\(_3\) fragment calculated with the \textit{ab initio} and scaled potentials are nearly identical (when averaged over all the initial quasibound states), even though they vary for the individual levels.

As can be seen in Tables VI and VII, the final rotational state distributions for the NH\(_3\) fragment are very different. One important feature is that none of them looks statistical, some being very selective [see Figs. 3(a) and 4(a) for instance, showing the final rotational state distribution for the \( \Sigma(1^+_1, v_z = 0) \) \textit{para} state with the \textit{ab initio} potential, for which the channels that get most of the population are the highest energetically allowed, 92\(_1^2 \) and 94\(_2^2 \) for the states with + parity, and 92\(_3^2 \) for the states with − parity, these channels accounting for 70\% of the population]. The final state distributions are not determined by the initial rotational content of the quasibound state wave function, since this involved only very few \( j_z \) levels with small values of the rotational quantum numbers (see Table IV). Looking for systematics in these distributions will give us information on the role of physical parameters in the vibrational predissociation process.

First we examine the effect of overall rotation by comparing dissociation from the \( J = 0 \) and \( J = 1 \) quasibound \( \Sigma \) and \( \Pi \) states. As mentioned before in the Results, the exact value of \( J \) does not affect the dynamics for low values of \( J \) (the lifetime and final rotational state distributions are very similar for corresponding \( \Sigma \) states with \( J = 0 \) and 1). The role of \( \Omega \) is more complex, since \( \Omega \) is also the projection of \( \hat{\jmath} \) on the intermolecular axis. For the \textit{ortho} initial quasibound states, if one is careful to compare states with the same nature [for example, the \( \Sigma(1^+_1, v_z = 1) \) \textit{ortho} state with the \textit{ab initio} potential should be compared with the \( \Pi(1^+_0, v_z = 1) \) \textit{ortho} state since they both correspond to stretching excitation], then it can be seen that the main channels showing up in the final state distribution are in general the same (but there are some spectacular exceptions), although their contributions to the final state distribution have different relative magnitudes. In some cases, channels that are very important for the decay of the quasibound \( \Pi \) state do not show up for the \( \Sigma \) state because they are not allowed. This is not so clear for the \textit{para} states, where exciting \( |\Omega \rangle \) from 0 to 1 seems to perturb much more the NH\(_3\) final state distribution.

Some similarities can also be found when one compares some of the van der Waals states within the same series. For instance, the similarity between the final state distributions from the two \textit{ortho} quasibound \( \Pi \) states with the scaled potential are striking. In this case, excitation in the van der Waals stretching mode does not modify the rotational state distribution of the NH\(_3\) fragment, although the lifetime is shortened (from 15 to 6 ns). Stretching excitation does not change much the rotational distributions with both the scaled potential and the \textit{ab initio} potentials, except that the lower \( j \) channels seem to gain more population. However, in the case of the \textit{ortho} \( \Pi \) states with the \textit{ab initio} potential, which also only have a different stretch excitation, the correlation between the final rotational state distributions is not so good, and it is even worse for the lowest two \textit{para} \( \Sigma \) states.
The potential anisotropy governs the final rotational state distribution. Hence it is expected to find differences between the *ab initio* potential energy surface and its scaled variation. For the contribution of + and — final tunneling states of NH$_3$, no clear propensity rules emerge. The + to — ratio is clearly affected by the scaling of the potential (Table V), but not in the same proportion for all the initial quasibound states. The $\Sigma(1^+_N, v_j=0)$ *ortho* *ab initio* quasibound state gives a larger contribution of + states while the scaled one leads to more population in the — states. The $\Pi(1^+_o, v_j=0)$ para state gives almost the same + to — population ratio with the *ab initio* and the scaled potentials. For the excited stretching states the situation is contrasted. The $\Sigma(1^+_o, v_j=1)$ *ortho* state leads to more difference between the — and + populations with the scaled potential than with the *ab initio* one, but the other three stretching states give nearly equal contributions of + and — NH$_3$ tunneling states. In the rotational distributions however, one main characteristic emerges. Although the final states that receive more population with the *ab initio* potential are still important with the scaled one, scaling the $v_{33}$ term in the potential expansion leads to repartition of the population amongst more final states, and seems to allow for more excitation in the k quantum number. For instance, with the *ab initio* potential, the lowest *ortho* quasibound $\Sigma$ state gives mainly NH$_3$ in the $8_0$ rotational state for the — parity, and in the $8_3, 7_0$ states for the + parity. With the scaled potential, the $8_0$ channel is still one of the most important ones for the — parity, but others have grown as well; $6_6$ and $9_3$. Similarly, for the + parity the $8_3$ and $7_0$ channels remain within the most populated channels but the $4_1, 5_9$, and $9_6$ channels have about the same or more population.

**VI. CONCLUSIONS**

We have performed quantum mechanical calculations to study the vibrational predissociation of the Ar–NH$_3$ van der Waals complex excited with one quantum of the $v_2$ (umbrella) vibrational mode of NH$_3$. We have investigated the vibrational predissociation of several initial quasibound states, corresponding to excitation in the stretching or bending van der Waals levels or in the tunneling motion of the NH$_3$ umbrella inversion, and for two values of the total angular momentum $J$ and its projection $\Omega$ onto the intermolecular axis $(J, \Omega)=(0,0), (1,0)$, and $(1, \pm 1)$. The calculations were performed within the framework of the Golden Rule, applying the Coriolis decoupling approximation. We have used two different intermolecular potential energy surfaces, one determined *ab initio* by Bulski et al.$^{14}$ and the other containing a scaling parameter chosen to account for spectroscopic data on bound states of Ar–NH$_3$, proposed by van Bladel et al.$^{16}$ Lifetimes obtained with the scaled potential are shorter than with the *ab initio* potential. The *ab initio* potential gives a lifetime compatible with the limits set by experiment for the $\Pi(1^+_o, v_j=0)$ *ortho* ground state which is the only level for which there are experimental results. The lifetime for this state obtained with the scaled potential lies just below the experimental limit. van der Waals excitation in the stretching mode leads to faster vibrational predissociation and lower final state rotational excitation. The fact that vibrational predissociation is faster may look in contradiction with the energy$^{30}$ or momentum$^{31}$ gap law since the excited van der Waals stretching level lies 31 cm$^{-1}$ higher in energy than the $v_2=0$ state. However, if we assume that the strength of the coupling responsible for vibrational predissociation is increased by exciting the van der Waals stretch, then not only can the lifetime become shorter, but also the fraction of the available energy that has to go into NH$_3$ rotation in order to reduce the energy gap can be smaller. The *ortho* nature of NH$_3$ does influence the efficiency of the process but not in a systematic way. Concerning the influence of overall rotation, the value of $J$ does not affect the dynamics. On the other hand, the *Pi* quasibound *ortho* states predissociate faster than the corresponding $\Sigma$ states, but the reverse is true for the *para* states.

Another important result of our calculations is the prediction of final NH$_3$ rotation-tunneling state distributions. The vibrational predissociation process tends to wash out the + or — character of the initial quasibound state, and in some cases inverts it. The fraction of the available energy that goes into NH$_3$ rotation is about one-third, with variations depending on the initial quasibound level. The van der Waals stretching excited states give final rotational state distributions similar to the ones with no stretching excitation, but with more weight to the lower $j$ channels. Exciting the overall rotation in $J$ does not affect the final NH$_3$ rotational state distribution, but going from $\Sigma$ to $\Pi$ states does have an effect, especially for the *para* states. Also, additional propensity rules apply for the $\Sigma$ states. Finally, since the potential anisotropy governs the final state distribution, there are differences between the *ab initio* and the scaled potentials. The scaled (more anisotropic) potential tends to distribute the population among more levels, and to populate levels with higher $k$ values.

All these conclusions indicate that there are many interesting effects to investigate in the vibrational predissociation of the Ar–NH$_3$ van der Waals complex. Hence it would be very interesting to compare with more experimental results, especially if the final state distributions can be determined.

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