Resonances in rotationally inelastic scattering of NH₃ and ND₃ with H₂

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Scattering of NH₃ by ortho- and para-H₂: Expansion of the potential and collisional propensity rules
We present theoretical studies on the scattering resonances in rotationally inelastic collisions of NH$_3$ and ND$_3$ with H$_2$. We use the quantum close-coupling method to compute state-to-state integral and differential cross sections for the NH$_3$/ND$_3$–H$_2$ system for collision energies between 5 and 70 cm$^{-1}$, using a previously reported potential energy surface [Maret et al., Mon. Not. R. Astron. Soc. 399, 425 (2009)]. We identify the resonances as shape or Feshbach resonances. To analyze these, we use an adiabatic bender model, as well as examination at the scattering wave functions and lifetimes. The strength and width of the resonance peaks suggest that they could be observed in a crossed molecular beam experiment involving a Stark-decelerated NH$_3$ beam. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4927074]

I. INTRODUCTION

Resonances are among the most intriguing phenomena in scattering experiments. In inelastic scattering, a resonance corresponds to formation of a quasibound level during the collision and usually manifests as structure in the energy dependence of cross sections. We use the term “shape” resonance if the quasibound level correlates with the initial or final monomer levels of the colliding partners, or “Feshbach” resonance, if the quasibound level correlates with a monomer level energetically inaccessible (“closed”) at the collision energy in question.

An accurate potential energy surface (PES) is the foundation for the theoretical study of collision dynamics. Although bound van der Waals states of the two collision partners depend mainly upon the attractive part of the PES, quasibound levels will be sensitive also to the repulsive portion of the PES. Since the position and shape of scattering resonances is a distinctive fingerprint of the PES, agreement with experiment gives confidence in the subsequent use of a PES in the prediction of rate coefficients and other kinetic quantities difficult or impossible to measure.

The observation of resonances in crossed molecular beam experiments requires low collision energy and high energy resolution, as well as high initial-state purity. Scattering resonances have been observed in mostly atomic, elastic collisions and in the reactive F + HD → HF + D system. Recently, in a merged-beam geometry, shape (also called orbiting) resonances were seen in Penning ionization collisions of metastable helium atoms with argon atoms or H$_2$ molecules at collision energies as low as 0.01 K. Both shape and Feshbach resonances were observed in rotationally inelastic atom-molecule and molecule-molecule collisions. Chefdeville et al. investigated the scattering of H$_2$ by CO and O$_2$, while Beigeat et al. studied CO–He scattering. In these experiments, the authors used Even–Lavie pulsed valves to cool the molecular beams. By crossing the two beams at a small angle, they were able to lower the collision energy down to 3.5 cm$^{-1}$.

For molecules with nearly degenerate pairs of levels (such as the A-doublets of OH and the inversion doublets of NH$_3$) and/or multiple nuclear spin symmetries, standard cooling techniques are insufficient to produce a beam with population restricted to a single level. For these molecules, Stark deceleration allows the production of cold beams confined to a single state. Scanning the collision energy would then provide an ideal means to search for resonances. Inspired by this possibility, our groups have searched theoretically for scattering resonances in the OH–He/Ne and the NH$_3$–He systems in calculations based on state-of-the-art PESs. Both these systems manifest significant shape and Feshbach resonances. The features are narrow, with widths of ~1 cm$^{-1}$. This poses a significant challenge to experiment.

Rotationally inelastic scattering of NH$_3$/ND$_3$ with H$_2$ has received considerable interest, not least because of the astrophysical importance. Earlier work has focused on collisions out of the ground rotational level of ortho-NH$_3$, which is not suitable for Stark selection. Strong resonance peaks do appear in the computed energy dependence of state-to-state cross sections (see Fig. 2 in Ref. 29). Inelastic collisions of ND$_3$ with H$_2$ were investigated experimentally and theoretically by...
Tkáč et al., with special attention for the hexapole-selected 11– state of ND₃ that is a candidate for Stark deceleration (see Sec. II for the notation of the rotational levels).

In the present work, we study in detail resonances in the state-to-state cross sections of NH₃ and ND₃ out of this 11– level, using the PES computed by Maret et al. This PES has been employed in a few studies of collision dynamics. We will show that this system has strong and broad resonance peaks along with relatively large state-to-state cross sections. In addition, these resonances are well suited for investigation with crossed molecular beams.

This paper is organized as follows: in Sec. II, we briefly present the theory for rotationally inelastic scattering between a symmetric top and a closed-shell (Σ⁺) diatomic molecule and describe our scattering calculations. In Sec. III, we introduce the PESs used in our calculations. We describe in Sec. IV the scattering resonances, both shape and Feshbach, that we found. To analyze these, we use the adiabatic bender model as well as examination of the scattering wave function. A discussion in Sec. V concludes.

II. SCATTERING CALCULATIONS

We label the rotational levels of the NH₃ and ND₃ symmetric top molecules as jkJz, where j is the total angular momentum of the molecule, k is the projection of j on the C₃ axis, and z is the umbrella inversion symmetry. The NH₃ and ND₃ molecules have, respectively, two (para and ortho) and three (E, A₁, and A₂) nuclear spin modifications that do not interconvert during inelastic scattering. The para or E nuclear spin rotational levels include k-stacks with k not a multiple of three, in particular the 11– level which is the candidate for Stark deceleration. For reference, we show in Fig. 1 the lower rotational levels of para-NH₃ and ND₃ (E nuclear spin symmetry).

We refer the reader to several previous papers for the full quantum description of inelastic collisions between a symmetric top molecule and a diatomic molecule in a Σ electronic state. We approximate the inversion doublet wave functions of NH₃/ND₃ as even and odd combinations of the two rigid equilibrium structures multiplied by rigid rotor wave functions, namely, |jkm⟩ = 2⁻¹/²[(|jkm⟩ + ε|jkm⟩) ± |jkm⟩ ± ε|jkm⟩],

The umbrella inversion symmetry is −ε(−1)j. Previous investigations of inelastic scattering in the NH₃/ND₃–He and NH₃/ND₃–Ar systems showed that this approximation gives excellent agreement with a more complete model based on full wave functions for the umbrella vibration–inversion.

Close-coupling calculations were performed both with the HIBRIDON suite of programs and with a set of scattering programs developed in Nijmegen. The availability of two totally distinct codes provided an ideal check of the accuracy and convergence of our calculations. We included in the close-coupling channel basis all para rotational levels of NH₃ with j ≤ 6 or E rotational levels of ND₃ with j ≤ 7. For collisions with para-H₂, the j = 0 and j = 2 levels of H₂ are included, while for ortho-H₂, only the j = 1 level. The maximum total angular momentum in the calculations was J = 20 for total energies <70 cm⁻¹. To determine the energy levels of isolated NH₃, we used rotational constants B = 9.9402 cm⁻¹ and C = 6.3044 cm⁻¹, while for ND₃, we used B = 5.1428 cm⁻¹ and C = 3.1246 cm⁻¹. We assume an inversion splitting of 0.7903 and 0.053 cm⁻¹ for NH₃ and ND₃, respectively, independent of j and k. More details on the calculation of differential cross sections for molecule-molecule systems are contained in the supplementary material.

III. POTENTIAL ENERGY SURFACES

To describe the NH₃–H₂ potential energy surface, we use the coordinate system defined in Fig. 2 of Ref. 28. The z axis lies along the three-fold symmetry axis of NH₃, and the Jacobian vector that connects the centers of mass of the molecules has the polar angles (θ₁, φ₁). The orientation of the H₂ bond axis relative to this frame is defined by the angles (θ₂, φ₂). The interaction potential can be expanded either in Clebsch-Gordan coupled products of angular basis functions

\[ V(R, \theta_1, \phi_1, \theta_2, \phi_2) = \sum_{l_{1\mu_1}l_{2\mu_2}} V_{l_{1\mu_1}l_{2\mu_2}}(R) \sum_{m_1} \langle l_{1m_1}l_{2,-m_1|00} \rangle \times D^{l_{1\mu_1}}_{m_1\phi_1}(0,-\theta_1,-\phi_1) \times D^{l_{2\mu_2}}_{m_2\phi_2}(\theta_2,\phi_2,0) \] (1)

or in an uncoupled product basis

\[ V(R, \theta_1, \phi_1, \theta_2, \phi_2) = \sum_{l_{1\mu_1}l_{2\mu_2}} V_{l_{1\mu_1}l_{2\mu_2}}(R)D^{l_{1\mu_1}}_{m_10}(0,-\theta_1,-\phi_1) \times D^{l_{2\mu_2}}_{m_20}(\phi_2,\theta_2,0). \] (2)

In the above equations, V_{l_{1\mu_1}l_{2\mu_2}} and V_{l_{1\mu_1}l_{2\mu_2}m_1} are expansion coefficients, \langle l_{1m_1}l_{2,-m_1|00} \rangle is a Clebsch-Gordan coefficient, and D^{l_{1\mu_1}}_{m_1\phi_1} are rotation matrix elements. The advantage of using the coupled expansion basis is that it is invariant under overall rotation of the system, so that the same expansion coefficients V_{l_{1\mu_1}l_{2\mu_2}} can be used independently of the orientation of the frame in which the potential is expanded. Another frequently adopted angular expansion of the PES uses a different set of angles to define the orientation of the molecules, but is in practice equivalent to Eq. (1).

We used the CCSD(T)/aug-cc-pVDZ PES with corrections from CCSD(T)/CBS calculations constructed by Maret et al. We obtained from the authors the potential fitted by the
expansions of both Eqs. (1) and (2). We performed scattering calculations with both PESs. Because of the sensitivity of resonances to the underlying PES, the two expansions predict a slightly different resonance structure, as displayed in Fig. S1 of the supplementary material. We recommend Eq. (1) for two reasons: (a) when similar terms in the two angular expansions are retained, the root mean square deviation (RMSD) is smaller [for example, at $R = 5$ bohr, the potential fitted to a 120-term expansion with Eq. (1) and a 167-term expansion with Eq. (2) has RMSD of 0.74 and 1.20 cm$^{-1}$, respectively] and (b) the evaluation of the potential matrix elements is easier.

To describe ND$_3$–H$_2$ collisions, the NH$_3$–H$_2$ PES needs to be modified to take into account the shift $\delta_{\text{COM}}$ of the center of mass. From the NH$_3$ geometry used in Ref. 29 ($\angle \text{NH}_3 = 1.9512 \, a_0$ and $\angle \text{NN} = 107.38^\circ$), we have $\delta_{\text{COM}} = 0.088$ $a_0$.

The ab initio NH$_3$–H$_2$ PES was determined on a grid of 29 values of $R$. At each value of $R$, 3000 orientations were used for the CCSD(T)/aug-cc-pVDZ PES but only 1000 for the CCSD(T)/CBS calculations. For ND$_3$–H$_2$, for each value of the NH$_3$–H$_2$ angle $\theta_1$ (see Fig. 2 of Ref. 28), we introduce a corresponding $\theta'_1$ defined by trigonometry as

$$
\theta'_1 = \arccos \left( \frac{R^2 + \delta_{\text{COM}}^2 - R^2}{2\delta_{\text{COM}} R} \right),
$$

where $R'$ is the intermolecular distance chosen to fit the ND$_3$–H$_2$ PES, and $R$ is the corresponding intermolecular distance for NH$_3$–H$_2$ calculated from

$$
R = -\delta_{\text{COM}} \cos \theta_1 + \sqrt{R^2 - \delta_{\text{COM}}^2 \sin^2 \theta_1}.
$$

We used these relations to transform the orientations $(\theta_1, \phi_1, \theta_2, \phi_2)$ for NH$_3$–H$_2$ to $(\theta'_1, \phi_1, \theta_2, \phi_2)$ for ND$_3$–H$_2$ for each $R'$ (from the same $R$ grid used in the NH$_3$–H$_2$ calculations) and estimated the interaction energy for that geometry by splining the $R$ dependence of the NH$_3$–H$_2$ interaction energies (ab initio points from Ref. 29) at this orientation. We then fit the ND$_3$–H$_2$ interaction energies with Eq. (1) and applied the long-range extrapolation using the method described in Ref. 29.

Figure 2 shows a comparison of $R$-dependence of the larger angular expansion coefficients for the NH$_3$ and ND$_3$ PESs. We see that the two PESs are quite similar, with three of the five larger expansion coefficients virtually identical and the other two showing only slight differences. This is not unreasonable given the small shift in the COM. The two expansion coefficients showing differences have significant contributions from multipole-multipole electrostatic interactions, with $V_{1023}$ associated with the NH$_3$/ND$_3$-dipole–H$_2$ quadrupole interaction and $V_{2024}$ with the quadrupole-quadrupole interaction.

IV. RESULTS AND DISCUSSION

A. Collisions between NH$_3$ and para-H$_2$

1. Overview of the resonances

We show in Fig. 3 the energy dependence of the state-to-state integral cross sections for transitions from the 11$^+$ initial level at collision energies below 70 cm$^{-1}$. Below the threshold for rotational excitation, transition between the inversion doublets (11$^+$ $\rightarrow$ 11$^-$) is the only inelastic process allowed. We observe rich resonance structure, with both broad and sharp peaks. Because of the deep well of the NH$_3$–H$_2$ PES [$D_e = 267$ cm$^{-1}$ (Ref. 29)], we do not observe distinct groups of resonances associated with the opening of a particular channel, as are seen in molecule–rare gas systems. We will show in Sec. IV A 2 that the resonances seen in Fig. 3 are Feshbach resonances. The broad peaks, a few wavenumbers in width and intensity more than three times the background inelastic cross sections, are particularly promising prospects for observation in a crossed beam experiment.

The 11$^+$ $\rightarrow$ 21$^+$ transition also shows several resonances with magnitudes twice that of the background cross section. The analysis in Sec. IV A 3 reveals that these are shape resonances corresponding to quasibound states associated with the 21$^+$ final level. Similar to the 11$^+$ $\rightarrow$ 21$^+$ transition, the cross section for the 11$^-$ $\rightarrow$ 21$^-$ transition also displays a few shape resonances at similar collision energies, though smaller in magnitude. The resonances in the 11$^-\rightarrow$ 22$^\pm$ transitions have contributions from both shape resonances, and Feshbach

![FIG. 2. Comparison between the larger expansion coefficients $V_{l,m,l',l}$ as defined in Eq. (1), only terms with non-negative $\mu$ plotted due to symmetry properties discussed in Ref. 42] as a function of intermolecular distance, $R$, of the NH$_3$–H$_2$ PES described in Ref. 28 (dotted lines) and the ND$_3$–H$_2$ PES described in the present work (solid lines).](image)

![FIG. 3. State-to-state integral cross section as a function of collision energy for transition from the 11$^+$ level of para-NH$_3$ in collisions with para-H$_2$ in the $j = 0$ level. The curves are labelled by the final rotational level.](image)
resonances caused by the quasibound states associated with the 21± levels.

The relative magnitudes of the state-to-state cross sections are significantly different for the NH₃–H₂ and NH₃–He systems. In particular, the transition to the 21+ level is much stronger when the collision partner is H₂. This can partly be explained with the differing anisotropies of the PESs. In collisions of NH₃ with H₂ (j = 0), the V₁₀₀₁ and V₂₀₀₃ terms directly couple the 11− and 21+ levels, while the V₂₀₀₂ term directly couples the 11− and 21− levels. These three coefficients in the NH₃–H₂ PES are comparable in magnitude at moderate to large intermolecular distances. For the NH₃–He PES, the corresponding V₁₀ and V₃₀ terms have significantly smaller magnitudes than the V₂₅₀ term (see Fig. 3 of Ref. 11), giving rise to smaller 11− → 21+ cross sections. Further, with H₂ (j = 2) in the close-coupling channel basis, expansion terms with l₂ > 0 can affect the cross sections. These correspond physically to the interactions involving the quadrupole moment of H₂, which is obviously not present for the interaction of NH₃ with a spherical target.

2. Feshbach resonances in the 11− → 11+ transition

To understand the resonances in the 11− → 11+ transition, we plot in Fig. 4 the contributions to the integral cross section (partial cross sections) from each partial wave, distinguished by the total angular momentum J and the parity of the scattering wave functions under inversion. We observe several series of resonance structures consisting of peaks of similar shape. These peaks shift to higher collision energies as J increases. We expect that peaks within a given series are resonances arising from quasibound states associated with the same rotational level of NH₃. As J increases, the corresponding orbital angular momentum L increases, which leads to a higher centrifugal barrier and a higher quasibound state energy.

To investigate the origin of the resonances, we performed an adiabatic bender analysis similar to that described in Sec. IV C of Ref. 10. Here, we diagonalize the Hamiltonian exclusive of the radial kinetic energy for a given partial wave to obtain adiabatic bender curves. The energies of the van der Waals stretch levels supported by those curves are computed using a discrete variable representation (DVR) method.

We display the derived adiabatic bender curves and quasibound level energies for the J = 6, ± parity partial wave in Fig. 5 as an example. We see that the stretch levels supported by the adiabatic bender curves associated with the NH₃ 22± levels, with energies 30, 15, 71, and 22 cm⁻¹ (red vertical lines in Fig. 4), are in reasonable agreement with the positions of the sharp resonance peaks that appear on the energy dependence of partial cross sections for this partial wave (the upper solid green curve in Fig. 4). The two lower stretch levels associated with the NH₃ 21± levels, with energies 19.49 and 26.44 cm⁻¹ (blue vertical lines in Fig. 4), agree with the positions of the broad resonance peaks. These results suggest that both the sharp and broad resonance peaks shown in Fig. 4 are Feshbach resonances, with the sharp peaks originating from quasibound states associated with the NH₃ 22± level and the broad peaks from the 21± level.

One of the adiabatic bender curves in Fig. 5 has a bound stretch level at 33.18 cm⁻¹, at which no resonance appears in Fig. 4. A close look reveals that this adiabatic bender curve has avoided crossings with other curves, including those associated with a different NH₃ level. This is an example of the limitations of the adiabatic bender model. Near an avoided
crossing, the scattering wave function would change dramatically, and the separation of radial and angular functions, as assumed in the adiabatic bender model, would no longer be a good approximation. Such a phenomenon is analogous to nonadiabatic effects\textsuperscript{37} in electronic structure theory. As shown in Fig. 5, the NH\textsubscript{3}–H\textsubscript{2} adiabatic bender curves have well depths comparable or greater than the rotational level separation, and the adiabatic bender analysis is particularly vulnerable to these avoided crossings.

An alternative method of studying the (shape or Feshbach) resonances is to examine the contributions to the radial scattering wave functions from different channels that correspond to various monomer rotational levels and partial wave quantum numbers \( L \).\textsuperscript{11} The Nijmegen scattering program uses a renormalized Numerov propagator and it is relatively easy to generate these radial scattering wave functions. We plot the continuum functions of the channels open at the corresponding quantum numbers. We show the expansion coefficients with different partial wave quantum numbers in Fig. 5, the NH\textsubscript{3} of about 0.6 cm\textsuperscript{−1}.

In electronic structure theory. As shown in Fig. 3, the energy spacings between the resonances and the assigned \( L \) values, one can deduce an effective end-over-end rotational constant of the quasi-bound NH\textsubscript{3}–para-H\textsubscript{2} complex. Both series of resonances correspond to a rotational constant of about 0.6 cm\textsuperscript{−1}. This value, combined with the reduced mass.

<table>
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<th>Parity</th>
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<th>( jk \pm (L) )</th>
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**TABLE I.** Resonance peaks in state-to-state cross sections and corresponding quasibound states giving rise to the resonances in the 11− → 11+ transition of NH\textsubscript{3} in collisions with para-H\textsubscript{2} (\( j = 0 \)). The associated NH\textsubscript{3} rotational levels \( jk \pm \) and partial wave quantum numbers \( L \) are obtained from the wave function analysis described in Sec. IV A 2.

![FIG. 6. Contributions of various rotational levels \( jk \pm \) of NH\textsubscript{3} and partial waves \( L \) to the square of the scattering wave function with \( J = 6 \). (a) Parity for the scattering of NH\textsubscript{3} in the 11− initial state and para-H\textsubscript{2} (\( j = 0 \)). Collision energies are (a) 20.65 cm\textsuperscript{−1} and (b) 22.65 cm\textsuperscript{−1}.](image-url)
of the complex, yields an effective \( R \) value of about 7.5 \( a_0 \), which agrees with the \( R \) value corresponding to the maximum in the dominant component of the scattering wave functions in Fig. 6. Noticeably, this is somewhat larger than the equilibrium distance \( R_e = 6.1 a_0 \).

We see that the two techniques for analyzing the resonances agree on the origin of the resonances. The scattering wave function analysis, while slightly more computationally demanding, does not suffer from avoided crossings in the adiabatic bender analysis.

Additional information on the resonances can be obtained by looking at the phase shifts in the scattering wave function. These phase shifts can be obtained from the eigenvalues of the scattering matrix.\(^1,\)\(^{58}\) The top panel (a) of Fig. 7 shows the sums of the phase shifts in all open channels for various total angular momenta \( J \) for collision energies up to 28.1 cm\(^{-1}\), where the 22+ channel opens and a jump in the phase shift sum occurs. Since we consider both parities \( \pm \), there are two curves for each \( J \). From scattering theory, it follows that when a resonance occurs, the phase shift sum rapidly increases by \( \pi \) as a function of the collision energy.\(^1,\)\(^{58}\) In Fig. 7(a), we see this happening at the collision energies where the Feshbach resonances are found in the elastic and inelastic cross sections.

The derivative of the phase shifts with respect to the energy gives the lifetime of the collision complex.\(^1\) These lifetimes are shown in Fig. 7(b). This figure illustrates that at the energies where resonances occur, we indeed get long-lived collision complexes. One can see that each pair of curves belonging to the same \( J \) and different parities \( \pm \) shows similar peaks, shifted by about 0.8 cm\(^{-1}\), which is the splitting between the \( \pm \) umbrella inversion tunneling states in NH\(_3\). By comparing this figure with Fig. 4, one observes that the narrower the resonance, the longer its lifetime.

![Fig. 7](image-url)

**FIG. 7.** (a) and (b) Phase shift sum and collision lifetime for different total angular momenta \( J \) for the scattering of NH\(_3\) in the 1\(1^-\) initial state and para-H\(_2\) \((j = 0)\). The two curves drawn for each \( J \) value correspond to the \( \pm \) parities of the overall scattering wave function.

We also computed the differential cross sections (DCSs) at several resonance and off-resonance energies; these are shown in Fig. 8. The pattern of increased backward scattering at energies close to a resonance, as we found for the OH/NH\(_3\)-rare gas systems,\(^10,\)\(^{11}\) is less clear for NH\(_3\)-H\(_2\) collisions. Figures 8(a) and 8(c) show DCSs at energies close to sharp resonance peaks, and we see significant backward scattering as expected. Backward scattering is even dominating at a collision energy of 4.265 cm\(^{-1}\), corresponding to the first sharp resonance peak shown in Fig. 3. Figures 8(b) and 8(d) correspond to energies at a peak and a valley, respectively, among a series of broad resonance peaks. Surprisingly, we do not see strong backward scattering at the near-resonance energy. We note that the differential cross sections are not from the \( J = 6 \), \( + \) parity partial wave alone and there are significant contributions and interferences involving other partial waves.

### 3. Shape resonances in the 11\(1^-\) \(\rightarrow\) 21\(+\) transition

In this section, we analyze the resonance structure shown in the energy dependent 11\(1^-\) \(\rightarrow\) 21\(+\) cross section. Although not as dramatic as the resonances in the 11\(1^-\) \(\rightarrow\) 11\(+\) transition, the resonances in this transition have a relatively simple structure, and these moderately broad resonance peaks at slightly higher collision energies may facilitate the observation of resonances in molecular beam experiments.

We first show the partial cross sections for this transition in Fig. 9. We see the contribution to the resonance peaks is quite different from those shown in Fig. 4. Namely, each of the three peaks at collision energies of \( \approx 40, 50 \), and 60 cm\(^{-1}\) has contributions from several partial waves. The three peaks have increasing widths as the energy increases. These are typical characteristics of a shape resonance.\(^10,\)\(^{59,60}\) This resonance structure, however, is distinguished from that observed in the NH\(_3\)-He and OH–He systems by the rapidly increasing background cross section and the large spacing between resonance...
peaks. The large spacing is a direct consequence of the small reduced mass of the system and large centrifugal barriers.

To confirm the origin of these resonances, we again applied the adiabatic bender model used in Sec. IV A 2. The adiabatic bender curves look similar to those shown in Fig. 5 and are not shown here. After computing the adiabatic bender curves, we treat them as in a conventional one-dimensional scattering problem and compute the phase shift as a function of collision energy. We plot in Fig. 10 the phase shifts for all adiabatic bender curves associated with the 21+ level with 6 ≤ J ≤ 9 that give rise to such changes in phase shift. We see clearly for each of the curves shown in Fig. 10 that the energy dependent partial cross section for the corresponding partial wave (Fig. 9) shows a resonance peak at a similar collision energy. Further, the widths of the resonances match those for the corresponding quasi-bound states associated with the final level of the transition.

We note that there are four rotational levels below the 21+ level and the adiabatic bender curves related to that level have large cardinal indices. There are many avoided crossings between the adiabatic bender curves that make such phase shift analysis difficult and inaccurate. For this particular case, we found such analysis unsatisfactory.

The nature of these resonances was further confirmed by the scattering wave function analysis. It showed in this case that at the collision energies where the resonances occur, the wave functions in the van der Waals well are strongly dominated by contributions from specific channels, open at the given collision energy. This is the signature of a shape (or orbiting) resonance, and we could determine which rotational levels of NH3 and which partial wave quantum numbers L mainly contribute to the corresponding quasi-bound states.

B. Collisions between NH3 and ortho- and normal H2

We show in Fig. 11 the collision energy dependence of the state-to-state cross sections out of the 11− level of NH3 in collisions with ortho-H2 in the j = 1 rotational level. We see that the 11− → 11+ transition dominates at the collision energies considered, and the cross section for this transition is considerably larger than the corresponding transition for collision with H2 j = 0, displayed in Fig. 3. Unlike H2 j = 0, the j = 1 level can polarize as it approaches the collision partner; the form of the j = 1 rotational wave function allows access to regions of the PES that are anisotropic in θ2, (or I2 > 0). Only I2 = 0 terms in the angular expansion [see Eq. (1)] of the PES directly couple channels in collisions with H2 j = 0, while many of the larger expansion coefficients have I2 > 0. A similar enhancement in cross sections for collisions of ortho-H2, as compared to those for para-H2, has also been found in other molecule–H2 inelastic collisions.61,62

We also see that the energy-dependent 11− → 11+ cross section plotted in Fig. 11 displays many overlapping resonances. This contrasts with the much smaller number of mostly
resolved resonances seen for collision of H\textsubscript{2} \textit{j} = 0 (see Fig. 3).
We also calculated the dissociation energy \(D_0\) of the various nuclear spin species of NH\textsubscript{3}–H\textsubscript{2}, see Table II. The results in this table show that \(D_0\) is considerably larger for NH\textsubscript{3}–ortho-H\textsubscript{2}(\textit{j} = 1) than for NH\textsubscript{3}–para-H\textsubscript{2}(\textit{j} = 0) since the effective PES for the former includes \(I_2 > 0\) terms and the H\textsubscript{2} rotational wave function can polarize to sample the most attractive geometry of the complex. This is similar to other molecule–H\textsubscript{2} complexes in which the dissociation energy of the complex is significantly larger for \textit{ortho}-H\textsubscript{2} than for \textit{para}-H\textsubscript{2}.\textsuperscript{63–68} Thus, there are more bound, and quasi-bound, levels associated with NH\textsubscript{3}–H\textsubscript{2}(\textit{j} = 1) than with NH\textsubscript{3}–H\textsubscript{2}(\textit{j} = 0), and the resonance structure in the cross section for the 11\textarrow{→}11\textsubscript{+} transition is much more complicated for collision with H\textsubscript{2} \textit{j} = 1 than for \textit{j} = 0. We have not carried out a detailed analysis of the resonances seen in Fig. 11.

The shape resonances in the cross sections for the 11\textarrow{→}21\textsubscript{±} transitions in collisions with H\textsubscript{2} \textit{j} = 1 are small in magnitude relative to the non-resonant background, as compared to those when H\textsubscript{2} \textit{j} = 0 is the collision partner. For the 11\textarrow{→}22\textsubscript{±} transitions, the shape and Feshbach resonances associated with the 21\textsubscript{±} levels overlap and are small in magnitude (see Fig. 11). We expect that the resonances in these transitions will be difficult to observe in crossed beam experiments.

Normal hydrogen has an \textit{ortho} to \textit{para} ratio of 3:1. We plot in Fig. 12 the cross section for the NH\textsubscript{3} 11\textarrow{→}11\textsubscript{+} transition in collision with \textit{para}-, \textit{ortho}-, and normal H\textsubscript{2}. Because of the larger nuclear spin statistical weight and the larger cross section, the resonance structures for NH\textsubscript{3}–normal H\textsubscript{2} (black lines in Fig. 12) are almost the same as for NH\textsubscript{3}–\textit{ortho}-H\textsubscript{2} (green lines in Fig. 12).

To estimate the feasibility of observing these resonances in molecular beam experiments, we also plot in Fig. 12 the cross sections for the 11\textarrow{→}11\textsubscript{+} transition of NH\textsubscript{3} in collisions with \textit{para}-, \textit{ortho}-, and normal H\textsubscript{2}, convoluted with Gaussian collision energy spreads of two different widths. We see that with a 2 cm\textsuperscript{-1} energy resolution, the sharp resonance peaks disappear, but the broad resonance peaks are still resolved. However, with an energy spread of 5 cm\textsuperscript{-1}, only relatively weak oscillatory structures corresponding to the broad resonance peaks are left. Such structures would be difficult to observe in experiments. The best prospect for observing resonances in NH\textsubscript{3}–H\textsubscript{2} collisions is with \textit{para}-H\textsubscript{2}.

### C. Collisions between ND\textsubscript{3} and H\textsubscript{2}

The ND\textsubscript{3} molecule has a smaller inversion splitting and is easier to manipulate with a Stark decelerator. Accordingly, we

![Diagram](image_url)

**Fig. 11.** State-to-state integral cross sections as a function of collision energy for transitions from the 11\textarrow{→} level of \textit{para}-NH\textsubscript{3} in collisions with \textit{ortho}-H\textsubscript{2} in the \textit{j} = 1 level. The final levels are indicated for each transition for which the cross section is plotted. The cross sections to the 21\textsubscript{±} and 22\textsubscript{±} levels are multiplied by 3 for clarity.

**Fig. 12.** Integral cross section as a function of collision energy for the 11\textarrow{→}11\textsubscript{+} transition of NH\textsubscript{3} in collisions with \textit{para}-, \textit{ortho}-, and normal (1:3 \textit{parato\textit{ortho}}) H\textsubscript{2}. Computed cross sections (solid lines) and cross sections convoluted with Gaussian energy spread of 2 cm\textsuperscript{-1} (dotted lines) and 5 cm\textsuperscript{-1} (dashed lines, only for NH\textsubscript{3}–\textit{para}-H\textsubscript{2}) are plotted.

**Fig. 13.** State-to-state integral cross sections as a function of collision energy for transitions from the 11\textarrow{→} level of ND\textsubscript{3} in collisions with \textit{para}-H\textsubscript{2} (\textit{j} = 0). The final levels are indicated for each transition for which the cross section is plotted.

<table>
<thead>
<tr>
<th>NH\textsubscript{3}–H\textsubscript{2}</th>
<th>(D_0) cm\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{ortho}–\textit{para}</td>
<td>32.43</td>
</tr>
<tr>
<td>\textit{para}–\textit{para}</td>
<td>34.25</td>
</tr>
<tr>
<td>\textit{ortho}–\textit{ortho}</td>
<td>59.78</td>
</tr>
<tr>
<td>\textit{para}–\textit{ortho}</td>
<td>66.00</td>
</tr>
</tbody>
</table>
investigate resonances in ND$_3$–H$_2$ collisions in this subsection. We present in Fig. 13 state-to-state integral cross sections as a function of collision energy for transitions from the 11– level of ND$_3$ in collisions with para-H$_2$ j = 0. There are pronounced resonance structures in the cross section for the 11– → 11+ transition. Similar to the NH$_3$–para-H$_2$ system, the broad peaks are Feshbach resonances associated with the 21± levels of ND$_3$, while the sharp peaks are Feshbach resonances associated with the 22± levels. While the NH$_3$–H$_2$ and ND$_3$–H$_2$ PESs are quite similar, the ND$_3$ rotational levels are more closely spaced. As a result, the ND$_3$ 22± and 21± levels become open at lower collision energies; this in turn lowers the energies of the quasibound levels associated with these levels relative to the energy of the initial 11– level. It is therefore reasonable to see the resonance peaks appear at lower collision energies. Also, two higher inversion doublets, 32± and 31±, open at ≈45 and ≈51 cm$^{-1}$, respectively. Quasibound states associated with these levels also give rise to weaker resonance peaks in the plotted collision energy range, making the resonance structure more complicated.

The propensities for various transitions are generally the same for NH$_3$–H$_2$ and ND$_3$–H$_2$, consistent with the similarity of the PESs. However, the resonances in the 11– → 21± and 11– → 22± transitions of ND$_3$ show significant overlap and would be difficult to observe cleanly in crossed beam experiments. We do not show a detailed analysis of these resonances here.

V. CONCLUSIONS

We have presented calculations and analysis of resonances in rotationally inelastic scattering of NH$_3$ and ND$_3$, in the 11– initial level, with H$_2$ in j = 0 and j = 1. The large width of many resonances and relatively large resonance contributions to the cross sections, particularly para-H$_2$ collisions resulting in 11– → 11+ transitions, suggest that these resonances could be observed in molecular beam experiments. This would require resolution of the collision energy to better than ≈2 cm$^{-1}$, similar to what would be required for the OH–He/Ne and NH$_3$–He systems. Notably, though, the NH$_3$–H$_2$ resonances are more prominent and the cross sections larger.

The required collision energy range could be achievable in Stark deceleration experiments in geometries where the beam crossing angle is less than 45°. The necessary energy resolution could be achieved by optimizing the kinematics of the experiment. In the most elegant implementation, both integral and differential cross sections are recorded as a function of collision energy using the velocity map imaging detection. The NH$_3$ molecule is particularly amenable to this combination of techniques, although the implementation of a recoil-free resonance-enhanced multi-photon ionization (REMPI) scheme can constitute a formidable challenge. Experiments of this type are currently underway.

With the heavier D$_2$ as the collision partner, the resonance structures are more complex, with significant overlapping between resonances associated with different asymptotic rotational levels. The energy dependence of the cross sections is plotted in the supplementary material. The reduced mass of NH$_3$–D$_2$ is almost twice that of NH$_3$–H$_2$. Thus, the zero-point energy of the deuterium complex will be smaller, so that the PES will support more bound and quasi-bound levels, including some levels with stretch quantum number greater than zero. Consequently, Feshbach resonances arising from quasi-bound levels associated with higher NH$_3$ rotational levels will appear at a lower energy and overlap significantly. In addition, the technique for ortho → para conversion is more efficient for H$_2$ compared to D$_2$. For all these reasons, then, D$_2$ is a less promising candidate for the study of resonances.

The ground rotational level (00+) of NH$_3$ is not amenable to Stark deceleration. Notwithstanding, we find that NH$_3$–H$_2$ cross sections for transitions from that level, particularly for the 00+ → 10+ transition, display interesting resonance structures with both broad and sharp resonance peaks. These energy-dependent cross sections are presented in the supplementary material.

For any given system, the location and heights of resonances in inelastic scattering are a sensitive function of the underlying PES. The PES we used is that of Maret et al., based on ab initio calculations at the CCSD(T)/aug-cc-pVDZ level, corrected by similar CCSD(T) calculations with an aug-cc-pVTZ basis. To check the accuracy of the PES, for 3000 orientations at $R = 5 \Omega$, we have performed more sophisticated CCSD(T)-F12a calculations with an aug-cc-pVQZ basis. We then fitted the interaction energy at these 3000 points using the same angular basis as used by Maret et al. We found that all ten expansion coefficients with the largest absolute values differ by less than 1% from those in this earlier PES. Therefore, we believe the PES of Maret et al. is sufficiently accurate for a careful study of the scattering resonance in this system.

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3HIBRIDON is a package of programs for the time-independent quantum treatment of inelastic collisions and photodissociation written by M. H. Alexander, D. E. Manolopoulos, H.-J. Werner, B. Follmeg, P. J. Dagdigian, and others. More information and/or a copy of the code can be obtained from the website http://www2.chem.umd.edu/groups/alexander/hibridon.


9See supplementary material at http://dx.doi.org/10.1063/1.4927074 for the difference in the scattering resonances obtained with the two expansions of the PES, the explicit equation for computing differential cross sections for molecule-molecule collisions, and the energy-dependent state-to-state integral cross sections for collisions between para-NH$_2$ and D$_2$ and between ortho-NH$_2$ and H$_2$.


