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Scattering of NH$_3$ by ortho- and para-H$_2$: Expansion of the potential and collisional propensity rules
Resonances in rotationally inelastic scattering of NH$_3$ and ND$_3$ with H$_2$

Qianli Ma (马千里),$^{1,a}$ Ad van der Avoird,$^{2,b}$ Jérôme Loreau,$^3$ Millard H. Alexander,$^4,c$ Sebastiaan Y. T. van de Meerakker,$^2$ and Paul J. Dagdigian$^{1,d}$

$^1$Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218-2685, USA
$^2$Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands
$^3$Service de Chimie Quantique et Photophysique C. P. 160/09, Université Libre de Bruxelles (ULB), 50 Ave. F. D. Roosevelt, 1050 Brussels, Belgium
$^4$Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218-2685, USA

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We present theoretical studies on the scattering resonances in rotationally inelastic collisions of NH$_3$ and ND$_3$ molecules with H$_2$ molecules. 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.$^{1–4}$ In inelastic scattering, a resonance corresponds to formation of a quasibound level during the collision$^{5,6}$ and usually manifests as structure in the energy dependence of cross sections.$^1$ 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.$^2$

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.$^5–11$ Scattering resonances have been observed in mostly atomic, elastic collisions$^{12–14}$ and in the reactive F + HD $\rightarrow$ HF + D system.$^{15}$ 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.$^{16,17}$ Both shape and Feshbach resonances were observed in rotationally inelastic atom-molecule and molecule-molecule collisions.$^{18–21}$ Chefdeville et al.$^{18–20}$ investigated the scattering of H$_2$ by CO and O$_2$, while Bergeat et al.$^{21}$ studied CO–He scattering. In these experiments, the authors used Even–Lavie pulsed valves$^{22}$ 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 Λ-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,$^{23,24}$ 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.$^{10,11}$ Both these systems manifest significant shape and Feshbach resonances. The features are narrow, with widths of $\sim$1 cm$^{-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.$^{25–35}$ 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 ND$_3$ that is a candidate for Stark deceleration (see Sec. II for the rotation of the rotational levels).

In the present work, we study in detail resonances in the state-to-state cross sections of NH$_3$ and ND$_3$ out of this 11– level, using the PES computed by Maret et al. \cite{30} This PES has been employed in a few studies of collision dynamics.\cite{29,30,36,37} 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 (3$^1\Sigma^+$) 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 bending model\cite{38,39} as well as examination of the scattering wave function.\cite{11} A discussion in Sec. V concludes.

II. SCATTERING CALCULATIONS

We label the rotational levels of the NH$_3$ and ND$_3$ symmetric top molecules as $j k \pm$, where $j$ is the total angular momentum of the molecule, $k$ is the projection of $j$ on the $C_3$ axis, and $\pm$ is the umbrella inversion symmetry.\cite{40} The NH$_3$ and ND$_3$ molecules have, respectively, two (para and ortho) and three (para, A$_1$, and A$_2$) nuclear spin modifications that do not interconvert during inelastic scattering.\cite{30,41} 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-NH$_3$ and ND$_3$ (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 $3\Sigma^+$ electronic state.\cite{20,28,42} We approximate the inversion doublet wave functions of NH$_3$/ND$_3$ as even and odd combinations of the two rigid equilibrium structures multiplied by rigid rotor wave functions, namely, $| j k m e \rangle = 2^{-1/2} [ | j k m \rangle + \epsilon | j k, -m \rangle ]$.

The umbrella inversion symmetry is $-\epsilon (-1)^j$. Previous investigations of inelastic scattering in the NH$_3$/ND$_3$–He and NH$_3}$/ND$_3$–Ar systems\cite{13,44} 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\cite{45} and with a set of scattering programs developed in Nijmegen.\cite{10,11,44,46} 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 NH$_3$ with $j \leq 6$ or $E$ rotational levels of ND$_3$ with $j \leq 7$. For collisions with para-H$_2$, the $j = 0$ and $j = 2$ levels of H$_2$ are included, while for ortho-H$_2$, 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 NH$_3$, we used rotational constants $B = 9.9402$ cm$^{-1}$ and $C = 6.3044$ cm$^{-1}$; for ND$_3$, we used $B = 5.1428$ cm$^{-1}$ and $C = 3.1246$ cm$^{-1}$.\cite{48} We assume an inversion splitting of 0.7903 and 0.053 cm$^{-1}$ for NH$_3$ and ND$_3$, respectively, independent of $j$ and $k$.\cite{48,49,50} More details on the calculation of differential cross sections for molecule-molecule systems are contained in the supplementary material.\cite{51}

III. POTENTIAL ENERGY SURFACES

To describe the NH$_3$–H$_2$ 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 NH$_3$, and the Jacobian vector $R$ that connects the centers of mass of the molecules has the polar angles ($\theta_1, \phi_1$). The orientation of the H$_2$ bond axis relative to this frame is defined by the angles ($\theta_2, \phi_2$). The interaction potential can be expanded either in Clebsch-Gordan coupled products of angular basis functions

$$V(R, \theta_1, \phi_1, \theta_2, \phi_2) = \sum_{l_1 \mu_1 l_2} V_{l_1 \mu_1 l_2}(R) \sum_{m_1} (l_1 m_1, l_2, -m_1 | 00) \times D^{l_1 *}_{m_1 \mu_1}(0, -\theta_1, -\phi_1) \times D^{l_2}_{m_1, 0}(\phi_2, \theta_2, 0)$$

(1)

or in an uncoupled product basis

$$V(R, \theta_1, \phi_1, \theta_2, \phi_2) = \sum_{l_1 \mu_1 l_2 m_1} V_{l_1 \mu_1 l_2 m_1}(R) D^{l_1 *}_{m_1 \mu_1}(0, -\theta_1, -\phi_1) \times D^{l_2}_{m_1, 0}(\phi_2, \theta_2, 0).$$

(2)

In the above equations, $V_{l_1 \mu_1 l_2}$ and $V_{l_1 \mu_1 l_2 m_1}$ are expansion coefficients, $(l_1 m_1, l_2, -m_1 | 00)$ is a Clebsch-Gordan coefficient, and $D^{l_1}_{m_1 \mu_1}$ are rotation matrix elements.\cite{52} 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 $V_{l_1 \mu_1 l_2}$ 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.\cite{30} 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.\textsuperscript{51} 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 ($r_{\text{NH}} = 1.9512 \ a_0$
and $\angle_{\text{NHN}} = 107.38^\circ$), we have $\delta_{\text{COM}} = 0.088530 \ a_0$.

The \textit{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
splineing the $R$ dependence of the NH$_3$–H$_2$ interaction energies
\textit{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$_3$

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.png}
\caption{Comparison between the larger expansion coefficients $V_{1\mu,1\ell,1j}$ [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).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.png}
\caption{State-to-state integral cross section as a function of collision energy
for transition from the 11$^\text{-}$ level of \textit{para}-NH$_3$ in collisions with \textit{para}-H$_2$ in
the $j = 0$ level. The curves are labelled by the final rotational level.}
\end{figure}

IV. RESULTS AND DISCUSSION

A. Collisions between NH$_3$ and \textit{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$^\text{-}$ initial
level at collision energies below 70 cm$^{-1}$. Below the threshold
for rotational excitation, transition between the inversion dou-
blets (11$^\text{-} \rightarrow$ 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
[$D_v = 267$ 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.\textsuperscript{10,11} 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$^\text{-} \rightarrow$ 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 reso-
nances corresponding to quasibound states associated with
the 21$^+$ final level. Similar to the 11$^\text{-} \rightarrow$ 21$^+$ transition, the
cross section for the 11$^\text{-} \rightarrow$ 21$^-$ transition also displays a few
shape resonances at similar collision energies, though smaller
in magnitude. The resonances in the 11$^\text{-} \rightarrow$ 22$^\pm$ transitions
have contributions from both shape resonances, and Feshbach
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 NH\(_3\). 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.\(^{55,56}\)

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 NH\(_3\) \( 22\pm \) levels, with energies 8.30, 15.71, and 22.30 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 NH\(_3\) \( 21\pm \) 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 NH\(_3\) \( 22\pm \) level and the broad peaks from the \( 21\pm \) 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 NH\(_3\) level. This is an example of the limitations of the adiabatic bender model. Near an avoided

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**FIG. 4.** Partial cross sections as a function of collision energy for the 11– → 11+ transition of \( \text{para-NH}_3 \) in collisions with \( \text{para-H}_2 \) in the \( J = 0 \) level. Solid lines represent the cross sections for + parity and dotted lines − parity for the given total angular momentum \( J \). The red and blue vertical lines on the \( J = 6, + \) parity partial cross sections show the stretch level energies of the adiabatic bender curves (shown in Fig. 5) associated to the \( 22\pm \) and \( 11\pm \) levels of NH\(_3\), respectively.

**FIG. 5.** Adiabatic bender curves for the interaction between \( \text{para-NH}_3 \) and \( \text{para-H}_2 \) for the \( J = 6, + \) parity partial wave. The colors of the lines indicate the asymptotic inversion doublet associated with the curves (the assignment is only approximate due to avoided crossings between curves). Quasibound states are shown as dotted horizontal lines. The zero of energy is the asymptotic energy of the 11− level of NH\(_3\) and the \( J = 0 \) level of H\(_2\).
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\(^7\) in electronic structure theory. As shown in Fig. 5, the \(\text{NH}_3-\text{H}_2\) 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 \(L\).\(^1\) The Nijmegen scattering program uses a renormalized Numerov propagator and it is relatively easy to generate these radial scattering wave functions. We plot in Fig. 6 such contributions to the squared scattering wave function of the \(J = 6, +\) parity partial wave at two collision energies. The two energies considered in Fig. 6 are close to each other, but the scattering wave functions are quite different. Figure 6(a) corresponds to a collision energy of 20.65 cm\(^{-1}\) where a broad resonance peak occurs. We see clearly that the 21\(^-\) channel with \(L = 4\) has a dominating amplitude in the region of the van der Waals well, but vanishes at larger \(R\) because this channel is still closed at this collision energy. This shows that the broad resonance peak around this energy corresponds to a Feshbach resonance with the 21\(^-\) level of \(\text{NH}_3\) and \(L = 4\). Figure 6(b) represents a collision energy of 22.65 cm\(^{-1}\) at which there is a sharp resonance peak. The major contributor to the scattering wave functions here is the 22+ channel with \(L = 6\), asymptotically closed at this collision energy. Hence, this sharp peak also corresponds to a Feshbach resonance, but involves the 22+ level of \(\text{NH}_3\). For comparison, we also plotted the scattering wave functions at some nearby, off-resonance energies, but these plots only show the continuum functions of the channels open at the given collision energy and no channels with particularly large amplitudes in the region of the van der Waals well.

An overview of the resonances in the 11\(^-\) \(\rightarrow\) 11\(^+\) transition is given in Table I. One series of Feshbach resonances involves the 21\(^\pm\) levels of \(\text{NH}_3\), just like the \(L = 4\) resonance illustrated in Fig. 6(a), with partial wave quantum numbers \(L = 4, 5, 6,\) and 7. The second series, illustrated for \(L = 6\) in Fig. 6(b), involves the 22\(^\pm\) levels of \(\text{NH}_3\) with \(L = 5, 6,\) and 7. Figure 3 shows that resonances in the first series are all broad, while those in the second series are all sharp. This is related to which terms in the expansion of the potential couple these closed states to the open 11\(^\pm\) states; for the 21\(^\pm\) levels in the first series, these are primarily the \(V_{l_1l_2l_3l_4}\) terms with \(l_1 = 1, 2,\) and 3 and \(\mu_1 = 0\), while for the 22\(^\pm\) levels in the second series, these are primarily the terms with \(l_1 = 3\) and \(\mu_1 = 3\). The plot of the expansion coefficients in Fig. 2 shows that the latter terms are considerably smaller, which explains why the resonances in the second series are much sharper than those in the first series. This agrees with the observation that the 11\(^-\) \(\rightarrow\) 21\(^\pm\) transitions have larger cross sections than the 11\(^-\) \(\rightarrow\) 22\(^\pm\) transitions, despite a larger energy gap (see Fig. 3).

From 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 \(\text{NH}_3-\text{para-H}_2\) complex. Both series of resonances correspond to a rotational constant of about 0.6 cm\(^{-1}\). This value, combined with the reduced mass

![FIG. 6. Contributions of various rotational levels \(jk\) of \(\text{NH}_3\) and partial waves \(L\) to the square of the scattering wave function with \(J = 6, +\) parity for the scattering of \(\text{NH}_3\) in the 11\(^-\) initial state and \(\text{para-H}_2\) \((j = 0)\). Collision energies are (a) 20.65 cm\(^{-1}\) and (b) 22.65 cm\(^{-1}\).](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.\footnote{We also computed the di} 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.\footnote{We also computed the di} 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.\footnote{We also computed the di} 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. (a) and (b) Phase shift sum and collision lifetime for different total angular momenta $J$ for the scattering of NH$_3$ in the $11^\rightarrow 11^+$ 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.](image)

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,\footnote{We also computed the di} 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 $J = 6$, $\pm$ parity partial wave alone and there are significant contributions and interferences involving other partial waves.

### 3. Shape resonances in the $11^\rightarrow 21^+$ transition

In this section, we analyze the resonance structure shown in the energy dependent $11^\rightarrow 21^+$ cross section. Although not as dramatic as the resonances in the $11^\rightarrow 11^+$ 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.\footnote{We also computed the di} 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 l₂ > 0). Only l₂ = 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 l₂ > 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 H₂ j = 0 (see Fig. 3). We also calculated the dissociation energy D₀ of the various nuclear spin species of NH₃–H₂, see Table II. The results in this table show that D₀ is considerably larger for NH₃–ortho-H₂ (j = 1) than for NH₃–para-H₂ (j = 0) since the effective PES for the former includes I₂ > 0 terms and the H₂ rotational wave function can polarize to sample the most attractive geometry of the complex. This is similar to other molecule–H₂ complexes in which the dissociation energy of the complex is significantly larger for ortho-H₂ than for para-H₂.63-68 Thus, there are more bound, and quasi-bound, levels associated with NH₃–H₂ (j = 1) than with NH₃–H₂ (j = 0), and the resonance structure in the cross section for the 11−→11+ transition is much more complicated for collision with H₂ j = 1 than for 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−→21± transitions in collisions with H₂ j = 1 are small in magnitude relative to the non-resonant background, as compared to those when H₂ j = 0 is the collision partner. For the 11−→22± transitions, the shape and Feshbach resonances associated with the 21± 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 ortho to para ratio of 3:1. We plot in Fig. 12 the cross section for the NH₃ 11−→11+ transition in collision with para-, ortho-, and normal H₂. Because of the larger nuclear spin statistical weight and the larger cross section, the resonance structures for NH₃–normal H₂ (black lines in Fig. 12) are almost the same as for NH₃–ortho-H₂ (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−→11+ transition of NH₃ in collisions with para-, ortho-, and normal H₂, convoluted with Gaussian collision energy spreads of two different widths. We see that with a 2 cm⁻¹ energy resolution, the sharp resonance peaks disappear, but the broad resonance peaks are still resolved. However, with an energy spread of 5 cm⁻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 NH₃–H₂ collisions is with para-H₂.

### Table II. Dissociation energies D₀ of the various nuclear spin species of NH₃–H₂.

<table>
<thead>
<tr>
<th>NH₃–H₂</th>
<th>D₀/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho–para</td>
<td>32.43</td>
</tr>
<tr>
<td>para–para</td>
<td>34.25</td>
</tr>
<tr>
<td>ortho–ortho</td>
<td>59.78</td>
</tr>
<tr>
<td>para–ortho</td>
<td>66.90</td>
</tr>
</tbody>
</table>

C. Collisions between ND₃ and H₂

The ND₃ molecule has a smaller inversion splitting and is easier to manipulate with a Stark decelerator. Accordingly, we...
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$^-\rightarrow$ 11$^+$ transition. Similar to the NH$_3$–para-H$_2$ system, the broad peaks are Feshbach resonances associated with the 21$^\pm$ levels of ND$_3$, while the sharp peaks are Feshbach resonances associated with the 22$^\pm$ 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$^\pm$ and 21$^\pm$ 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$^\pm$ and 31$^\pm$, 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$^-\rightarrow$ 21$^\pm$ and 11$^-\rightarrow$ 22$^\pm$ 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$^-\rightarrow$ 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 $\rightarrow$ 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$^-\rightarrow$ 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 $R = 5\ a_0$, we have performed more sophisticated CCSD(T)-F12a calculations with an aug-cc-pVTZ 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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