

High-Resolution Absorption Spectroscopy of ND₃ between 59,000 and 93,000 cm⁻¹

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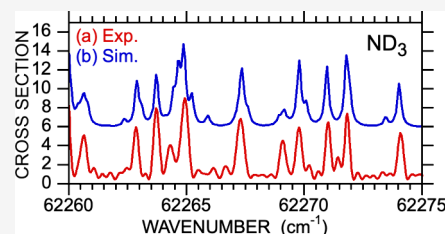


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ABSTRACT: Complementing our recent work on ammonia [Pratt et al., *J. Mol. Spectrosc.* **2023**, 396, 111810], we here present new high-resolution photoabsorption spectra of deuterated ammonia, ND₃, spanning the region between 59,000 and 93,000 cm⁻¹. This region extends from just above the Franck–Condon envelope for the $\tilde{X}^1A_2'' \leftarrow \tilde{X}^1A_1'$ transition to well above the ND₃⁺ $\tilde{X}^2A_2''$ ionization threshold. The absolute photoabsorption cross sections were recorded at room temperature using the Fourier transform spectrometer at the Synchrotron SOLEIL with a measured spectral resolution of 0.22 cm⁻¹, which is a factor of 10–100 times higher than in any previously reported broadband spectrum of ND₃. The spectra reveal partially resolved rotational structure in several different vibrational progressions, which allows the reassignment of some of the higher energy bands, enabling proposed assignments for the P1 and P2 progressions reported by Wu et al. [*J. Chem. Phys.* **2007**, 127, 154311] and an expanded appraisal of the pattern of lower-lying Rydberg states of ammonia.



I. INTRODUCTION

The vacuum ultraviolet (VUV) photochemistry of ammonia, NH₃, and its isotopologues (NH₂D, NHD₂, and ND₃) is important for characterizing isotopic fractionation in planetary atmospheres.^{1,2} The isotope ratios of ammonia and its deuterated analogues also provide useful probes of cold molecular clouds and the early stages of star formation.^{3–5} We have recently reported a high-resolution absorption spectrum of NH₃ between 59,000 and 93,000 cm⁻¹, a region that starts just above the 3s $\tilde{A}^1A_2'' \leftarrow \tilde{X}^1A_1'$ band system and extends well above the first ionization threshold and up to the $\tilde{X}^2A_2''$, $v_2^+ = 14$ limit (where v_2 is the umbrella vibration of the molecule).⁶ This spectrum was recorded using the Fourier transform spectrometer (FTS) at the Synchrotron SOLEIL, which provides considerably higher resolution than previous comprehensive measurements. NH₃ spectra were obtained both at room temperature (298 K) and in a supersonic expansion (~70 K). As a complement to this earlier work, we now report the absolute absorption cross section for a room-temperature ND₃ sample across the same energy range and with comparable photon energy resolution.

Ammonia has a pyramidal equilibrium geometry in its electronic ground state, but the inversion barrier is sufficiently low that its spectroscopy is traditionally described using the D_{3h} point group. Removal of an electron from the highest occupied 2p_{a₂} molecular orbital (HOMO) of ND₃ in its (pyramidal) $\tilde{X}^1A_1'$ ground state results in a planar equilibrium structure for the $\tilde{X}^2A_2''$ ground state of ND₃⁺ and for

members of all Rydberg series converging to it.⁷ As a result, the band system accompanying each Rydberg $n\ell\gamma \leftarrow 2p_{a_2}''$ electron promotion displays a long progression in the ν_2 umbrella bending vibration of the upper state.^{8–11} (Here, γ is used to label a generic irreducible representation for the Rydberg electron.) The band systems at a low principal quantum number (e.g., for the 3s $\tilde{A}^1A_2'' \leftarrow \tilde{X}^1A_1'$ transition) are well separated, but at higher energy, the long progressions associated with different $n\ell\gamma$ quantum numbers are strongly overlapped. Interactions among levels with different $n\ell\gamma$ and vibrational quantum numbers could give rise to perturbations and complex resonances that further complicate assignments. The strength of such perturbations depends on the value of Δv_2 between the perturbing levels, with larger values of Δv_2 expected to result in significantly weaker perturbations. To help navigate the data that follow, Table 1 lists the relevant electronic states, their effective principal quantum numbers (i.e., $n^* = n - \delta$, where δ is the quantum defect), and corresponding configurations for the Rydberg states of ND₃ considered in the present study.^{11–16} This table includes states

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Table 1. ND₃ States and Their Dominant Electronic Configurations in the Vertical Region

state	configuration	term energy (cm ⁻¹)	<i>n</i> *
$\tilde{X}^1A_1'$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^2$	0.0	
$\tilde{A}^1A_2''$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(3sa_1')^1$	46,713.8 ¹¹	1.757
$\tilde{B}^1E''$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(3pe')^1$	59,391.396 ¹²	2.190
$\tilde{C}^{a1}$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(3pe')^1$		
$\tilde{C}'^1A_1'^b$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(3pa_2'')^1$	63,955.5 ^{13,19}	2.448
$\tilde{D}^1E'$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(3de'')^1$	69,832 ¹⁴	2.971
$\tilde{D}'^1A_2''^c$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(4sa_1')^1$	70,097 ¹⁴	3.003
$\tilde{D}''^1A_2''^c$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(3da_1')^1$	70,067 ¹⁴	3.000
$\tilde{D}'''^1E''^b$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(4pe')^1$	71,349 ²¹	3.171
$\tilde{E}^1E'$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(4de'')^1$	75,366 ¹⁴	3.989
$\tilde{E}'^1A_1'^b, d$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(4pa_2'')^1$	72,995 ¹⁵	3.441
P1 $^1A_2''$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(5s/4da_1')^1$	75,421 ^c	4.005
$\tilde{F}^1E'$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(5de'')^1$	78,045 ¹⁴	5.101
$\tilde{F}'^1A_1'^b$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(5pa_2'')^1$	76,770 ¹⁵	4.470
P2 $^1A_2''$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(6s/5da_1')^1$	77,920 ^c	5.027
$\tilde{G}^1E'$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1(6de'')^1$	78,927 ¹⁴	5.736
$\tilde{X}^+ 2A_2''$	$(1sa_1')^2(2sa_1')^2(2pe')^4(2pa_2'')^1$	82,261.7 ¹⁶	

^aThe $\tilde{C}$ – $\tilde{X}$ bands were originally attributed¹¹ to excitation to the $3pa_2''$ Rydberg orbital. It was later shown that these bands actually corresponded to $2_0^m3_0^1$ combination bands of the $\tilde{B}$ – $\tilde{X}$ transition. The true Rydberg state from $3pa_2'' \leftarrow$ HOMO excitation was first characterized by Nieman and Colson,^{18,19} who labeled it $\tilde{C}'^1A_1'$. ^bThe three states of $^1A_1'$ symmetry highlighted in bold are not observed in the present single-photon absorption study. The present analysis also concludes that the $\tilde{D}'''^1E''$ state identified in multiphoton ionization spectroscopy studies²¹ of NH₃ and ND₃ does not align with features previously assigned as $\tilde{D}'''$ – $\tilde{X}$ absorptions¹⁴—see Section IIIC. ^cThe $\tilde{D}'$ and $\tilde{D}''$ state labels were initially associated with excitations to the $3da_1'$ and $4sa_1'$ orbitals,^{20–22} respectively, but these were subsequently interchanged. For consistency, the labeling scheme used by Li and Vidal¹⁷ and by Wu et al.¹⁴ is used throughout this paper. ^dThe dominant configuration underpinning this state was misprinted in ref 6. ^ePresent work. The term energies for the P1 and P2 states were determined from the data in Table SIII using the ion vibrational spacings of ref 26.

identified and refined in the present work, as well as data drawn from previous single-photon and multiphoton studies.

Between $\sim 59,000$ and $\sim 70,000$ cm⁻¹, the one-photon spectrum of ND₃ shows a long progression of bands displaying resolved rotational structure corresponding to the $3pe' \tilde{B}^1E'' \leftarrow \tilde{X}^1A_1' 2_0^m$ transitions.^{10,11,17} (In what follows, *m* and *v*₂ will be used interchangeably for the vibrational quantum number of *v*₂.) Weaker $2_0^m3_0^1$ and $2_0^m3_0^14_0^1$ progressions have been identified also (where *v*₃ and *v*₄ are, respectively, the doubly degenerate asymmetric in-plane stretch and in-plane bending vibrational modes), and rotational analyses have been reported for many of these bands. Multiphoton ionization studies with two- and three-photon resonant excitation have allowed detailed characterization and rotational analysis of these bands as well as those associated with the $3pa_2'' \tilde{C}'^1A_1' \leftarrow \tilde{X}^1A_1' 2_0^m$ progression.^{12,13,18–23}

In what follows, we first present a description of the FTS,²⁴ the experimental approach, and the analysis methods. We then focus on the principal body of the spectrum between 59,000 cm⁻¹ and the first ionization threshold at 82,261.7 cm⁻¹.¹⁶ Much of the discussion builds on the extensive previous work,^{14,25–28} but we emphasize the use of isotope shifts (between corresponding transitions in ND₃ and NH₃) to clarify and correct some earlier assignments and the observation and identification of two long, partially rotationally resolved progressions. Next, we discuss the spectrum above the ionization threshold and the interaction/competition between autoionization and predissociation before summarizing the present findings.

As shown in previous works, few of the bands in the one-photon absorption spectrum of NH₃ above 70,000 cm⁻¹ display even partially resolved rotational structure. Exceptions include the $3de'' \tilde{D}^1E' \leftarrow \tilde{X}^1A_1' 2_0^m$ (*m* = 0–3) and $4de'' \tilde{E}^1E' \leftarrow \tilde{X}^1A_1' 2_0^m$ (*m* = 0–3) bands, which do show poorly resolved structure in the jet-cooled spectrum, but efforts to simulate

these bands have met with only limited success.⁶ One motivation for the present study is that the predissociation rates from excited states of ND₃ are expected to be smaller than those for the corresponding states of NH₃, as a result of which rotational structure in the ND₃ spectrum can be expected to be better defined and more readily analyzed. Indeed, Li and Vidal observed partially resolved rotational structure in the jet-cooled ND₃ $3de'' \tilde{D}^1E' \leftarrow \tilde{X}^1A_1' 2_0^m$ (*m* = 0–3) bands and presented a rotational analysis of the origin (2_0^0) band.¹⁷

II. METHODS

The FTS on the DESIRS undulator beamline of the Synchrotron SOLEIL has been described previously,^{24,29,30} and the experimental details are discussed only briefly here. The ND₃ sample was used directly from the cylinder without dilution. Spectra were recorded using two different configurations of the sample cell. Most of the spectra were recorded using a 100 mm long windowless flowing cell. Because the determination of the sample density is difficult in this configuration, spectra were also recorded in the region below 70,000 cm⁻¹ using a static 80 mm long cell equipped with MgF₂ entrance and exit windows. This configuration allows the determination of absolute absorption cross sections and the calibration of the flowing cell measurements. In the present experiments, ND₃ spectra recorded in the static cell revealed the presence of an $\sim 10\%$ contribution from NHD₂, which hampered the absolute cross-section calibration. The NHD₂ was likely produced by photolysis of ND₃ by the continuum of undulator radiation followed by reactions with water from the walls of the cell. No evidence for NHD₂ is observed in the spectra obtained using the flowing cell. While the calibration provided absolute photoabsorption cross sections in good agreement with previous experiments, ultimately the entire spectrum was scaled by using the cross section reported in ref 14 in the structureless portion of the spectrum above 90,000 cm⁻¹.

Nine different undulator settings were used to cover the spectral region of the present study. The full undulator bandwidth was passed through a harmonic-filtering gas cell and into the sample. The

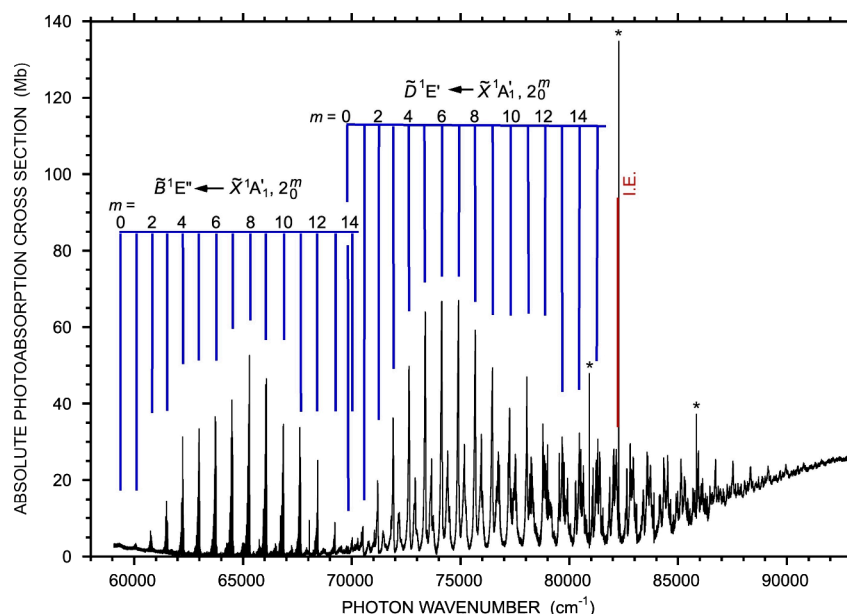


Figure 1. Room-temperature (298 K) absorption spectrum of ND₃ between 59,000 and 93,000 cm^{−1}. The dominant $\tilde{B}-\tilde{X}$ and $\tilde{D}-\tilde{X}$ 2_0^m progressions are indicated, as is the ionization energy (I.E., in red). Impurity absorption lines from Kr, H, and D are indicated with an asterisk, *. On the scale of the figure, the H and D Lyman α absorption lines are overlapped with the ionization energy of ND₃.

separate spectra were spliced together, and the energy scale was calibrated using impurity absorption lines from Xe and Kr in the gas filter and H and D atoms produced by photolysis by the continuum source. The full resolution corresponded to a 0.22 cm^{−1} full width at half-maximum peak height (FWHM) in the 59,000–81,310 cm^{−1} region. At yet higher wavenumbers, the spectra were computed at somewhat lower resolution to improve the signal-to-noise ratio, corresponding to 0.44 cm^{−1} (FWHM) in the range 81,310–86,460 cm^{−1} and to 3.45 cm^{−1} (FWHM) above 86,460 cm^{−1}. The full spectrum of ND₃ between 59,000 and 93,000 cm^{−1} is shown in Figure 1.

III. RESULTS AND DISCUSSION

A. Cross Sections and Oscillator Strengths

As in the case of NH₃, the peak photoabsorption cross sections in Figure 1 are somewhat larger than those reported in previous studies,^{14,31} particularly for the $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$ band system. This difference is due to the substantially higher resolution of the present measurements (0.22 cm^{−1} vs 11 cm^{−1} at 75,000 cm^{−1} in ref 14). The oscillator strength, f , is defined by³²

$$f = 1.13 \times 10^{-6} \int_a^b \sigma d\tilde{\nu} \quad (1)$$

where σ is the absolute cross section in Mb, $\tilde{\nu}$ is the wavenumber in cm^{−1}, and a and b determine the spectral range of interest. Table 2 compares the oscillator strengths determined in the regions reported in refs 14 and 31. The agreement is generally good, typically differing from the previous measurements by ~2–5%, with the exception of the region between 60,606 and 69,444 cm^{−1}, corresponding to the $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$ system, where the present oscillator strength is ~36% greater than the values of Cheng et al.³¹ Figure 2 shows a significant continuum signal at the low energy side of the spectrum under the well-resolved $\tilde{B} \leftarrow \tilde{X}$ system, from the tail of the $\tilde{A} \leftarrow \tilde{X}$ system at lower wavenumbers. This continuum is much weaker in the data of Cheng et al. A simple polynomial fit to the present continuum between 60,606 and 69,444 cm^{−1}

Table 2. Oscillator Strengths for ND₃

spectral region (cm ^{−1}) ^a	oscillator strength (f)	reference
60,606–69,444	0.0122	this work
	0.0090	ref 31
continuum only	0.0023	this work
continuum subtracted	0.0099	this work
69,444–78,125	0.0915	this work
	0.0964	ref 14
78,125–84,746	0.0848	this work
	0.0864	ref 14
84,746–90,909	0.1225	this work
	0.1261	ref 14
69,444–81,967	0.1385	this work
	0.1445	ref 14
81,967–89,286	0.1205	this work
	0.1228	ref 14

^aThese wavenumber ranges correspond to those used in ref 14.

gives an oscillator strength of 0.0023. Subtracting this from the corresponding total oscillator strength for this region gives 0.0099, in closer agreement with the value of Cheng et al. (0.0090).³¹ This finding suggests that further investigation of the continuum absorption throughout this region of the ammonia spectrum is worth pursuing.

B. The 59,000–70,000 cm^{−1} Region: The $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$ Bands of ND₃

Figure 2 shows the ND₃ absorption spectrum between 59,000 and 70,000 cm^{−1}. This region is dominated by the $3pe' \tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$ band system, which displays a long, rotationally resolved 2_0^m progression and, as observed in previous one-photon absorption studies,^{10,17} significantly weaker features attributed to $2_0^m3_0^1$ and $2_0^m3_0^14_0^1$ combination bands. The $3pa_2'' \tilde{C}'^1A_1' \leftarrow \tilde{X}^1A_1'$ 2_0^m band system, now well-characterized by multiphoton spectroscopies,^{18–22} also falls in this wavenumber region, but no recognizable structure associated with this transition is evident in the one-photon spectrum.

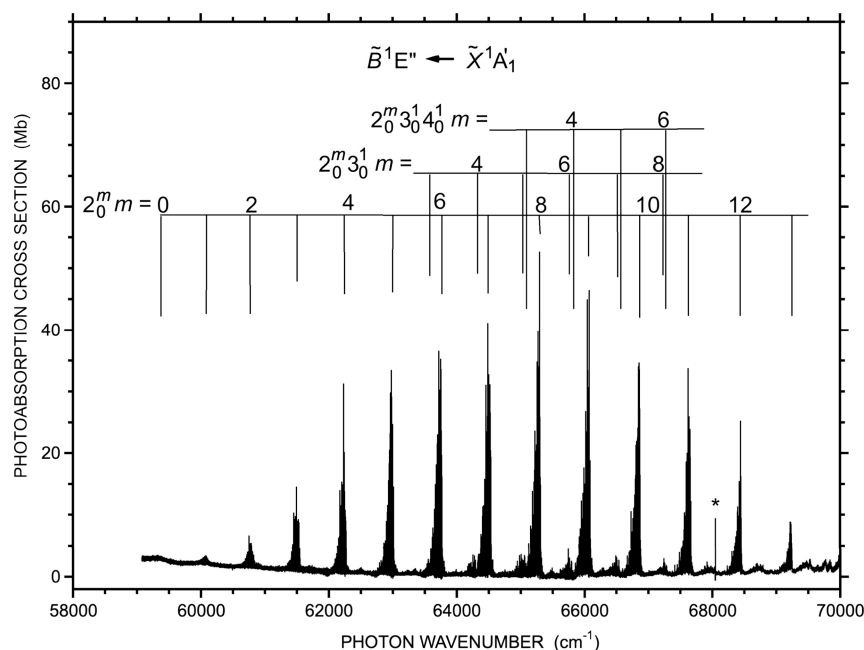


Figure 2. Room-temperature (298 K) absorption spectrum of ND₃ between 59,000 and 70,000 cm⁻¹. Features attributed to the $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$ 2_0^m , $2_0^m 3_0^1$, and $2_0^m 3_0^1 4_0^1$ progressions are indicated, as is one Xe impurity absorption line, with an asterisk, *.

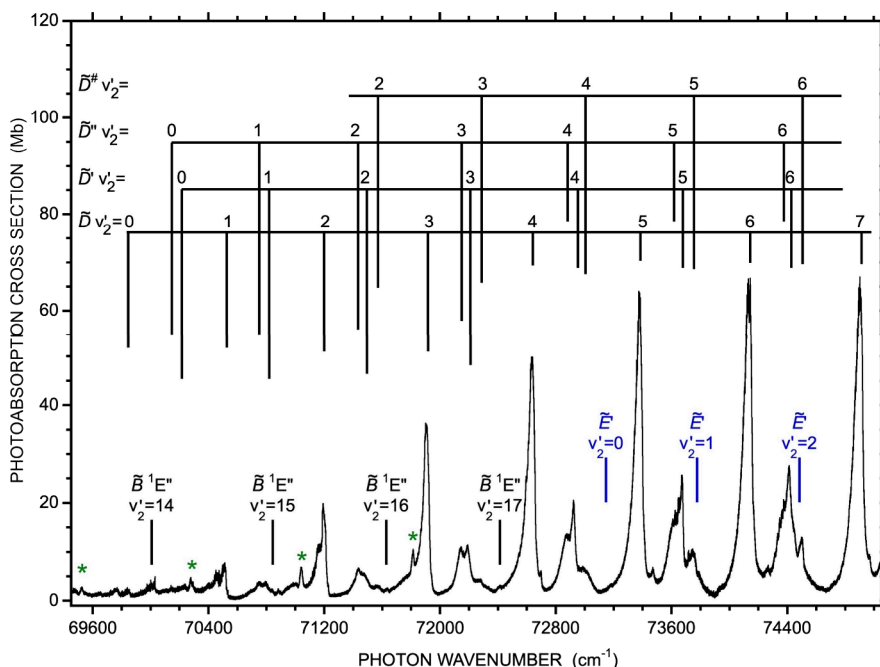


Figure 3. An expanded view of the room-temperature absorption spectrum of ND₃ between 69,500 and 75,000 cm⁻¹. The 2_0^m progressions associated with transitions to the $\tilde{B}^1E''$, $\tilde{D}^1E'$, $\tilde{D}'^1A_2''$, and $\tilde{D}''^1A_2''$ electronic states are indicated. As discussed in the text, the $\tilde{D}^{\#}$ bands correspond to the $\tilde{D}'''$ bands of ref 14 but with the present renumbering. The weak peaks labeled with green asterisks belong to an unassigned progression. The reported wavenumbers of the origins of the first few $\tilde{E}'^1A_1' \leftarrow \tilde{X}^1A_1'$, 2_0^m bands are also indicated (in blue), but these bands are not observed in single-photon absorption.

Using a combination of Doppler-free two-photon spectroscopy and the single-photon absorption data of Douglas and Hollas,¹⁰ Ashfold et al.¹² presented a detailed analysis of the $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$ 2_0^m ($m = 0-8$) bands in NH₃ and the $m = 0-6$ bands in ND₃. Douglas also analyzed a number of combination bands in ND₃.¹¹ More recently, Li and Vidal¹⁷ used a combination of fragment fluorescence and ionization detection to record jet-cooled VUV absorption spectra for ND₃ and

presented analyses of the $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$ 2_0^m ($m = 7-12$) bands, as well as for a number of combination bands. Using two-photon excitation, Langford et al. subsequently extended the ND₃ ($\tilde{B} \leftarrow \tilde{X}$) 2_0^m progression up to $m = 17$ but without any rotational analysis.¹⁵

As discussed in more detail in Section S1 of the Supporting Information (SI), we have used the PGOPHER^{33,34} simulation software and the ground and excited-state rotational constants

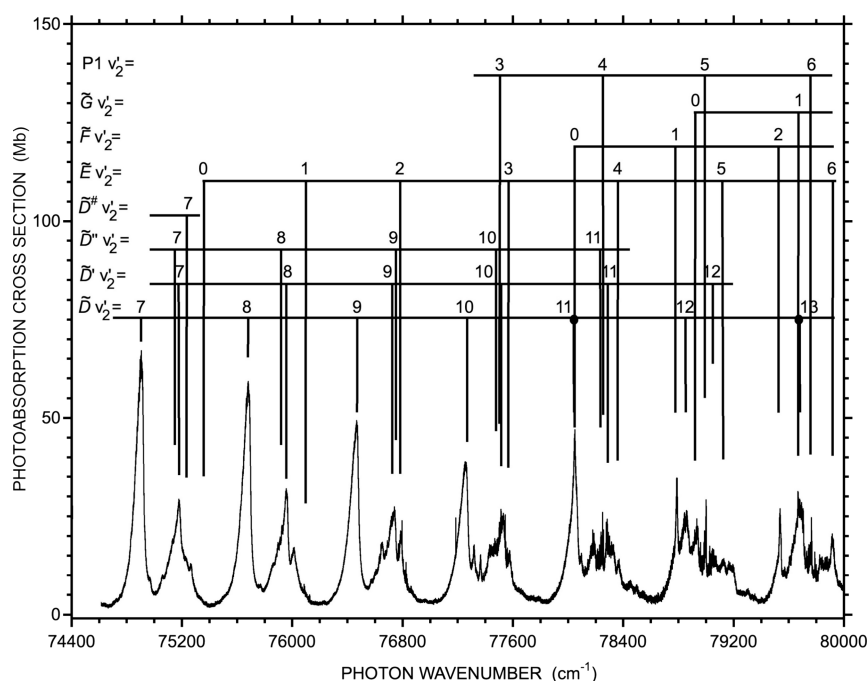


Figure 4. An expanded portion of the room-temperature absorption spectrum of ND₃ between 74,600 and 80,000 cm^{−1}, along with combs indicating progressions to the $\tilde{D}^1E'$, $\tilde{D}'^1A_2''$, $\tilde{D}''^1A_2''$, $\tilde{D}^\#$, $\tilde{E}^1E'$, $\tilde{F}^1E'$, and $\tilde{G}^1E'$ states, and the previously unassigned P1 progression with the vibrational numbering discussed in Section IIID.

returned by, respectively, Fusina et al.³⁵ and the Doppler-free two-photon experiments¹² to simulate the present single-photon spectra. The agreement is excellent for the $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1' 2_0^m$ ($m < 6$) bands, providing a testament to the quality of the previous data and analysis. Excited state rotational constants for vibrational levels with $m = 7-10$ were reported by Li and Vidal;¹⁷ these yielded simulated profiles in reasonable agreement with the spectra measured in the present work. For transitions to yet higher levels, e.g., the $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1' 2_0^m$ ($m = 11, 12$) bands, the fits using the parameters of Li and Vidal were less successful. Section S1 also reports a spectrum of the $\tilde{B} \leftarrow \tilde{X} 2_0^3$ band (without analysis) and examination of several weaker features assigned to $\tilde{B} \leftarrow \tilde{X} 2_0^{m1}$ ($m = 4-8$) and $2_0^3 3_0^1 4_0^1$ ($m = 3-5$) combination bands previously studied by Douglas¹¹ and by Li and Vidal.¹⁷ Simulations based on their analyses allow us to confirm and/or correct a number of their assignments, as detailed in Table SI.

C. Assignments above 70,000 cm^{−1}

Figures 3 and 4 show expanded views of the ND₃ spectrum in the regions 69,500–75,000 and 74,600–80,000 cm^{−1}, respectively, along with many of the previous assignments of Wu et al.¹⁴ The content of these spectra is now discussed in turn, and we start by noting that the peak wavenumbers of some of the bands in the present data differ slightly from those reported previously, probably as a result of the improved resolution and wavelength precision in the current experiments. Apart from the $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1' 2_0^{14}$ band evident at $\sim 70,015$ cm^{−1}, all of the bands in Figure 3 are quite broad, with only traces of underlying rotational structure. The longer-lived nature of the $\tilde{B}$ state levels allowed Langford et al.¹⁵ to follow the $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1' 2_0^m$ progression up to $m = 17$ in their jet-cooled (2 + 1) REMPI studies. The positions of these higher 2_0^m bands are also indicated in Figure 3, as are the wavenumbers of the $4pa_2'' \tilde{E}^1A_1' \leftarrow \tilde{X}^1A_1' 2_0^m$ ($m = 0-2$) band origins identified in the jet-cooled (2 + 1) REMPI

spectrum.³⁶ As with the $3pa_2'' \tilde{C}^1A_1' \leftarrow \tilde{X}^1A_1'$ transition, a careful comparison reveals no evidence for these $\tilde{E}' \leftarrow \tilde{X}$ transitions in the single-photon absorption spectrum. We return to discuss this point further in Section IIID.

Figures 3 and 4 are dominated by the well-documented $3de'' \tilde{D}^1E' \leftarrow \tilde{X}^1A_1' 2_0^m$ progression¹⁴ followed—at slightly higher wavenumber—by the $4sa_1' \tilde{D}'^1A_2'' \leftarrow \tilde{X}^1A_1' 2_0^m$ and $3da_1' \tilde{D}''^1A_2'' \leftarrow \tilde{X}^1A_1' 2_0^m$ progressions.¹⁴ For consistency with ref 6, the narrative here maintains the association between the excited state label and orbital excitation suggested by Li and Vidal¹⁷ and by Wu et al.,¹⁴ rather than the alternative earlier attribution.²¹ As with the transitions to the $\tilde{A}^1A_2''$ and $\tilde{B}^1E''$ states, these progressions each begin with weak 2_0^0 bands (supplemented by the corresponding 2_1^1 hot band), become progressively more intense up to $m = 7-8$ and thereafter slowly decline in intensity. Wu et al.¹⁴ reported wavenumbers for the maxima attributed to the $4sa_1' \tilde{D}'^1A_2'' \leftarrow \tilde{X}$ and $3da_1' \tilde{D}''^1A_2'' \leftarrow \tilde{X}$ progressions for ND₃. As Figures 3 and 4 show, for each value of m , the wavenumber separations between the assigned $\tilde{D}' \leftarrow \tilde{X}$ and $\tilde{D}'' \leftarrow \tilde{X}$ maxima are small ($\sim 20-60$ cm^{−1}). Given that these neighboring transitions involve the same excited state symmetry and have the same vibrational quantum number, they can be expected to interact. Such s/d mixing is common in diatomic molecules³⁷ and can lead to significant energy shifts and intensity redistribution effects, so the energetic proximity of the assigned $\tilde{D}'$ and $\tilde{D}''$ bands is noteworthy. Even though the bands are not rotationally resolved, the rotational envelopes can still make significant contributions to the observed widths. For example, the FWHM of the rotational envelopes accompanying the various $\tilde{A} \leftarrow \tilde{X}$ and $\tilde{B} \leftarrow \tilde{X} 2_0^m$ bands in the room-temperature absorption spectrum of ND₃ are ~ 150 and ~ 85 cm^{−1}, respectively, so one should expect significant overlap between rotational contours of two vibronic transitions spaced by less than 100 cm^{−1}. We return to consider this point further later in this section.

Li and Vidal¹⁷ observed some (at least partially) resolved rotational structure in their jet-cooled, single-photon excitation spectra of the $\tilde{D}^1E' \leftarrow \tilde{X}^1A_1' 2_0^m$, $m = 0-4$ bands of ND₃ and were able to perform a rotational analysis of the origin band. Rotational structure is also evident in the room-temperature spectrum of this band, which, as shown in Section S2 of the SI, is reproduced reasonably well by a PGOPHER simulation using the reported spectroscopic constants.¹⁷ Our attempts to refine the fit did not produce significant changes in these constants.

Above 71,500 cm⁻¹, Wu et al.¹⁴ assigned a fourth series of bands to the $4pe' \tilde{D}'''E'' \leftarrow \tilde{X}^1A_1' 2_0^m$ progression in ND₃ and attributed corresponding transitions in NH₃, NH₂D, and NHD₂. Glowia et al.^{20,21} had previously assigned an alternative progression observed in multiphoton ionization studies to the $4pe' \tilde{D}'''E'' \leftarrow \tilde{X}^1A_1'$ transition in both NH₃ and ND₃. The $\tilde{D}'''$ band positions of Glowia et al.^{20,21} for ND₃ are consistently 200–300 cm⁻¹ lower than those of Wu et al., suggesting that these are not the same progressions. As discussed below, to avoid confusion, we henceforth refer to the $\tilde{D}'''$ state of Wu et al.¹⁴ as the $\tilde{D}^\#$ state and do not provide a configuration or symmetry label. To address these assignments, Figure 5 shows the isotope shift, $(\tilde{\nu}(\text{NH}_3) - \tilde{\nu}(\text{ND}_3))$, plotted

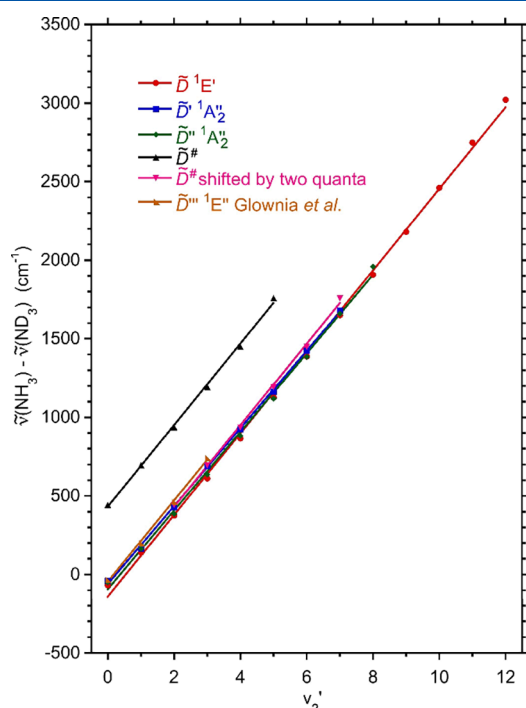


Figure 5. Isotope shift, $(\tilde{\nu}(\text{NH}_3) - \tilde{\nu}(\text{ND}_3))$, plotted as a function of v_2' for the $\tilde{D}^1E' \leftarrow \tilde{X}$, $\tilde{D}''^1A_2'' \leftarrow \tilde{X}$, $\tilde{D}'''^1A_2'' \leftarrow \tilde{X}$, $\tilde{D}'''^1E'' \leftarrow \tilde{X}$, and $\tilde{D}^\# \leftarrow \tilde{X}$ bands. All data are from the work of Wu et al.,¹⁴ except for the $\tilde{D}'''^1E'' \leftarrow \tilde{X}$ bands from Glowia et al.^{20,21} Also shown is a plot of the $\tilde{D}^\# \leftarrow \tilde{X}$ isotope shifts of Wu et al. that have been renumbered by increasing the originally proposed v_2' values by 2. (As discussed in the text, the $\tilde{D}'''$ bands of Wu et al. are labeled $\tilde{D}^\#$ in this figure.)

as a function of v_2' , for the $\tilde{D}$, $\tilde{D}'$, $\tilde{D}''$, and $\tilde{D}^\#$ bands reported by Wu et al.¹⁴ and for the $\tilde{D}'''$ bands reported Glowia et al.²⁰ Figure S11 shows equivalent plots of the isotope shift in the $\tilde{B} \leftarrow \tilde{X}$, $\tilde{C}' \leftarrow \tilde{X}$, and $\tilde{E}' \leftarrow \tilde{X} 2_0^m$ transitions of NH₃ and ND₃ established by REMPI spectroscopy. In all but one case, the isotope shift is near zero for $v_2' = 0$, and increases linearly with v_2' . The one exception is the $\tilde{D}^\# \leftarrow \tilde{X}$ data of Wu et al.,¹⁴

which falls far from this expected line, suggesting that the assignment is in need of revision. As Figure 5 shows, the $\tilde{D}^\# \leftarrow \tilde{X}$ data¹⁴ can be brought into line with all other data by increasing the previously proposed v_2' quantum numbers by 2. With this change in v_2' , the electronic origin of the progression identified by Wu et al. is $\sim 70,200$ cm⁻¹, very close to the origins of the $\tilde{D}' \leftarrow \tilde{X}$ and $\tilde{D}'' \leftarrow \tilde{X}$ transitions. The corresponding quantum defect is near integer (the effective principal quantum number, $n^* \sim 3.02$), suggesting that this $\tilde{D}^\# \leftarrow \tilde{X}$ progression arises as a result of electron promotion to a $3d/4s$ Rydberg state rather than, as proposed previously, $4pe' \leftarrow a_2''$ orbital promotion.

This situation creates a new difficulty, however, as the one-photon electric dipole selection rules only allow transitions to three excited states (two of $^1A_2''$ symmetry, the other of $^1E'$ symmetry) upon excitation from the highest occupied a_2'' orbital in the electronic ground state to $3d/4s$ Rydberg orbitals. (The remaining component of the $3d$ orbital has e' symmetry, but the $3de' \leftarrow a_2''$ excitation is forbidden in D_{3h} symmetry.) Thus, the current $\tilde{D}$, $\tilde{D}'$, and $\tilde{D}''$ state assignments already 'use up' the three excited states predicted for single-photon absorption from the ground state. The assignment of the $3de' \tilde{D}^1E' \leftarrow \tilde{X}^1A_1' 2_0^m$ bands appears solid, which leaves the $4sa_1' \leftarrow a_2''$ and $3da_1' \leftarrow a_2''$ orbital promotions as plausible carriers of the features hitherto attributed to the $\tilde{D}'$, $\tilde{D}''$, and $\tilde{D}^\#$ states. As hinted above, one possibility is that one (or more) of these purported 'transitions' actually represent different features within the overall rotational band contour associated with a transition to a single upper state. For example, the features assigned to the $\tilde{D}^\# \leftarrow \tilde{X}$ transition in NH₃ (labeled $\tilde{D}''' \leftarrow \tilde{X}$ in ref 6) are weaker in the jet-cooled spectra than in the room temperature spectra,^{6,38} which might suggest that this absorption is associated with higher rotational quantum number transitions within a branch of a $\tilde{D}' \leftarrow \tilde{X}$ or $\tilde{D}'' \leftarrow \tilde{X}$ band. Conversely, however, only features attributed to $(2+1)$ REMPI via $\tilde{D}'''$ levels as assigned by Glowia et al.^{20,21} were recognized in the REMPI-photoelectron studies of Langford et al.¹⁵ Finally, we also note that the very well-documented $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$ band system discussed in Section IIIB is a significant contributor to the one-photon absorption spectrum of ammonia. Allowing some analogous vibronic transition probability to the nominally 'forbidden' $3de' ^1E'' \leftarrow \tilde{X}'$ excitation could give rise to a fourth 2_0^m progression with the deduced quantum defect. Double-resonance spectra^{13,39} via selected intermediate rotational levels that allow some resolution of the final-state rotational structure might well offer the best route to resolving what remains a congested spectroscopic problem.

For completeness, we note an additional progression in v_2' in the region between 69,500 and 71,800 cm⁻¹. These features, which are indicated by green asterisks in Figure 3, are evident on the high energy side of the documented $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1' 2_0^m 3_0^1$ and $2_0^m 3_0^1 4_0^1$ combination bands. Similar, albeit weaker, features are observed at 68,030 and 68,789 cm⁻¹. While these features could also be associated with combination bands, their relative intensities appear to be increasing with increasing wavenumber in a region where those of the recognized $\tilde{B}^1E'' \leftarrow \tilde{X}^1A_1'$ features are decreasing. The expected position of the next member of this additional progression lies beneath the intense $\tilde{D} \leftarrow \tilde{X} 2_0^4$ transition and is not apparent in Figure 3.

As Figure 4 also shows, it is possible to follow the $\tilde{D} \leftarrow \tilde{X}$, $\tilde{D}' \leftarrow \tilde{X}$ and $\tilde{D}'' \leftarrow \tilde{X}$ progressions up to $\sim 78,000$ cm⁻¹, but the spectrum is becoming increasingly structured and complicated

as transitions to higher Rydberg states become energetically allowed. Specifically, the $4d$ and $5s$ Rydberg states built on the ground-state cation have their origins just above $75,000\text{ cm}^{-1}$, while the $5d/6s$ and $6d/7s$ Rydberg states can be predicted to have origins near $78,000$ and $79,200\text{ cm}^{-1}$, respectively.¹⁴ The $4de'' \tilde{E}^1E' \leftarrow \tilde{X}^1A_1' 2_0^m$ $m = 0$ and 1 bands are weak, and the spectral patterns below $\sim 76,000\text{ cm}^{-1}$ are similar to those in Figure 3. As the Franck–Condon factor grows with increasing m , however, new features appear, and the assignment of spectral features to specific transitions becomes less certain, especially since most of the bands are broad and rotationally unresolved. Nevertheless, Wu et al.¹⁴ assigned 15 members of the $4de'' \tilde{E}^1E' \leftarrow \tilde{X}^1A_1' 2_0^m$ progression, as well as 13 and 15 members to the $5de'' \tilde{F}^1E' \leftarrow \tilde{X}^1A_1' 2_0^m$ and $6de'' \tilde{G}^1E' \leftarrow \tilde{X}^1A_1' 2_0^m$ progressions, respectively. The first few of their assignments are indicated in Figure 4. Saraswathy et al.²⁷ (and later Limão-Vieira et al.²⁸) suggested reassigning the $6de'' \tilde{G}^1E' \leftarrow \tilde{X}$ progression in NH_3 to the $7sa_1' \tilde{A}_2'' \leftarrow \tilde{X}$ transition based on quantum defect considerations, notwithstanding the evident intensities of the transitions to lower members of the $nde'' \leftarrow a_2''$ Rydberg series (i.e., the $3de'' \tilde{D}$, $4de'' \tilde{E}$, and $5de'' \tilde{F}$ states). Here, we retain the $6de'' \tilde{G}^1E'$ assignment of Wu et al.¹⁴ The unassigned 2_0^m progression that Wu et al. labeled as P1 is also indicated in Figure 4. Note that Wu et al. did not assign vibrational quantum numbers to the P1 progression, or to a second unassigned progression, P2, but labeled them only with a running integer index. As discussed in Section IIID, in Figure 4 we label these progressions with the present assignments for v_2' .

We now focus on a single cluster of features in Figure 4 between $78,600$ and $79,400\text{ cm}^{-1}$. An expanded view of this region is shown in Figure S12 in the SI, along with the corresponding region of the spectrum of Wu et al.¹⁴ (We note that the peak wavenumbers reported in the earlier work are consistently ~ 12 – 15 cm^{-1} below the band maxima observed in the present work.) These data have two significant features.

First, this spectral region shows more maxima and peaks than there are assignments. In principle, $4da_1'/5sa_1' \leftarrow a_2''$ and $5da_1'/6sa_1' \leftarrow a_2''$ excitations analogous to the $3da_1'/4sa_1' \leftarrow a_2''$ promotions traditionally associated with the $\tilde{D}'$ and $\tilde{D}''$ states should be observed in this region, but more definitive evidence is required before offering such assignments. Additionally, as noted above, it is also possible that more than one ‘feature’ may arise from the overall band contour of a single vibronic transition. Details of the positions and assignments of the various features should thus remain tentative.

The second noteworthy aspect of Figure 4 and Figure S12 is that the feature labeled as the P1 2_0^5 band shows rotational fine structure, as do the corresponding P1 2_0^4 and 2_0^6 bands that can be seen in Figure 4. These bands are discussed in more detail in Section IIID.

In addition to the increasing density of states, a second factor contributing to the complexity of the spectrum at higher wavenumbers is the likely increasing strength of perturbations among the Rydberg series. For example, the $4d/5s$, 2^0 levels lie at a similar energy to the $3de'' \tilde{D}^1E'$, 2^7 level. The very different v_2' values suggest that perturbations between these levels will be small. However, the $5d/6s$, 2^0 levels are near resonant with the $4de'' \tilde{E}^1E'$, 2^4 level, and the $6d/7s$, 2^0 levels have similar energy to the $5de'' \tilde{F}^1E'$, 2^1 level. In the latter case, $\Delta v_2 = 1$ interactions can be expected to produce stronger perturbations, as is borne out in the discussion of auto-

ionization processes in Section IIIE. Nonetheless, even in this higher energy region, the perturbations (at least within the 2_0^m progressions) appear to be relatively weak.

Figure 1 displays similar patterns in the spectrum above $80,000\text{ cm}^{-1}$, albeit with somewhat less regularity. Expanded spectra for this region are shown in Figures S13 and S14 in Section S3 of the SI. It is noteworthy that no members of Rydberg series with $n > \sim 7$ can be convincingly identified in the absorption spectrum, and essentially all of the observed structure appears to correspond to transitions to relatively low- n , high- v_2' Rydberg levels.

D. Rotationally Resolved Bands and Progressions

Close examination of Figure 4 and Figure S13 reveals two 2_0^m progressions that show resolved rotational structure. A subset of members of each progression appears to correlate with members of the unassigned P1 and P2 progressions reported by Wu et al.,¹⁴ but the resolution of the earlier spectra was insufficient to reveal the rotational structure evident in the present data. Note also that in a subsequent study of NH_3 , also without rotational resolution, Saraswathy et al.²⁷ attributed the P1 and P2 progressions to excitations to higher 2^m levels of states arising from, respectively, $4da_1' \leftarrow a_2''$ and $6sa_1' \leftarrow a_2''$ orbital promotions. The present ND_3 data allow further discussion of these bands.

Figure 6a shows an expanded view of the P1 2_0^5 band (previously labeled¹⁴ P1,3) in Figure S12 together with PGOPHER-predicted band contours assuming that the absorption arises from one-photon dipole allowed excitation to electronic states with (Figure 6b) $^1A_2''$ (consistent with the suggested $nsa_1' \leftarrow a_2''$ orbital promotion) or (Figure 6c) $^1E'$

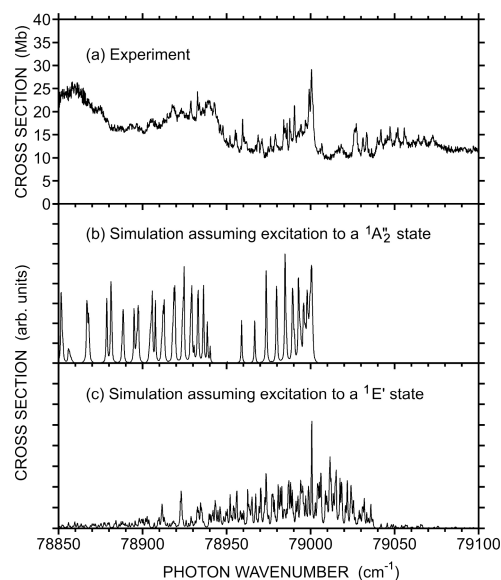


Figure 6. (a) Expanded view of the region around the P1 2_0^5 band in Figure 4, together with predicted contours for this band if it was carried by a (b) $^1A_2'' \leftarrow \tilde{X}^1A_1'$ and (c) $^1E' \leftarrow \tilde{X}^1A_1'$ electronic transition. Both predictions assume excitation to a 2^5 level and a temperature $T = 298\text{ K}$. The simulation shown in (b) therefore starts from the 0^- inversion level in the $\tilde{X}$ state³⁵ and assumes excited state parameters $T_0 = 78,941\text{ cm}^{-1}$, $B' = 4.71\text{ cm}^{-1}$, $C' = 2.75\text{ cm}^{-1}$, and a uniform transition line width, $w_0 = 0.5\text{ cm}^{-1}$. The illustrative simulation shown in (c) assumes the excited state constants reported previously for the $\tilde{B}^1E'$ 2^5 level, along with $T_0 = 79,012\text{ cm}^{-1}$ and $w_0 = 0.5\text{ cm}^{-1}$.

symmetry. Given the high density of electronic states at the energies of present interest (recall Figure S12), perturbations to the rotational fine structure—both in terms of excited rovibrational level term values and relative line intensities—are to be expected, and the contours shown in panels (b) and (c) are intended to be indicative rather than fits. Excited states at these energies may also be subject to heterogeneous (*i.e.*, rotational (Coriolis) induced) predissociation, which would introduce further J', K' level-dependent variations to the intensities and widths of lines predicted in the present simulations.

The predicted band contours are sensitive to the values of the rotational constants selected. Trial parallel band contours were derived by drawing on the B and C rotational constants for the well-documented ν_2' levels of the $\tilde{C}'$ and $\tilde{E}'$ Rydberg states of ND₃.^{15,18,19} This encouraged the assignment to the ${}^1A_2'' \leftarrow \tilde{X} {}^1A_1' 2_0^5$ transition, with a prominent R branch band head at high wavenumbers. Figure 6c shows the contour predicted for an analogous ${}^1E' \leftarrow \tilde{X} {}^1A_1' 2_0^5$ transition, using the published constants for the $\tilde{B} {}^1E'' 2_0^5$ level.¹² Obviously, there is considerable flexibility when it comes to positioning the contour (*i.e.* the assumed band origin), but the parallel band interpretation (Figure 6b) is judged to provide a much better match to the measured contour—both in terms of line density and overall band profile.

Similar comparisons and simulations for the P1, 2_0^m ($m = 4, 6$, and 8) bands (previously labeled P1,2; P1,4; and P1,6) are presented in Section 3 of the SI. Analogy with the progressions observed at lower wavenumber (recall Figures 2–4) suggest that transitions to these 2_0^m levels should all have substantial Franck–Condon factors. Again, the excited state rotational constants chosen in each case mirror those determined for the corresponding ν_2' levels of the $\tilde{C}' {}^1A_1'$ and $\tilde{E}' {}^1A_1'$ Rydberg states of ND₃,^{15,18,19} and the dominant consideration guiding the ‘alignment’ of the predicted versus observed contours was matching the respective Q/P branch envelopes. The match is tolerable in all cases, and the analysis points to the presence of another rotationally structured band centered at slightly higher wavenumber. As seen in Table SIII in the SI, the wavenumber separations between successive vibronic origins deduced in this way mimic those found previously for the corresponding levels of the $\tilde{C}'$ and $\tilde{E}'$ Rydberg states of ND₃,¹⁵ thus providing further support to the proposed numbering of the ν_2' levels.

The wavenumbers of these additional bands in ND₃ are provided in Table SIII in the SI. Note that the wavenumbers reported in that table are for the observed band heads, which in most cases correspond to the strongest feature in the band, whereas the values reported in Table SII are band origins estimated by the simulations. At first sight, the wavenumbers of members within the P1 progression might appear to match reasonably well with the $4p_2'' \tilde{E}' {}^1A_1' \leftarrow \tilde{X} {}^1A_1' 2_0^m$, $m = 4$ – 13 bands identified in the $(2 + 1)$ REMPI studies of Langford et al.¹⁵ This possible attribution required consideration, as the simulated contours of bands within an ${}^1A_2'' \leftarrow \tilde{X} {}^1A_1' 2_0^m$ progression and those in an ${}^1A_1' \leftarrow \tilde{X} {}^1A_1' 2_0^m$ progression (*i.e.*, a vibronically induced progression originating from the upper inversion level in the ground state) would be indistinguishable in the present data. Careful comparison, however, showed that the band energies and rotational constants do not agree sufficiently to make such an assignment. This is not surprising, since transitions to the $4p_2'' \tilde{E}' 2_0^m$ levels can be expected to mirror those to the analogous $3p_2'' \tilde{C}' 2_0^m$ levels, which, as

noted above, have no intensity in the one-photon absorption spectrum.

There are rather few other potential sources of singly degenerate excited states (*i.e.*, states with ${}^1A_1'$ or ${}^1A_2''$ symmetry) in this energy region. First, $2_0^m 3^1$ and $2_0^m 3^1 4^1$ combination levels of excited states with ${}^1E''$ electronic symmetry include levels with ${}^1A_1'$ vibronic symmetry. However, as observed in the $\tilde{B} \leftarrow \tilde{X}$ band system, the Herzberg–Teller interactions⁷ that promote transitions to such combination levels are expected to be quite small, and it would be unusual for any such combination levels to be much more resistant to predissociation, *i.e.*, to show rotational fine structure, when transitions to the Franck–Condon-allowed 2_0^m levels do not. This leaves only the $(n+1)s/nda_1' \leftarrow a_2''$ Rydberg excitations that, for $n = 3$, have been assigned to the $\tilde{D}'$ and $\tilde{D}''$ states. As discussed above, the $(n+1)s$ and nda_1' Rydberg states are likely to be mixed,³⁷ and we will henceforth refer to these as excitations to $(n+1)sa_1'/nda_1'$ states.

Using the ν_2' numbering deduced from the analysis of rotational structure, we can calculate the effective principal quantum number, n^* , by using the Rydberg formula and the corresponding vibrational threshold of the ND₃ $\tilde{X} {}^2A_2''$ state. Here, we use the adiabatic ionization threshold of Duggan et al.,¹⁶ and the vibrational intervals between higher $\tilde{X} {}^2A_2''$, ν_2^+ levels from Loch et al.²⁶ The latter intervals are reported to a precision of $\pm 8 \text{ cm}^{-1}$, with a larger absolute uncertainty (80 cm^{-1}), but a recent determination of the $\tilde{X} {}^2A_2''$, $\nu_2^+ = 5$ threshold by Kuijpers et al.⁴⁰ differs by only 13 cm^{-1} from the value determined from refs 16 and 26, suggesting a significantly smaller uncertainty for the thresholds in Table SIII. This calculation yields n^* values of ~ 4.0 for the P1 progression, in line with the expectations for a $5s/4d$ Rydberg state. Further, varying the ν_2 vibrational quantum number by ± 1 results in a much less consistent sequence of n^* values, thus providing additional support for the present vibrational numbering and level assignments. Note that the members of the P1 progression reported for NH₃¹⁴ lie at significantly higher wavenumbers than those in the reported P1 progression in ND₃, suggesting that the former are likely associated with transitions to a state with higher principal quantum number.

A series of bands in the P2 progression of ND₃ are shown in Figure S18, where the present proposed vibrational numbering is used. The structure within these bands shows some similarities with that of the P1 progression, favoring their assignment to a ν_2' vibrational progression in the $6s/5da_1'$ Rydberg state. The wavenumbers of the P2 bands identified in the present work are also provided in Table SIII. Again, the values correspond to the position of the observed band head, which generally corresponds to the strongest feature in the band. With the given choice of vibrational numbering, the n^* values for the P2 bands are all ~ 5.0 , as expected for $6s/5d$ Rydberg states. This analysis suggests that, for ND₃, the previously proposed P1 and P2 progressions correspond to $5s/4da_1' {}^1A_2'' \leftarrow \tilde{X} {}^1A_1' 2_0^m$ and $6s/5da_1' {}^1A_2'' \leftarrow \tilde{X} {}^1A_1' 2_0^m$ transitions, respectively. These states have been included in Table 1. We note that this assignment is close to that of Saraswathy et al.,²⁷ who assigned the progressions to the $4da_1'$ and $6sa_1'$ upper states, respectively.

The proposed interpretation implies that, while the $3s \tilde{A} {}^1A_2''$ excited state of ammonia is highly predissociative, higher excited states with significant s character are, relatively, much longer lived (as evidenced by the observed rotational fine structure). Such a conclusion parallels that seen for other

prototypical hydrides, e.g., H_2O ^{41,42} and H_2S .⁴³ In both of these cases, the first $n\text{s}a_1 \leftarrow \text{HOMO}$ absorption (with $n = 3$ and 4, respectively) is a broad continuum feature—reflecting population of a very short-lived, mixed Rydberg/valence state with substantial antibonding character. However, the absorptions attributed to higher $n\text{s}a_1 \leftarrow \text{HOMO}$ transitions in H_2O and H_2S are dominated by the respective origin bands (reflecting the very similar equilibrium geometries of the neutral molecule and the ground state ion in each case), which show sufficient rotational fine structure to allow determination of the excited state symmetry.

E. Autoionization and Predissociation

As shown in Figure S19 in the SI, and as in NH_3 , the ionization yield for ND_3 grows slowly at energies above the adiabatic ionization threshold ($82,261.7(15) \text{ cm}^{-1}$, ref 16), and dissociation remains the major decay channel up to $\sim 88,000 \text{ cm}^{-1}$. Above this energy, the ionization and dissociation yields are approximately equal up to $\sim 93,000 \text{ cm}^{-1}$ (the highest wavenumbers investigated in the present work). The competition between ionization and dissociation is similar to that in NH_3 and is discussed in more detail in Section S4 of the SI.

IV. CONCLUSIONS

New high-resolution absolute photoabsorption cross sections for a room-temperature ND_3 sample between $59,000$ and $93,000 \text{ cm}^{-1}$ have been obtained using the Fourier transform spectrometer at the Synchrotron SOLEIL. These new measurements complement an earlier photoabsorption study of NH_3 under similar conditions.⁶ The spectral resolution of the present ND_3 data is a factor of 10 – 100 higher than any broadband spectral data previously reported for this molecule. This enhanced resolution results in higher peak cross sections of some sharp resonances, but the integrated oscillator strengths over individual vibronic bands and over selected broader wavenumber ranges are generally in good agreement with previous results.¹⁴ The new data allow some extension of the $\tilde{B}^1\text{E}'' \leftarrow \tilde{X}^1\text{A}_1'$ band system, particularly some of the weaker Herzberg–Teller induced combination band features, and provide new insights and some reassignments of higher energy features, particularly those associated with various $(n+1)s/nd$ Rydberg complexes. The higher resolution of the present study also reveals previously unobserved rotational structure in a number of higher energy bands. With this additional information, the unassigned P1 and P2 progressions observed by Wu et al.¹⁴ have been assigned to components of the mixed $5\text{s}a_1'/4\text{d}a_1'$ and $6\text{s}a_1'/5\text{d}a_1'$ Rydberg states.

Another noteworthy aspect of the present study is the seeming lack of strong perturbations among the Rydberg series converging to each v_2^+ level of the cation. Although the long v_2' progression associated with excitation to any one Rydberg state of the neutral generally overlaps with the equivalent progressions for many other Rydberg states (and other principal quantum numbers), vibronic interactions appear to be rather weak. Thus, even in regions where multiple progressions overlap, the observed structure remains quite regular. A second factor contributing to the relative simplicity of the spectrum is that the first excited electronic state of the ammonia cation lies $\sim 40,000 \text{ cm}^{-1}$ above the ground-state cation, so there are no interloping Rydberg series converging to the excited state cation in the region of present interest. These simplifying factors, as well as the success of a recent

measurement and analysis of the ND_3 spectrum based on multichannel quantum defect theory,^{40,44} and the obvious prospects for more double-resonance excitation studies, all provide hope that a yet more comprehensive analysis of the electronic spectrum of ammonia and its isotopologues is within reach.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.6c03163>.

Additional experimental data and spectra accompanied by spectral simulations. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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