Self-broadening and self-shift in the $3\nu_2$ band of ammonia from mid-infrared-frequency-comb spectroscopy

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We report the broadband absorption spectrum of the $3\nu_2$ band of $^{14}$NH$_3$ near 4 μm. The data were recorded using a mid-infrared frequency comb coupled to a homebuilt Fourier-transform spectrometer with a resolution of 0.00501 cm$^{-1}$. Line positions, line intensities, self-broadening, and self-shift parameters for six rovibrational lines were determined at room temperature ($T = 296$ K). Comparison with HITRAN 2016 shows good agreement at improved precision. The high precision and the rapid tunability of our experiment enables advanced fast spectroscopy of molecular gases.

I. INTRODUCTION

Ammonia is one of the spectroscopically most-studied molecules due to its importance in the atmosphere, astrophysics, chemistry, medicine and biology. Ammonia exists in a wide range of astrophysical environments and was the first polyatomic molecule detected in the interstellar medium. It was used as one of the most accurate “molecular thermometers” to measure the temperature of C/2001 Q4(Neat) and other comets by detecting the ortho-para ratio. Ammonia also formed the basis for modern laser technology through the original demonstration of the MASER. Ammonia spectra have been extensively studied and disentangled, both in theory and experiment.

The spectra of ammonia were extensively measured from the microwave to the ultraviolet. Yurchenko et al. calculated the spectra for ammonia covering a large part of the infrared region using a variational approach. Recently, we calculated hyperfine-resolved rotation-vibration line lists of ammonia, which agree very well with experimental results. The rotation-vibration-spectroscopy data were all critically re-

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II. EXPERIMENT

A schematic diagram of the experimental setup is shown in Fig. 1. It consists of three parts: the DFG-based MIR...
FC source, the gas cell, and the FTS. The MIR FC source consists of a Yb:fiber FC and a DFG setup. The Yb:fiber FC is mode-locked by a saturable absorber with the repetition rate of 150 MHz and phase-locked to a cw laser (Coherent Mephisto) with kHz-level linewidth at ~1064 nm and frequency stability to 1 MHz/minute. Using chirped-pulse amplification, 1.5 W average power is delivered in pulses of 130 fs duration with a center wavelength of 1050 nm and a bandwidth of 25 nm. The Yb:fiber FC is split into pump and signal driver of the DFG process, with the signal generated as the longest Raman soliton from the supercontinuum process in a highly-nonlinear suspended-core fiber. By controlling the input power, we could adjust the wavelength of the longest Raman soliton from 1.2 µm to 1.6 µm. The signal and pump pulse are temporally overlapped in a fan-out periodically poled Lithium Niobate (PPLN) crystal (HCPhotonics) for DFG by locking a mechanical delay-line in the pump arm. This yielded MIR radiation ranging from 3 µm to 6 µm. The MIR FC was tuned to near 4 µm (2390 cm⁻¹ to 2510 cm⁻¹), and the light passed through the gas cell together with a frequency stabilized (1 MHz/minute) HeNe laser (SIOS SL4), which was used to calibrate the absolute frequency of the spectroscopic signals.

Ammonia (¹⁴NH₃, Linde HiQ 6.0) was contained in a 35.4646(12) mm long gas cell with wedged CaF₂ windows (30 arcmin) at 296 K. The optical path length was determined using low-coherence interferometry utilizing the residual 1050 nm laser light from the DFG process as the input signal. The optical path difference (OPD) of the four reflected beams from the two gas cell windows are detected by interfering the reflections with a reference laser. Before the measurements, the reservoir was pumped (HiCube 80 Eco) to <3.1 × 10⁻⁴ mbar, filled to 699.75 mbar of ammonia, and then pumped to 543.85 mbar, 500.01 mbar, 400.50 mbar, 300.70 mbar, 199.90 mbar, 98.90 mbar, 50.00 mbar, and 10.00 mbar, respectively. All pressures were measured using calibrated ceramic capacitance gauges (Pfeiffer Vacuum CMR 361 and CMR 364) with a relative accuracy of 0.2%.

The two laser were both directed to our homebuilt FTS, which is based on a Michelson interferometer with two liquid-nitrogen-cooled indium antimonide (InSb) detector (InfraRed Associates IRA 20-00060). The interferograms of both MIR FC and HeNe laser were acquired at 5 MSa/s sampling rate with 20 bit resolution by a computer-controlled data acquisition board (National Instruments PCI-5922). The interferogram of the HeNe laser was used to measure the OPD and provides steps to resample the MIR FC interferogram by determining the positions of the zero-crossings. By matching the delay range of the FTS to the repetition rate of the MIR FC, we overcame the resolution limitation of conventional FTS given by the maximum delay range and removed the instrumental line shape oscillations, which allowed a reduction of the instrument size and acquisition time. The grid spacing was equal to the comb spacing of 150 MHz, yielding a resolution of the FTS of 0.00501 cm⁻¹. After performing a fast Fourier transform (FFT) to MIR FC interferograms, we obtained MIR absorption spectra of ammonia at the different specified pressures. To extract the transmittance, we first measured the reference spectra before filling ammonia when the reservoir was under vacuum.

The top panel of Fig. 2 a shows the raw spectrum in the range 2434 to 2459 cm⁻¹ at 98.90 mbar and at 296 K. The recorded spectra had oscillatory background signals that not only decreased the SNR.
of the spectra, but also changed the center and linewidth of the absorption line profiles. We assigned this regular signal to etalon effects of the optical components in the experimental setup. In order to remove this etalon signal, we used a numerical approach based on FFT analysis. Firstly, we calculated the power spectral density (PSD) for different FFT sample frequencies of the spectra, shown in [Fig. 2 b]. The unit of sample frequencies was in cm, which exactly corresponded to the OPD of the FTS. Then we set the FFT values for the four sample frequencies between 4.10 cm and 4.18 cm to be zero, and performed an inverse FFT, resulting in the filtered spectrum shown in [Fig. 2 a]. Analyzing the sample frequencies of the filtered signal, [Fig. 2 a, bottom panel] we suppose that the etalon signal most likely comes from an Germanium (Ge) filter in the experimental setup; the length and refractive index of the Ge filter at 4 µm are around 5 mm and 4, resulting in a 4 cm OPD that matches the free spectral range of these oscillations. The FFT filtering might have introduced some small errors as the filtered frequencies also included real spectral information. Nevertheless, these errors should be smaller than profile fitting error and the approach clearly improved the precision and SNR. In the future, the Ge filter shall be replaced by wedged optics.

III. RESULTS AND DISCUSSION

Direct multipeak Voigt fit for the transmittance data was performed to retrieve spectral information. Voigt profile was still valid because the transmittance was more than 90% for all transitions due to the low sensitivity with the short gas cell and the pressures of gas sample were relatively high.\(^{37}\) The four basic spectroscopic line parameters – the pressure-broadening \(\gamma_{p,t}\), the Doppler-broadening \(\alpha_D\), line transition frequency \(\nu_{ij}\), and the spectral line intensity \(I_{ij}\) – were determined from individual spectra to extract details on the molecular motions and collisions through a non-linear least-squares fit. Since \(\alpha_D\) depends on \(\nu_{ij}\) and temperature, which was 296 K here, we could reduce the Voigt fit to the three other parameters, as shown in Equation 1.

\[
T(\nu) = e^{I_{ij}(T)/I_{path} V(\nu - \nu_{ij}; \gamma_{p,t})} + a_0 \tag{1}
\]

Here, \(N\) is the number density of ammonia, equals to \(p/\kappa_b T\) assuming the ideal gas law, and \(I_{path}\) is the optical path length (35.4646 mm in our experiment). In addition, small instrumental baseline \(a_0\) was added in the fit. We assumed \(a_0\) to be a constant value around 0 since the low sensitivity, more general baseline fitting process could be found from Ref. 37.

For the fit we chose six typical peaks with high absorption, corresponding to the \(aR(2, K)\) and \(aR(3, K)\) multiplets in the 3ν\(_2\) band. In order to show the performance of the fit, we show the \(aR(2, K)\) multiplet in Fig. 3, which fit very well. The small dip at the low-wavenumber end of the residual difference corresponds to a \(sP(6, 1)\) transition in \(\nu_2 + \nu_4\) band. From the fit, we obtained the line-transition frequencies \(\nu_{ij}\), line intensities \(I_{ij}\), and the pressure-broadening component \(\gamma_{p,t}\) specifically the self-broadening component \(\gamma_{self}\) since the gas cell only contained pure \(^14\)NH\(_3\).

We recorded and averaged 25 spectra at each of the nine different pressures ranging from 10.00 mbar to 700.00 mbar. It took around 1 minute for recording the spectra and pressures stayed the same during the 25 measurements. Fig. 3 shows the performance of the global multipeak Voigt fit and the extraction of self-broadening and self-shift coefficients for the \(aR(2,0)\) transition. For each pressure, \(\nu_{ij}\), \(I_{ij}\) and \(\gamma_{self}\) were determined as described above. The mean value of \(I_{ij}\) and \(\gamma_{self}\) was extracted. From a linear regression of the line transition wavenumbers \(\nu_{ij}\) as a function of pressure, see Fig. 4, the vacuum transition wavenumber \(\nu_0^{ij}\) was determined as the y intercept and its self-shift parameter \(\gamma_{self}\) as the slope \(k\).

Line wavenumbers \(\nu_0^{ij}\), line intensities \(I_{ij}\), self-broadening \(\gamma_{self}\), and self-shift \(\delta_{self}\) components of the \(aR(2, K)\) and \(aR(3, K)\) multiplet in the 3ν\(_2\) band of \(^14\)NH\(_3\) are presented in Table 1. Specified uncertainties for line wavenumbers and self-shifts are their standard deviations from the fit, the uncertainties for line intensities and self-broadenings were the combination of statistical errors from the averaging of multiple scans and the standard deviations from the fit. Other systematic errors such as misalignments of the HeNe laser and MIR FC, the line mixing, the FFT filter etc. were neglected because they were relatively small in relation to the errors from the fit. Line-transition wavenumbers and intensities show good agreement with the HITRAN database values.\(^{37}\) Our
TABLE I. Line transitions, line intensities, self-broadening, and self-shift coefficients for the 3ν2 band of 14NH3 at 296 K.

| Transition (R branch) | ν\text{ij, exp.} | ν\text{ij, ref.} | I\text{ij, exp.} | I\text{ij, ref.} | γselfexp | γselfref | δself |
|----------------------|-----------------|-----------------|-----------------|-----------------|----------|----------|--------|
|                      | (ν\text{cm}^{-1}) | (ν\text{cm}^{-1}) | (cm/molec.) | (cm/molec.) | (cm\text{-1}/atm) | (cm\text{-1}/atm) | (cm\text{-1}/atm) |
| aR(2, 0)             | 2437.76258(18)  | 2437.7655       | 5.12(19) × 10^{-22} | 4.590 × 10^{-22} | 0.225(13) | 0.302 | 0.0016(5) |
| aR(2, 1)             | 2438.14454(106) | 2438.1475       | 2.35(21) × 10^{-22} | 2.078 × 10^{-22} | 0.320(33) | 0.396 | -0.0112(28) |
| aR(2, 2)             | 2439.31026(421) | 2439.3148       | 1.70(20) × 10^{-22} | 1.372 × 10^{-22} | 0.445(63) | 0.496 | -0.0139(110) |
| aR(3, 1)             | 2454.62688(68)  | 2454.6298       | 2.26(16) × 10^{-22} | 2.323 × 10^{-22} | 0.263(31) | 0.36 | -0.0073(18) |
| aR(3, 2)             | 2455.73934(231) | 2455.7392       | 1.93(15) × 10^{-22} | 1.963 × 10^{-22} | 0.397(43) | 0.448 | 0.0006(62) |
| aR(3, 3)             | 2457.66941(317) | 2457.6615       | 2.27(21) × 10^{-22} | 2.508 × 10^{-22} | 0.464(62) | 0.541 | -0.0351(83) |

* Data from the HITRAN 2016 database [10, 21, 36], the uncertainty range for ν0, Iij and γself are 0.0001 cm\text{-1} to 0.001 cm\text{-1}, 10% to 20%, and 2% to 5%, respectively.

IV. CONCLUSIONS

We recorded the broadband absorption spectra of the 3ν2 band of ammonia (14NH3) near 4 μm using a MIR-FC-based FTS system. Spectra were background corrected by FFT-filtering raw spectra for experimental etalon. A global multipake Voigt fit allowed us to determine transition wavenumbers and intensities, pressure self-broadening and self-shift parameters at room temperature (T = 296 K) for 6 prototypical R branch rovibrational transitions.

The recorded line wavenumbers and line intensities are in good agreement with the HITRAN database. As no literature values were available for the self-broadening and self-shift parameters, our new experimental data on these parameters provide useful information about the molecular motions and collisions, which could help to improve their theoretical modeling.

Our experimental system is capable of trace-gas detection of different molecular species in the spectral range of 3...6 μm with a current resolution of 0.00501 cm\text{-1}. We plan to implement a liquid-nitrogen-cooled multi-pass-cell cryostat to increase the sensitivity.

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FIG. 4. Extraction of the self-broadening and self-shift parameters from the lineshape of the aR(2, 0) transition at various pressures, i.e., from top to bottom 10.00 mbar, 50.00 mbar, 98.90 mbar, 199.90 mbar, 300.70 mbar, 400.50 mbar, 500.01 mbar, 543.85 mbar, and 699.75 mbar, respectively. The black curves show the fitted Voigt profiles. For clarity, all lines are successively offset by -0.01 from top to bottom. The bottom panel shows the relative line transition wavenumbers (red squares) with respect to the vacuum line transition. Error bars depict the standard deviation from the multipake Voigt fit. The black line is a linear fit of these transition frequencies from which the vacuum transition wavenumber and the self-shift are derived.

retrieved self-broadening parameters were around 20% smaller than in the HITRAN database, which were derived from measurements at 10 μm. Our results provide new laboratory data allowing to improve pressure-self-broadening models.
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