

Infrared Spectroscopy and Interferometry as Methods for Structural Determination of Ammonia

Purpose

This paper details how the usage of a novel new technique, interferometer-coupled Fourier-transform infrared spectroscopy, can be used to resolve previously imperceptible transitions which can be used for the accurate structural characterization of ammonia. The N-H bond length, H-N-H bond angle, and constant-volume vibrational heat capacity along with its temperature dependence are derived using the finely-resolved rotational transitions previously hidden within a vibrational mode. This method provides a wealth of future possibilities for future determination of the structural and physical properties of molecules.

Special Considerations

No special considerations are requested to ensure a fair review process.

Reviewing Colleagues

This paper has been reviewed by colleagues Raymond Yu and David Gygi. The author would also like to give thanks to David Hasselhoff.

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Statement of Authenticity

We hereby verify that none of the material detailed in this article has been published or is under consideration elsewhere, including the Internet.

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Thank you for your time and consideration.

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The structural properties of a compound are often crucial to understanding the physical and chemical interactions of a molecule with its environment. Complete characterization of the conformation of a given molecule, however, often necessitates careful excitation and measurement of its normal modes. The developing field of infrared spectroscopy may be the key to unlocking the conformational properties of a wide variety of molecules. Spectra of ammonia have been gathered, through the use of a high-resolution Fourier-Transform infrared spectrometer with Michelson interferometer, from which previously imperceptible rotational transitions can be resolved inside vibrational modes. Structural characteristics of the molecule, such as bond length and angle, as well as physical properties such as constant-volume vibrational heat capacity, can be derived from the calculable rotational transition energy. This high-resolution technique offers a new approach with unprecedented accuracy and precision for investigators to determine the microscopic physical characteristics that govern macroscopic chemical interactions.

Human inquiry into the nature and interactions of ammonia dates back into antiquity, though the so-called “alkaline air” was only first isolated by J. Priestley in 1774 (1). However, it was not until the development of the Haber-Bosch process in 1913 that an abundance of commercial uses for ammonia unfolded (2). Since then, ammonia has been used as a nitrogenous fertilizer on a truly global scale, providing food for some 40% of the world population and, by several reckonings, supporting a human population that would be untenable by purely natural, agrarian means (3–5). Besides agriculture, ammonia is also used as a precursor to many nitrogenous compounds, as a common coordinating ligand, a refrigerant, a household cleaning agent, and more (1–4, 6, 7). It is a complete surprise, then, that the structural properties of this ubiquitous compound were, until recently, relatively unknown. Though infrared spectroscopy has proved historically useful in the “fingerprinting” of distinctive moieties, previous attempts at analysis of the infrared spectra of ammonia were stymied by insufficient resolution of peaks where the normal vibrational modes would be found (8). However, through the usage of new Michelson interferometer instruments and utilizing a Fourier Transform Infrared (FTIR) spectrometer, a high-resolution spectrum of ammonia has been produced, from which various structural and chemical properties can be elucidated.

In order to capture the infrared spectrum of ammonia in the gas phase, a gas cell like that shown in Fig. 1 was used. The Pyrex-glass cell was sandwiched between two KBr plates that were held together by metal panels connected by elongated screws. The panels contained glass apertures to allow light to pass through the cell, which could be filled or evacuated of gas using

a Schlenk adapter. By this method, the cell was evacuated to a pressure of 5 mmHg before being filled with 50 mmHg of sample. To ensure the accuracy of the instrument, CO₂ and SO₂ spectra were first taken for calibration purposes and verified with past results (10, 11). Next, the ammonia was dosed in and analyzed in the region from 4000-400cm⁻¹ with a 2 cm⁻¹ resolution for 32 cycles.

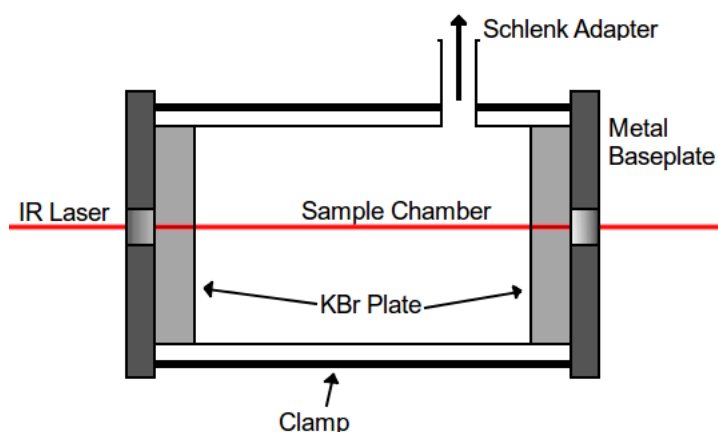


Fig. 1: Diagram of the glass cell used to contain sample for measurement. The cell is sandwiched by KBr plates clamped into place by two metal panels held together by screws.

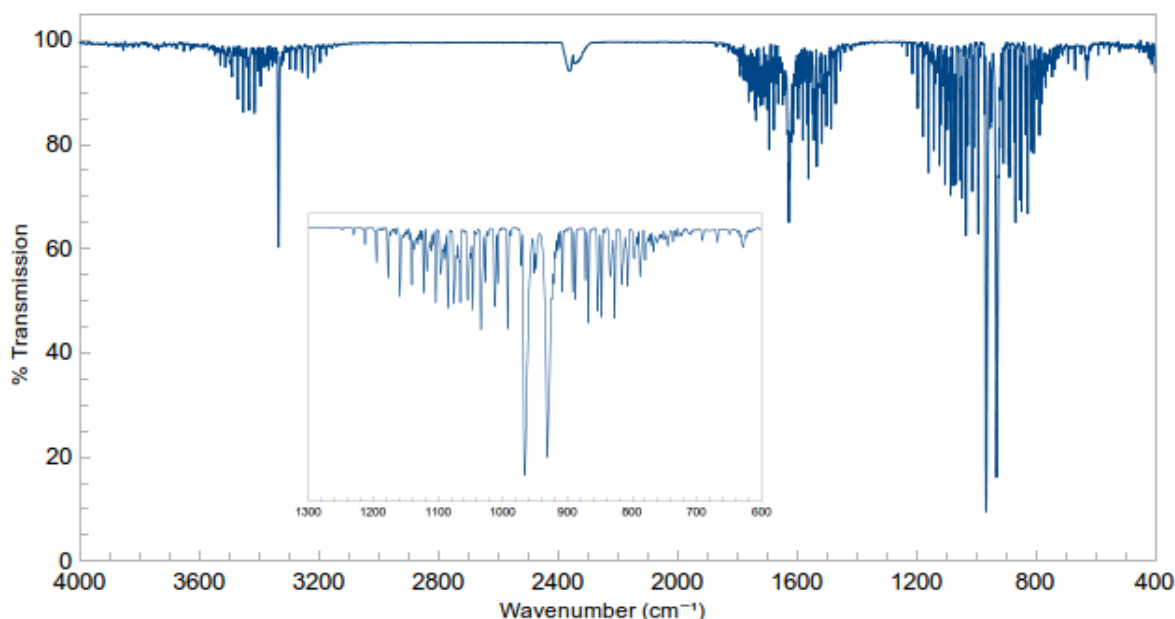


Fig. 2: Complete FTIR spectrum of ammonia.

Inset: Magnified portion of the spectrum around 950 cm⁻¹, showing detail of the P, Q, and R branch transitions.

Fig. 2 shows the IR spectrum of ammonia collected by the preceding methods. The coarse structure of the spectrum corroborates with theoretical and previous experimental work; observed modes are present at 1139 cm⁻¹, 1757 cm⁻¹, 3464 cm⁻¹, and 3525 cm⁻¹, which are in line with previous findings. More salient is the increased resolution in the range 600 cm⁻¹-1300 cm⁻¹ (Fig. 2, inset), which are resolved to a degree not possible in preceding works. Finer resolution

of this range allows us to identify the twin peaks of greatest magnitude centered about 950 cm^{-1} , which correspond to the Q-branch of the lowest-energy vibrational mode. A peculiarity of the “puckered” trigonal pyramidal structure of ammonia is that it allows for the inversion of vibrational modes by everting the hydrogens about the nitrogen, like an umbrella turning inside-out in a strong wind. The two seemingly overlaid peaks exist due to the availability of this inversion to the vibrational mode, frameshifted from each other by a distance equal to the activation energy for such an inversion. More importantly, the spacing of the supporting P and R transitions that flank the Q-peaks (roughly 20 cm^{-1}) allows us to calculate an average value for the energy spacing of the rotational states, $B = 10.32(2)\text{ cm}^{-1}$. Plugging this value into Equation 1, the moment of inertia about the rotational axis perpendicular to the principal C_{3v} rotational axis (henceforth I_b) can be determined:

$$I_b = \frac{h}{8cB\pi^2} \quad (1)$$

This value can then be used to calculate the N-H bond distance using an experimentally determined value of $4.437 \times 10^{-39}\text{ kg}\cdot\text{m}^2$ for the moment of inertia about the principal C_{3v} rotational axis (henceforth I_c) in Equation 2.

$$r_{N-H} = \sqrt{\frac{I_c \left(1 - \frac{3m_H}{m_N}\right) + 2I_b \left(1 + \frac{3m_H}{m_N}\right)}{6m_H}} \quad (2)$$

This value can be used to find the angle between the N-H bonds and the principal C_{3v} axis of rotation of the trigonal pyramid (β), using Equation 3:

$$\beta = \arcsin \left(\sqrt{\frac{I_c}{3m_H r_{N-H}^2}} \right) \quad (3)$$

At last, the calculated constants, with the aid of some “simple” trigonometry, provide us with enough information to solve for the structural specifications of the NH_3 trigonal pyramid, as seen in Fig. 3.

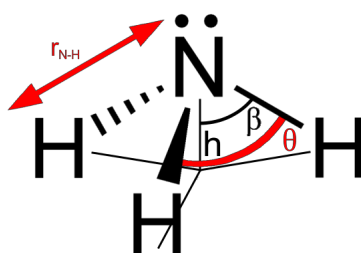


Fig. 3: Structural diagram of the geometric quantities evaluated in this study.

The importance of these results (compiled in Table 1) cannot be overstated. Merely the fact that these values were calculable from a single high-resolution IR spectra is astounding, to say nothing of the fact that these values corroborate Valence-Shell Electron-Pair Repulsion (VSEPR) predictions for ammonia bond angle, down to the squeezing of the hydrogen atoms beyond the tetrahedral 109.5° due to the oversized lone-pair lobe. These results show incredible promise for structural characterization of arbitrary single-center molecules using only a high-resolution FTIR, a process that is accurate, rapid, and largely amenable to automation.

Impressively enough, there are still more physical properties that can be derived from these derived values. The equipartition theorem states that energy is distributed equally among all

Property	Units	Value
B_{avg}	cm^{-1}	10.32(2)
I_b	$\text{kg}\cdot\text{m}^2$	$2.710(6)\times 10^{-47}$
$r_{\text{N-H}}$	\AA	1.001(5)
β	$^\circ$	69.8(1)
h	\AA	0.345(2)
θ	$^\circ$	108.7(2)

Table 1: Structural values of the NH_3 trigonal pyramid and their calculated values.

degrees of freedom of a system; each mode should contribute $k_B T$ to the total energy of the system, and $k_B N_A = R$ (the ideal gas constant) to the heat capacity. Because ammonia is a nonlinear molecule consisting of four atoms ($N = 4$), it should have $3N - 6 = 6$ vibrational degrees of freedom, and thus the heat capacity should approach $6R$ as temperature approaches infinity, causing higher-energy vibrational energy states to become more equally occupied. Because we have access to the IR spectrum of ammonia, we can look directly at the wavenumbers of the vibrational modes and solve for the constant-volume vibrational heat capacity $C_{v,vib}$, using Equation 4, to see that it approaches the theoretical value:

$$C_{v,vib} = R \sum_{DoF} \frac{(\beta h \nu)^2 e^{-\beta h \nu}}{(1 - e^{-\beta h \nu})^2} \quad (4)$$

As shown in Fig. 4, the vibrational volumetric heat capacity does indeed asymptotically approach its idealized value of $6R$ as the temperature increases. This demonstration clearly showcases both the impressive breadth and depth of information belied by the simple form of the high-resolution FTIR. This technique will certainly be a powerful tool for elucidating chemical structures and vibrations for many years to come.

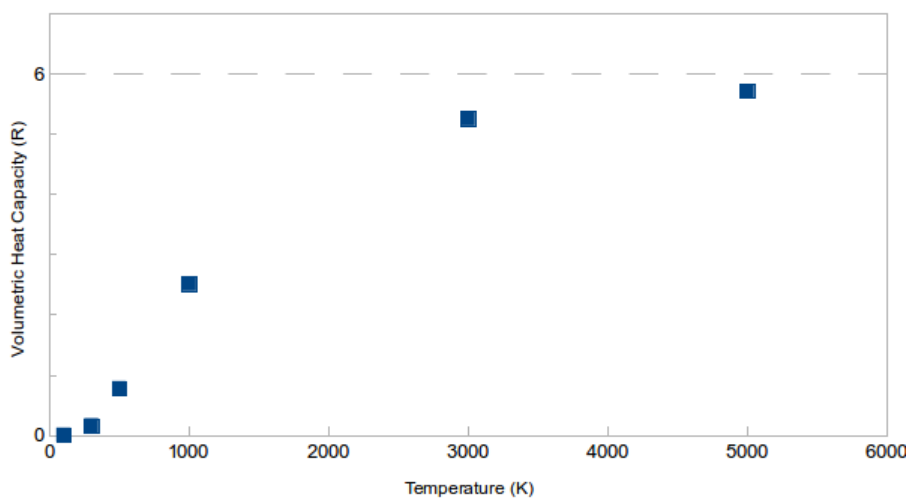


Fig. 4: Constant-volume vibrational heat capacity of ammonia as a function of temperature. The dashed line at $6R$ represents the theoretical limit of the heat capacity as predicted by the equipartition theorem, as well as the apparent experimental horizontal asymptote of the data.

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