

Inversion Doubling of Ammonia

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Key Words

Ammonia, FT-IR, Gas Analysis, Infrared, Quantum

Introduction

Ammonia is a trigonal pyramid, with three identical N-H bonds. However, the gas phase spectrum displays two peaks where one is expected. The physical origin and theoretical description of this doubling is presented, followed by a description of the experimental measurement. The inversion doubling of about 35 cm^{-1} represents an excellent coupling of a simple infrared measurement with a quantum mechanical description involving many aspects of the wave nature of vibrations.

Theory

The energy of a molecule is determined by the translational, rotational, and vibrational components. The contributions to the infrared spectrum arise from the latter two, whose energy is given by (ignoring second order effects such as anharmonicity)

$$E_{\text{vib-rot}} = hv(v + \frac{1}{2}) + J(J + 1)\hbar^2/(2I)$$

Here, h is Planck's constant, $\hbar = h/(2\pi)$, I is the moment of inertia about the axis of rotation and the values J and v are the rotational and vibrational quantum numbers, respectively. In liquids, the rotation is hindered sufficiently that only the vibrational component is seen, resulting in single peaks for each vibration under normal circumstances.

In gases, however, the molecule can freely rotate, so changes in J can be reflected in spectral features. The spacing between rotational levels is very small – on the order of $1\text{--}10\text{ cm}^{-1}$ – so many rotational transitions can be seen. Further, as the energy differences are small, the Boltzmann distribution indicates that there is significant population of higher rotational states ($J > 0$). Thus, transitions which may be allowed include $J \rightarrow J - 1$, $J \rightarrow J$, and $J \rightarrow J + 1$ ($\Delta J = -1, 0, +1$). The resulting series of peaks are designated as P, Q and R bands, respectively.



The separation between peaks in the P and R branches is determined by the value of I , where $I = \mu r^2$, r being the bond length and μ being the reduced mass. As the mass of the rotor increases, the energy level spacing decreases, and the P and R branches become closely packed, as in CO (carbon monoxide). Small reduced masses give the expansive P and R branches seen in HCl.

The Q branch is typically a singlet, as the rotational contribution effectively is zero when there is no change in J . The parallel bands of symmetric-top (including linear, like HCl) molecules show no Q branch at all. For instance, the vibration-rotation of carbon monoxide shows no Q branch (the dipole change is parallel to the symmetry axis), and its high moment of inertia results in a tightly spaced P and R structure. In contrast, the bending of carbon dioxide at 667 cm^{-1} changes the dipole perpendicularly to the symmetry axis, and shows a Q-branch and tight P and R branches.

In seeming conflict with this description, it was observed that trigonal pyramidal molecules like ammonia showed *two Q branches*. There is only one type of N-H bond (the C_{3v} symmetry exchanges all three bonds), so the origin of the doublet arises from some other source. The source is inversion of the molecule; the phenomenon is called *inversion doubling*.

Imagine the three hydrogens of ammonia being labeled uniquely a-b-c, with the hydrogens all pointing down and the nitrogen up. If the molecule is compressed to a planar configuration and then through to the inverted form (hydrogens up), the two conformations will not be superimposable – the a-b-c labels are swapped on two hydrogens (build a model using different colored balls for the hydrogens to prove this). The barrier for this rotation is not excessive, so the molecule can tunnel through the planar state and flip between the two conformations.

The harmonic oscillator potential wells for the “down” and “up” conformations are shown on the left side of Figure 1. The vibrational levels are shown evenly spaced (harmonic, which for the lowest levels is a satisfactory approximation here). This part of Figure 1 assumes the barrier to inversion is infinite, so the two wells are independent.

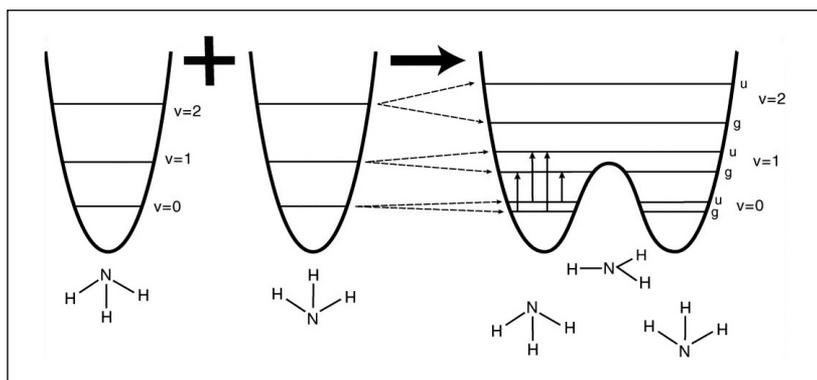


Figure 1

When the inversion barrier is lowered, the energy levels do not remain independent – they combine through linear combinations. The right side of Figure 1 shows this mixing. This is analogous to the quantum description of bond formation, where the interaction between two wavefunctions produces energy levels formed from linear combinations of the pure wavefunctions (hybridization is another example). In ammonia, each of the original levels is the same (the two configurations are degenerate), so the mixing results in two new wavefunctions, $\Psi_g = \Psi_1 + \Psi_2$ and $\Psi_u = \Psi_1 - \Psi_2$ symmetrically distributed about their original (unmixed) energies. The subscripts g and u stand for *gerade* and *ungerade*, or even and odd, respectively, referring to their spatial symmetry. As examples of this, the sine function is even, so that an integral over all space is not zero, while cosine is odd giving an integral over all space of zero. This can be seen from a plot of sine and cosine.

There are four transitions possible with $\Delta v = +1$ (for state $0 \rightarrow 1$) in the infrared (note we are discussing the Q branch, so $\Delta J = 0$). These are $0g \rightarrow 1g$, $0g \rightarrow 1u$, $0u \rightarrow 1g$ and $0u \rightarrow 1u$, as shown in Figure 1. However, the full integral for the vibrational transition involves the dipole moment operator μ , which is an odd function itself for ammonia. Thus, the four normalized transition moment integrals are

$$c(gg) = \int \Psi_g^* \mu \Psi_g d\tau$$

$$c(gu) = \int \Psi_g^* \mu \Psi_u d\tau$$

$$c(ug) = \int \Psi_u^* \mu \Psi_g d\tau$$

$$c(uu) = \int \Psi_u^* \mu \Psi_u d\tau$$

and

The integrals run over all space (the x, y, and z coordinates), and the asterisk indicates the complex conjugate, making the overall integral real.

As in multiplication, the result of multiplying these functions can be simply stated as (even * even) = even, (odd * odd) = even, (odd * even) = odd and (even * odd) = odd. Applying these rules, the integrals simplify to (recall they are normalized, the integral over all space of an odd function is zero and apply the rules left to right):

$$c(gg) = \int (\text{even})(\text{odd})(\text{even}) d\tau = 0$$

$$c(gu) = \int (\text{even})(\text{odd})(\text{odd}) d\tau = 1$$

$$c(ug) = \int (\text{odd})(\text{odd})(\text{even}) d\tau = 1$$

$$c(uu) = \int (\text{odd})(\text{odd})(\text{odd}) d\tau = 0$$

and

Thus, the $0u \rightarrow 1u$ and $0g \rightarrow 1g$ transitions are forbidden, while the other two result in allowed transitions. As seen from the length of the vectors in Figure 1, this leads to two transitions of slightly different frequency, and two Q bands.

Experimental

The ammonia bands are centered around 950 cm^{-1} , and the separation of the two Q-branches is over 30 cm^{-1} , so data collection does not require extremely high resolution or extended frequency ranges. Thus, the Thermo Scientific™ Nicolet iS™5 FT-IR spectrometer is capable of measuring this effect (as are the Nicolet iS10 or Nicolet iS50 FT-IR systems). The absorptivity of ammonia is quite high, so a 5 cm pathlength gas cell provides plenty of absorption.

The gas cell should be loaded with ammonia vapor at low pressure, typically about 5–10 psi (or up to 1 atm, which is safe in the glass cells), using a manifold in a hood. Note, if the gas cell has been used for HCl previously, then the cell should be pumped under vacuum or at least purged thoroughly, as the two gases react to form a white powder. The Nicolet iS5 spectrometer should also be located in the hood for safety in handling ammonia gas; the small size and easy portability make this simple. A background of the cell (preferably under vacuum) should be obtained first. Fill the gas cell with a small amount of ammonia, and place the cell into the sample chamber. Acquire 32 to 64 scans covering the range $600\text{--}1200 \text{ cm}^{-1}$ at a resolution of 4 cm^{-1} or better. The ammonia doublet is clearly resolved, and the spacing should be about 35 cm^{-1} , as seen in Figure 2.

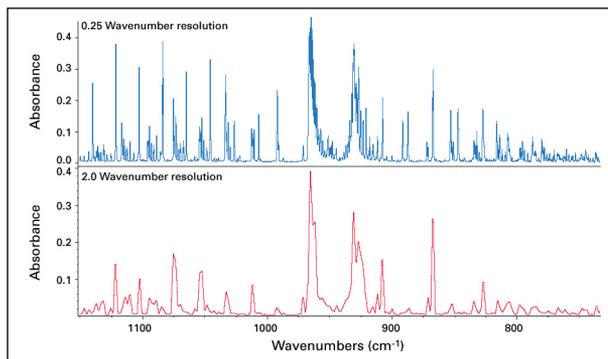


Figure 2

There are many P and R bands around the central Q-branches, which can present interesting teaching points for rotational moments of inertia. Ammonia has two axes, and the doubling mixes in to cause several sets of P and R branches. The spectrum, collected at high resolution (1 cm^{-1} or better), shows an intricate interplay of the two branches and isotopic influences (if present in the ammonia), so the analysis and discussion of the spectrum can be very rewarding. This is one of the richest, yet explicable, gas phase spectra easily attainable in the physical chemistry laboratory.

Conclusion

The most common physical chemistry experiment involving IR spectroscopy is the HCl/DCl rotation-vibration experiment, which usually ends with the measurement of the bond length. This experiment provides a more complex theoretical framework with a similarly simple experimental procedure (the gas is no more hazardous than HCl). However, the ability of quantum mechanics to explain the doubling of the ammonia spectrum in a sufficiently complex derivation without being tedious, presents students with a fascinating glimpse into the possibilities of quantum. In a lab setting, this experiment would follow (or conjoin) with the HCl experiment to provide a second look into the inner workings of spectroscopy.

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