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The Microwave Spectrum of Quinuclidine

by

Lauren G. Johnson

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Robert F. Curl

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INTRODUCTION

Quinuclidine has the empirical formula $C_7H_{13}N$. It may be prepared from 4-(β -hydroxyethyl) piperdine by the action of HBr followed by alkali (1). Since it is well known that piperdine has a six membered heterocyclic ring it was expected that quinuclidine would have a bicyclic structure consisting only of six member rings with the nitrogen at one of the bridgeheads. The assumed structure is shown in Figure I. It was further expected that quinuclidine would have a three fold axis of symmetry which passes through the two bridgehead positions.

It was hoped that from the investigation of the microwave spectrum of quinuclidine the three fold symmetry axis might be confirmed and some information about the molecular geometry might be obtained.

Somewhat more remote was the prospect of finding the dipole moment, the centrifugal distortion constants, and the quadrupole coupling constant.

FIGURE II. ASSUMED STRUCTURE OF QUINUCLIDINE

$r_{NC} = 1.47\text{\AA}$

$\angle CNC = 108.7^\circ$

$r_{CC} = 1.54\text{\AA}$

$\angle CCC = 111.0^\circ$

$r_{CH} = 1.09\text{\AA}$

$\angle HCH = 109.5^\circ$

II. EXPERIMENTAL

The spectrum of quinuclidine was examined with a microwave spectrometer of the usual design, employing 100 kc Stark modulation and phase sensitive detection. The general features of such a system are more fully explained in references 2 and 3. However, a brief description seems in order. The microwave power is generated by a klystron and passes through the sample cell to a crystal detector. The sample cell consists of a piece of wave guide divided by a metal septum to which the 100 kc voltage is applied.

After amplification the 100 kc signal arising from the crystal goes into a phase sensitive detector. Here the amplified signal is compared with the original 100 kc source. The lines and Stark, being out of phase, appear on opposite sides of the base line of a recorder.

Once the lines are observed they must be measured accurately. Their approximate frequency can be measured with a wave meter (a tunable cavity coupled to a wave guide), but for precise measurements a frequency standard must be employed. The source of the standard frequency is a General Radio Corporation crystal controlled 100 kc oscillator of excellent stability.

This signal is multiplied into the 500 to 1,000 Mc range where it is used to control the oscillation of a cavity. The signal emerging from the cavity (500 to 1,000 Mc) is multiplied to approximately the klystron frequency and heterodyned with the frequency from the klystron. The beat note is detected by a radio receiver.

At one stage in the multiplication of the 100 kc signal a 5 Mc signal is generated. This signal is then beat against the 5 Mc National Bureau of Standards station, WWV, signal. WWV is good to 1 part in 10^8 per day (4). A beat of a cycle per second can be detected giving an accuracy of .01 Mc after the 5 Mc signal is multiplied to 20,000 Mc.

Although the marker can be read to 0.01 Mc in this work, the frequencies were reported only to 0.1 Mc. Because the lines are broad, due to a quadrupole coupling and centrifugal distortion, the estimated accuracy is 0.2 Mc.

If there had been resolvable splitting of the lines, the hyperfine structure could have been measured more accurately.

The sample was obtained for the author from A. C. Boyd, Jr., of Purdue University, by Dr. E. S. Lewis, of the Rice Institute, and was believed to be fairly pure.

Quinuclidine adsorbed on the walls of the wave guide quite rapidly and small amounts of the sample had to be admitted frequently to maintain the working pressure of 35 microns.

The observed lines are shown in Figure II. The intensities of the lines could not be measured to very high accuracy. The intensities are the average of a large number of recorder tracings. The estimated uncertainty is about $\pm 20\%$.

The spectrum was measured at room temperature, ice temperature, and -20°C , which was obtained by an ice-salt bath. This is not a large enough range to give good data on the temperature dependence of the intensity, but the vapor pressure of quinuclidine was not large enough at lower temperatures to observe the lines. The lines assigned to the ground vibrational state were observed to increase slightly in intensity with decreasing temperature, while the excited vibrational states decreased in intensity.

As will be discussed later, the three sets of lines seen were assigned as the 4 to 5, 5 to 6, and the 6 to 7 rotational transitions.

The signal to noise ratio for the ground vibrational state line of the 4 to 5 transition was 10. For the 5 to 6 line it was 25, and for the 6 to 7 line the signal to noise ratio was about 50. Thus for the

4 to 5 transition the weakest line that could possibly be seen would be $1/4$ as intense as the ground state line, while for the 5 to 6 transition the limit would be lines about $1/10$ as intense, and for the 6 to 7 transition lines about $1/20$ as intense as the ground vibrational line could be seen.

On the basis of the above assignment, the 1 to 2 ground state line was predicted to lie at 9,727.3 Mc. In the absence of centrifugal distortion, the peak intensity for a transition J to $J+1$ summed over all K increases approximately as ν^4 (5). The effect of centrifugal distortion is to decrease the exponent somewhat from 4. Thus a line at 9,727.3 would be approximately .025 as intense as the line at 24,311.5, which is a weak line itself. A careful search was made, but no adsorption was detected at 9,727.

FIGURE II. MEASURED LINES

The frequency scale is adjusted so that each vibrational state is in vertical alignment.

The relative intensities are illustrated by line height. + indicates increasing intensity with decreasing temperature, - indicates decreasing intensity with decreasing temperature.

III. INTERPRETATION OF THE SPECTRUM AND COMPARISON TO EXPECTED SPECTRUM

Because the microwave spectrum of quinuclidine is so very simple, the molecule must possess a three fold axis of symmetry. Molecules having a three fold or higher axis of symmetry have an especially simple rotational energy level pattern.

In the rigid rotor approximation the rotational energy of these molecules is simply:

$$B \cdot J \cdot (J+1) + (C-B)K^2.$$

The selection rules for dipole radiation of a nonplanar symmetric top such as this are: $\Delta J = 0, \pm 1$, $\Delta K = 0$ (6). These selection rules lead to a line every 2B Mc in the rotational spectrum. In this approximation the rotational spectrum of quinuclidine would be a series of equally spaced lines.

There are, however, a number of effects which lead to a deviation from this pattern. The most general features of the spectrum are left intact but instead of a single line every 2B Mc, a set of lines is observed at approximately the expected frequency.

These effects are the interactions between rotation and vibration, centrifugal distortion, coupling of the quadrupole moment of the nitrogen nucleus to the molecular frame, ℓ -type doubling, and lines

arising from species containing C^{13} . Each effect will now be discussed in detail.

The interaction of the rotational and vibrational energies leads to slightly different values of B and consequently to rotational transitions of slightly different frequencies for molecules in excited vibrational states. This was observed.

Three sets of lines were measured and assigned as the $J=4$ to 5 , 5 to 6 , and 6 to 7 transitions. The strongest line of each set is assigned as the ground state due to its greater intensity and to its temperature dependence. The rest of the lines are interpreted as excited vibrational satellites but no specific assignment is attempted due to the multiplicity of these lines and the lack of knowledge about the infrared spectrum.

The line at $24,311.5$ Mc was assigned as the ground state 4 to 5 transition. The line at $29,173.5$ Mc as the ground state 5 to 6 , and the line at $34,033.7$ Mc as the ground state 6 to 7 transition.

The 4 to 5 line was not strong enough to see more than the three strongest satellites. However, the 5 to 6 transition was fairly intense and six definite satellite lines were observed as well as numerous recorder deflections which were too weak to be recorded as definite lines. The 6 to 7 transition was even more

intense; however, it was impossible to get the klystron to oscillate over the entire range of this transition and this explains the apparent absence of some of the expected vibrational satellites.

A value of B could be assigned to each vibrational satellite. Table I lists the values of B obtained. The numbering of the B's corresponds to the numbering of the observed lines.

Because the molecule is not rigid, each of the lines observed will be slightly displaced by the effect of centrifugal distortion. Centrifugal distortion also removes some of the K degeneracy of the lines, particularly for higher J transitions.

The amount of centrifugal distortion of the molecule cannot depend on the sign of the angular rotation (7). Therefore, the change in rotational energy must involve only even powers of the momentum, such as the square of the total angular momentum, $J \cdot (J+1)$, or of the component of angular momentum along the symmetry axis, K^2 . Thus the rotational energy may be written:

$$W(J,K) = B \cdot J \cdot (J+1) + (C-B) \cdot K^2 - D_J J^2 \cdot (J+1)^2 - D_{JK} J \cdot (J+1) \cdot K^2 - D_K K^4$$
, plus higher order terms. Since $\Delta K = 0$, for a transition all the terms involving only K will vanish and only terms in J and coupling terms will remain. The frequency can then be written:

$\nu = 2 \cdot (J+1) \cdot (B - D_{JK}K^2) - 4D_J \cdot (J+1)^3$, plus higher order terms.

The centrifugal distortion constants are always relatively small, but as J becomes large the lines will be displaced from their rigid rotor position by the D_J term and if D_{JK} is appreciable, the K degeneracy will be lifted in higher transitions. In the present case, the K degeneracy was not lifted sufficiently to resolve the individual lines.

D_J was obtained by fitting the expression $2 \cdot (J+1)B - 4D_J \cdot (J+1)^3$ to the center of gravity of the three lines. This leads to a B of 2,431.78 Mc and a D_J of $10 \text{ kc} \pm 5 \text{ kc}$. As expected, D_J was positive since centrifugal forces due to rotation about an axis always tend to increase the moment of inertia about that axis or decrease the rotational constant.

Since the hyperfine components were not resolved, the only possible information on D_{JK} comes from the line widths. If the quadrupole coupling constant of quinuclidine is assumed to be about equal to that of trimethyl amine, which seems very reasonable, and the width of the measured line is 2Mc, then D_{JK} is less than 15 kc.

Even in the absence of centrifugal distortion, each of the vibrational satellites and the main line are split still further by interaction of the nitrogen quadrupole moment with molecular fields. This hyperfine interaction arises from the axial nitrogen nucleus which

has a spin of one and thus has a nonzero expectation value for the interaction of its quadrupole moment with the gradient of the molecular electron field. This effect is quite small and in this case no splitting was resolved. Lide and Mann report that eqQ has a value of -5.47 for trimethyl amine (8). The eqQ for quinuclidine should be similar.

Since there are always a number of degenerate vibrational modes in symmetric tops, there is also the possibility of ℓ -type doubling. Every degenerate mode can produce an angular momentum which interacts with the angular motion of rotation.

If one of the excited vibrational states corresponding to a satellite line happens to be a degenerate state, two weak lines should be present symmetrically placed about the satellite line in question. These ℓ -type doubling satellites (perhaps more correctly sub-satellites) arise from the interaction between the vibrational angular momentum and the molecular rotation. No such sub-satellites were observed, probably because they are too weak. Thus the satellite lines arising from degenerate vibrational states could not be identified by this effect.

There are also two sets of asymmetric top lines for quinuclidine arising from isotopic substitution in the two sets of equivalent carbon atoms. C^{13}

occurs in 1.2% natural abundance and so due to the three fold axis, each asymmetric variety will occur in 3.6% abundance.

No lines were assigned asymmetric top lines since the intensities of these transitions are so small that they were not observable. The asymmetric tops occur in only 3.6% abundance so that the maximum possible intensity would be $\frac{3.6}{92.8}$ of the ground state line. The intensities are further reduced by the K splitting of the symmetric transition, making it virtually impossible to see the lines. Thus the only moment of inertia obtained is B.

The effect of an electric field on the lines might have led to a measurement of the electric dipole moment. However, in the case of quinuclidine it was not possible to get an accurate measure of the dipole moment since the lines displaced by the electric field were too weak to be resolved. The fact that the normal lines were very weak tells us that the dipole is small. The dipole for trimethyl amine was found to be $0.612 \pm 0.003D$ (9).

In conclusion, it is possible to propose a structure for quinuclidine by piecing the molecule together from trimethyl amine and a tertiary butyl struc-

ture. It is not intended to propose this as the exact structure for quinuclidine, but rather to show that the present work is at least consistent with these previously determined structures.

The structure for trimethyl amine has been given by Lide and Mann (10). It is as follows:

The tertiary butyl structure is given by Andersen, Bak, and Rastrup-Andersen (11) as:

The $\angle HCH$ is assumed to be $109^\circ 28'$ and the hydrogen atoms to be symmetric with respect to the $\angle CCC$ and $\angle CCN$ and $r_{CC}=1.54\text{\AA}$.

This structure leads to a B of 2,507. Mc as compared to the measured B of 2,431.78 Mc.

TABLE I. ASSIGNED VALUES OF B

<u>Vibrational Satellite</u>	<u>B (Mc)</u>
1	2,427.47
2	2,430.80
3	2,433.02
4	2,436.64
5	2,438.32
6	2,441.90

The numbering of the lines corresponds to that of Figure II.

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