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Jackson Koo and Yu-Nian Hsieh

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N^{14} Nuclear Quadrupole Coupling Constants In Imidazole*

Jackson Koo and Yu-Nian Hsieh

Department of Physics, University of California
and
Inorganic Materials Research Division,
Lawrence Radiation Laboratory,
Berkeley, California 94720

ABSTRACT

All six N^{14} nuclear quadrupole resonances in imidazole have been observed. Using Townes-Dailey theory and experimental observation, we are able to make the first unambiguous identification of the quadrupole coupling constants at a bi-coordinate N site.

This letter reports the observation of all six N^{14} nuclear quadrupole resonances in imidazole (see Figure 1 for structural formula) by means of the level crossing detection technique.[1] Nitrogen has a nuclear spin I=1, thus it has at most three pure nuclear quadrupole resonances, denoted by ν_+, ν_-, ν_o, for each nuclear site. There are two independent non-equivalent nitrogen sites in imidazole: one of them forms a bi-coordinate bond with its neighbor carbon nuclei (C-N=C), the other forms a tri-coordinate bond (C-$\overset{C}{\overset{|}{N}}$-H). From the transition frequencies, both the quadrupole coupling constant e^2qQ and the asymmetry parameter η can be determined.[2] The experimental data, taken at a temperature of 77°K, and the calculated values of e^2qQ and η are shown in Table 1. Spectrum 1 in Table 1 has been previously reported by Schempp and Bray.[3] It may be remarked that the value η=0.98 calculated from our experimental data is the largest asymmetry parameter yet observed in a N compound. Since only polycrystalline samples were used in the experiments, the directions of the principal axes of the electrical field gradients (EFG) could not be determined experimentally. It remains to determine, however, which of the spectra (1 and 2 in Table 1) corresponds to the bi-coordinately bonded N site, and which corresponds to the tri-coordinate N site. The simplest theoretical approach has been given by Townes and Dailey, for symmetrical molecules. The molecules of imidazole do not have two fold symmetry at its nitrogen sites. The directions of the principal axes of its EFG are thus generally not the same as those of the bonding orbitals, as assumed in the simple Townes-Dailey analysis. However, these deviations are expected to be quite small.[4] The Townes-Dailey analysis should thus be sufficiently accurate to distinguish the origins of the spectra, since the quadrupole coupling constants and η's here are grossly different.

For the three coordinate nitrogen atom, the principal axes of the EFG are shown in Figure 1. Since P_π orbital of the nitrogen atom contains the lone pair of electrons, it is assumed that Z axis is in this direction and is perpendicular to the molecular plane. The N-C sigma orbital populations are usually less than N-H sigma orbital populations which implies that the X-axis is in the N-H orbital direction.[5] The S-P^3 hybrid orbitals are given by:

$$\begin{aligned}
\phi_1 &= \psi_z \\
\phi_2 &= \cot\theta\, \psi_s + (1-\cot^2\theta)^{1/2}\, \psi_x \\
\phi_3 &= [(1-\cot^2\theta)^{1/2}\, \psi_s - \cot\theta\, \psi_x + \psi_y]/\sqrt{2} \\
\phi_4 &= [(1-\cot^2\theta)^{1/2}\, \psi_s - \cot\theta\, \psi_x - \psi_y]/\sqrt{2}
\end{aligned} \tag{1}$$

where ψ_s, ψ_x, ψ_y, and ψ_z are 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals of the nitrogen atom and 2 θ is the C-N-C bond angle. Then if the population of ϕ_1, ϕ_2, ϕ_3 ($\simeq \phi_4$) are a, b, and c respectively, it may be shown from Townes-Dailey analysis that the coupling constants are given by:

$$\begin{aligned}
\frac{e^2qQ}{e^2q_oQ}\,(1 + \eta/3) &= (a - c) \\
\eta\,\frac{e^2qQ}{e^2q_oQ} &= 3(1 - \cot^2\theta)\,(b - c)/2
\end{aligned} \tag{2}$$

By substituting the experimental data into these equations and assuming the typical value[5] of b = 1.33, one can obtain the values for a and c corresponding to the two different sets of spectra, as shown in Table 2. The values for the first spectrum correspond to those of usual three coordinate nitrogen atom.[5-7] The values for the second spectrum

are rather small by comparison. Thus, it seems from this simple theoretical analysis that the first spectrum is likely to be that of the three coordinate nitrogen resonances.

For the two coordinate nitrogen atoms, the principal axes of the EFG are chosen as shown in Figure 2. The S-P^3 hybrid orbitals are given by simply exchanging the x and z in the Equation 1. If the population of the $P_\pi(\phi_1)$ and bonding sigma (ϕ_3, ϕ_4) orbitals are represented as a and b respectively, the coupling constants are given by:

$$(a-b) = 2\eta \frac{e^2qQ}{3e^2q_oQ} \qquad (3)$$

$$(2-b) = \frac{1}{(1-\cot^2\theta)} \quad (1 + \eta/3) \quad \frac{e^2qQ}{e^2q_oQ}$$

The values of a and b calculated from experimental data for the spectrum 1 are given in reference [5]. Values of a and b calculated for spectrum 2 are shown in Table 3 where two different values of bonding angles 2 θ are assumed. The values of a and b with the smaller bonding angle in Table 3 seem to be quite close to the values found for spectrum 1. The calculation here thus does not help to correlate the spectra with the sites.

This simple Townes-Dailey analysis indicates that the nuclear quadrupole coupling constant and the asymmetry parameter for the three coordinate nitrogen atoms in imidazole are 3.2714 Mc/s and 0.128, respectively, and for two coordinate nitrogen atoms, these are 1.4245 Mc/s and 0.98 respectively.

In order to verify this conclusion experimentally, a sample of deuterated imidazole was used in which most of the hydrogen atoms which form chemical bonds with the three coordinate nitrogen atoms are replaced by

deuterium atoms. With a rather strong r.f. irradiation field, a search was made by employing the same level crossing detection technique for the forbidden transition due to simultaneously exciting both nitrogen and deuterium at the sum frequencies:

$$\nu = \nu_N + \nu_D$$

where ν_N and ν_D are the quadrupole resonance frequencies of nitrogen and deuterium atoms respectively. The typical value for the transition frequencies of deuterium are known to be around 150 kc/s. Only one doublet was observed as shown in Figure 3. This corresponds to the transition frequency for nitrogen around ν_Q = 210.5 kc/s together with the transition frequencies of deuterium around ν_{D-} = 131 kc/s and ν_{D+} = 143.5 kc/s. Since the transition probability of a forbidden line is directly proportional to the square of the dipolar coupling constant between the nitrogen and deuterium nuclei, one concludes that the nitrogen atoms with transition frequency at 210.5 kc/s of spectra 1 are much more strongly coupled to the deuterium. This means that spectrum 1 arises from three coordinate nitrogen atoms which form chemical bonds with deuterium. Thus, this provides experimental confirmation of the Townes-Dailey analysis.

The failure to observe the forbidden transitions at the high frequencies $V_{N\pm}+\nu_{D\pm}$ can be explained by the fact that the forbidden transition probabilities are inversely proportional to the square of the transition frequencies. This can be shown for the case of both interacting nuclear spins having I=1 which is true for N and D. The dip at the frequency of 375 kc/s in Figure 3 is thought to be a high order transition due to proton nuclei, for a large shift of its frequency as a function of d.c.

magnetic field was observed.

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Footnotes

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1) Jackson C. Koo, Ph.D. Thesis, University of California, Berkeley, Calif., 1969; paper to be published; J. C. Koo and E. L. Hahn, Bull. Am. Phys. Soc., Series 11, 13, 356 (1968).

2) T. P. Das and E. L. Hahn, Solid State Physics Supplement (1) Seitz and Turnbull, editors (Academic Press, 1958).

3) E. Schempp and P. J. Bray, Phys. Lett. 25A, 414 (1967).

4) These deviations are expected to be smaller than those of pyridazine, because of the direct bond between the two nitrogen atoms in this molecule. But the deviation in pyridazine is only about 9° which introduces only a few present changes in the calculated values of η.

5) E. A. C. Lucken, Chapter 11, "Nuclear Quadrupole Coupling Constants" (Academic Press, 1969).

6) C. A. Coulson and H. C. Longuet Higgins, Rev. Sci. Paris 85, 929 (1947).

7) R. D. Brown, Australian J. Chem. 12, 152 (1959).

FIGURE CAPTIONS

Fig. 1 Principal axes of the electric field gradient of three-coordinate nitrogen atoms in imidazole.

Fig. 2 Principal axes of the electric field gradient of bi-coordinate nitrogen atoms in imidazole.

Fig. 3 Forbidden transitions in deuterated imidazole. H_1 (rf) $\approx$ 20 gauss. H_o (low field) $\approx$ 15 gauss. A resonance is observed as a decrease in S.

Table I. N^{14} Nuclear Quadrupole Resonance in Imidazole (Mc/s)

Spectrum	ν_+	ν_-	ν_o	e^2qQ	η
1	2.5588	2.3483	0.2105	-3.2714	0.128
2	1.4175	0.7193	0.6982	-1.4245	0.98

Table II. Orbital Populations in Imidazole for Three Coordinate Nitrogen Atoms e^2q_oQ is assumed equal to -9.0 Mc/s and the Bond Angle 2θ equal to 108°.

Spectrum	e^2qQ (Mc/s)	η	a	b	c
1	-3.2714	0.128	1.65	1.33	1.27
2	-1.4245	0.98	1.33	1.33	1.12

Table III. Orbital Populations in Imidazole for Two Coordinate Nitrogen Atoms with EqQ equal to 1.4245 Mc/s and $\eta = 0.98$. e^2Qq_o is Assumed Equal to -9.0 Mc/s.

2θ	a	b
108°	1.68	1.58
100°	1.35	1.25

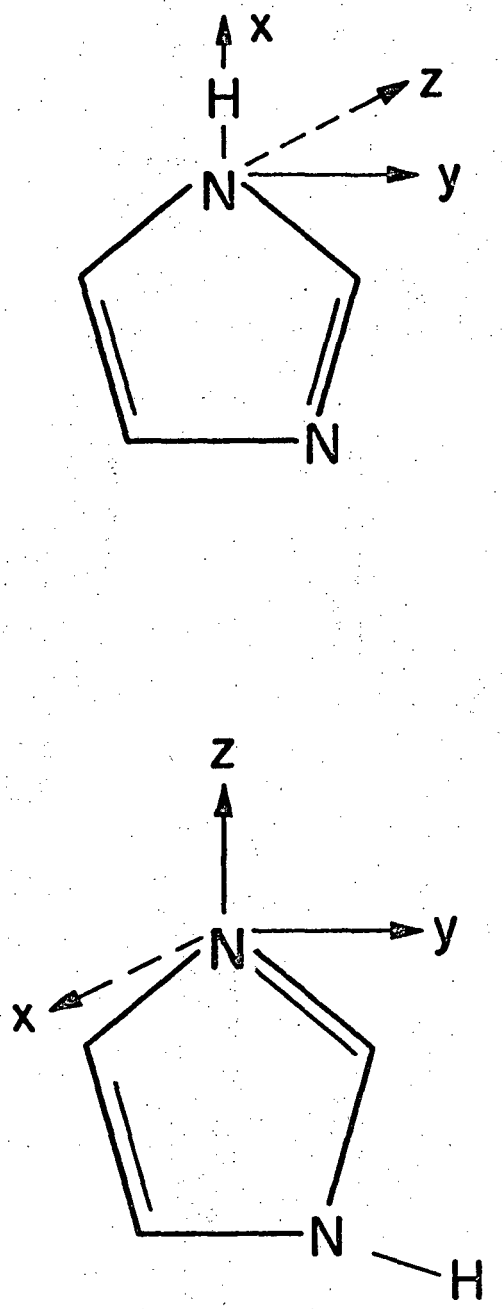

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Fig. 1

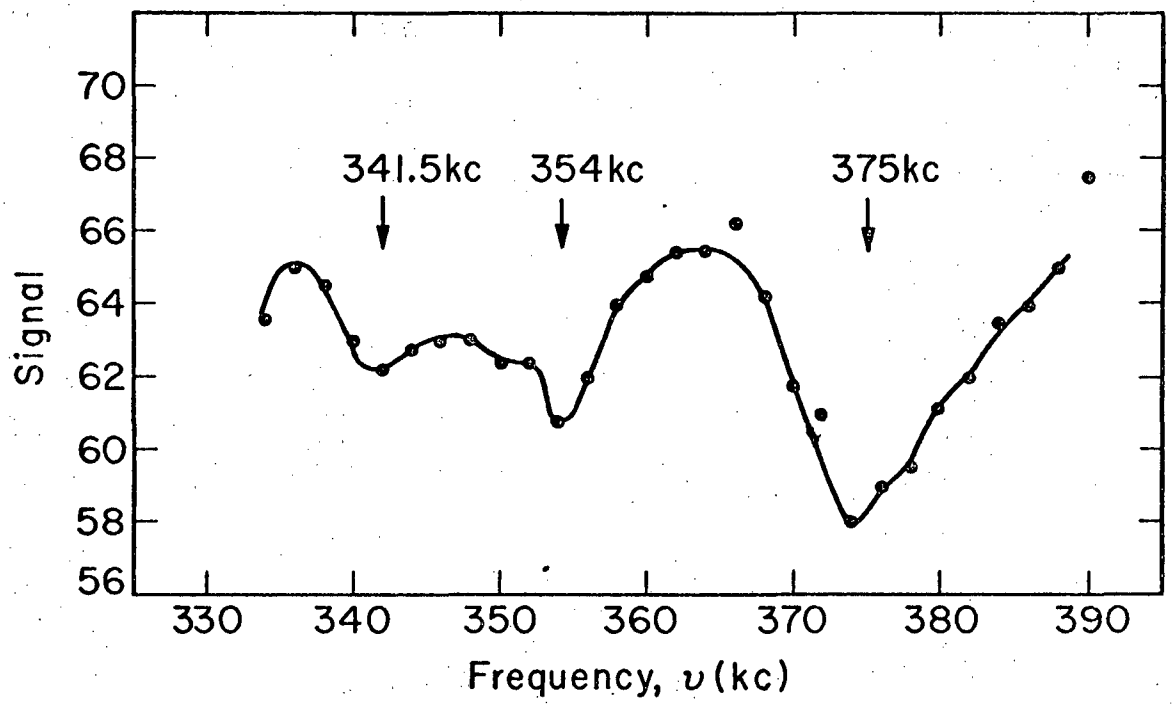

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Fig. 2

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