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Study of Potential Interstellar Molecules: Nuclear Quadrupole Coupling Constants of the Nitrogen Atom in Pyrrole

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Abstract

The nuclear quadrupole coupling constants of the nitrogen atom in pyrrole have been redetermined by analysis of the hyperfine structure for several low J rotational transitions. The resulting values are $\chi_{aa} = 1{\cdot}400 \pm 0{\cdot}008$ MHz and $\chi_{bb} = 1{\cdot}300 \pm 0{\cdot}008$ MHz. Small modifications to the previously reported rotational constants are given.

Recent interest in the discovery of molecules in interstellar space led us to investigate the possibility of finding pyrrole, a simple heterocyclic compound containing atoms of only carbon, hydrogen and nitrogen. The importance of pyrrole in relation to the exobiology of porphyrins has recently been emphasized and a plea made for a search in the region of Sagittarius (Hodgson 1971). As a preliminary to the interstellar search, it was necessary to study several low J absorptions of pyrrole in the laboratory. The microwave spectrum, including the nitrogen quadrupole analysis,was published by Nygaard *et al.* (1969) but during our study of the 1_{11}–1_{10} transition it became evident that the multiplet structure of the absorption could not be accurately predicted using the published microwave data. We therefore decided to study several multiplets of pyrrole in order to obtain more accurate values of the nitrogen quadrupole coupling constants.

Pyrrole (Koch–Light. pure grade) was used without further purification. Spectra were recorded using a conventional 5 kHz Stark-modulated G band spectrometer. Frequency measurements were made with a Hewlett–Packard 5246L electronic counter which was calibrated periodically against a Sulzer 2·5C laboratory standard. Absolute frequencies of hyperfine components are quoted to an accuracy of ± 10 kHz whereas frequency differences, between various components of the multiplet, can be determined to within ± 5 kHz. The pyrrole sample was contained in a dry-ice cooled absorption cell at pressures of approximately 1 μmHg (0·13 Pa). Time constants of the orders of 1 s were used whilst scanning the multiplets.

A maximum resolution of 20 kHz half-width was achieved for the 1_{11}–1_{10} transition. Substitution of the frequency separation between successive members of this multiplet into the well-known relationship of Casimir (1936) yielded the following accurate values of the coupling constants

$$\chi_{aa} = 1{\cdot}40 \text{ MHz}, \qquad \chi_{bb} = 1{\cdot}30 \text{ MHz}.$$

Fig. 1 shows an experimental tracing of the 1_{11}–1_{10} multiplet together with computer-simulated plots obtained using (A) the above coupling constants and (B) the coupling constants of Nygaard *et al.* (1969). Even on the scale of Fig. 1 the discrepancies

between the observed hyperfine structure and the calculated structure B can be seen, particularly for the separation between the $F = 1$–2 and 0–1 components of the multiplet. For these components the observed splitting is $0{\cdot}165 \pm 0{\cdot}005$ MHz and the calculated splitting (Nygaard *et al.*) is $0{\cdot}1095$ MHz. The values of χ_{aa} and χ_{bb} quoted above, however, predict all the components of the multiplet to within the precision of the measurements (± 5 kHz). This can be seen by reference to Fig. 1 or Table 1. Once the coupling constants have been determined the centre frequency of the multiplet can be evaluated directly (Table 1).

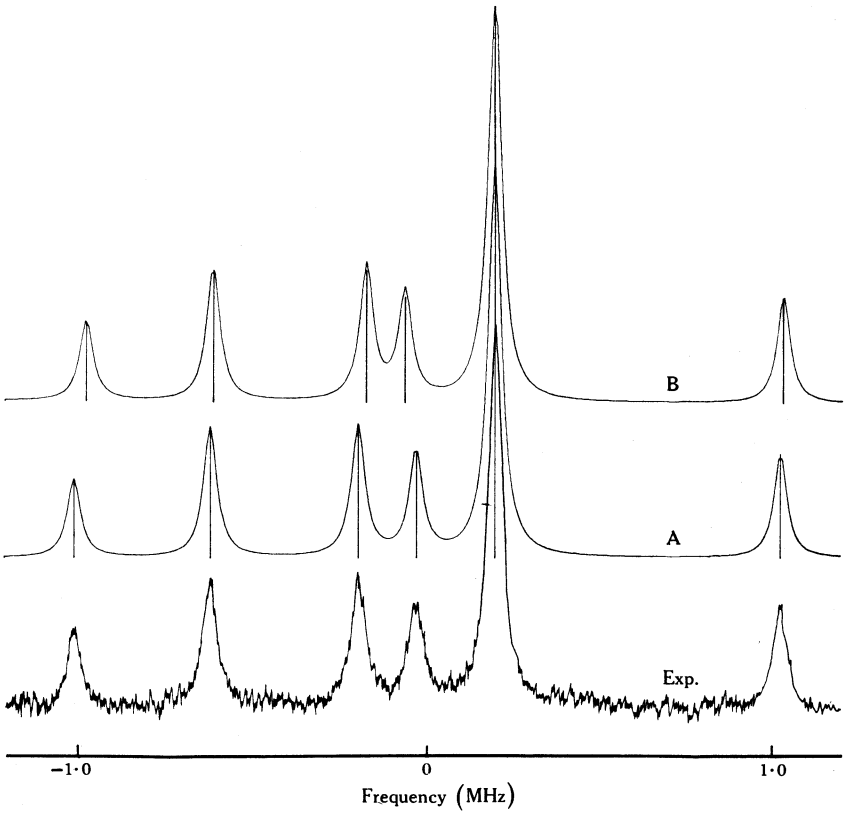

Fig. 1. Comparison between experimental and computed line shapes for the 1_{11}–1_{10} transition in pyrrole. The computer-simulated plots A and B were obtained using the present coupling constants and those of Nygaard *et al.* (1969) respectively; a half-width of 23 kHz was assumed for both plots.

The coupling constants χ_{aa} and χ_{bb} above were used to calculate the multiplet structure of the 0_{00}–1_{01}, 2_{12}–2_{11}, 2_{21}–2_{20} and 3_{31}–3_{30} transitions. Each of these transitions was investigated under conditions of high resolution and their experimental tracings were compared with the computer-simulated plots. The discrepancies between the observed and calculated frequencies (Table 1) are very small and well within the precision of the measurements (such close agreement must be regarded as entirely fortuitous). The coupling constants can be quoted then to a high degree of certainty, i.e.

$$\chi_{aa} = 1{\cdot}400 \pm 0{\cdot}008 \text{ MHz}, \qquad \chi_{bb} = 1{\cdot}300 \pm 0{\cdot}008 \text{ MHz}.$$

The accurate centre frequencies, as given in Table 1, allow the calculation of the rotation constants of pyrrole. The results (MHz) are:

$$A = 9130{\cdot}637 \pm 0{\cdot}010, \qquad B = 9001{\cdot}360 \pm 0{\cdot}010, \qquad C = 4532{\cdot}120 \pm 0{\cdot}010.$$

These values are slightly different from those quoted by Nygaard *et al.* (1969).

Since the 1_{11}–1_{10} transition of pyrrole is relatively intense and has a well-resolved, and well-documented, quadrupole multiplet pattern, it provides an excellent candidate for an interstellar search. An account of the search for this line, using the radio telescope at Parkes, N.S.W., will be published separately.

Table 1. Comparison between observed and calculated hyperfine transition frequencies in pyrrole

Transition $J \rightarrow J'$	$F \rightarrow F'$	Frequency (MHz) Observed*	Calculated†	Transition $J \rightarrow J'$	$F \rightarrow F'$	Frequency (MHz) Observed*	Calculated†
1_{11}–1_{10}	1–1	4468·255	4468·255	2_{21}–2_{20}	1–2	4341·700	4341·700
	2–1	4468·645	4468·645		3–2	4341·950	4341·950
	1–2	4469·065	4469·065		2–2	4342·400	4342·400
	0–1	4469·230	4469·230		3–3	4342·820	4342·818
	2–2	4469·455	4469·455		1–1	4343·050	4343·050
	1–0	4470·280	4470·280		2–3	4343·270	4343·268
Centre frequency		4469·255 ± 0·01			2–1	4343·750	4343·750
				Centre frequency		4342·725 ± 0·01	
3_{31}–3_{30}	2–3	4157·060	4157·060				
	4–3	4157·300	4157·302	2_{12}–2_{11}	2–2	13 406·715	13 406·715
	3–3	4157·990	4157·994		2–3	13 407·135	13 407·133
	4–4 }	4158·220	4158·202		2–1	13 407·365	13 407·365
	2–2 }		4158·275		3–2	13 407·585	13 407·583
	3–4	4158·890	4158·894		3–3	13 408·000	13 408·001
	3–2	4159·205	4159·209		1–2	13 408·065	13 408·065
Centre frequency		4158·150 ± 0·01			1–1	13 408·715	13 408·715
				Centre frequency		13 407·715 ± 0·01	
0_{00}–1_{10}	1–0	13 532·780	13 532·780				
	1–2	13 533·410	13 533·410				
	1–1	13 533·830	13 533·830				
Centre frequency		13 533·480 ± 0·01					

* Relative frequency ±0·005 MHz.

† Assuming same centre frequency as observed.

Note added in proof

Abstracts recently received from the Symposium on Molecular Structure and Spectroscopy, Ohio, June 1973, show that beam-maser measurements by L. Gaines and G. R. Tomasevich of the Columbia Radiation Laboratory, Columbia University, New York, are in complete agreement with our data on the quadrupole coupling constants of the nitrogen atom in pyrrole. The values quoted are:

$$\chi_{aa} = 1{\cdot}4057 \pm 0{\cdot}0011 \text{ MHz}, \qquad \chi_{bb} = 1{\cdot}2945 \pm 0{\cdot}0010 \text{ MHz}.$$

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