NOTIZEN

Nuclear Quadrupole Resonance of N^{14} in Pyridine Complexes

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Shifts in the nuclear quadrupole coupling are detected for N^{14} in pyridine complexes by pure nuclear quadrupole resonance spectroscopy (NQR). These are compared with values obtained by the Townes-Dailey method using a simple molecular-orbital (MO) calculation for the pyridine-pyrrole system.

The purpose of this note is to present nuclear quadrupole data for N^{14} in hydrogen bonded pyridine complexes (pyridine-chloroform, pyridine-pyrrole, and pyridine-CH_3OH), and to show that NQR spectroscopy is also a very useful tool in the studies of electronic distribution and structure of hydrogen bonded complexes along with more standard spectroscopic methods[1]: (i. e. IR, UV, NMR, etc.). 1 : 1 mixtures of pyridine-pyrrole, pyridine-chloroform, and pyridine-CH_3OH were prepared. The samples were very slowly cooled to liquid nitrogen temperature. A modified Pound-Knight-Watkins type marginal NQR-spectrometer[2] with a frequency modulation (sine-wave, 500 Hz) was employed with a tank coil of large diameter (~ 8 cm), by which the saturation effects caon be avoided and a better signal to noise ratio can be achieved at higher oscillation level of the spectrometer[3]. By a phase diagram study, it is found that the 1 : 1 complexes of these compounds are stable. Unfortunately X-ray studies for these complexes are not yet available, and a detailed structural analysis in terms of crystal structure is not yet possible.

Table 1 summarizes the observed NQR frequencies, the quadrupole coupling constants ($e\,Q\,q_{\mathrm{mol}}$) and the asymmetry parameter (η) of N^{14} in these complexes, measured at 77 °K. Corresponding values for gaseous and pure solid pyridine and pyrrole are also listed as a comparison. In Table 1 we notice a small shift in the quadrupole coupling constant as well as the asymmetry parameter of the complexes, compared with the pure compound. This shift, we believe, is due to the hydrogen bond formation in the complexes. Similar and extensive studies have been carried out on the solid state shift in the quadrupole coupling of N^{14} in ammonia and it has been concluded that the lone pair electron of the nitrogen is mainly responsible for this shift[4, 5]. As in the case of solid ammonia, the lone pair electrons of nitrogen are considered to be hydrogen bonded in these complexes. The systems under study represent prototypes of N...H−C, N...H−N, and N...H−O of the hydrogen bond and it is of interest to notice that the NQR shifts in these systems follow the hydrogen bond strength[1]. In the system pyridine-pyrrole we notice the N^{14} quadrupole coupling to be less affected in the pyrrole molecule than in the pyridine molecule by the formation of the hydrogen bond, as shown in Table 1. This is presumably due to the fact that the nitrogen lone pair electrons in pyrrole are not directly associated with the N...H−N hydrogen bond formation in this complex.

Compounds	$e\,Q\,q_{\mathrm{mol}}$ [a]; $\nu_\pm$			η
pyridine (gas)	4.88 [b]			0.41 [b]
pyridine (solid)	4.60 [c]			0.39 [c]
pyrrole (solid)	2.069 [d]			0.269 [d]
pyridine-chloroform	4.535;	3.833;	2.969	0.44
pyridine-pyrrole				
(pyridine-N)	4.287;	3.605;	2.825	0.48
(pyrrole-N)	2.122;	1.645;	1.522	0.10
pyridine-CH_3OH	— ;	— ;	2.686	

[a] in MHz.
[b] G. SORENSEN, J. Mol. Spectr. **22**, 325 [1967].
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Table 1. Quadrupole Coupling at N^{14} in pyridine complexes.

An Extended Hückel MO calculation with charge iteration (self-consistent charge method) has been per-

	Experiment [a] (f; η)		MO (f; η)	
pyridine	0.527;	0.41	0.563;	0.55
pyrrole	0.227;	0.26	0.513;	0.29
pyridine-pyrrole				
(pyridine-N)	0.470;	0.48	0.536;	0.68
(pyrrole-N)	0.233;	0.10	0.491;	0.47

[a] We used $e\,Q\,q_{\mathrm{at}} = 9.10$ MHz, which was obtained from the Hartree-Fock-Roothaan SCF value of $q_{\mathrm{at}}(N^{14})$ and $Q(N^{14}) = 1.56 \cdot 10^{-26}\ \mathrm{cm}^3$: see C. T. O'KONSKI and T.-K. HA, J. Chem. Phys. **49**, 5354 [1968] and C. T. O'KONSKI and T.-K. HA, Quadrupole Coupling Constants of N^{14}, to be published in J. Chem. Phys.

Table 2. Comparison of f and η values in pyridine-pyrrole.

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formed for pyridine, pyrrole, and the pyridine-pyrrole system with standard atomic parameters[6], and the TOWNES-DAILEY method[7] has been used to evaluate the f_z values (number of unbalanced p_z-electrons) and the asymmetry parameter, which is defined as:

$$\begin{aligned} f_z &= e\,Q\,q_{\text{mol}}/e\,Q\,q_{\text{at}} \\ &= N_z - \tfrac{1}{2}\,(N_x+N_y)\,, \\ \eta &= 3\,(N_x-N_y)/(2\,N_z-N_x-N_y) \end{aligned}$$

where N_x, N_y, and N_z are number of electrons in p_x, p_y, and p_z-orbitals. In the MO-calculation we used the experimental geometry for pyridine and pyrrole, and the N – N distance $R(\text{N}\ldots\text{H}-\text{N})$ in the complex was set equal to 3·10 Å[1]. The $R(\text{N}\ldots\text{H})$ distance is varied to obtain a potential energy curve for the complex. We obtained an asymmetric double minimum with energy minima at

$$R(\text{N}\ldots\text{H}) = 0.80\ \text{Å} \quad \text{and} \quad R(\text{N}\ldots\text{H}) = 2.40\ \text{Å}.$$

In the frame of these MO calculations the complex is more stable than the isolated molecules by an amount of 4.3 eV and 4.8 eV at these respective distances. Table 2 summarizes a comparison of the experimental and calculated values. f and η values for the pyridine-pyrrole system are obtained from the population analysis of the molecular orbitals at

$$R(\text{N}\ldots\text{H}-\text{N}) = 3.10\ \text{Å} \quad \text{and} \quad R(\text{N}\ldots\text{H}) = 2.40\ \text{Å}.$$

While for the pyridine-N the MO-calculation provides a resonable qualitative trend, f and η values for the pyrrole-N are not at all satisfactory. One could further refine the analysis to obtain better agreement with experiment in the framework of the Townes-Dailey method, as done recently by WHITE and DRAGO[8], but we have not pursued this further.

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Pion Finite Size and Mesic Atoms

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Contrary to the point-like muon the pion has a spatial extension. The effect of this finite size on levels of π-mesic atoms is estimated to be small but not necessarily negligible.

The levels of π-mesic atoms are usually treated with an optical potential[1–4]. Involved numerical computations are necessary to obtain fair agreement with the experimental data. The shape of the nucleus is taken from electromagnetic data, i. e. data of muonic atoms or electron scattering. Muon and electron are considered as point-like particles. The pion, on the other hand, has a spatial extension which has not yet been taken into account in previous work on π-mesic atoms. In this note the electromagnetic size of the pion[5], with a radius equaling that of the proton[6], will be taken as strong-interaction "size" of the pion.

In order to estimate the effect of the additional finite range of the π-nucleus interaction due to the pion size a simple model shall be used. The additional finite interaction range is taken into acount by describing the pion as a sphere of equivalent radius R_π uniformly charged with strong interaction of range zero. The nucleus is considered as a uniform sphere of radius R_{N} where R_{N} is the equivalent electromagnetic radius[6]. The probability of finding the pion center of mass at a (small) distance r from the center of mass of the nucleus is, for $l > 0$, approximately given by

$$P = a\,r^{2l+2}$$

where a is a constant and l is the orbital quantum number (for s states the distortion of the pion wave function by the nuclear potential is too large). If the center of mass of the pion is well inside the nucleus, at $r \leqq R_{\text{N}} - R_\pi$, the pion finite size has almost no effect on the properties of the π-mesic level (the change in electromagnetic finite size effect is very small). The same is true for $r \geqq R_{\text{N}} + R_\pi$. In the region of $R_{\text{N}} - R_\pi < r < R_{\text{N}} + R_\pi$, however, there is an effect which always yields a net increase in the π-nucleus interaction compared with the case $R_\pi = 0$. In the approximation $R_\pi \ll R_{\text{N}}$ the effect of the relative interaction change is easily calculated and equals approximately the changes in nuclear shift and width:

$$\frac{\Delta V}{V_0} \approx \frac{\Delta S}{S_0} \approx \frac{\Delta \Gamma}{\Gamma_0} \approx \frac{2\,l+3}{8} \cdot \frac{R_\pi}{R_{\text{N}}} \tag{1}$$

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