

## Ab-initio Study of Hydrogen Bonded Systems: (H<sub>2</sub>NO...H<sub>2</sub>O)<sup>-</sup> and H<sub>2</sub>NO...H<sub>2</sub>O

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Yonezawa et al.<sup>1</sup> have recently studied hydrogen bonds between radicals and proton donors. The prediction that the binding energy (hydrogen bond energy) is of a magnitude comparable to the value of the normal (closed shell) hydrogen bonded complex has been made on the basis of semiempirical (INDO) calculations. There are some indications<sup>2</sup> that the INDO method overestimates the importance of the hydrogen bond and the aim of this work is to report results of a more sophisticated method. The Hartree-Fock-Roothaan and the unrestricted Hartree-Fock method of Pople and Nesbet<sup>3</sup> were used with the minimal basis set STO-3G of Pople et al.<sup>4</sup> Too large values for the binding energies were obtained in previous calculations (review article ref. 2) using the same minimal basis set. Two hydrogen bonded complexes (H<sub>2</sub>NO...H<sub>2</sub>O)<sup>-</sup> and (H<sub>2</sub>NO...H<sub>2</sub>O) were investigated and only the comparison of them is reasonable. The geometry optimizations of the proton donor (H<sub>2</sub>O) and acceptors (H<sub>2</sub>NO, H<sub>2</sub>NO<sup>-</sup>) were done separately. The constituents were put together at  $\theta = 60^\circ$  (for the molecular scheme cf. Table 2) and the distances O<sub>2</sub>O<sub>4</sub> and O<sub>2</sub>H<sub>3</sub> were varied only. Some sensitive indicators of the hydrogen bond strength are given in Table 1.

Table 1. Binding energies and distances in the hydrogen bonded complexes.

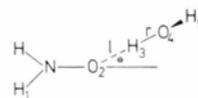
	(H <sub>2</sub> NO...H <sub>2</sub> O) <sup>-</sup>	(H <sub>2</sub> NO...H <sub>2</sub> O)
Binding energy (kcal/mol)	48.04	1.63
R <sub>O<sub>2</sub>O<sub>4</sub></sub> (Å)	2.468	2.695
r <sub>H<sub>3</sub>O<sub>4</sub></sub> (Å)	1.096	0.999

An extreme difference in binding energies is predicted. In the bonded radical the distance *R* corresponds to the values in the closed shell systems of medium hydrogen bond strength. Nevertheless the calculation predicts a very small binding energy. The elongation [*r* - *r*(H<sub>2</sub>O)] is substantial for the

first complex (0.102 Å) and very small (0.005 Å) for the second one. This is in accordance with the other two quantities in Table 1. The results of the population analysis (electronic charge density) are given in Table 2.

Table 2. Electronic charge densities.

	(H <sub>2</sub> NO...H <sub>2</sub> O) <sup>-</sup>	H <sub>2</sub> NO <sup>-</sup>	(H <sub>2</sub> NO...H <sub>2</sub> O)	H <sub>2</sub> NO	H <sub>2</sub> O
N	7.394	7.417	7.317	7.327	—
O <sub>2</sub>	8.498	8.629	8.046	8.055	—
H <sub>3</sub>	0.785	—	0.805	—	0.838
O <sub>4</sub>	8.490	—	8.375	—	8.323
H <sub>5</sub>	0.975	—	0.865	—	0.838
H <sub>1</sub>	0.927	0.976	0.794	0.808	—



A particularly large change of the atomic charge on H<sub>3</sub> from free (H<sub>2</sub>O) to bonded proton is predicted. This change is much larger in the first complex in spite of the fact that the flow of the electronic charge is from (H<sub>2</sub>NO)<sup>-</sup> to H<sub>2</sub>O. In Fig. 1

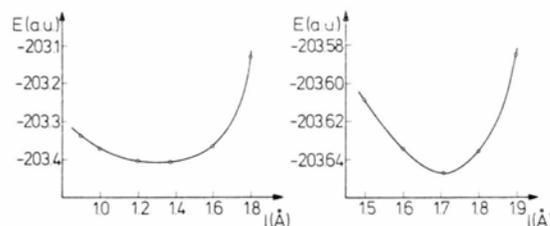


Fig. 1. Potential for the proton vibration in [H<sub>2</sub>NO...H<sub>2</sub>O]<sup>-</sup> and (H<sub>2</sub>NO...H<sub>2</sub>O).

the potential for the proton vibration in both species is given. A great difference in the form of the potentials is observed. One can expect quite different IR (Raman) spectra of both complexes. This can be reflected in the width of the O-H stretching vibrations since the potential of the first complex is much more anharmonic than that of the second one. As a result of this anharmonicity the ratio between the stretching vibrations OH/OD is more different from the ratio of the harmonic oscillator in the first case than in the second one. The second derivative of the potential at the minimum energy (harmonic force constant) is lower for the first complex and there-

fore the OH stretching vibration would be at lower wave numbers than in the hydrogen bonded radical complex.

- <sup>1</sup> I. Morishima, K. Endo, and T. Yonezawa, *Chem. Phys. Letters* **9**, 143 [1971].  
<sup>2</sup> P. Schuster, *Z. Chem.* **13**, 41 [1973].

## Nuclear Magnetic Resonance Studies of <sup>43</sup>Ca

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The ratio of the Larmor frequencies of <sup>43</sup>Ca and <sup>37</sup>Cl has been measured and a magnetic moment for <sup>43</sup>Ca of  $\mu(^{43}\text{Ca}^{2+} \text{ in } \text{D}_2\text{O}) = -1.315645(7) \mu_N$  has been calculated. <sup>43</sup>Ca chemical shifts have been determined in aqueous calcium salt solutions with <sup>43</sup>Ca in natural abundance, also at low concentrations. The latter result is interesting for <sup>43</sup>Ca studies in biological systems.

### Introduction

<sup>43</sup>Ca, the only stable Calcium isotope which can be studied by the NMR-method, has a natural abundance of 0.129%. Therefore there exist no <sup>43</sup>Ca NMR studies in natural abundance, although <sup>43</sup>Ca is an interesting element in biological systems. A few studies in this area were done by Bryant<sup>1</sup> with enriched material.

Jeffries<sup>2</sup> has determined the nuclear magnetic moment of <sup>43</sup>Ca,  $\mu(^{43}\text{Ca}) = -1.3152(2) \mu_N$  by measuring the ratio of the Larmor frequencies of <sup>43</sup>Ca and <sup>2</sup>H in an aqueous solution of CaBr<sub>2</sub> enriched to 68 percent <sup>43</sup>Ca, with a paramagnetic catalyst. With the optical pumping method, Olschewski<sup>3</sup> determined the nuclear magnetic moment on free <sup>43</sup>Ca-atoms; the value is

$$\mu(^{43}\text{Ca}) = -1.31537(60) \mu_N.$$

We have done NMR measurements of naturally abundant <sup>43</sup>Ca in aqueous solutions of CaBr<sub>2</sub>, CaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> and have measured the ratio of the Larmor frequencies of <sup>43</sup>Ca and <sup>37</sup>Cl for calculating a magnetic moment of <sup>43</sup>Ca and for evaluating a shielding constant<sup>4</sup>.

### Experimental

Because of its low natural abundance and the spin  $I=7/2$ , the <sup>43</sup>Ca NMR signal has only a relative sensitivity of  $8.3 \cdot 10^{-8}$  in a 1 molal aqueous solution of CaCl<sub>2</sub> compared with 1 for the proton NMR

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- <sup>3</sup> J. A. Pople and R. K. Nesbet, *J. Chem. Phys.* **22**, 571 [1954].  
<sup>4</sup> W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51**, 2657 [1969].

signal in this solution. This is the reason for the failure of any NMR study in natural abundance. But with the aid of Fourier transform NMR spectroscopy<sup>5</sup> studies of the weak <sup>43</sup>Ca NMR signals in natural abundance are possible within a reasonable time.

The nuclear magnetic resonance signals of <sup>43</sup>Ca at about 5.178 MHz were detected in a highly stabilized field of 1.807 Tesla. For further experimental details see for example Reference<sup>4</sup>. The <sup>43</sup>Ca NMR signals were observed by the QFT method<sup>6</sup>. Figure 1 shows a typical <sup>43</sup>Ca resonance curve of a 7.2 molal

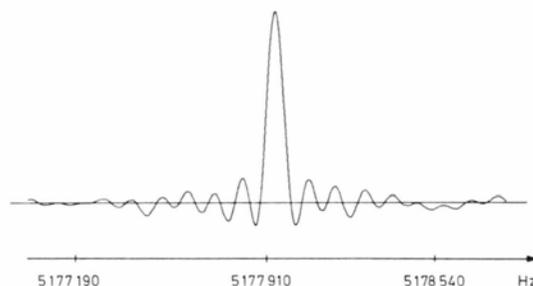


Fig. 1. Absorption curve of <sup>43</sup>Ca in a 7.2 molal CaCl<sub>2</sub> solution in H<sub>2</sub>O at a Larmor frequency of 5.177 944 MHz, measured by the QFT-technique<sup>6</sup>, using a pulse repetition frequency of 90 Hz. Accumulation time: 12 min.

aqueous CaCl<sub>2</sub> solution. Within a measuring time of 48 minutes, a reasonable signal-to-noise ratio was achieved for solutions down to 0.5 molal.

The chemical shifts were measured relatively to an external standard by the sample exchange technique; the NMR signal of <sup>43</sup>Ca in a 7.2 molal solution of CaCl<sub>2</sub> in H<sub>2</sub>O was our external standard. The chemical shift is given by  $\delta = \nu_{\text{sample}} - \nu_{\text{standard}}$ , a negative value means a shift to lower frequency in a constant field. Cylindrical samples of 10 mm diameter were used, no bulk susceptibility corrections were made, since they are smaller than the other errors. The temperature for all the measurements was  $(303 \pm 3) \text{K}$ .

### Chemical shifts of <sup>43</sup>Ca

The dependence of the Larmor frequency of <sup>43</sup>Ca was measured in solutions of CaCl<sub>2</sub>, CaBr<sub>2</sub> and

$\text{Ca}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . Results are given in Figure 2.

The behaviour of the chemical shifts in the chloride and bromide solutions is opposite to that found in corresponding magnesium solutions by  $^{25}\text{Mg}$  NMR studies<sup>7</sup>. The size of the  $^{43}\text{Ca}$  chemical shifts is larger than that of  $^{25}\text{Mg}$ .

Although one must assume that  $^{43}\text{Ca}$  has a quadrupole moment, the size of which is unknown, the linewidths are smaller than 30 Hz for concentrated chloride solutions.

A further result is, that  $^{43}\text{Ca}$  investigations are possible also at low concentrations, which seems to be important for direct studies of calcium environments in systems of biological interest.

*The ratio of the Larmor frequencies of  $^{43}\text{Ca}$  and  $^{37}\text{Cl}$  and the magnetic moment of  $^{43}\text{Ca}$*

In an aqueous solution of  $\text{CaCl}_2$  the ratio of the Larmor frequencies of  $^{43}\text{Ca}$  and  $^{37}\text{Cl}$  (at about 6.275 MHz) was determined. The sample consisted of 41.36 mol%  $\text{D}_2\text{O}$ , 46.92 mol%  $\text{H}_2\text{O}$  and 11.72 mol%  $\text{CaCl}_2$ . The Larmor frequencies were measured alternately in this sample in a constant field only by varying the excitation frequency. On four dif-

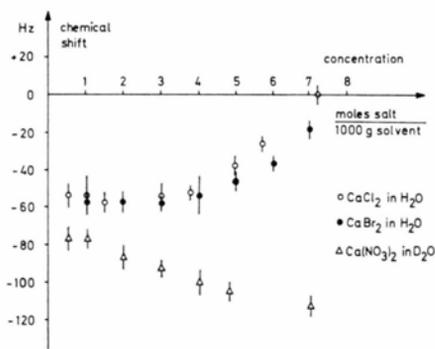


Fig. 2.  $^{43}\text{Ca}$  chemical shifts in aqueous solutions of calcium salts. Negative values are to lower frequencies. Cylindrical probes (10 mm diameter) were used; no bulk susceptibility correction was made, since this correction is smaller than the given errors (standard deviation). Reference solution: 7.2 molal  $\text{CaCl}_2$  solution in  $\text{H}_2\text{O}$ .

ferent days 64 measurements of the ratio were carried out. The result is:

$$\nu(^{43}\text{Ca})/\nu(^{37}\text{Cl}) = 0.825\,175\,3(16).$$

The uncertainty is twice the standard deviation. The linewidth of the  $^{37}\text{Cl}$  signal was 330 Hz, that of  $^{43}\text{Ca}$  was 70 Hz.

Using the ratio  $\nu(^{37}\text{Cl})/\nu(^2\text{H}) = 0.531\,294\,38(4)$  of Blaser et al.<sup>8</sup> measured in a 4.5 molal solution of  $\text{NaCl}$  in  $\text{D}_2\text{O}$ , and taking into account the measured chemical shifts of  $^{37}\text{Cl}$  of +193(10) Hz and of  $^2\text{H}$  of +9(3) Hz between the  $\text{CaCl}_2$  and  $\text{NaCl}$  solution, we get for the used  $\text{CaCl}_2$  solution  $\nu(^{43}\text{Ca})/\nu(^2\text{H}) = 0.438\,424\,2(12)$ . Taking the measured dependence of  $^{43}\text{Ca}$  and  $^2\text{H}$  on the concentration of  $\text{CaCl}_2$  we get the following ratio of the Larmor frequencies for vanishing concentration:

$$\nu(^{43}\text{Ca})/\nu(^2\text{H}) = 0.438\,418\,9(23).$$

From this ratio one can derive a nuclear magnetic moment using  $\nu(^2\text{H})/\nu(^1\text{H}) = 0.153\,506\,083(60)$  of Smaller<sup>9</sup> and the uncorrected magnetic moment of proton in water  $\mu_p = 2.792\,709(17)\mu_N$  of Taylor et al.<sup>10</sup>.

The value of the magnetic moment is

$$\mu(^{43}\text{Ca}) = -1.315\,645(7)\mu_N.$$

This moment is affected by the uncertainty of the magnetic moment of the proton and is not corrected for the ionic diamagnetism. The negative sign results from<sup>2</sup>.

For evaluating the shielding constant<sup>4</sup>  $\sigma^* = 1 - \mu_{\text{NMR}}/\mu_{\text{atom}}$ , the  $\mu_{\text{atom}}$  of Olschewski<sup>3</sup> is used, but the accuracy of this measurement is too low, the only possible result is  $\sigma^*(^{43}\text{Ca}^{2+} \text{ in } \text{D}_2\text{O}) = -0.0002(5)$ .

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<sup>1</sup> R. G. Bryant, J. Amer. Chem. Soc. **91**, 1870 [1969].

<sup>2</sup> C. D. Jeffries, Phys. Rev. **90**, 1130 [1953].

<sup>3</sup> L. Olschewski, Z. Physik **249**, 205 [1972].

<sup>4</sup> O. Lutz and A. Nolle, Z. Naturforsch. **27 a**, 1577 [1972].

<sup>5</sup> A. Schwenk, Z. Physik **213**, 482 [1968].

<sup>6</sup> A. Schwenk, J. Mag. Res. **5**, 376 [1971].

<sup>7</sup> M. M. Ellenberger, and M. Villemin, C. R. Acad. Sci. Paris **B 266**, 1430 [1968].

<sup>8</sup> J. Blaser, O. Lutz, and W. Steinkilberg, Z. Naturforsch. **27 a**, 72 [1972].

<sup>9</sup> B. Smaller, Phys. Rev. **83**, 812 [1951].

<sup>10</sup> B. N. Taylor, W. H. Parker, and D. N. Langenberg, Rev. Mod. Phys. **41**, 375 [1969].