Ab-initio Study of Hydrogen Bonded Systems: 
\((\text{H}_2\text{NO} \ldots \text{H}_2\text{O})^- \text{ and H}_2\text{NO} \ldots \text{H}_2\text{O}\)

J. Koller, M. Kodrič, and A. Ažman

Chemical Institute Boris Kidrič, University of Ljubljana, 
Ljubljana, Yugoslavia

(Z. Naturforsch. 28 a, 1533 - 1534 [1973]; received 18 June 1973)

Yonezawa et al.\(^1\) 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\(^2\) 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\(^3\) were used with the minimal basis set STO-3G of Pople et al.\(^4\). 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 (\((\text{H}_2\text{NO} \ldots \text{H}_2\text{O})^-\) and \((\text{H}_2\text{NO} \ldots \text{H}_2\text{O})\)) were investigated and only the comparison of them is reasonable. The geometry optimizations of the proton donor (\(\text{H}_2\text{O}\)) and acceptors (\(\text{H}_2\text{NO}, \text{H}_2\text{NO}^-\)) were done separately. The constituents were put together at \(\theta = 60^\circ\) (for the molecular scheme cf. Table 2) and the distances \(\text{O}_2\text{O}_4\) and \(\text{O}_3\text{H}_3\) 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.

<table>
<thead>
<tr>
<th></th>
<th>((\text{H}_2\text{NO} \ldots \text{H}_2\text{O})^-)</th>
<th>((\text{H}_2\text{NO} \ldots \text{H}_2\text{O}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy</td>
<td>48.04</td>
<td>1.63</td>
</tr>
<tr>
<td>R_{\text{O}_2\text{O}_4} (Å)</td>
<td>2.468</td>
<td>2.695</td>
</tr>
<tr>
<td>R_{\text{H}_2\text{O}} (Å)</td>
<td>1.096</td>
<td>0.999</td>
</tr>
</tbody>
</table>

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 \([r - r(\text{H}_2\text{O})]\) 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.

<table>
<thead>
<tr>
<th></th>
<th>((\text{H}_2\text{NO} \ldots \text{H}_2\text{O})^-)</th>
<th>((\text{H}_2\text{NO} \ldots \text{H}_2\text{O}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>7.394</td>
<td>7.417</td>
</tr>
<tr>
<td>O_2</td>
<td>8.498</td>
<td>8.629</td>
</tr>
<tr>
<td>O_3</td>
<td>8.490</td>
<td>8.375</td>
</tr>
<tr>
<td>O_4</td>
<td>0.973</td>
<td>0.865</td>
</tr>
<tr>
<td>H_1</td>
<td>0.927</td>
<td>0.976</td>
</tr>
</tbody>
</table>

A particularly large change of the atomic charge on \(\text{H}_2\text{O}\) from free (\(\text{H}_2\text{O}\)) 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 \((\text{H}_2\text{NO})^-\) to \(\text{H}_2\text{O}\). In Fig. 1, the potential for the proton vibration in \([\text{H}_2\text{NO} \ldots \text{H}_2\text{O}]^-\) and \((\text{H}_2\text{NO} \ldots \text{H}_2\text{O})\) 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.


Acknowledgements

The ab initio program was obtained from Dr. W. J. Hehre. The work was supported by the Boris Kidrič Fund.


Nuclear Magnetic Resonance Studies of $^{43}$Ca

O. Lutz, A. Schwenk, and A. Uhl

Physikalisches Institut der Universität Tübingen

(Z. Naturforsch. 28a, 1534—1535 [1973]; received 21 July 1973)

The ratio of the Larmor frequencies of $^{43}$Ca and $^{37}$Cl has been measured and a magnetic moment for $^{43}$Ca of $\mu (^{43}\text{Ca}) = -1.3156 (7) \mu_N$ has been calculated. $^{43}$Ca chemical shifts have been determined in aqueous calcium salt solutions with $^{43}$Ca in natural abundance, also at low concentrations. The latter result is interesting for $^{43}$Ca studies in biological systems.

Introduction

$^{43}$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 $^{43}$Ca NMR studies in natural abundance, although $^{43}$Ca is an interesting element in biological systems. A few studies in this area were done by Bryant with enriched material.

Jeffries has determined the nuclear magnetic moment of $^{43}$Ca, $\mu (^{43}\text{Ca}) = -1.3152 (2) \mu_N$ by measuring the ratio of the Larmor frequencies of $^{43}$Ca and $^2\text{H}$ in an aqueous solution of $\text{CaBr}_2$ enriched to 68 percent $^{43}$Ca, with a paramagnetic catalyst. With the optical pumping method, Olschewski determined the nuclear magnetic moment on free $^{43}$Ca-atoms; the value is $\mu (^{43}\text{Ca}) = -1.315 (37) \mu_N$.

We have done NMR measurements of naturally abundant $^{43}$Ca in aqueous solutions of $\text{CaBr}_2$, $\text{CaCl}_2$ and $\text{Ca(NO}_3)_2$ and have measured the ratio of the Larmor frequencies of $^{43}$Ca and $^2\text{H}$ for calculating a magnetic moment of $^{43}$Ca and for evaluating a shielding constant.

Experimental

Because of its low natural abundance and the spin $I=7/2$, the $^{43}$Ca NMR signal has only a relative sensitivity of $8.3 \cdot 10^{-8}$ in a 1 molal aqueous solution of $\text{CaCl}_2$ compared with 1 for the proton NMR signal in this solution. This is the reason for the failure of any NMR study in natural abundance.

The nuclear magnetic resonance signals of $^{43}$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 4. The $^{43}$Ca NMR signals were observed by the QFT method. Figure 1 shows a typical $^{43}$Ca resonance curve of a 7.2 molal aqueous $\text{CaCl}_2$ 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 $^{43}$Ca in a 7.2 molal solution of $\text{CaCl}_2$ in $\text{H}_2\text{O}$ 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 $^{43}$Ca

The dependence of the Larmor frequency of $^{43}$Ca was measured in solutions of $\text{CaCl}_2$, $\text{CaBr}_2$ and...
Ca(NO₃)₂ in H₂O and D₂O. 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 ²⁵Mg NMR studies ⁷. The size of the ⁴³Ca chemical shifts is larger than that of ⁵⁵Mg.

Although one must assume that ⁴³Ca 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 ⁴³Ca 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 ⁴³Ca and ³⁷Cl and the magnetic moment of ⁴³Ca

In an aqueous solution of CaCl₂ the ratio of the Larmor frequencies of ⁴³Ca and ³⁷Cl (at about 6.275 MHz) was determined. The sample consisted of 41.36 mol% D₂O, 46.92 mol% H₂O and 11.72 mol% CaCl₂. The Larmor frequencies were measured alternately in this sample in a constant field only by varying the excitation frequency. On four different days 64 measurements of the ratio were carried out. The result is:

\[ \nu(⁴³Ca)/\nu(³⁷Cl) = 0.825 175 3(16). \]

The uncertainty is twice the standard deviation. The linewidth of the ³⁷Cl signal was 330 Hz, that of ⁴³Ca was 70 Hz.

Using the ratio \( \nu(³⁷Cl)/\nu(²H) = 0.531 294 38(4) \) of Blaser et al. ⁸ measured in a 4.5 molal solution of NaCl in D₂O, and taking into account the measured chemical shifts of ³⁷Cl of +193(10)Hz and of ²H of +9(3)Hz between the CaCl₂ and NaCl solution, we get for the used CaCl₂ solution \( \nu(⁴³Ca)/\nu(²H) = 0.438 424 2(12) \). Taking the measured dependence of ⁴³Ca and ²H on the concentration of CaCl₂ we get the following ratio of the Larmor frequencies for vanishing concentration:

\[ \nu(⁴³Ca)/\nu(²H) = 0.438 418 9(23). \]

From this ratio one can derive a nuclear magnetic moment using \( \nu(²H)/\nu(³H) = 0.153 506 083(60) \) of Smaller ⁹ and the uncorrected magnetic moment of proton in water \( \mu_p = 2.792 709(17) \mu_N \) of Taylor et al. ¹⁰.

The value of the magnetic moment is

\[ \mu(⁴³Ca) = -1.315 645(7) \mu_N. \]

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 ².

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

Acknowledgement

We like to thank Prof. Dr. H. Krüger for his continuous support of this work. We are indebted to Dipl.Phys. A. Nolle for helpful discussions. We thank the Deutsche Forschungsgemeinschaft for the financial support.

---

5. A. Schwenk, Z. Physik 213, 482 [1968].

⁹ B. Smaller, Phys. Rev. 83, 812 [1951].