

Density Functional Theory Calculation of Adsorption of NaCl on Chlorophyll

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ABSTRACT We have calculated the vibrational frequencies of chlorophyll-a, chlorophyll-a + 1 NaCl and chlorophyll-a + 2 NaCl from the first principle. We are able to find the vibrational frequencies as well as the structural parameters in all of the three cases. The Mg atoms are found to absorb Na atoms which distort the structure. The vibrational frequencies calculated for the chlorophyll-a are in reasonable agreement with those found from the Raman Spectra.

(Chlorophyll, density functional, Raman spectra of chlorophyll)

INTRODUCTION

The “chloro” in chlorophyll means colour and “phyl” means a leaf. It looks green to the human eye but it does not have a green band in the energy level diagram. The leaves appear green every where except when they become old when they look yellow or red. As the cold weather starts, the green leaves change to yellow and red before dropping. One Mg ion is found in the centre of a porphyrin group in the chlorophyll and there is a long phytol chain. The Mg ion uses the light energy to synthesize the molecules. If one of the terminating groups is CH₃ it is called a-form and when this CH₃ is replaced by CHO, it is called b-form. In the a-form, there are two strong absorption bands one at 430 nm (blue) and the other at about 642 nm (red). In the b-form they are shifted to 453 nm and 642 nm. The fluorescence occurs at 673 nm. The frequencies depend on the method of extraction, in particular, on the solvent used to extract chlorophyll from the leaf.

The red colour in the blood is due to heme group which has Fe ion, the breathing process is to change the Fe ions by means of oxygen absorption. Hence the importance of oxygen absorption is quite different from the absorption of light in plants. Some time ago, Amru Boyce [1] has prepared assays to characterize the oxidative cyclise that synthesizes the chlorophyll. We refer the reader to the “Amru

method” for the preparation of the actual material. The absorption of light from 6800Å till 4250Å is given by Mackinney [2]. The vibrational equilibration is reported by Struve [3]. A very detailed Raman study is given by Diers et al [4]. The data are very rich in absorption lines. There are a lot of peaks in the vibrational Raman spectra which give information about the peculiarities of the molecular structure. The vibrations are very complicated and require a detailed study.

In this paper, we simulate the chlorophyll-a structure by using the density-functional theory so that as a first step we optimize the molecule and determine the Mg-N distance for which the energy of the quantum mechanical Schrodinger equation is a minimum. The actual molecule has the formula C₅₅H₇₂O₅N₄Mg, which has 137 atoms including 482 electrons. The secular determinant of the size of 482 x 482 is indeed too large for us to solve. Hence we eliminate the phytol part which is far away from Mg and consider only C₃₈H₃₄O₅N₄Mg part of the molecule which has 82 atoms containing 342 electrons. This problem is tractable by our duo Pentium which takes about 10 days to optimize one configuration, which has 342 x 342 secular determinant. We are interest in obtaining the absorption of NaCl on the Mg site. Hence we perform two more optimizations, one with chlorophyll-a with one molecule of NaCl and another with one chlorophyll with two molecules

of NaCl. In all of the three calculations, the structure is determined along with the vibrational spectra. We are therefore able to predict the distance between Na and Mg atoms and show all of the vibrations. It is thus possible to calculate the vibrational frequencies which are indeed very exhaustive and give information about the vibrations in the molecules including those with NaCl absorbed. Our programme takes into account that Na^+ and Cl^- exist and NaCl is electrically neutral.

Theory.

The density-functional theory makes it possible to solve the Schrodinger equation for a large number of electrons on a large number of atoms [5]. The present problem has 342 electrons on 5 atoms identified by the atomic numbers, 1, 6, 7, 8 and 12 (H, C, N, O and Mg). The Schrodinger equation requires the kinetic energies of all of the electrons and that of all of the nuclei. The potential energy consists of the repulsive Coulomb forces between nuclei, electrons and the attractive forces between electrons and nuclei. In short we can write the Schrodinger equation as,

$$\left[\frac{1}{2} \nabla^2 - \sum_n \frac{Z_n}{|r-R_n|} + \int d^3r' n(r') \frac{1}{|r-r'|} + V_{xc}[n](r) \right] \psi_k(r) = \epsilon_k \psi_k(r)$$

where $n(r)$ is the electron density which depends on the coordinates. The computer program solves this equation and provides the energy values as well as the bond angles for which the energy is a minimum. We have made considerable effort to obtain energies as well as vibrational frequencies in several systems. The calculated values are in reasonable agreement with the experimental values deduced from the Raman spectra [6-10].

Calculated Structures and Vibrations.

A model of chlorophyll-a without the phytol is shown in Fig. 1. It has $\text{MgO}_5\text{N}_4\text{C}_{38}\text{H}_{34}$ atoms.

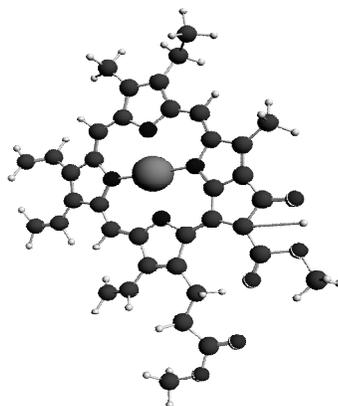


Fig. 1. A model of chlorophyll-a without the phytol

After the secular equation of the size 342x342 is solved and energy minimized, it is found that Mg-N distance is 201.1 picometer at one bond and 198.0 pm at the other. Hence MgN_4 is not a perfect square. When it is smallest the calculated value of 1.98Å is indeed very reasonable. The total binding energy is -549.5 eV for 342 electrons which shows strong binding of Mg with nearest N atoms. The vibrational spectrum calculated by using the density-functional theory is shown in Fig. 2. All of the vibrational peaks have only positive energies. A few weak lines are seen near negative energies which show that there are bound states in addition to free oscillations.

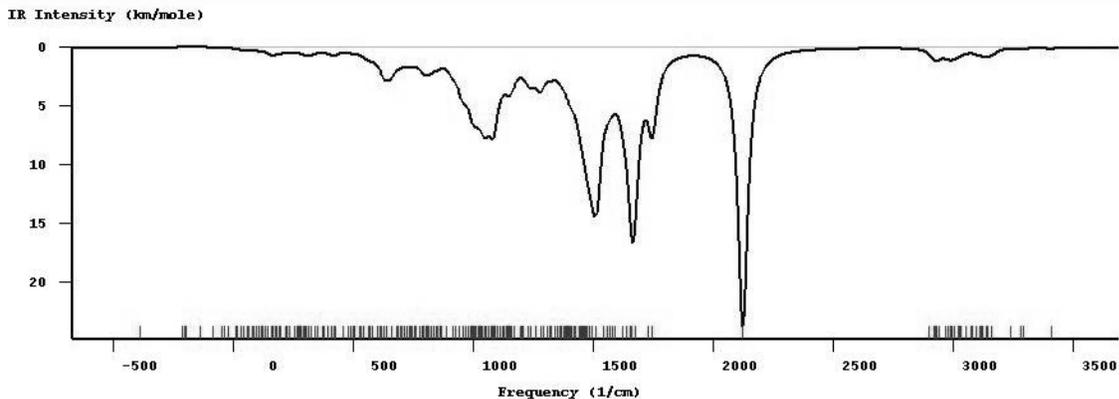


Fig. 2: The vibrational frequencies of the chlorophyll-a without the phytol

We adsorb one NaCl molecule on $\text{MgO}_5\text{C}_{38}\text{H}_{34}$ molecule near the Mg site. We find that the optimized distance are Mg – Na 352.4 pm, Cl – Na 285 pm, Mg – N 228.0 pm and Mg – N' 230 pm. Thus we see that the effect of NaCl is to change the Mg – N distance from 198 pm to 228 pm. Therefore we see that $2.28 - 1.98 = 0.3 \text{ \AA}$ is the displacement of Mg atom. The chlorophyll-a is thus considerably modified by absorption of NaCl. The leaves which are more salty have therefore slightly different structural parameters than these which are more salty. The structure of the chlorophyll is thus influenced by the salt. The bond energy of the chlorophyll with one NaCl is -492.6 eV which is less than the value without NaCl. The optimized structure with one NaCl is given in Fig. 3. The vibrational spectrum is shown in Fig. 4. Now for the negative frequencies, some amplitudes are clearly visible.

We make an effort to adsorb 2 NaCl molecules on $\text{MgO}_5\text{N}_4\text{C}_{38}\text{H}_{34}$ near the Mg site. In this case it is seen that NaCl adsorb near the Mg site and distort the Mg-N bond. The optimized bond lengths are now Mg – Na 379.2 pm, Cl – Na 283.9 pm, Mg – N 226.3 pm and Mg – N' 228.5 pm. The Mg – Na distance is 589.1 pm and Cl – Na 284.0 pm. One of the NaCl is nearer to Mg than the next one by a small distance. One of the Cl – Na and the other Cl – Na' are off by $2.84 - 2.839 \text{ \AA}$. First one Mg – NaCl is formed and then the next NaCl is slightly differently interacting. In this case the bonding energy is found to be -526.6 eV which shows the character of bonding. The system with 2 NaCl is shown in Fig. 5. The vibrational spectrum calculated from the first principles is shown in Fig. 6.

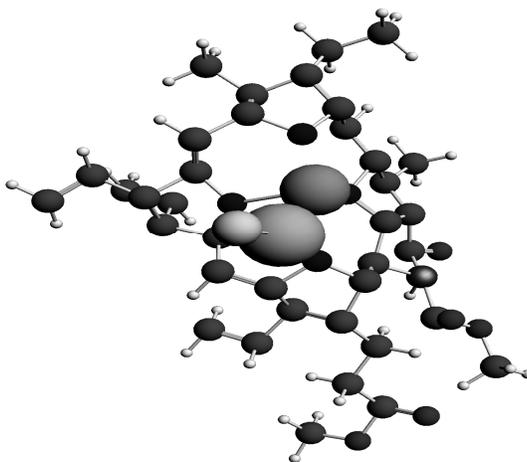


Fig. 3: A model of chlorophyll-a with 1 NaCl.

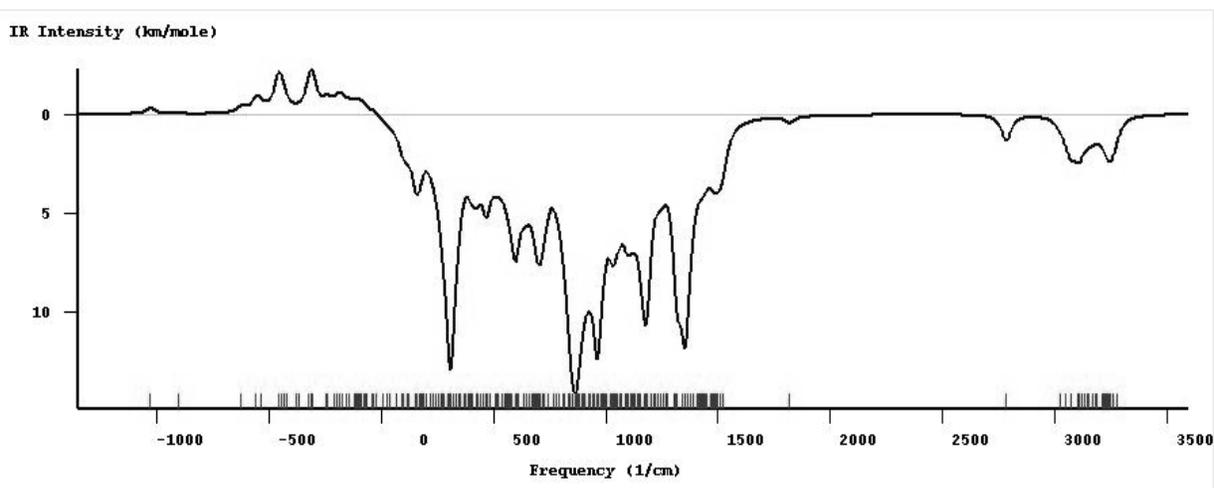


Fig. 4: A vibrational spectrum of chlorophyll-a with 1 NaCl calculated using first principle.

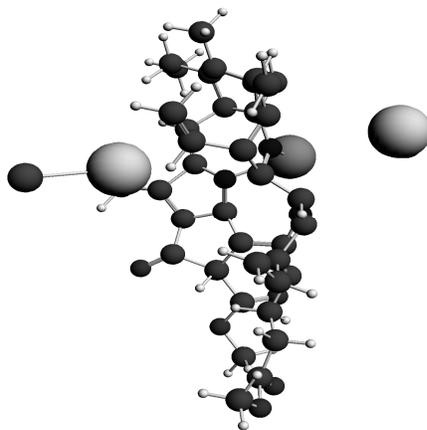


Fig. 5: A model of chlorophyll-a with 2 NaCl

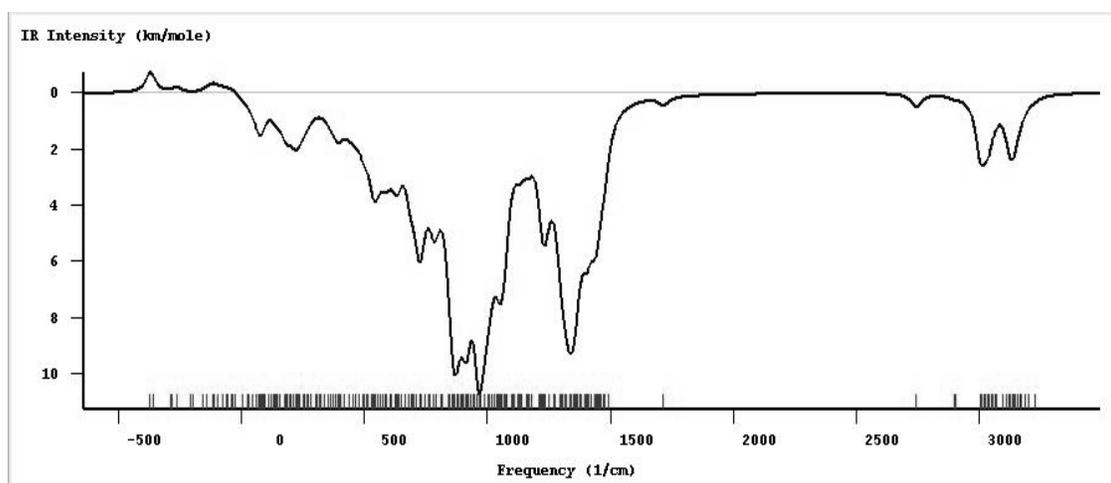


Fig. 6: A vibrational spectrum of chlorophyll-a + 2NaCl calculated by using first principles

Experimental Raman of Chlorophyll-a.

The experimental measurement of the resonant Raman spectra of chlorophyll-a have been performed by Diers et al [4]. We also show the experimental Raman spectra of Chlorophyll-a in Fig. 7. The experimentally found peaks are at 101, 130, 211, 260, 356, 390, 409, 476, 519, 546, 562, 569, 585, 605 and 643 cm^{-1} . The temperature of measurement is about 15K and the excitation used is 647 nm. Most of the measured frequencies are very near those calculated by us as given in Fig. 1.

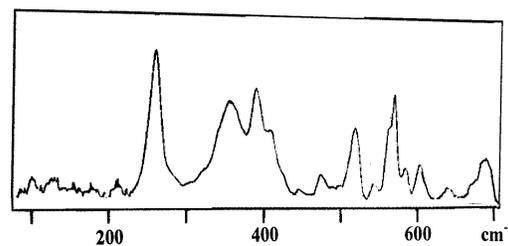


Figure 7: The experimental Raman spectra of Chlorophyll-a. It helps to compare the calculated values with the experimental data.

CONCLUSION

We have calculated the vibrational frequencies of Chlorophyll-a with one NaCl molecule as well as with two NaCl molecules. We find that the structure is modified by NaCl molecules. We also calculated the vibrational spectra of pure chlorophyll-a which is compared with that deduced from the experimental Raman spectra. The calculated values agree well with those measured. Although there are several studies of biological molecules[11,12], we are able to diagonalize the secular determinant of a very large number of electrons as presented in this work.

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