# Second Moment Simulations for Different Models of Rotations and Oscillations in Polycrystalline Thiourea Pyridinium Nitrate Inclusion Compound and its Two Perdeuterated Analogues

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The second moment of $^1$H NMR absorption spectra was calculated for three samples of $[(NH_2)_2CS]_2(C_5H_5NH)^+NO_3^-$, two of which were deuterated at different positions. The calculations were performed for different rotations and oscillations, and for a wide range of frequencies of these motions. These frequencies were then transformed into temperatures resulting in the temperature dependence of the second moment. The calculations were undertaken in order to analyze the experimental results obtained in our laboratory. Special attention was paid to molecular reorientations through unequal potential barriers. Comparison of the second moment values calculated for different models of rotation with the experimental ones enabled a deeper insight into the internal motion in this material as a function of temperature.

*Key words:* NMR; Second Moment; Simulation; Internal Reorientation; Inclusion Compounds.

## 1. Introduction

The second moment of the proton NMR absorption spectra of the polycrystalline thiourea pyridinium nitrate inclusion compound $[(NH_2)_2CS]_2(C_5H_5NH)^+NO_3^-$ and its two deuterated analogues was calculated on the basis of the Van Vleck [1] formula. Crystallographic data required for such calculations were obtained at our institute and will be published separately [2]. The experimental values of the second moment of these compounds were measured in our laboratory and were published in [3].

For clarity and simplicity of the description the names of the compounds in question were abbreviated as follows:

$T_2(PyH)NO_3$: compound without deuterons, $T_2(d_5PyH)NO_3$: with deuterons in the pyridinium ion (proton attached to nitrogen), $d_8T_2(PyD)NO_3$: with thiourea molecules deuterated and one deuteron attached to nitrogen in the pyridinium ion.

Some introductory analysis of the experimental second moment calculated from the proton NMR absorption spectra is present in an already published paper [3], but the necessity of a more quantitative consideration was mentioned there. In order to continue this work, we performed calculations of the second moment for each of the samples measured. The calculations, based on the crystallographic data, were performed for the rigid structure of these compounds and for a few different models of rotations and oscillation of groups of atoms constituting these compounds. This type of calculation is often called a computer experiment, because one simulates the internal dynamics of the studied compound and evaluates parameters which can be measured in a real experiment.

These types of studies by means of a computer experiment are increasingly popular, because they allow for nearly unlimited changes of the experimental conditions. There is no problem in simulating very high or very low temperatures or pressures or any other "experimental" conditions.

A general description and theoretical basis of the computer experiment in the field of studying the internal dynamics by the NMR second moment is presented in [4]. A computer program which allows the implementation of such an experiment was published recently [5]. This program and its modification allowing simulation of self-diffusion was used to analyze NMR experimental results obtained in two different Laboratories [6, 7].

Analytical calculation of the second moment whose value is averaged by internal motion of molecules or ions is possible only for a few very simples cases, simple from the point of view of the geometry of the aver-

aged motion. On the other side, numerical calculations based on the Van Vleck formula can be performed for any type of reorientations without any restrictions as to the model and geometry of rotation. The only limitation of such simulations may be the available computing power, but as pointed in published papers [5 – 7] this is not the case for these types of calculations.

Such a procedure of a computer experiment was applied to the three compounds measured previously [3] in our laboratory. Different models of internal dynamics were considered, and the Van Vleck second moment was calculated for every model as a function of the frequency of this motion as well as for different amplitudes, in case of oscillations of groups of atoms. Comparing results obtained from calculations with experimental ones allows for reasonably good assignment of models of motion to different temperature ranges. The results of these assignments will be presented in this paper.

## 2. Possible Models of Internal Motions

To start the computer experiments, that is the calculations of the second moment based on the Van Vleck formula, we must define the conditions for these calculations. In this case the calculations must be performed for different models of internal motions. Therefore all possible models of such motions have to be defined.

From the point of view of the symmetry of our three modifications (due to deuteration) of the studied compounds, there are three types of motion possible. We denote them by *m1*, *m2*, and *m3*, and define them as follows:

*m1*: reorientation of the pyridinium ion about the pseudo hexagonal axis $C_6'$, *m2*: reorientation of thiourea about the axis passing through sulfur and carbon atoms, *m3*: reorientation of $NH_2$ groups about the axis passing through carbon and nitrogen atoms.

Preparing our computer experiments we assumed different modifications for each type of reorientation.

For *m1* reorientation we decided to consider the model of motion *m1_f*: full rotation by random jumps $+/-60$ degrees.

Preliminary calculations of the second moment as well as the calculation of the potential barrier as a function of the angle of rotation about each axis showed that *m2* reorientation, if only possible, may occur according to model *m2_angle* with the value of the angle below 4 degrees. So, for *m2* reorientation we expected only "thermal oscillations" by rather small angles ($< 10$ degrees). The corresponding models of motion were denoted *m2_angle*, where for *angle* we substituted the value used in numerical calculation.

For *m3* reorientation we assumed the following models:

*m3_f*: full rotation by random jumps by arbitrary chosen steps expressed in degrees, *m3_angle*: "thermal oscillations" by angles smaller than 90 degrees.

Here we used the rather non standard expression "thermal oscillation", by which we mean the motion which geometrically looks like oscillation, but it is of random nature, thermally activated. That is, the frequency of jumps $\nu_c$ increases with increasing temperature according to Arrhenius relation

$$\nu_c = \nu_0 \exp(-E_a/RT),$$

where $E_a$ is the activation energy.

The assumption that the frequency increases with temperature is necessary to get a continuous decrease of the calculated Van Vleck second moment with increasing temperature as observed in the experiment. The classical oscillations with well defined frequency would not give such a result. The onset of such oscillations would result in a stepwise decrease of the second moment, if only the frequency of this oscillation was higher than the NMR absorption line width [8].

### *2.1. Rotation through Unequal Potential Barriers*

Due to the departure from the pseudo $C_6$ symmetry of the pyridinium ion, the barriers hindering the rotation about the pseudo hexagonal $C_6'$ axis are expected to be unequal. The analysis of the experimental results [3] confirms such a suggestion. Unequal potential barriers must be assumed to explain experimental results in the temperature region 100 K to 280 K.

We assign numbers 1 to 6 to each possible position of the pyridinium ion, the 1 corresponding to the position given by crystallographic studies, when the ion is in the equilibrium position. This situation is depicted in Figure 1. The difficulty with this situation is how to construct an algorithm which allows simulation of rotation through unequal barriers. With thermally activated rotational jumps, the pyridinium ions taking positions 2 to 6 are equally probable, and the probability of being in position 1 is higher. The difference in these probabilities depends on the difference in barrier heights between position 1 and positions 2 to 6.

An in depth analysis of the influence of the unequal height of the potential barriers hindering the

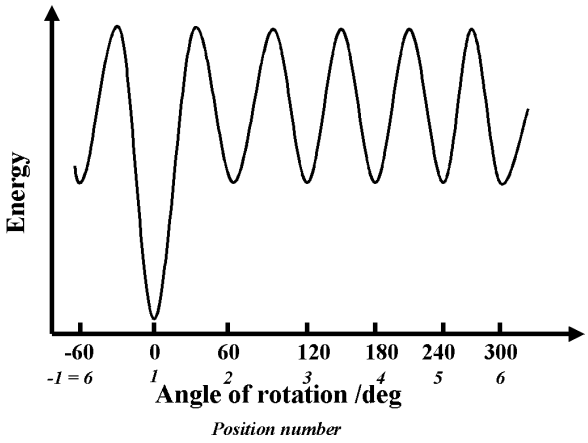

Fig. 1. The shape of the potential barriers.

pyridinium ion rotation leads to the conclusion that the average frequency of rotation will decrease with the increase of the "inequality" of the barriers. This isn't quite surprising, but the problem is how to incorporate this decrease into an algorithm used to simulate rotation and calculate the Van Vleck second moment. Two methods of achieving this aim were tested "experimentally", that is, introduced into an algorithm, incorporated into the computer program and the second moment values calculated with such modifications of the program were compared with the experimental ones.

### *2.2. Algorithm 1*

First we assign different probabilities of jumps to the different positions of the pyridinium ion. Denoting the probabilities of leaving positions 2 to 6 as $P_{2-6}$, and the probability of leaving position 1 as $P_1$, we can simulate an increase of the height of the barrier in position 1 by making the ratio $P_{2-6}/P_1$ greater than 1.0. For clarity of the program we set probabilities

$$P_{2-6} = 1.0 \tag{1}$$

and

$$P_1 < 1.0 = 1.0/N_{not}, \tag{2}$$

where $N_{not}$ is the average number of not successful attempts to perform a jump before the jump occurs. $N_{not}$ must be an integer. $P_{2-6} = 1$ means that each attempt to perform a jump is successful. The algorithm to perform jumps through unequal barriers is as follows:

1. The pyridinium ion which should jump is randomly chosen by a program procedure.

2. If the ion pointed to by this procedure is in one of the positions 2 to 6, it will be rotated to the neighboring position, left or right (also chosen randomly).

3. If the ion is in position 1, then the random number $N_r$ from the range between 1 and $N_{not} + 1$ will be generated. – If $(N_r = or > N_{not})$ a jump is performed. – If $(N_r < N_{not})$ no jump is performed, the next ion is chosen for a jump.

This algorithm results in performing only 1 jump per $N_{not}$ attempts if the ion was in position 1, that is in the deeper potential well. We use the words "random number", but actually we are dealing with "pseudo random" numbers, because they are generated by computer program. This is a separate problem, but for our calculations these pseudo random numbers fulfill the requirements of being random, we will not devote more space and time to this problem.

The simulation of the Van Vleck second moment with this algorithm happened to be unsuccessful in fitting the experimental values for these compounds. Even at the "highest temperatures" simulated, the second moment did not decrease to the experimental value, averaged by thermal motion. The conclusion is obvious – this algorithm did not properly represent the internal dynamics in this compound.

We carefully analyzed the intermediate results of calculation with the above described algorithm. A special subroutine counted how many pyridinium ions where in each position after every complete cycle of jumps. As a complete cycle of jumps we defined the completion of all reorientations for a given number of jumps (then recalculated into a particular temperature) of all pyridinium ions in a block of unit cells. From this analysis we got information that our algorithm reflecting the unequal barriers hindering the rotation, results in the dependence of the average abundance of each position (1 to 6) of the pyridinium ion on the height of the potential wall around the given position. In other words, this algorithm created something like two substructures: one with all pyridinium ions in position 1 (the highest potential walls), the second with pyridinium ions equally distributed between positions 2 to 6.

Regardless of the conclusions that can be drawn from the above analysis. The algorithm did not allow the reproduction of experimental results. The decrease of the calculated second moment values was slower compared to the decrease of the second moment calculated for equal barriers, and this is in agreement with the experiment. The calculated values did not, how-

ever, go down to the experimental value determined at the highest temperature. Summarizing:

• The assumption of equal barriers gives calculated second moment values that decrease more rapidly than the experimental ones, but the final calculated and experimental values are in good agreement.

• Introducing unequal barriers through algorithm 1 described above gives calculated second moment values that decrease as the experimental ones at the low temperature side, but the high temperature plateau is higher than the experimental one.

### *2.3. Algorithm 2*

We looked for another algorithm which could better reflect the experimental temperature dependence of the second moment. After analyzing many possibilities we ended up with a simple decreasing of the average frequency of reorientation with increasing of the inequality of the barriers hindering reorientation of the pyridinium ions. Such an algorithm may be justified by the stochastic nature of the thermally activated reorientations. A more detailed justification for such an algorithm is given below.

Averaging of the dipole-dipole interaction which leads to the decrease of the NMR second moment takes place during time intervals of the same order as the inverse of the NMR absorption line width. This time is approximately equal to the time of the decrease of the Free Induction Decay signal [8] to the level of noise. This time for the NMR signals on protons in typical solids is of the order of microseconds, usually from 20 $\mu$s to 100 $\mu$s. Let's assume it to be $6 \times 10^{-5}$ s. The average time between jumps of the reorienting molecule $\tau_c = 1/\nu_{ic}$, where $\nu_{ic}$ is the frequency of molecular reorientation, also known as a correlation frequency. The averaging of dipole-dipole interactions starts when the correlation frequency $\nu_{ic}$ is of the order of the line width for the rigid structure [4, 8], that is of about $1 \times 10^{-5}$ s$^{-1}$. When the averaging is effective enough to decrease the second moment to the value corresponding to the center of the slope on the $M2 = f(T)$ graph, the correlation frequency is a few orders of magnitude higher ($10^7$ to $10^8$ s$^{-1}$) as it increases exponentially with the temperature. With such aghast rate of jumps of molecules or ions, "stopping" for a moment at the position of the deepest potential well does not influence averaging at this particular instant of time, but can be seen as slowing down the average correlation frequency by a factor depending on the barriers inequality, that is how much deeper the barrier in position 1 is.

On the basis of the above reasoning we came to the conclusion, that the barriers' inequality may be taken into account by introducing the numerical factor $N_{sl}$, which will slow down the reorientation of the pyridinium ions. The algorithm which will perform such a slowing down is very simple.

The number of jumps given as input is $N_j$ and this number will then be used to recalculate the number of jumps at the corresponding temperature [6], but the number of jumps performed by the pyridinium ions during the calculation is reduced by $1/N_{sl}$. We introduce this algorithm into the computer program, and some preliminary calculations show that we can reproduce the experimental dependence of the second moment on the temperature in a satisfactory way. The values of the second moment calculated with this algorithm decreased more and more slowly with temperature as the slowing factor $N_{sl}$ was increased. And, what is important, the final (at the highest temperatures) values of the calculated second moment were very close to the experimental ones. There was no effect of the dependence of the calculated high temperature plateau on the barriers' inequality introduced by this algorithm, as there was, when calculations were performed, with algorithm 1.

The problem is that we were fitting calculated values of the second moment to the experimental ones choosing the slowing factor $N_{sl}$ with a trial-and-error method. We really did not find a reasonably justified dependence between the $N_{sl}$ and the inequality of the barrier in position 1. This would require a number of calculations for specially modelled potential barriers, and we intend to do this as the next step on our path to in depth interpretation of experimental NMR data.

## 3. Computer Simulations of the Second Moment for Different Models of Internal Motion

As the first step of our simulations the Van Vleck second moment was calculated for the rigid structure of the studied compound and its perdeuterated analogues. The term "rigid structure" in the solid state NMR terminology means that any possible internal reorientations occur with the average frequency much lower than the NMR absorption line-width for an absolutely rigid structure [8].

In Table 1 experimental and calculated values of the second moment for the rigid structure are given. The

Table 1. The experimental and calculated values of the second moment for the rigid structure.

| | $M_2$ [$G^2$] experimental ($T = 100$ K) | $M_2$ rigid [$G^2$] calculated |
|---|---|---|
| $T_2(PyH)NO_3$ | 13.9 | 13.7 |
| $T_2(d_5PyH)NO_3$ | 15.6 | 15.8 |
| $d_8T_2(PyD)NO_3$ | 3.6 | 3.4 |

experimental values were determined at 100 K, which is the lowest temperature available in our spectrometer. The error in experimental values of second moment is about $+/-4\%$. The calculated values can be reproduced in subsequent runs of the simulating program with accuracy better than $+/-1\%$, but the absolute values of the calculated second moment depend on the accuracy of the structure parameters from X-ray studies. We estimated the final error for calculated values to be less than $+/-4\%$.

### *3.1. Motion of Pyridinium Ion – m1_f*

Only the motion of the type *m1* was considered. The best situation for the analysis is presented by the sample $d_8T_2(PyD)NO_3$, because the observed NMR spectrum is due only to protons in the pyridinium ion and those ions are well separated by deuterated thiourea molecules. Therefore the motion of these ions is the only reason of the NMR second moment changes.

Previous analysis of the experimental data [3] suggests that in phase II and III (see Fig. 2 in this paper) reorientation occurs through unequal potential barriers. At the highest temperature of our measurements in phase I the analysis from paper [3] suggests symmetrical barriers. Simulation of the NMR second moment for the case of equal potential barriers was discussed and presented in [4, 6], but simulations for unequal barriers are presented by us for the first time in this paper.

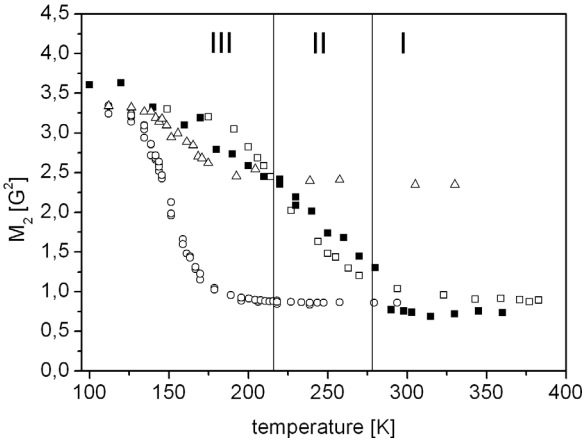


Fig. 2. The experimental (■) and calculated second moment: (○) $M_2$ for equivalent barriers; (△) $M_2$ for unequal barriers – algorithm 1; (□) $M_2$ for unequal barriers – algorithm 2.

Table 2. The experimental and calculated values of the second moment for the pyridinium ion reorientation followed by $NH_2$ group motion.

| | Averaged $M_2$ [$G^2$] $T_2(PyH)NO_3$ | $T_2(d_5PyH)NO_3$ |
|---|---|---|
| Experimental at $T = 360$ K | 4.5 | 6.6 |
| Reorientation of pyridinium ion + – $NH_2$ group flip-flop motion | 9.9 | – |
| Reorientation of pyridinium ion + – $NH_2$ oscillations ($+/-15$ deg) | 6.3 | – |
| Reorientation of pyridinium ion + – $n$-fold reorientation of $NH_2$ group ($n = 4$) | 4.3 | 4.9 |
| Reorientation of pyridinium ion + – $NH_2$ oscillations ($+/-45$ deg) | 5.0 | 6.1 |

From Fig. 2 it is evident that simulating the second moment assuming equal barriers hindering reorientation gives a temperature dependence of the second moment completely different form the experimental one. Simulation of the second moment assuming unequal barriers and applying described previously algorithm 1 is also unsuccessful, we cannot reach the value of the high temperature plateau.

Finally, the calculations based on algorithm 2 give a simulated temperature dependence of the second moment in good agreement with the experimental one. The problem is that the numerical factor $N_{sl}$, which decreases the effective frequency of reorientation, must be chosen by a trial and error method. We are in the process of extensive simulation of the second moment for well defined, simple structures to determine the relation between the inequality of potential barriers and this numerical factor $N_{sl}$. At this point we can only state that our simulations confirm the inequality of barriers hindering the reorientation of pyridinium ions.

### *3.2. Motion of Thiourea*

Simulations of the second moment were performed for two samples: $T_2(PyH)NO_3$ and $T_2(d_5PyH)NO_3$ (Table 2). The measured NMR second moment is due to the dipole-dipole interactions between all protons in the sample. Therefore results for the first sample $T_2(PyH)NO_3$ are more difficult to interpret, as protons in the pyridinium ion mask the dependence of the second moment on temperature due to protons in thiourea. The second sample $T_2(d_5PyH)NO_3$ with only one pro-

ton left in the pyridinium ion constitutes a much better structure for studying the influence of thiourea motion on the second moment.

The simulations were performed for all temperatures at which the second moment was experimentally determined, that is for the whole range of frequencies of jumps corresponding to these temperatures. The analysis based on the comparison of the calculated values with the experimental ones was done only for the highest temperatures, as scaling such a complex type of rotations into temperatures for the whole range of numbers of jumps seems too unambiguous.

The motion of the previously defined *m2* type (about the S-C axis) must be excluded from the analysis because, as already mentioned in point 2, the crystal structure does not allow for oscillations with amplitudes larger than 2 degrees. Thermal oscillations with such a small amplitude result in a decrease of the Van Vleck second moment by less than one half percent. The error in the experimentally determined second moment is about $+/-4\%$, far above the calculations error. Nevertheless, this model of motion was included in our calculation for rigorous consideration of all motions and for checking the possibility of mutual interactions between different types of motion.

The *m3* type of reorientation of the $NH_2$ groups is not prohibited, at least from the structure point of view. Different modifications of this type of motion were used in simulations and we found that reorientation of the type *m_45*, that is thermal oscillations about the C-N axis by $+/-45$ degrees gives the best agreement between the experimental and simulated temperature dependence of the second moment.

## 4. Conclusions

With the computing power available to scientist growing very rapidly, all kinds of so called computer experiments seem to be increasingly promising. They allow not only very deep analysis of experimental data, but can often be used for "studies under experimental conditions" that are very difficult to obtain in a laboratory.

The results of our numerical simulations seem to add valuable information not available by other means, in this case by analytical calculations.

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