

# A study on the molecular aspects of ignition in energetic materials through simplified means

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## 1 Introduction

One of the most sought parameter in the field of energetic materials is the burning rate of a given formulation. At the present, this parameter can only be obtained through measurements made in a closed vessel. The theoretical prediction of burning rates has been and remains an important goal in propellant modeling research. Important advances have been made in the gaseous phase part of the modeling and calculations codes are now readily available. The modeling of the condensed phase zone combustion has proven over time to be a more difficult undertaking. One of the reasons for these difficulties is the challenge in obtaining reliable experimental data in the harsh conditions imposed by the combustion. Another main source of difficulties is the need to apply molecular dynamics to understand the chemical reactions happening [1]. This last requirement has important ramifications with respect to the complexity of the calculations and the computing power required. As a result, the best attempts made to predict burning rates were made by ignoring the condensed phase part through a guess of the initial reaction and the use of empirical reaction rates [2]. Recently, a simplified approach which uses spectroscopic data has been devised in order to eliminate the guessing step for the initial reaction [3]. The qualitative results of the spectroscopic approach were shown to agree with current ideas pertaining to initial reactions [3].

Ignition is defined as the onset of a self sustained reaction known as combustion [4]. The phenomenon of ignition is directly linked to the above considerations as the initial part of the combustion process in solids occurs in the condensed phase. Ignition has been recognized in various sources as being a thermal problem [5, 6]. However, the term “thermal” is a quite general one that can be resumed to simple molecular properties. This study uses the ideas introduced in [3] along with basic considerations taken from statistical mechanics to look more closely at the molecular aspect of ignition.

## 2 Theoretical foundations

In order to look at ignition with the spectroscopic approach, the three following important assumptions are made:

- Molecular bonds will break only because of vibrational excitation
- Vibrational modes are linked to the fundamental wavelength through a second order Morse type potential function

$$E_n = (n + \frac{1}{2})h\nu - \chi_e(n + \frac{1}{2})^2 h\nu$$

where  $E_n$  is the vibrational energy,  $n$  is the vibrational quantum number,  $h$  is the Planck constant,  $\nu$  is the frequency and  $x_e$  is a dimensionless anharmonicity constant linked to the dissociation energy,  $D_e$ , by the following relation [7]:

$$\chi_e = \frac{h\nu}{4D_e}$$

- Dissociation energies of various bonds are those found in the literature

It must be noted that these assumptions are known not to be true in all cases but will be shown to be sufficient for the present calculations. The molecular modes of energetic materials can be determined readily through the use of spectroscopy (either infrared or ultraviolet-visible) and detailed records of measurements are available in the literature (for example in the Sigma Aldrich Catalogue [8]). The fundamental vibrational frequencies of a given material are obtained from its infrared spectrum.

In order for ignition to occur, a sufficient amount of chemical bonds must be able to break. From the above considerations, the last affirmation can be rephrased as follows: a sufficient amount of bonds must have the dissociation energy. It is thus necessary to compute the distribution of bonds with dissociation energy for various temperatures. Assuming a system of distinguishable quantum oscillators, the general expression for this distribution is as follows:

$$N = \frac{e^{-\frac{D_e}{k_b T}}}{Z}$$

where  $k_b$  is the Boltzmann constant,  $T$  is the temperature, and  $Z$  the partition function [9]. For this type of statistics, the partition function will have the following form:

$$Z = \prod_i \left[ \sum_n \left( e^{-\frac{E_n}{k_b T}} \right) \right]$$

where the sum is over the  $n$  vibrational energy levels of a specific bond, and the product is over the  $i$  bonds of the molecule being studied [9].

Hence, it is important to note here that rotational and translational modes are neglected (as is be mostly the case for solids). In addition, the present methodology does not take into account collisions with gaseous molecule at the surface of the solid. One must thus imagine a solid mass of molecules idealized as anharmonic oscillators at a given temperature. Since only vibrational modes are considered, the temperature here must be viewed as the measure of the vibrational energy of the system. Upon performing the above calculations for a given molecule for a range of temperatures, it is expected that the distributions will show a notable increase around a certain temperature.

### 3 Examples

The case of nitroguanidine (abbreviated NQ), a crystalline energetic material from the nitramine family, is discussed here (for a schematic representation of the NQ molecule, the reader is referred to [10]). The infrared spectrum of NQ can be obtained from the Sigma Aldrich Catalogue [8] and the spectrum analysis has been performed in [3]. The results of the NQ spectrum analysis along with the calculated values of the anharmonic constant are shown on Table 1. It must be noted that the dissociation energies found on Table 1 were obtained from [11]. The analysis results can be directly used to calculate the distribution of bond with dissociation energy following the methodology introduced in the previous section. The distribution for the N-N bond case is shown on Fig. 1. The reason for showing the N-N case is that it yields the lowest temperature for the increase (around 200K) and that the fraction of bonds affected is largely superior to that of the other cases. As an example, the case with the second lowest temperature is that of the  $\text{NO}_2$  group single bonds with a significant increase around 500K and a fraction of bonds in the order of  $10^{-6}$ .

Table 1: Analysis of nitroguanidine infrared spectroscopy data.

<i>Mode description</i>	<i>amount</i>	<i>wavenumber (1/cm)</i>	<i>De (eV)</i>	<i>λ (m)</i>	<i>ν (Hz)</i>	<i>n</i>	<i>limit λ (nm)</i>	<i>χe</i>
<i>NH2 asym stretch</i>	1	3350	4.01	3.0E-06	1.0E+14	20	149	0.0259
<i>NH2 sym stretch</i>	1	3270	4.01	3.1E-06	9.8E+13	20	153	0.0253
<i>NH2 wagging</i>	1	780	4.01	1.3E-05	2.3E+13	83	154	0.0060
<i>NH2 scissoring</i>	1	1630	4.01	6.1E-06	4.9E+13	58	106	0.0126
<i>NH stretch</i>	4	3450	4.01	2.9E-06	1.0E+14	19	153	0.0267
<i>C=N stretch</i>	1	1660	6.38	6.0E-06	5.0E+13	62	97	0.0081
<i>C-N stretch (NH2)</i>	1	1050	3.17	9.5E-06	3.2E+13	49	194	0.0103
<i>C-N stretch (NO2)</i>	1	1160	3.17	8.6E-06	3.5E+13	45	192	0.0114
<i>NO2 sym stretch (N-O)</i>	1	1300	2.3	7.7E-06	3.9E+13	29	265	0.0176
<i>NO2 sym stretch (N=O)</i>	1	1300	6.3	7.7E-06	3.9E+13	79	97	0.0064
<i>NO2 asym stretch (N-O)</i>	1	1530	2.3	6.5E-06	4.6E+13	25	261	0.0207
<i>NO2 asym stretch (N=O)</i>	1	1530	6.3	6.5E-06	4.6E+13	67	98	0.0075
<i>NO2 rocking (in)</i>	1	480	2.3	2.1E-05	1.4E+13	78	267	0.0065
<i>NO2 wagging (out)</i>	1	570	2.3	1.8E-05	1.7E+13	65	270	0.0077
<i>NO2 bending (in)</i>	1	650	2.3	1.5E-05	2.0E+13	57	270	0.0088
<i>N-N bond</i>	1	1400	1.73	7.1E-06	4.2E+13	14	510	0.0251

## 4 Discussion and conclusion

The interpretation of the temperature at which the sudden increase shown on Fig. 1 takes place must be made carefully. What this particular result says is that at around 200K, the fraction of N-N bonds with enough vibrational energy to dissociate increases several order of magnitude to the values shown. It should not be interpreted from these considerations that the solid mass is expected to ignite at a temperature around 200K. It is important to remember that, even if the calculations presented here are made applying equilibrium statistical mechanics, ignition remains a dynamic process. Hence, this initial dissociation of bonds is the beginning of a process that will generate an amount of energy dependent on the nature of the bond and which will partly be absorbed by the mass of material with the effect of raising its temperature. This temperature increase will occur over a variable amount of time depending on the fraction of bonds undergoing scission. In fact, previous studies have shown the dependence of temperature on the time to ignition of several energetic molecules (for a good example, the reader is referred to [12]).

From the previous argument, it is clear that the present results should, in the near future, be applied to a calculation where the energy release transfer would be taken into account. The updated model would thus yield a better representation of the dynamic aspect of the system and the results could be compared with empirical data on ignition temperatures.

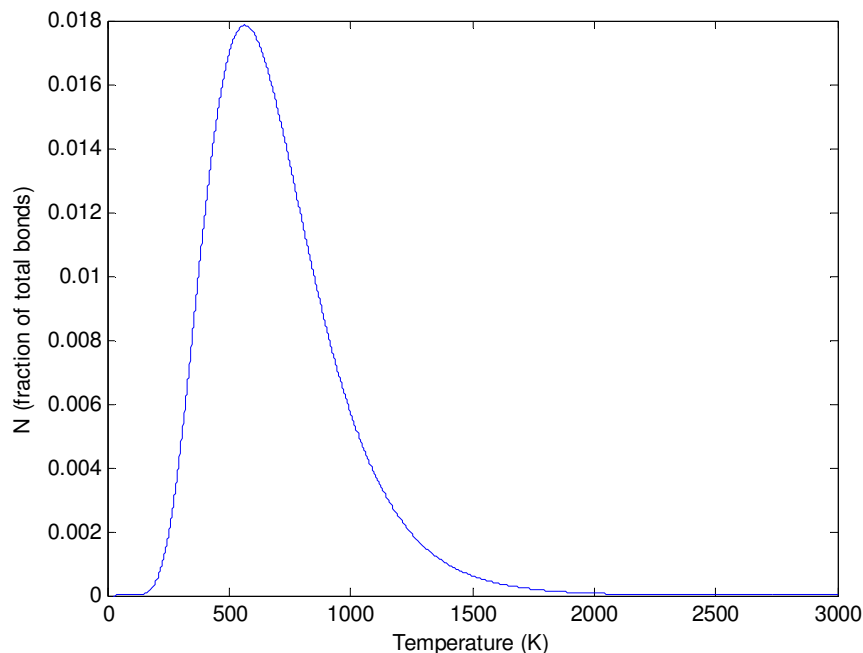


Figure 1. Distribution of N-N bonds at different temperatures for the nitroguanidine molecule.

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