A simple mathematical model for prediction of nitrogen dioxide molecular structure

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Where it is shown that one can numerically compute the angle between atomic bonds and length bonds in NO_2 *molecule with a good agreement with experimental data.*

In this paper we assume that nitrogen and oxygen atoms have valence electronic configuration $2s^2 2p^3$ and $2s^2 2p^4$ respectively. In NO_2 nitrogen dioxide molecule, N atom and each O atom share two pairs of electrons while N preserves a single unpaired electron (see [1]ChEBI). The pairs of electrons shared by N and O are bonding pairs, according to VSEPR theory terminology (see [1,2]Gillespie).

From VSEPR theory, in this molecule the three atoms have a planar configuration. Let be α = ONO the angle with vertex at N nucleus, that is the angle between atomic bonds. Also, we consider the circle C_N centred on N nucleus and having radius R_N equal to Van der Waals radius of N (see [1]Gillespie), and the two circles C_O centred on O nuclei and having radii R_O equal to Van der Waals radius of O, positioned along the line NO with O nucleus at a distance, from N, equal to a value d to be defined. Let be A the point of intersection between C_N and the vertical line traced from N nucleus, and B and C the two intersections between C_O and the lines NO respectively (see Fig.1). Finally, denote with χ_N and χ_O the nitrogen and oxygen electronegativities.

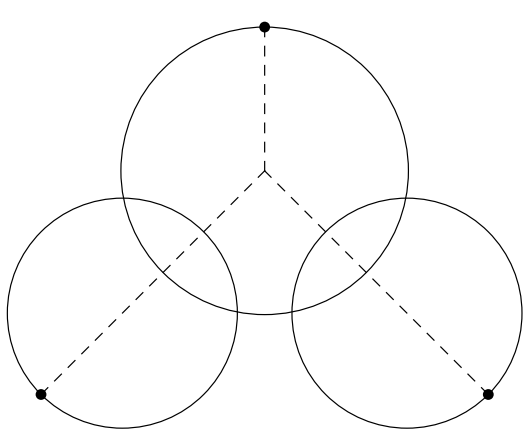

Fig. 1 *The geometrical representation of nitrogen dioxide molecule.*

In the most simple representation, assuming cr_N and cr_O the covalent radius of N and O respectively, the length d of the bonds N-O is assumed to be the sum $cr_N + cr_O$. But nitrogen and oxygen are two chemical elements having great electronegativity values, so the real length bond d is lower than the sum of the two covalent radii (see [2]Gillespie). Also, $\chi_O > \chi_N$, so O atom attracts valence electrons and the extension of the bond electronic pair domain decreases along the NO direction. We can think that $d : (cr_N + cr_O) = \chi_N : \chi_O$, therefore the length bond is

$$d = (cr_N + cr_O)\,\frac{\chi_N}{\chi_O}$$

If Q is the charge concentration at point A of the nitrogen unpaired electron, then for the double bonds N-O the charge concentrations at points B and C, due to two valence electrons of oxygen, are $2Q$. The Coulomb electrostatic energy among the three electronic pairs domains is

$$W = Q\ 2Q\,\frac{1}{d_{NO}} + Q\ 2Q\,\frac{1}{d_{NO}} + 2Q\,2Q\,\frac{1}{d_{OO}}$$

where is d_{NO} the distance between N and O atoms, and d_{OO} is the distance between O atoms in the molecule. If we consider a cartesian system with origin at the middle point of the segment BC, then the cartesian coordinates of A, B and C are A = {0, R_N + (d + R_O) cos $\alpha/2$}, B = {–(d + R_O) sin $\alpha/2$, 0} and C = {(d + R_O) sin $\alpha/2$, 0} respectively. The geometric configuration of the molecule in its ground state is determinated by atoms positioning so that W is minimum.

We can find numerically, using a mathematical software, the value of α for which W has its minimum (see [1]Trott). Note that, for this purpose, it is not restrictive to suppose $Q = 1$. These are the values of geometric parameters used for computation (see [1]CCCBDB and [1]Gillespie): R_N =150 *pm*, R_O =140 *pm*, cr_N = 70 *pm*, cr_O = 60 *pm*, χ_N = 3.1, χ_O = 3.5 .

In Fig. 2 there is a plot of the Coulomb energy as function of the angle α the N-O bonds. Minimum is obtained for a value of 2.35 *rad*, that is α = 134.65°. Note that this value is in good agreement with experimental values reported in technical literature, e.i. α = 134.1° in [1]CCCBDB.

Note that the d length bond, computed using previous formula, is 120.5 *pm*, to be compared with the value of 119.4 *pm* from experimental data (see [1]CCCBDB).

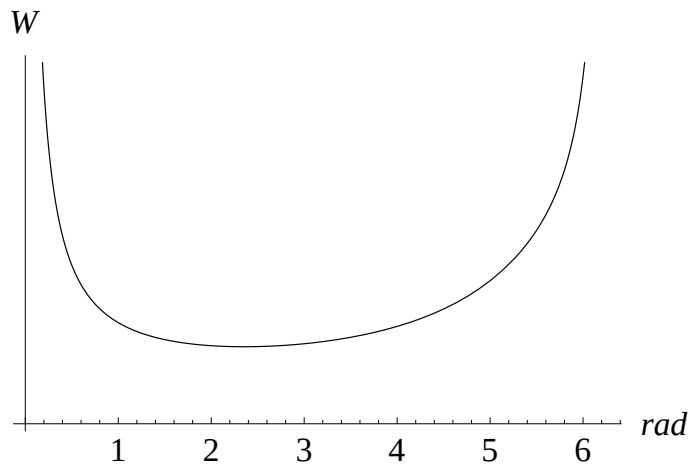

Fig. 2 *Graph of the Coulomb energy vs the angle* α = ONO, *due to electronic pairs in nitrogen dioxide molecule.*

Summary Table

	Experimental	*This model*
ONO angle [°]	134.1	134.65
bond length [*pm*]	119.4	120.5

References

[1] CCCBDB, Computational Chemistry Comparison and Benchmark DataBase, http://cccbdb.nist.gov/, 2013

[1] ChEBI, Chemical Entities of Biological Interest, https://www.ebi.ac.uk/chebi, 2014

[1] R. J. Gillespie and I. Hargittai, *The VESPR Model of Molecular Geometry*, Boston, Allyn and Bacon, 1991

[2] R. J. Gillespie and P. L. A. Popelier, *Chemical Bonding and Molecular Geometry*, Oxford & New York, Oxford University Press, 2001

[1] M. Trott, *The Mathematica Guidebook for Numerics*, New York, Springer, 2006

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