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Empirical Correlation Between the Stretching Force Constant and the Bond Order for Nitrogen—Oxygen Systems

Short Communication

Yoshiyuki Hase

Instituto de Química, Universidade Estadual de Campinas,
13100 Campinas, SP, Brasil

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The stretching force constant correlates satisfactorily with the *Wiberg*'s bond order, $K(\text{N—O}) = 11.791\ [p(\text{N—O})] - 9.565$, with a correlation coefficient of 0.958, for nitrogen—oxygen systems.

(Keywords: Force constant; Bond order; Empirical correlation; Nitrogen—oxygen system; MNDO method)

Empirische Korrelation zwischen der Kraftkonstante der Streckschwingung und der Bindungsordnung in Stickstoff—Sauerstoff-Systemen (Kurze Mitteilung)

Die Kraftkonstante K der Streckschwingung läßt sich in befriedigender Weise mit der *Wiberg*schen Bindungsordnung p korrelieren: $K(\text{N—O}) = 11.791\ [p(\text{N—O})] - 9.565$. Für Stickstoff—Sauerstoff-Systeme beträgt der Korrelationskoeffizient 0.958.

In a recent paper[1], the vibrational force field for the orthonitrate anion, NO_4^{3-}, was numerically investigated by normal coordinate analysis and based on the differences between the observed and calculated fundamental wavenumbers; the *Urey-Bradley* force constants were found to be $K(\text{N—O}) = 1.743$, $H(\text{ONO}) = 0.574$, $F(\text{O}\cdots\text{O}) = 1.261$ mdyn/Å, and $\kappa(NO_4^{3-}) = 0.25$ mdyn/Å. Since the force constants are one of the useful parameters to discuss the bond nature of molecules, its appropriate values may be examined in relation with other suitable molecular parameters.

In this communication, an empirical correlation between the *Urey-Bradley* stretching force constant and the *Wiberg*'s bond order is first studied for simple nitrogen—oxygen systems, and then the result is applied to NO_4^{3-} to examine the force field previously proposed.

Table 1. *Stretching force constant and bond order for nitrogen—oxygen systems*

Species	Force constant[a] K(N—O)	Bond order[b] p(N—O)
NO^+	22.73	2.856
NO	15.55	2.142
NO^-	8.02	1.436
NO^{2-}	3.54	1.192
NO_2^+	17.18	1.907
NO_2	8.46	1.560
NO_2^-	5.80	1.489
NO_3^-	5.62	1.278
NO_4^{3-}	1.743[c]	0.958

[a] *Urey-Bradley* force constant in mdyn/Å.
[b] *Wiberg*'s MNDO bond order.
[c] For $\kappa(NO_4^{3-}) = 0.25$ mdyn/Å, Ref. [1].

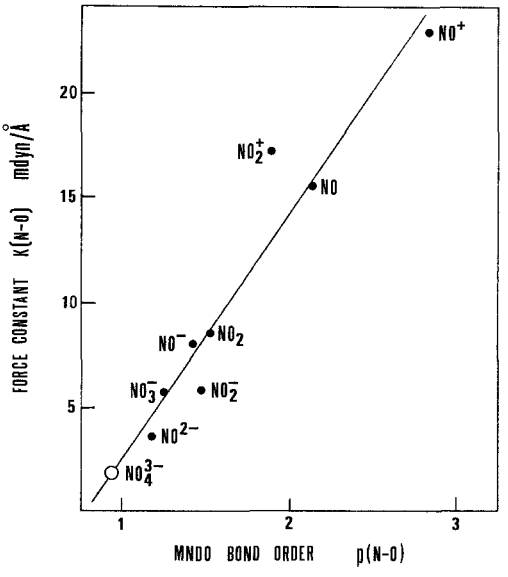

Fig. 1. Plot of the stretching force constant, K(N—O), vs. the *Wiberg*'s bond order, p(N—O)

Table 1 shows the stretching force constants and the bond orders calculated for 8 simple nitrogen-oxygen systems. The force constants were obtained for the *Urey-Bradley* force field using the spectral data available in the literature[2]. The bond orders by *Wiberg*'s definition[3] were evaluated by the MNDO method[4]. When the stretching force constants, K(N—O), are plotted against the bond orders, p(N—O), as shown in Fig. 1, a reasonable correlation is obtained,

$$K(\text{N—O}) = 11.791\,[p(\text{N—O})] - 9.565,$$

with a correlation coefficient of 0.958. For NO_4^{3-}, the MNDO bond order is calculated to be 0.958, and accordingly the evaluated force constant is 1.73 mdyn/Å. This value is comparable with the experimental one of 1.743 mdyn/Å which is found for the best value of $\kappa(NO_4^{3-})$, 0.25 mdyn/Å, from normal coordinate calculations. Consequently, the force field of NO_4^{3-} obtained from the empirical correlation developed in the present work is very consistent with that determined from the normal coordinate treatment in terms of the wavenumber differences.

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