Badger's rule revisited

Jerzy Cioslowski [a],*, Guanghua Liu [a], Ricardo A. Mosquera Castro [b]

[a] *Department of Chemistry and CSIT, Florida State University, Tallahassee, FL 32306-3006, USA*
[b] *Departamento de Quimica Fisica e Quimica Organica, Facultade de Ciencias Lagoas-Marcosende, 36200 Vigo, Spain*

Abstract

Numerical experiments demonstrate that the accuracy of stretching force constants k_e provided by Badger's rule is unlikely to be substantially improved either by modification of the functional dependence on the equilibrium bond length R_e or the inclusion of bond parameters related to electron density. These results, based upon both the experimental and QCISD/6-311++G(3d2f, 3p2d) values of R_e and k_e, imply that most of the universal characteristics of the bond strength vs. bond length dependence are accounted for by Badger's rule, the more detailed features being unexplainable by first-order response properties such as electron density. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In 1934, Badger put forward a simple empirical formula

$$k_e = A(R_e - B)^{-3}, \qquad (1)$$

relating the force constant k_e for stretching a bond X–Y to its equilibrium length R_e [1,2]. Many decades later, numerous attempts were made [3–14] to improve the accuracy of the Badger rule, which involves a universal constant A and a parameter B that depends on the rows of the periodic table to which the nuclei X and Y belong. Those attempts produced approximate expressions for k_e in terms of R_e, atomic charges on X and Y, and values of electron density at particular points in Cartesian space. Since, despite increased complexity, those expressions offered at most only a minor improvement over Badger's rule, interest in the estimation of k_e gradually waned, especially after rigorous calculations of second-order response properties became routinely available.

With the advent of advanced methods for geometry optimization, the demand for computationally inexpensive estimates of force constants has reemerged. Consequently, Badger's rule was investigated again [15,16]. A recent study in which a set of over 80 molecules was employed, found Eq. (1) to yield values of k_e with an absolute error of 11.9% and standard deviation of 9.0% [16]. However, since the testing set did not include charged species or less common bonding arrangements, these error statistics may not reflect the actual performance of Badger's rule.

In this Letter, we report on our recent research aiming at assessing and possibly improving the accuracy of Badger's rule. As the first step toward attaining these objectives, we present here a new,

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* Corresponding author. Fax: +1-850-644-8281.
E-mail address: jerzy@kyoko.chem.fsu.edu, http://www.scri.fsu.edu/~jerzy (J. Cioslowski).

Table 1
The testing set of 108 diatomic molecules and ions

Species	State	R_e (au)		k_e (au)	
		Calc.[a]	Exp.[b]	Calc.[a]	Exp.[b]
AlCl	$^1\Sigma^+$	4.0514	4.7294	0.1321	0.1335
AlF	$^1\Sigma^+$	3.1467	3.1263	0.2655	0.2715
AlH	$^1\Sigma^+$	3.1182	3.1139	0.1054	0.1041
AlH$^+$	$^2\Sigma^+$	3.0393	3.0270	0.1047	0.0965
AlN	$^3\Pi_i$	3.4084	3.3758	0.1918	0.1946
AlO	$^2\Sigma^+$	3.0862	3.0574	0.3370	0.3644
AlS	$^2\Sigma^+$	3.8573	3.8342	0.1984	0.2109
BCl	$^1\Sigma^+$	3.2530	3.2426	0.2204	0.2231
BF	$^1\Sigma^+$	2.3925	2.3859	0.5149	0.5186
BH	$^1\Sigma^+$	2.3298	2.3289	0.1944	0.1958
BN	$^3\Pi$	2.5004	2.4207	0.5622	0.5351
BO	$^2\Sigma^+$	2.2764	2.2762	0.8939	0.8775
BO$^+$	$^1\Sigma$	2.2752	2.2775	0.9041	0.7880
BS	$^2\Sigma^+$	3.0448	3.0410	0.4393	0.4316
BeAr$^+$	$^2\Sigma^+$	3.9789	3.9401	0.0346	0.0379
BeCl	$^2\Sigma^+$	3.4093	3.3960	0.1922	0.1944
BeF	$^2\Sigma^+$	2.5856	2.5719	0.3665	0.3599
BeH	$^2\Sigma^+$	2.5430	2.5372	0.1448	0.1457
BeH$^+$	$^1\Sigma^+$	2.4869	2.4797	0.1660	0.1693
BeO	$^1\Sigma^+$	2.5387	2.5150	0.4531	0.4826
BeS	$^1\Sigma^+$	3.3000	3.2910	0.2667	0.2650
C$_2$	$^1\Sigma_g^+$	2.3600	2.3480	0.7762	0.7811
C$_2^-$	$^2\Sigma_g^+$	2.3971	2.3966	0.7284	0.7203
C$_2^+$	$^2\Pi_u$	2.4758	2.4585	0.5805	0.4138
CCl	$^2\Pi_{1/2}$	3.1250	3.1086	0.2565	0.2540
CF	$^2\Pi_r$	2.4062	2.4034	0.4741	0.4763
CH	$^2\Pi_r$	2.1130	2.1163	0.2918	0.2875
CH$^-$	$^3\Sigma^-$	2.1439	2.0579	0.2465	0.3220
CH$^+$	$^1\Sigma^+$	2.1317	2.1371	0.2920	0.2641
CN$^+$	$^1\Sigma$	2.1990	2.2165	0.9667	1.0108
CO	$^1\Sigma^+$	2.1300	2.1322	1.2512	1.2216
CS	$^1\Sigma^+$	2.9021	2.9006	0.5557	0.5453
Cl$_2$	$^1\Sigma_g^+$	3.7905	3.7566	0.2031	0.2073
Cl$_2^+$	$^2\Pi_{3/2g}$	3.5899	3.5744	0.2807	0.2758
ClF	$^1\Sigma^+$	3.0822	3.0771	0.2950	0.2879
ClO	$^2\Pi_i$	2.9840	2.9662	0.2992	0.3028
F$_2$	$^1\Sigma_g^+$	2.6382	2.6682	0.3574	0.3020
F$_2^-$	$^2\Sigma_u^+$	3.6288	3.5527	0.0742	0.0935
F$_2^+$	$^2\Pi_{g,i}$	2.4370	2.4982	0.5203	0.4141
FO	$^2\Pi$	2.5518	2.5058	0.3799	0.3478
H$_2$	$^1\Sigma_g^+$	1.4021	1.4011	0.3701	0.3694
H$_2^+$	$^2\Sigma_g^+$	1.9975	1.9880	0.1032	0.1028
HCl	$^1\Sigma^+$	2.4062	2.4085	0.3371	0.3316
HCl$^+$	$^2\Pi_i$	2.4791	2.4844	0.2729	0.2650
HF	$^1\Sigma^+$	1.7245	1.7325	0.6343	0.6203
HF$^+$	$^2\Pi_i$	1.8805	1.8918	0.3544	0.3459
HO	$^2\Pi_i$	1.8260	1.8324	0.5149	0.5013
HO$^-$	$^1\Sigma^+$	1.8135	1.8330	0.5185	0.4912
HO$^+$	$^3\Sigma^-$	1.9336	1.9443	0.3584	0.3478
He$_2^+$	$^2\Sigma_u^+$	2.0463	2.0424	0.2179	0.2185
He$_2^{2+}$	$^1\Sigma_g^+$	1.3315	1.3304	0.8082	0.8222
HeH$^+$	$^1\Sigma^+$	1.4641	1.4632	0.3159	0.3176

Table 1 (Continued)

Species	State	R_e (au)		k_e (au)	
		Calc.[a]	Exp.[b]	Calc.[a]	Exp.[b]
$HeNe^+$	$^2\Sigma^+$	2.7285	2.4566	0.0999	0.2160
LiCl	$^1\Sigma^+$	3.8544	3.8185	0.0889	0.0915
$LiCl^-$	$^2\Sigma^+$	4.0360	4.1196	0.0570	0.0510
LiF	$^1\Sigma^+$	2.9923	2.9553	0.1563	0.1607
LiH	$^1\Sigma^+$	3.0423	3.0154	0.0643	0.0659
LiO	$^2\Pi_i$	3.2230	3.2031	0.1189	0.1338
MgCl	$^2\Sigma^+$	4.1901	4.1557	0.1137	0.1150
MgF	$^2\Sigma^+$	3.3362	3.3070	0.2041	0.2032
MgH	$^2\Sigma^+$	3.2907	3.2687	0.0809	0.0818
MgH^+	$^1\Sigma^+$	3.1506	3.1216	0.1035	0.1057
MgO	$^1\Sigma^+$	3.3384	3.3051	0.1890	0.2238
MgS	$^1\Sigma^+$	4.0869	4.0487	0.1374	0.1450
N_2	$^1\Sigma_g^+$	2.0707	2.0743	1.5349	1.4740
N_2^-	$^2\Pi_g$	2.2341	2.2544	0.9058	1.0262
N_2^+	$^2\Sigma_g^+$	2.1061	2.1097	1.3329	1.2906
N_2^{2+}	$^1\Sigma_g^+$	2.1369	2.1386	1.0943	1.0178
NCl	$^3\Sigma^-$	3.0618	3.0508	0.2568	0.2588
NF	$^3\Sigma^-$	2.4875	2.4887	0.4080	0.3974
NH	$^3\Sigma^-$	1.9548	1.9582	0.3904	0.3833
NH^+	$^2\Pi_r$	2.0153	2.0220	0.3344	0.3038
NO	$^2\Pi_r$	2.1728	2.1746	0.9345	1.0246
NO^-	$^3\Sigma^-$	2.3911	2.3773	0.5538	0.5249
NO^+	$^1\Sigma^+$	2.0031	2.0092	1.6757	1.5957
NS	$^2\Pi_r$	2.8229	2.8233	0.5516	0.5473
NS^+	$^1\Sigma^+$	2.7061	2.7212	0.8037	0.7379
Na_2	$^1\Sigma_g^+$	6.0022	5.8182	0.0101	0.0110
NaCl	$^1\Sigma^+$	4.5291	4.4613	0.0662	0.0703
NaF	$^1\Sigma^+$	3.7413	3.6395	0.1156	0.1131
NaH	$^1\Sigma^+$	3.6257	3.5667	0.0472	0.0502
NaO	$^2\Pi$	3.9332	3.8739	0.0833	0.0988
Ne_2^+	$^2\Sigma_u^+$	3.2445	3.3070	0.1326	0.0984
NeH^+	$^1\Sigma^+$	1.8638	1.8689	0.3118	0.3090
O_2	$^3\Sigma_g^-$	2.2689	2.2819	0.8307	0.7557
O_2^-	$^2\Pi_{g,i}$	2.5290	2.5511	0.4271	0.3596
O_2^+	$^2\Pi_g$	2.0953	2.1097	1.2313	1.0980
P_2^+	$^2\Pi_{u3/2}$	3.7215	3.7528	0.2951	0.2648
PF	$^3\Sigma^-$	3.0183	3.0041	0.3158	0.3195
PF^+	$^2\Pi_r$	2.8492	2.8352	0.4903	0.4944
PH	$^3\Sigma^-$	2.6862	2.6878	0.2097	0.2066
PH^-	$^2\Pi_i$	2.7105	2.6588	0.1912	0.1837
PH^+	$^2\Pi_r$	2.6877	2.7121	0.2145	0.1953
PN	$^1\Sigma^+$	2.8097	2.8173	0.7013	0.6526
PO	$^2\Pi_r$	2.7904	2.7891	0.6316	0.6072
PO^-	$^3\Sigma^-$	2.9068	2.9102	0.4447	0.3992
S_2	$^3\Sigma_g^-$	3.5770	3.5701	0.3244	0.3186
S_2^+	$^2\Pi_{g,r}$	3.4404	3.4487	0.4181	0.3776
SH	$^2\Pi_i$	2.5316	2.5339	0.2735	0.2719
SO	$^3\Sigma^-$	2.7958	2.7988	0.5707	0.5329
SO^+	$^2\Pi_r$	2.6860	2.6910	0.7426	0.7462
SiCl	$^2\Pi_r$	3.9146	3.8891	0.1643	0.1687
SiF	$^2\Pi_r$	3.0419	3.0256	0.3101	0.3146
SiH	$^2\Pi_r$	2.8745	2.8726	0.1554	0.1535
SiH^-	$^3\Sigma^-$	2.9293	2.7855	0.1287	0.1741

Table 1 (Continued)

Species	State	R_e (au)		k_e (au)	
		Calc.[a]	Exp.[b]	Calc.[a]	Exp.[b]
SiH^+	$^1\Sigma^+$	2.8423	2.8423	0.1738	0.1713
SiO	$^1\Sigma^+$	2.8598	2.8530	0.6004	0.5937
SiS	$^1\Sigma^+$	3.6525	3.6459	0.3228	0.3173

[a] Computed at the QCISD/6-311++G(3d2f, 3p2d) level of theory.
[b] [17].

more extensive testing set as well as several modifications of Eq. (1).

2. Methodology

A large set of diatomic molecules and ions composed of elements belonging to the first three rows of the periodic table was taken from Herzberg's compilation [17]. Electronic structure calculations of equilibrium bond lengths and quadratic force constants were carried out for ground electronic states of all the members of this set, out of which 108 species with computed values of R_e spanning the range of 1.33–6.00 (au) were selected. The calculations were performed at the QCISD/6-311++G(3d2f, 3p2d) level of theory with the GAUSSIAN 98 suite of programs [18]. Species with unrestricted wavefunctions suffering from high spin contamination were excluded from the final testing set listed in Table 1. In general, an excellent agreement between the predicted and experimental equilibrium bond lengths is observed, AlCl, $HeNe^+$, and Na_2 being notable exceptions (Table 1). This is also the case for the computed force constants, which range from 0.01 to 1.68 (au).

When used in conjunction with the previously published parameters [16], Eq. (1) performs poorly (Table 2), yielding estimates of k_e with an average absolute error of ca. 17%. Both positive and negative deviations from the actual force constants are observed, with k_e for species such as He_2^{2+} being underestimated by as much as 47% and that predicted for $BeAr^+$ being too high by over 100%. Reoptimization of both the constant A and the six-membered set of the row-dependent parameters B drastically reduces the errors, bringing them on average to the previously reported levels. However, there is only a slight improvement for the species with the underestimated force constants, and the maximum error still exceeds 90% (Table 2).

Table 2
Error statistics of various estimators for k_e[a]

Estimator	Standard deviation (%)	Absolute error (%)	Error range (%)
Badger's rule[b]	27.1	16.6	-46.5 (He_2^{2+})...156.2 ($BeAr^+$)
	26.2	17.3	-47.4 (He_2^{2+})...133.9 ($BeAr^+$)
Badger's rule[c]	17.8	12.0	-46.3 (He_2^+)...91.3 ($BeAr^+$)
	18.8	13.0	-58.1 ($HeNe^+$)...80.3 ($BeAr^+$)
Generalized rule[d]	16.4	11.1	-46.3 (He_2^+)...82.6 ($BeAr^+$)
	18.1	13.1	-58.3 ($HeNe^+$)...74.7 ($BeAr^+$)
Generalized rule[e]	16.5	11.6	-49.0 (He_2^+)...70.2 ($BeAr^+$)
	17.9	13.0	-49.4 (He_2^+)...63.3 ($BeAr^+$)

[a] Errors for the QCISD/6-311++G(3d2f, 3p2d) data followed by those for the experimental data.
[b] Eq. (1) with the parameters taken from [16].
[c] Eq. (1) with reoptimized parameters.
[d] Eq. (2).
[e] Eq. (1) with the constant A made row-dependent.

Out of the 108 species in the testing set, only two have their values of k_e predicted within 1%, whereas for 30 species, the error is greater than 20%.

Simple generalizations of Badger's rule perform only marginally better. The formula

$$k_e = A(R_e - B)^{-\beta}, \tag{2}$$

with an optimized exponent β, produces estimates of k_e that are barely more accurate than those afforded by the original rule. Interestingly, the optimized exponent deviates significantly from 3, equaling 4.33 and 5.02 for the testing sets based upon the experimental and QCISD/6-311++ G(3d2f, 3p2d) data, respectively. Even more disappointing are the results obtained with Eq. (1) in which the constant A is made row-dependent as, despite the increase in the number of the fitted parameters from 7 to 12, both the average errors and error ranges remain almost unaffected (Table 2).

More involved empirical estimators of the general form

$$k_e = F_1(\rho_c, \lambda_c)[F_2(\rho_c, \lambda_c)R_e - F_3(\rho_c, \lambda_c)B]^{-\beta}, \tag{3}$$

where ρ_c and λ_c are, respectively, the magnitudes of the electron density and its Laplacian at the bond critical point (i.e. the point along the bond at which the electron density attains its minimum), were also investigated. Rather surprisingly, none of the tested formulae with F_1, F_2 and F_3 being either power or exponential functions was found to offer a substantial improvement over Eq. (2).

3. Conclusions

The aforedescribed numerical experiments demonstrate that the level of accuracy provided by Badger's rule is unlikely to be substantially improved either by modification of the functional dependence on the equilibrium bond length or the inclusion of bond parameters related to electron density. Apparently, most of the universal characteristics of the bond strength (as measured by the stretching force constant) vs. bond length dependence are accounted for by the simple power law of Badger's rule, the more detailed features being unexplainable by first-order response properties such as electron density.

The crudeness of the force constant estimates that enter initial Hessian guesses translates into increased numbers of iterations in geometry optimizations. For this reason, in cases of less usual bonding situations, it may be advisable to employ look-up tables for such guesses.

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