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Transition Metal Dimer Internuclear Distances from Measured Force Constants

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Several empirical rules, which correlate force constants and equilibrium internuclear distances, have been extended to the transition metal dimers to test which one gives the most accurate fit. It is also of interest to determine to what extent their use can accurately predict internuclear distances for dimers for which there are no available experimental values. Pauling showed by using crystallographic data that internuclear distance can be correlated with the logarithm of the bond order, which itself is closely related to the force constant. Another empirical rule, due to Badger, indicates an inverse correlation between the force constant and the third power of the internuclear distance. Badger's relationship is the most widely used; therefore, it has found considerable application in various branches of chemistry. Guggenheimer proposed a correlation between force constant and the inverse of the internuclear distance raised to the power 2.46. We find that Pauling's rule provides a considerably better fit to existing data than Badger's and Guggenheimer's for the transition metal dimers. Although Pauling's rule gives the best results, the remarkable accuracy of Guggenheimer's relation is of considerable theoretical interest.

I. Introduction

Recently, accurate experimental values for force constants for almost all of the homonuclear transition metal dimers, and many of the internuclear distances, have become available.[1] This compilation leads to the question as to whether various existing correlations between force constants and equilibrium internuclear distances can be extended to transition metal dimers, and to what extent they can be used to predict accurate internuclear distances for those dimers for which no experimental data has yet been obtained. The most well-known of such correlations is that of Badger, for which the force constant is shown to be inversely proportional to the cube of the internuclear distance. A complete discussion of the application of Badger's rule[2] has been given by Herschbach and Laurie.[3] Other correlations include one between the internuclear distance and logarithm of the bond order, due to Pauling,[4] as well as a relationship due to Guggenheimer[5] between force constant and the inverse of the internuclear distance raised to the power 2.46. All of these relationships are empirical, and have found varying degrees of applicability, but all are remarkable in their accuracy.

Previously, there were not enough available force constant data and accurate measurements of the internuclear distances in transition metal clusters to test these theories. Transition metals are special in regard to the availability of d electrons for bonding. This leads to an enormous range of bond orders (from near zero to over five) as well as the possibility of high spin ground states, numerous low lying states, possible ferroelectric coupling, and, especially in the heavier metals, severe relativistic effects. It is therefore of considerable interest to determine the extent to which the above empirical correlations can be extended to transition metal dimers and to examine whether they are of any predictive value for internuclear distances which cannot be measured experimentally.

We have found that there is reasonably good agreement in almost all cases between the calculated internuclear distances and the experimental results. Overall, Pauling's relationship is more closely in agreement with the experimental values than Badger's. The calculated values obtained by using Guggenheimer's formula are remarkably good as well, but this relationship requires some reformulation for application to transition metals.

II. Existing Experimental Data on Transition Metals

In this section, we examine the existing experimental data on transition metal dimers. In Table 1, we present the measured vibrational frequencies (ω in cm^{-1}). In most cases, these have been obtained in Raman or fluorescence spectroscopy either in the gas phase or in matrix isolation. Below each vibrational frequency is given the force constant (k_e in mdyne/Å) calculated from the observed harmonic frequency using the expression $k_e = {}^1/_2 m\omega^2$, with the conversion factor 1 amu cm^{-2} = 5.8919×10^{-7} mdyne/Å. The masses used were the natural abundance-weighted average of the isotopic masses unless isotopic resolution was reported in the spectra, in which case the individual isotopic mass was used. Only the vibrational frequencies for Tc_2, Os_2, and Ir_2 have not been measured. The force constants listed in Table 1 for these three dimers were obtained through a correlation between force constant and diabatic dissociation energy[1] and, thus, may be considered only indirectly measured experimentally. However, the values determined in this manner fit well the periodic trends observed and are therefore reasonable.

Also of interest in application of the empirical correlations is the bond order n. The bond order, like the force constant, is a measure of the bond strength, and it is usually defined formally as ${}^1/_2$ the difference between the number of bonding electrons and antibonding electrons. However, a more realistic definition involves calculation of the electron occupation number for a given bond from the wave function. This enables the determination of noninteger values for bond order. For transition metals,

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TABLE 1: Experimental Vibrational Frequencies (in cm^{-1}), Force Constants (Å), and Bond Orders (n) for the Transition Metal Dimers[a]

	Sc_2[7]	Ti_2[8]	V_2[9]	Cr_2[10]	Mn_2[11]	Fe_2[12]	Co_2[13]	Ni_2[14]	Cu_2[15]	Zn_2[16]
ω	239.9	407.9	536.9	480.6	76.4	299.6	296.8	259.2	266.5	25.9
k_e	0.76	2.35	4.33	3.54	0.09	1.48	1.53	1.16	1.33	0.01
n	0.57	1.77	3.26	2.66	0.07	1.11	1.15	0.87	1.00	0.01
	Y_2[17]	Zr_2[18]	Nb_2[19]	Mo_2[20]	Tc_2[1]	Ru_2[21]	Rh_2[22]	Pd_2[23]	Ag_2[24]	Cd_2[16]
ω	184.4	305.7	420.5	473.3	(389)	347.1	283.9	210.0	192.4	23.0
k_e	0.89	2.51	4.84	6.33	(4.37)	3.59	2.44	1.38	1.18	0.02
n	0.76	2.13	4.12	5.38	(3.72)	3.05	2.07	1.17	1.00	0.02
	Lu_2[25]	Hf_2[26]	Ta_2[27]	W_2[28]	Re_2[29]	Os_2[1]	Ir_2[1]	Pt_2[30]	Au_2[31]	Hg_2[32]
ω	121.6	176.2	300.2	336.8	337.9	(334)	(280)	222.5	190.9	18.5
k_e	0.76	1.63	4.80	6.14	6.26	(6.26)	(4.44)	2.84	2.12	0.02
n	0.36	0.77	2.27	2.90	2.96	(2.96)	(2.10)	1.34	1.00	0.02

[a] Values in parentheses were obtained indirectly from a fit of force constants with dissociation energies (see ref 1).

TABLE 2: Experimental Ground State Dimer Internuclear Distances (Å)

Sc_2	Ti_2[33]	V_2[34]	Cr_2[35]	Mn_2[36]	Fe_2[37]	Co_2	Ni_2[38]	Cu_2[39]	Zn_2[15]
	1.94	1.77	1.679	3.4	2.02		2.154	2.22	4.19
Y_2	Zr_2[40]	Nb_2[41]	Mo_2[42]	Tc_2	Ru_2	Rh_2	Pd_2	Ag_2[43]	Cd_2[16]
	2.24	2.078	1.929					2.53	4.07
Lu_2	Hf_2	Ta_2	W_2	Re_2	Os_2	Ir_2	Pt_2[44]	Au_2[45]	Hg_2[32]
							2.33	2.47	3.63

there exist relatively few good calculations because of the same problems associated with the existence of d electrons discussed above. It is therefore of use to obtain an experimental value for the bond order, and it would be valuable to be able to compare bond strengths across the periodic table. We are assisted in this regard by a derivation due to Johnston.[6] He showed that the bond order, as defined by Pauling[4] is proportional to the force constant by the formula

$$n = k_e/k_e^{(1)}$$

where k_e is the experimental force constant in mdyne/Å, $k_e^{(1)}$ is the force constant for a single bond, and n is the bond order. The only problem is the determination of $k_e^{(1)}$. For transition metal dimers, we consider that for the coinage metals (Cu, Ag, and Au) the ground-state atomic configuration is $d^{10}s^1$. The filled d shell precludes the participation of d electrons in bonding, and because there is only one s electron per atom available for bonding, we may take the force constant for the coinage metal dimers to be $k_e^{(1)}$ for each row of the periodic table. In the third row under each metal in Table 1, we present the bond order calculated for each dimer using this procedure. Note these experimental values range in magnitude from as low as 0.01 (for Zn_2, Cd_2, and Hg_2), which are essentially van der Waals complexes, to 5.38 (for Mo_2), which implies considerable participation of d-electrons to provide an extremely strong chemical bond.

Accurate experimental data for equilibrium internuclear distances exist for 16 transition metal dimers as exhibited in Table 2. Most of these have been measured either by high-resolution absorption or fluorescence spectroscopy in the gas phase. Such studies are hampered by the fact that, especially for the heavier elements, the moments of inertia are large, leading to rather small rotational constants. Thus, the rotational spacings obtained in spectra may often be comparable to or less than the laser or Doppler line width. This causes spectral congestion resulting in inability to resolve rotational structure.

We should also point out at this stage that in previous work[1] we have focused exclusively on transition metals, referring to the *first, second, and third* row of the transition metal series. However, for comparison with work on other parts of the periodic table, it is best to revert to the nomenclature of the table as a whole, and that involves reference to the *third, fourth, and fifth* row (for the first, second, and third transition metal rows). Also, because of the paucity of experimental internuclear distances in row five, we do not consider the fits presented below for this row to be very reliable.

III. Empirical Correlations

Among the several empirical rules relating the force constant with other properties of chemical bonds, those proposed by Pauling, Badger, and Guggenheimer are used in this study to predict the internuclear distances for the transition metal dimers.

A. Pauling's Rule. By using crystallographic data, Pauling empirically developed a relationship between bond order (n) and the equilibrium internuclear distances. This is expressed by

$$r_n = r_1 - b_{ij} \log (n)$$

where r_n is the internuclear distance when the bond order is n (r_1 is for a single bond) and b_{ij} is a constant that depends on the rows of the periodic table in which the two atoms reside. In this article, all of the dimers are homonuclear, so that in principle, we need only b_{ii}, but we retain the more general notation for consistency. Originally, Pauling[4] estimated b_{ij} to be about 0.6 for many species with fractional bonds and 0.71 for bond orders of 1 and higher. Using best-fit procedures, with the experimentally derived bond orders from Table 1 and the known internuclear distances from Table 2, for dimers of the third row of the periodic table, we obtain $b_{33} = 1.02$; for the fourth and fifth row, we obtain $b_{44} = 0.78$ (this is in agreement with the value of 0.75 for the second row obtained by Pettifor,[46] who also provided a theoretical justification for Pauling's relationship derived from a pairwise potential function) and $b_{55} = 0.67$, respectively. The fits obtained are illustrated for rows 3 and 4 in Figure 1. Note that these values differ slightly from those previously reported,[1] because in these fits we have included the van der Waals bonded dimers of Zn, Cd, and Hg. With these parameters, we may then calculate internuclear distances for all of the transition metal dimers. The results are displayed in Table 6 in the rows just below the experimental results. For the third row of the periodic table, the standard deviation is 0.07. Out of eight elements for which internuclear

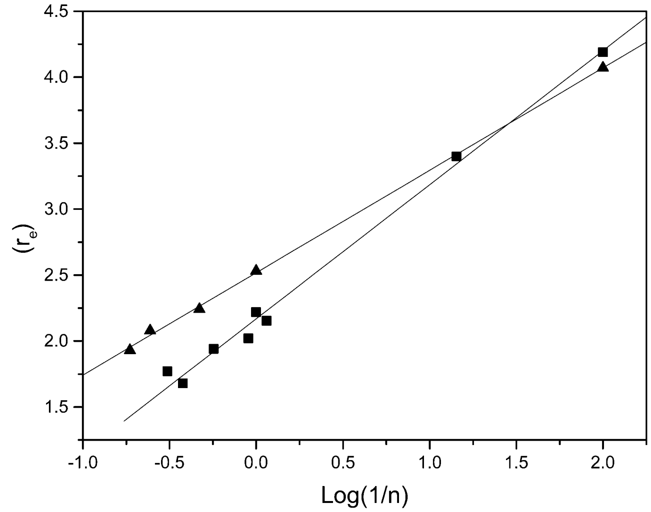


Figure 1. Correlation of force constant and internuclear distance for rows 3 (square) and 4 (triangle) of the transition metal dimers using Pauling's empirical relationship. The straight line represents to best fit of the data for each row.

TABLE 3: Parameters for Pauling's Rule Fits of Transition Metal Dimers

row	b_{ij}
3	1.02
4	0.78
5	0.67

TABLE 4. Parameters for Badger's Rule Fits of Transition Metal Dimers[a]

row	m	b	a_{ij}	d_{ij}
3	0.62	1.52	2.14	1.52
4	0.64	1.74	2.38	1.74
5	0.42	2.09	2.51	2.09

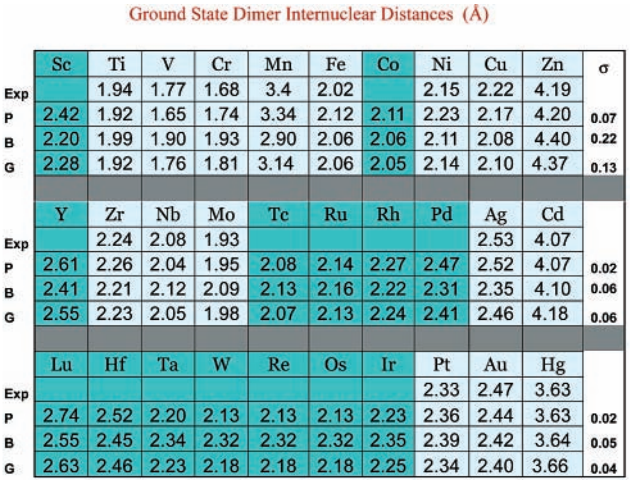
[a] Defined by $r_e = m(k_e^{-1/3}) + b$ using a linear fit of r_e vs $k_e^{-1/3}$; $m = a_{ij} - d_{ij}$; $b = d_{ij}$.

TABLE 5: Parameters for Guggenheimer's Rule Fits for Transition Metal Dimers[a]

row	m	b	s
3	0.15	0.34	6.7
4	0.13	0.40	7.7
5	0.09	0.41	11.

[a] Defined by $\log(r_e) = m \log(1/n) + b$ using a linear fit of $\log(r_e)$ vs $\log(1/n)$.

TABLE 6. Comparison between Experimental and Calculated Internuclear Distances (in Å) for the Transition Metal Dimers[a]



Ground State Dimer Internuclear Distances (Å)

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	σ
Exp		1.94	1.77	1.68	3.4	2.02		2.15	2.22	4.19	
P	2.42	1.92	1.65	1.74	3.34	2.12	2.11	2.23	2.17	4.20	0.07
B	2.20	1.99	1.90	1.93	2.90	2.06	2.06	2.11	2.08	4.40	0.22
G	2.28	1.92	1.76	1.81	3.14	2.06	2.05	2.14	2.10	4.37	0.13
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
Exp		2.24	2.08	1.93					2.53	4.07	
P	2.61	2.26	2.04	1.95	2.08	2.14	2.27	2.47	2.52	4.07	0.02
B	2.41	2.21	2.12	2.09	2.13	2.16	2.22	2.31	2.35	4.10	0.06
G	2.55	2.23	2.05	1.98	2.07	2.13	2.24	2.41	2.46	4.18	0.06
	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	
Exp								2.33	2.47	3.63	
P	2.74	2.52	2.20	2.13	2.13	2.13	2.23	2.36	2.44	3.63	0.02
B	2.55	2.45	2.34	2.32	2.32	2.32	2.35	2.39	2.42	3.64	0.05
G	2.63	2.46	2.23	2.18	2.18	2.18	2.25	2.34	2.40	3.66	0.04

[a] Exp: experimental values; P: Pauling's rule; B: Badger's rule; G: Guggenheimer's rule; σ: standard deviation for each fit of the observed internuclear distances.

distance experimental data are available, six agree very closely with the calculated values. For V_2 and Fe_2, the deviation is a little larger. For Cr_2, we might have expected difficulties because of the unusual potential function for this dimer. Requiring a function with terms up to the sixth power of the internuclear distance, Casey and Leopold[10] found a harmonic force constant of 3.54 mdyne/Å, a value that is higher than that of any third row dimer, except for V_2. Furthermore, in Ni_2, there is evidence for unusually low d-electron contribution to the bonding.[14,47] Despite these potential problems, our fits for Cr_2 and Ni_2 are not bad. The results obtained for the fourth and fifth rows are also in very close agreement with experimental values, although, with so little internuclear distance data available, the fifth row fit must be regarded as tentative, at best. The standard deviations for rows 4 and 5 are 0.02 and 0.02, respectively. It is especially gratifying that the van der Waals dimers of Mn, Zn, Cd, and Hg are fit so well (all within 0.06 Å). Note also the excellent fit for Zr, Nb, and Mo dimers. The quality of these fits encourages us to extend the calculations to dimers of each row for which internuclear distances have not yet been measured, and we include these predictions in the table.

B. Badger's Rule. The second empirical relationship used in this study is the one proposed by Badger in 1934. In the case of diatomic molecules, Badger[2] observed that the internuclear distance may be expressed with fair accuracy as a function only of the "bond force constant" at the equilibrium separation and of the positions of the periodic table from which the molecules reside. This rule states that there exists an inverse correlation between the force constant and the third power of the internuclear distance as expressed by the formula

$$k_e(r_e - d_{ij})^3 = C$$

where k_e is the force constant in mdyne/Å, r_e is the internuclear distance in Å, d_{ij} is a constant that depends on the rows of the periodic table to which the nuclei of atoms i and j reside, and C is a universal constant equal to 1.86×10^5 dyn/cm. Badger also suggested that to obtain a more accurate fit C should be allowed to take different values from group to group. This relationship may then be expressed more generally as $r_e = d_{ij} + (C_{ij}/k_e)^{1/3}$. However, because of the lack of available data about vibrational spectra of the molecules, this relationship was not at the time applied to polyatomic molecules. With few exceptions, it is believed that the above relationship holds for both ground and excited states of molecules.[2] A valuable contribution to such studies has been presented by Herschbach and Laurie.[3] They showed how Badger's rule could be extended to anharmonic constants, including cubic and quartic constants, and assembled considerable data for numerous diatomic species. They also proposed an alternative form of Badger's rule with the formula

$$r_e = d_{ij} + (a_{ij} - d_{ij})\, k_e^{-1/3}$$

where a_{ij} may be considered to be a standard bond length ($k_e = 1$ at $r_e = a_{ij}$) and d_{ij} as a distance of closest approach of the two nuclei ($k_e \to \infty$ at $r_e = d_{ij}$). Herschbach and Laurie then compiled extensive tables of the parameters a_{ij} and d_{ij}, which have been quite useful for predicting equilibrium internuclear

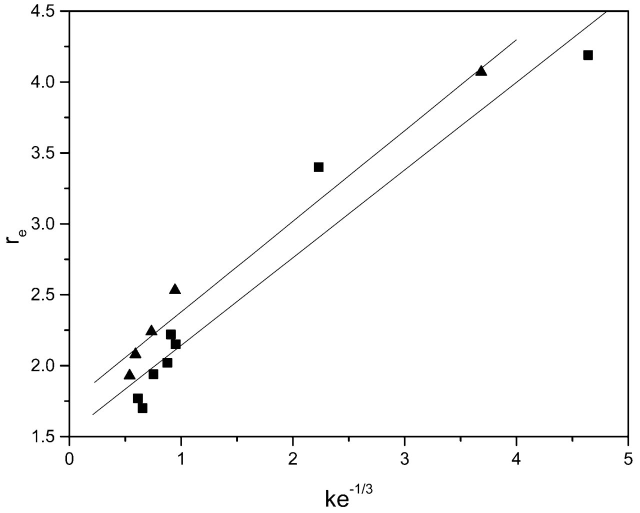


Figure 2. Correlation of force constant and internuclear distance for rows 3 (square) and 4 (triangle) of the transition metal dimers using Badger's empirical relationship. The straight line represents to best fit of the data for each row.

distances.[17] We shall use this form of Badger's rule in our fits of transition metal dimers. Weisshaar[48] has applied Badger's rule to the third row metal diatomics, including transition metals, but since then, much more data has been obtained, and we utilize it here.

Using the available data for transition metal dimers, we show in Figure 2 the best fit of the above relationship for the third and fourth row of the periodic table. The best-fit parameters are displayed in Table 4. The resulting values of internuclear distances are displayed in the third row below the metal of Table 6. They can be seen to be reasonable in the light of the results of Herschbach and Laurie, who, with considerably less data available, obtained values of 2.58 (a_{33}) and 2.85 (a_{44}) for the third and fourth row values of a_{ij} and 1.41(d_{33}) and 1.62 (d_{44}) for d_{ij}. In a fit of diatomic molecules containing one or two metal atoms across the entire periodic table, Weisshaar[48] obtained $a_{33} = 2.12$ and $d_{33} = 0.906$. Fang et al.[17] obtained $a_{44} = 2.60$ and $d_{44} = 1.09$ for the fourth row, once again with considerably less data than currently available. The standard deviations for the fits (0.22 for row three, 0.06 for row four, and 0.05 for row five) are adequate but can be seen to be nowhere near as good as for Pauling's rule fits for the rows (3 and 4) for which the best data is available. This is consistent with a more recent examination of Badger's rule.[49] Especially problematic are the values for the van der Waals dimers Zn_2 and Mn_2, although the value for Ni_2 is somewhat better than that of Pauling. Poor fits are also obtained for Cr_2, Cu_2, and Ag_2. Once again, the fifth row results should not be taken too seriously. Predicted values for dimers for which there are no measured values are also presented.

C. Guggenheimer's Rule. Guggenheimer[5] showed that the force constant and the bond length may be related by the formula

$$k_e = C(z_1 z_2)^{1/2} r_e^{-s}$$

where k_e is the force constant mdyne/Å, C is a constant, and z_1 and z_2 are the total number of s and p valence electrons contributed from each of the two atoms. The exponent (s) of r_e as well as C was obtained by a least-squares fit of the series H_2, Li_2, Na_2, and K_2, and the best fit was found to be for a value of $s = 2.46$ and $C = 273.8$. It was then shown that this formula could accurately predict the vibrational frequencies of over 70 diatomic species with an average deviation of 1.6%. The above formula was used only for molecules with single bonds, but he also showed that a double bond contributes a factor of 2 to the force constant[5] and that the same values of s and C are obtained. For hydrides, an optimal value of $s = 1.84$ was found.

It is worthwhile to examine the possibility of extending Guggenheimer's relationship to transition metals. One difficulty is to choose the factor z_1z_2. The contribution of s and p electrons, plus the added factor of 2 added for formal double bonds, indicates that this is related in some way to the bond order. However, we must search for an extension of this relationship, which in some way accounts for the contribution of d electrons. For transition metal dimers, it is well-known that the best bonding occurs when the atoms are in an s^1 configuration. However, many transition metals have a $d^N s^2$ ground-state configuration. To explain the rather strong bonds observed for many dimers, it is therefore necessary to consider promotion energies to a $d^{N+1}s^1$ configuration, and where this promotion energy is low enough, we may presume that the latter configuration may be used. Indeed it was shown that a better correlation between observed force constants and dissociation energies is obtained when considering the diabatic dissociation energies[1], i.e., those for which promotion energies are included. Thus, we assume that all of the transition metal dimers dissociate diabatically to two $d^{N+1}s^1$ atoms. Exceptions to this doubly promoted diabatic limit would exist for the dimers of Sc, Y, Lu, and Re, which are known to dissociate to $d^N s^2 + d^{N+1}s^1$ configurations, and Pd, which is thought to dissociate to a $d^{10} + d^9 s^1$ separated atom limit. Also of concern are the van der Waals dimers (Mn_2, Zn_2, Cd_2, and Hg_2) which may be regarded as consisting of two s^2 atoms. The experimental bond order n, introduced in section II, provides us with a way to include all of the contributions to bonding. As was shown by application of Pauling's rule (A), this holds over a wide range of values of n. Remembering that the bond order $n = k_e/k_e^{(1)}$, it is perhaps convenient to rewrite Guggenheimer's relation as

$$k_e/k_e^{(1)} = (r_e^{(1)}/r_e)^s$$

We see that in this interpretation, Guggenheimer's parameter $C(z_1z_2)^{1/2}$ is replaced by $k_e^{(1)}(r_e^{(1)})^s$ and, despite the suggestive notation ($r_e = r_e^{(1)}$ for $n = 1$), we may regard $r_e^{(1)}$ as an adjustable parameter, along with s. Taking logarithms

$$\log(r_e) = m \log(k_e^{(1)}/k_e) + b = m \log(1/n) + b$$

where it may be seen that $m = 1/s$ and $b = \log(r_e^{(1)})$. We now use the experimental data to obtain best values of m and b. The fits obtained are illustrated in Figure 3 for rows 3 and 4, and the values obtained for m_{ij} and b_{ij} are listed in Table 5. The standard deviations for the three rows are 0.13, 0.06, and 0. 04, respectively.

As above, the values for row 5 should not be taken too seriously because of such few data points. Note, however, how close the values are to those of row 4. In fact, the values for all three rows are seen to be quite similar. The values for s ($=1/m$), however, differ considerably from those obtained by Guggenheimer for nontransition metals, perhaps reflecting the effect of d-electron contributions to bonding. The fits are not as good as those obtained with Pauling's relationship but still are rather remarkable. The internuclear distances obtained for Ti_2, V_2, Fe_2, Ni_2, Zr_2, Nb_2, and even Cd_2 are quite close, whereas for Cu_2 and Ag_2, they are relatively poor. Considering those dimers for which we have no measurements, the Guggenheimer

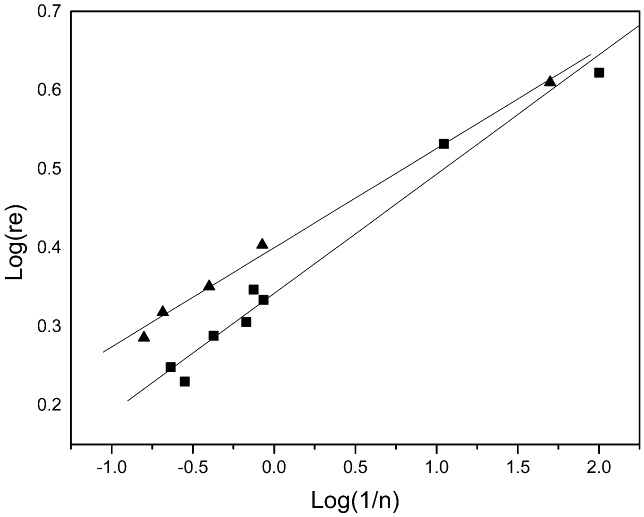


Figure 3. Correlation of force constant and internuclear distance for rows 3 (square) and 4 (triangle) of the transition metal dimers using Guggenheimer's empirical relationship. The straight line represents to best fit of the data for each row.

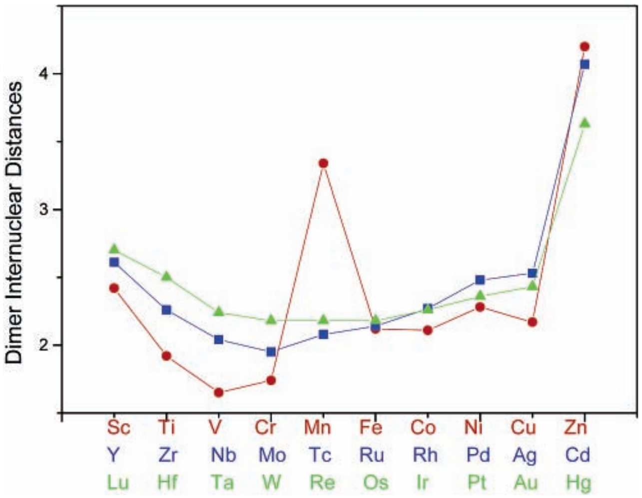


Figure 4. Transition metal dimer internuclear distances (in Å) calculated using Pauling's relationship. Circles (red) are for the third row (Sc−Zn), squares (blue) are the fourth row (Y−Cd), and triangles (green) are for the fifth row (Lu−Hg).

predictions are often close to the Pauling predictions, but both tend to differ considerably from those of Badger's rule.

IV. Discussion

Examining the results of all of the correlations collected in Table 6, we can make several observations. First, it is clear that Pauling's rule provides the best fit overall, both in terms of standard deviation, as well as range of applicability. Even the van der Waals molecules are accurately fit. We thus expect that most of the predicted dimer internuclear distances that have not been measured will also be accurate. In Figure 4, we display the calculated internuclear distances for all of the transition metal dimers using Pauling's relationship. Note that with the exception of the van der Waals dimers (Mn_2, Zn_2, Cd_2, and Hg_2) the internuclear distances track quite closely from row to row. The values drop toward the center of the series (somewhat skewed in row 3) from highs on either side, reflecting the increased availability of d electrons for bonding near the center of the periodic table, at least for rows 4 and 5.

Also of interest is the relatively good fits obtained using the Guggenheimer relationship. Although not as good as found with Pauling's, the consistency of parameters among the rows of the periodic table and the apparent wide applicability observed by Guggenheimer justify more detailed investigation into possible theoretical justifications for this relationship. The reformulation presented here is suggestive of a possible route for interpretation of this relationship, but this will require further study.

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References and Notes

(1) Lombardi, J. R.; Davis, B. *Chem. Rev.* **2002**, *102*, 2431.

(2) Badger, R. M. *J. Chem. Phys*. **1934**, *2*, 128; *J. Chem. Phys*. **1934**, *2*, 131; *J. Chem. Phys*. **1935**, *3*, 710

(3) Herschbach, D. R.; Laurie. V. W. *J. Chem. Phys*. **1961**, *35*, 458.

(4) Pauling, L. *The Nature of The Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 255.

(5) Guggenheimer, K. M. *Proc. Phys. Soc*. **1946**, *63*, 456; also *63*, 459.

(6) Johnston, H. S. *Gas-Phase Reaction Rate Theory*; The Ronald Press Co.: New York, 1966; p 82.

(7) Moskovits, M.; DiLella, D. P.; Limm, W. *J. Chem. Phys*. **1984**, *80*, 626.

(8) Cossé, C.; Fouassier, M.; Mejean, T.; Tranquille, M.; DiLella, D. P.; Moskovits, M. *J. Chem. Phys*. **1980**, *73*, 6076.

(9) Hu, Z.; Shen, B.; Zhou, Q.; Deosaran, S.; Lombardi, J. R.; Lindsay, D. M.; Harbich, W. *J. Chem. Phys*. **1991**, *95*, 2206.

(10) Casey, S. M.; Leopold, D. G. *J. Chem. Phys*. **1993**, *97*, 816.

(11) Bier, K. D.; Haslett, T. L.; Kirkwood, A. D.; Moskovits, M. *J. Chem. Phys*. **1988**, *89*, 6.

(12) Moskovits, M.; DiLella, D. P. *J. Chem. Phys*. **1980**, *73*, 4917.

(13) Dong, J. G.; Hu, Z. H.; Craig, R.; Lombardi, J. R.; Lindsay, D. M. *J. Chem. Phys*. **1994**, *101*, 9280.

(14) Wang, H.; Haouari, H.; Craig, R.; Lombardi, J. R.; Lindsay, D. M. *J. Phys. Chem*. **1996**, *100*, 3420.

(15) Ram, R. S.; Jarman, C. N.; Bernath, P. F. *J. Mol. Spectrosc*. **1992**, *156*, 468.

(16) Czajkowski, M. A.; Koperski, J. *Spectrochim. Acta* **1999**, *A55*, 2221

(17) Fang, L.; Chen, X.; Shen, X.; Liu, Y.; Lindsay, D. M.; Lombardi, J. R. *Fiz. Nizk. Temp*. **2000**, *26*, 1011. See also: *Low Temp. Phys*. **2000**, *26*, 752.

(18) Hu, Z.; Zhou, Q.; Lombardi, J.R.; Lindsay, D.M., *Physics and Chemistry of Finite Systems: From Clusters to Crystals.* II, 969; Jena, P., Khanna, N. S., Rao, B. K., Eds.; Kluwer: Amsterdam, The Netherlands, 1992.

(19) Hu, Z.; Shen, B.; Zhou, Q.; Deosaran, S.; Lombardi, J. R.; Lindsay, D. M. *SPIE* **1991**, *1599*, 65.

(20) Fang, L.; Davis, B.; Lu, H.; Chen, X.; Shen, X.; Lombardi, J. R. *Chem. Phys. Lett*. **2002**, *352*, 70.

(21) Wang, H.; Liu, Y.; Haouari, H.; Craig, R.; Lombardi, J. R. Lindsay, D. M. *J. Chem. Phys*. **1997**, *106*, 6534.

(22) Wang, H.; Haouari, H.; Craig, R.; Liu, Y.; Lombardi, J. R.; Lindsay, D. M. *J. Chem. Phys*. **1997**, *106*, 2101.

(23) Ho, J.; Ervin, K.M.; Polak, M.L.; Giles, M.K.; Lineberger, W. C. *J. Chem. Phys*. **1991**, *95*, 4845. Ho, J.; Polak, M. L.; Ervin, K. M.; Lineberger, W. C. *J. Chem. Phys*. **1993**, *99*, 8542.

(24) Brown, C. M.; Ginter, M. L. *J. Mol. Spectrosc*. **1978**, *69*, 25.

(25) Fang, L.; Chen, X.; Shen, X.; Lombardi, J. R. *J. Chem. Phys*. **2000**, *113*, 10202.

(26) Hu, Z.; Dong, J. G.; Lombardi, J. R.; Lindsay, D. M. *J. Phys. Chem*. **1993**, *97*, 9263.

(27) Hu, Z.; Shen, B.; Lombardi, J. R.; Lindsay, D. M. *J. Chem. Phys*. **1992**, *96*, 8757.

(28) Hu, Z.; Dong, J. G.; Lombardi, J. R.; Lindsay, D. M. *J. Chem. Phys*. **1992**, *97*, 8811.

(29) Hu, Z.; Dong, J. G.; Lombardi, J. R.; Lindsay, D. M. *J. Chem. Phys*. **1994**, *101*, 95.

(30) Fabbi, J. C.; Langenberg, J. D.; Costello, Q. D.; Morse, M. D.; Karlsson, L. *J. Chem. Phys*. **2001**, *115*, 7543.

(31) Ruamps, J. *Ann. Phys. (Paris)* **1959**, *4*, 1111.

(32) van Zee, R. D.; Blankespoor, S. C.; Zwier, T. S. *J. Chem. Phys.* **1988**, *88*, 4650.

(33) Doverstäl, M.; Lindgren, B.; Sassenberg, U.; Arrington, C. A.; Morse, M. D. *J. Chem. Phys*. **1992**, *97*, 7087. Doverstål, M.; Karlsson, L.; Lindgren, B.; Sassenberg, U. *Chem. Phys. Lett*. **1997**, *270*, 273.

(34) Spain, E. M.; Behm, J. M.; Morse, M. D. *J. Chem. Phys*. **1992**, *96*, 2511.

(35) Bondybey, V. E.; English, J. H. *Chem. Phys. Lett.* **1983**, *94*, 443.

(36) Baumann, C. A.; Van Zee, R. J.; Bhat, S. V.; Weltner, W., Jr. *J. Chem. Phys.* **1983**, *78*, 190.

(37) Purdum, H.; Montano, P. A.; Shenoy, G. K.; Morrison, T. *Phys. Rev. B.* **1982**, *25*, 4412.

(38) Morse, M. D.; Hansen, G. P.; Langridge-Smith, P. R. R.; Zheng, L. S.; Geusic, M. E.; Michalopoulos, D. L.; Smalley, R. E.. *J. Chem. Phys.* **1984**, *80*, 5400. Pinegar, J. C.; Langenberg, J. D.; Arrington, C. A.; Spain, E. M.; Morse, M. D. *J. Chem. Phys*. **1995**, *102*, 666.

(39) Ram, R. S.; Jarman, C. N.; Bernath, P. F. *J. Mol. Spectrosc*. **1992**, *156*, 468.

(40) Doverstål, M.; Karlsson, L.; Lindgren, B.; Sassenberg, U. *J. Phys. B: At. Mol. Opt. Phys*. **1998**, *31*, 795.

(41) James, A. M.; Kowalczyk, P.; Fournier, R.; Simard, B. *J. Chem. Phys*. **1993**, *99*, 8504.

(42) Efremov, V. M.; Samoilova, A. N.; Kozhukhovsky, V. B.; Gurvich, L. V. *J. Mol. Spectrosc*. **1978**, *73*, 430.

(43) Simard, B.; Hackett, P. A.; James, A. M.; Langridge-Smith, P. R. R. *Chem. Phys. Lett*. **1991**, *186*, 415.

(44) Airola, M. B.; Morse, M. D. *J. Chem. Phys*. **2002**, *116*, 1313.

(45) Simard, B.; Hackett, P. A. *J. Mol. Spectrosc.* **1990**, *142*, 310.

(46) Pettifor, D. G. *Bonding and Structures of Molecules and Solids*; Clarendon Press: Oxford, U.K., 1995.

(47) Pinegar, J. C.; Langenberg, J. D.; Arrington, C. A.; Spain, E. M.; Morse, M. D., *J. Chem. Phys*. **1995**, *102*, 666.

(48) Weisshaar, J. C. *J. Chem. Phys*. **1989**, *90*, 1429.

(49) Cioslowski, C., Liu, G., Mosquers Castro, R. A. *Chem. Phys. Lett*. **2000**, *331*, 497.