# CHEMICAL BONDS DISSOCIATION ENERGY

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In previous publications dealing with experimental mass spectrometry of tungsten hexacarbonyl, hexafluoroacetylacetone and its bidentate metal complexes M(hfac)$_2$; M = Cu, Pd the obtained data have been not adequately systematized. In this paper, we analyse the previously published experimental data of the various bond dissociation energy. A modified Yukawa potential, which is the exact solution of the problem dependence the chemical bond energy of its length, is used to analyse the experimental data. Experimental results of the formation of ions can be interpreted only in terms of the formation of fractionally charged quasi-particles. As an experimental technique, mass spectrometry of negative ions in electron resonance capture mode ranks next to the fractional quantum Hall effect in which fractional values of the charge quantization are observed. Also noted the resonance possibility capture of electron with “negative” kinetic energy.

The recent reports of Wnorowski *et al.*[1,2] on investigations of the decay of tungsten hexacarbonyl, $W(CO)_6$, using electron ionization (EI)[1] and dissociative electron attachment (DEA)[2] methods were of particular interest to the low-temperature plasma and nanotechnology communities. Furthermore, the dissociative photoionisation of $W(CO)_6$ was, however, discussed in an earlier paper.[3] It was shown that the bond dissociation of $[W(CO)_n^+]$–CO (n = 0-5) most likely proceeds differently if $n < 3$ or if $n \geq 3$ and that the dissociation occurs from both vibrational excited states or from the electronic-vibrational excited states. The interaction of low-energy electrons with $W(CO)_6$ was, however, discussed in a much earlier paper.[4] Our interest here is with the predominantly sequential detachment of a CO ligand from $W(CO)_6$, as well as presenting a comparison of the chemical bond dissociation energy BDE(W−CO) as calculated with the EI and DEA processes.

In Ref. 1, the EI (Eqns. (1) and (3)) and dissociative ionizations (Eqns. (2) and (4)) of $W(CO)_6$ in the gas phase were given as

$$e^- + M \rightarrow M^+ + 2e^-, \tag{1}$$
$$e^- + M \rightarrow (M - X)^+ + X + 2e^-, \tag{2}$$
$$e^- + M \rightarrow M^{2+} + 3e^-, \tag{3}$$
$$e^- + M \rightarrow (M - X)^{2+} + X + 3e^-, \tag{4}$$

where M is $W(CO)_6$ and X is CO. The EI method was used to estimate BDE(W−CO) as 2.15 ± 0.1 eV, and it was pointed out that there was a serious problem with calculations in that the internal energy of the initial molecule and fragment ions could not be calculated accurately. To address this, the electron affinity (EA) of the fragment ions of $W(CO)_x$ (x = 2, 3, 4, and 5) was estimated in Ref. 2 using

$$EA[W(CO)_x] = (6 - x)\cdot BDE(W\text{-}CO) - AE[W(CO)_x^-], \tag{5a}$$

where

$$AE[W(CO)_x^-] = (6 - x)\cdot BDE(W{-}CO) - EA[W(CO)_x], \tag{5b}$$

$$BDE(W\text{-}CO) = AE[W(CO)_5^-] + EA[W(CO)_5], \tag{5c}$$

and AE is the appearance energy of the given ion. The authors of Ref. 2 pointed out that these EA values are only estimates because of the uncertainty in the values of BDE(W−CO) of the anions. In their experimental investigation into the interaction of low-energy electrons with $W(CO)_6$, Wnorowski *et al.*[2] studied the reactions

$$
\begin{aligned}
e + W(CO)_6 \rightarrow W(CO)_6^{-\#} &\rightarrow W(CO)_5^{-} + CO &(6)\\
&\rightarrow W(CO)_4^{-} + 2CO &(7)\\
&\rightarrow W(CO)_3^{-} + 3CO &(8)\\
&\rightarrow W(CO)_2^{-} + 4CO. &(9)
\end{aligned}
$$

The ion yields and electron energy dependence of the metastable decay reaction are shown in Figs. 1 and 2.[2] The experimental results reported in Refs. 1, 2 and 3 therefore warrant some further discussion.

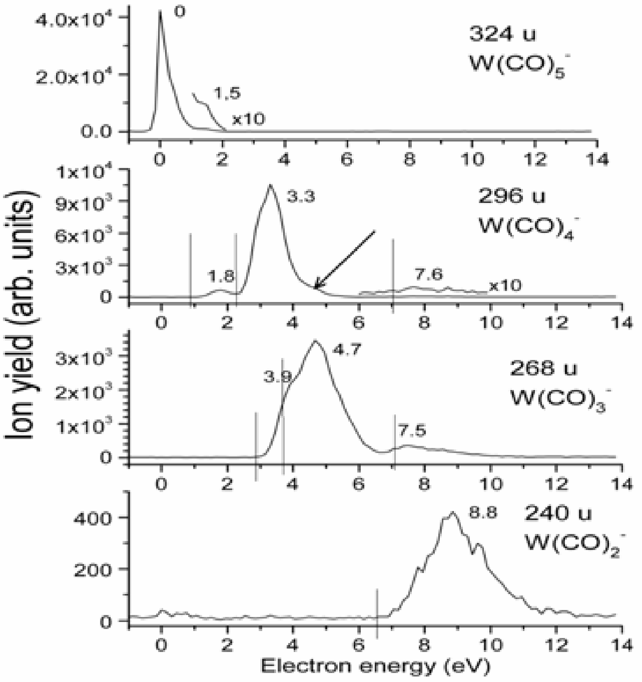

**Figure 1.** Ion efficiency curves of negatively charged fragments formed by DEA to tungsten hexacarbonyl. The vertical lines indicate the AE of the anion, and the arrow indicates the unidentified resonance. Reproduced with permission from Wnorowski *et al*. *Rapid Commun. Mass Spectrom*. **2012**, *26*, 2093. © 2012 John Wiley & Sons.

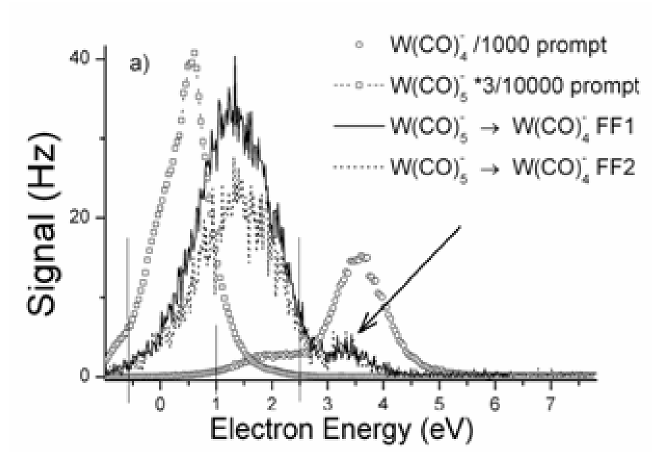

**Figure 2.** The electron energy dependence of the metastable decay reaction in Eqn. (5a). Prompt ion yields of the fragmentary anions involved are shown for comparison. The vertical lines indicate the AE of the anion, and the arrow indicates a small resonance. Reproduced with permission from Wnorowski *et al*. *Rapid Commun. Mass Spectrom*. **2012**, *26*, 2093. © 2012 John Wiley & Sons.

Wnorowski *et al*.[2] noted that several resonance peaks in the DEA reaction were not detected in the earlier study.[3] However, neither the origin of these resonances nor their position were discussed. The presence of several resonance peaks can be interpreted as the presence of several discrete energy levels, and some insight may be gained by calculating all the BDE(W−CO) values for a loss of only one CO group.

The recent reports of Engmann *et al*[5] on investigations of the decay hexafluoroacetylacetone (hfac) and its bidentate metal complexes M(hfac)$_2$; M = Cu, Pd (Figure 3), using dissociative electron attachment (DEA).

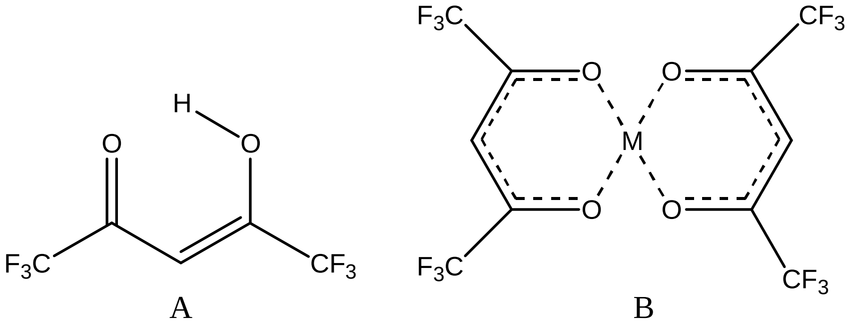

**Figure 3.** A is hexafluoroacetylacetone (hfac). B is bidentate metal complexes $M(hfac)_2$; M = Cu, Pd.

Engmann *et al*[4x] studied the reactions

$$e + hfac \rightarrow hfac^- + H \tag{10}$$
$$e + M(hfac)_2 \rightarrow hfac^- + M(hfac) \tag{11}$$

In reactions (10-11) observed several resonance peaks. Quantitative interpretation of the experimental data made is not correct.. The ion yields and electron energy dependence hexafluoroacetylacetone (hfac) and its bidentate metal complexes $M(hfac)_2$; M = Cu, Pd decay reaction are shown in Figure 4[5]

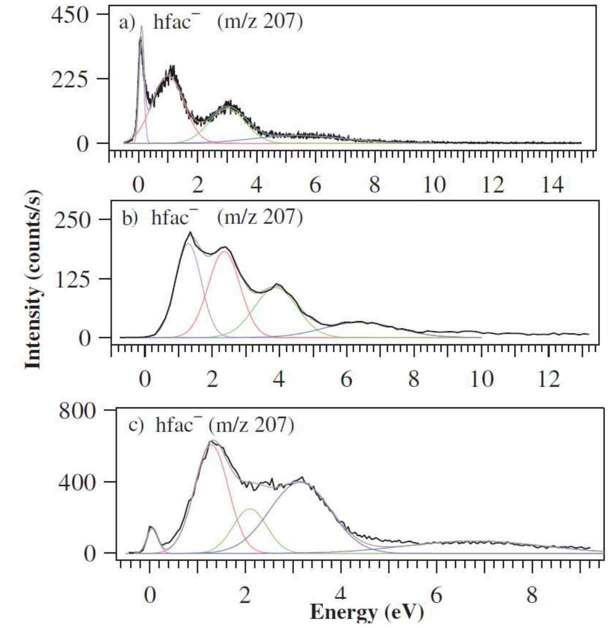

**Figure 4**. Ion yield curves from dissociative electron attachment as a function of incident electron energy; a) hexafluoroacetylacetone (hfac), b). $Pd(hfac)_2$, c) $Cu(hfac)_2$. Reproduced with permission from Engmann *et al*. *J. Chem. Phys.* **2013,** 138, 234309. © 2013 AIP Publishing LLC.

The problem of the energy dependence of a chemical bond on its length has been solved using quantum field theory.[6,7] Results obtained with a modified Yukawa potential and a Lewis electron pair as the interaction transfer quantum are in very good agreement with the experimental data listed in Refs. 8 and 9. The propagation velocity of Lewis pairs is constant and equals $\alpha c$, where $\alpha$ is the fine structure constant and $c$ is the velocity of light. An important characteristic of Lewis pairs is that the kinetic energy of the interaction transfer quantum is always larger than the chemical bond energy. Thus, the amplitude of the wave function of a Lewis electron pair must be zero on atoms forming a chemical bond. This, in turn, imposes the condition that the interatomic spacing be a half-wavelength of the Lewis electron pair ($\lambda$) and hence implies chemical bond energy quantization[1].

The chemical bond energy $U$ is expressed as

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[1] Note that in classical chemistry there is always a clear understanding of the fact that a symmetry breakdown is accompanied by the appearance of a compensating electromagnetic field, i.e. the transition from a symmetric to asymmetric biatomic molecule is accompanied by the appearance of a dipole moment in the latter. A quantitative assessment of the phenomenon was made by Pauling by introducing electronegativity. The difference in the electronegativities and the phase difference in the wave function of a Lewis electron pair on atoms forming a chemical bond are identical concepts.

$$U = \frac{n \cdot z_1 \cdot z_2}{r} \cdot e^{-\frac{n \cdot r}{k \cdot \bar{\lambda}}} \qquad (12)$$

where

$$\bar{\lambda} = \frac{\alpha \cdot \hbar \cdot c}{2 \cdot \left( m \cdot \alpha^2 \cdot c^2 - I_D \right)}, \qquad (13)$$

$$r = R + \bar{\lambda} \cdot \sum_{i=0}^{2} t_i \cdot \left( \frac{\beta}{\alpha} \right)^{2i}, \qquad (14)$$

$$\beta = \frac{g^2}{\hbar \cdot c}, \qquad (15)$$

and $n$ is the chemical bond order, $\hbar$ is the reduced Planck constant, $m$ is the rest mass of an electron, and $I_D$ is the first ionization potential of the donor atom, that is, the atom with the lower electronegativity. In the case under consideration here, the donor is the carbon atom. The parameter $k$ is an integer number equal to twice the number of valence electrons of the acceptor (exceptions are $k_N = 5$, $k_O = 6$, and $k_F = 7$), and $z_i$ is an interaction constant (charge) that assumes values of $e = \sqrt{\alpha \cdot \hbar \cdot c} = 1.518885 \times 10^{-14} J^{1/2} \cdot m^{1/2}$, $q = \frac{1}{3} e = 5.06295 \times 10^{-15} J^{1/2} \cdot m^{1/2}$, or $g = 1.03682 \times 10^{-14} J^{1/2} \cdot m^{1/2}$, where the subscript $i$ denotes an atom in the bonded pair such that a charge combination of $e^2$ corresponds to an ionic bond, $g^2$ to a covalent bond, and $q^2$ to a hydrogen bond. Note that $g \approx \frac{2}{3} e$ is only an approximation. The effective bond length $r$ is determined from the bond length $R$ and an additional term to compensate for local symmetry breakdown[2]. The quantum numbers $t_i$ that determine the main, fine, and hyperfine structure of a discrete spectrum of chemical bond energies assume values of $t_0 = 0, \pm 1, \pm 2, \pm 3, \ldots$, $t_1 = 0, \pm 1, \pm 2, \pm 3, \ldots$ and $t_2 = 0, \pm \frac{1}{4}, \pm \frac{1}{2}, \pm \frac{3}{4}, \pm 1, \ldots$ respectively.

## RESULTS AND DISCUSSION

In Ref. 1, the BDE(W−CO) of bonds broken via a single ionization event (Eqn. (1)) were calculated as

$$\mathrm{BDE}[(\mathrm{CO})_{n-1}\mathrm{W}^+ - \mathrm{CO}] = \mathrm{AE}[(\mathrm{CO})_{n-1}\mathrm{W}^+] - \mathrm{AE}[(\mathrm{CO})_n\mathrm{W}^+] \ (n = 1\text{–}6), \qquad (16)$$

and the average value was calculated as

$$\mathrm{BDE}(\mathrm{W–CO}) = [\mathrm{AE}(\mathrm{W}^+) - \mathrm{IE}(\mathrm{W})]/6, \qquad (17)$$

where IE(W) = 7.98 eV is the ionization energy of the tungsten atom.[10] It is also useful, however, to calculate the average values of each singly charged ion:

$$\mathrm{BDE}[(\mathrm{CO})_n\mathrm{W}^+ - \mathrm{CO}] = \{\mathrm{AE}[(\mathrm{CO})_n\mathrm{W}^+] - \mathrm{AE}[(\mathrm{CO})_6\mathrm{W}^+]\}/n \ (n = 1\text{–}5). \qquad (18)$$

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[2] Rather than introducing this treatment in a gauge electromagnetic field, a space warp was used, which greatly simplifies the mathematical calculations when its discrete character is taken into account.

Table 1 lists the BDEs obtained from Eqns. (16)–(18) for the electron ionisation (EI) method and the dissociative photoionisation (PI) method from Ref.3. For comparison purposes, the results obtained using Eqn. (10) to calculate BDE(W-CO), with $k_C = 8$, $R_{W-C} = 2.06 \times 10^{-10} m$, ,[11] $t_0 = 0$, and $t_2 = 0$, are also listed. For the EI method, the variable parameter is $t_1$, and this range of energies corresponds to the vibrational energies of the W-CO bonds. For the PI method, the variable parameter is $t_1$, and/or the $z_i$ charge combinations were also varied.

**Table 1. Calculated BDE(W−CO) values for several CO group loss events via electron ionization and dissociative photoionization.**

| Species | BDE[eV][2] (EI) | | BDE[eV] calc . | | | BDE[eV] [3] (PI) | BDE[eV] calc. | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Eqn.18** | **Eqn.16** | $t_1$ | **Eqn.12** | $z_1 \cdot z_2$ | | $t_1$ | **Eqn.12** | $z_1 \cdot z_2$ |
| $(CO)_5W^+ - CO$ | 1.84 | 1.84 | 0 | 1.84 | $g \cdot g$ | 1.80 | 0 | 1.84 | $g \cdot g$ |
| $(CO)_4W^+ - CO$ | 1.77 | 1.70 | 1 | 1.71 | $g \cdot g$ | 2.13 | -2 | 2.15 | $g \cdot g$ |
| $(CO)_3 W^+ - CO$ | 1.81 | 1.90 | 0 | 1.84 | $g \cdot g$ | 1.31 | 0 | 1.36 | $e \cdot q$ |
| $(CO)_2W^+ - CO$ | 1.99 | 2.52 | -4 | 2.53 | $g \cdot g$ | 1.03 | -2 | 1.07 | $g \cdot q$ |
| $(CO) W^+ - CO$ | 1.98 | 1.92 | -1 | 1.98 | $g \cdot g$ | 4.03 | 0 | 4.08 | $e \cdot e$ |
| $W^+ - CO$ | 2.07 | 2.52 | -4 | 2.53 | $g \cdot g$ | 3.46 | -3 | 3.47 | $e \cdot g$ |
| $W(CO)_6$ | — | 2.15[a] | -2 | 2.15 | $g \cdot g$ | 2.33[a] | -3 | 2.33 | $g \cdot g$ |

[a] This is average value.

According to the thermodynamic data from NIST,[10] $\Delta H_f(CO) = -110.53$ kJ/mole, $\Delta H(W) = 851.03$ kJ/mole, and $\Delta H_f[W(CO)_6] = -882.9$ kJ/mole, which gives a thermodynamic mean BDE(W–CO) value of 1.85 eV[3] that is consistent with the value calculated here for $t_1 = 0$ (1.84 eV). All the other experimental values agree with the calculated values for different vibrational states of the W−CO bond. However, while Eqn. (12) largely removes the uncertainty in regard to the internal energy of initial molecules and fragmentary ions, it does not resolve the question of how these vibrational states are filled. The experimental data obtained using the EI method does indicate that the detachment of CO ligands proceeds with the excitation of different vibrational levels. Note that the EI and PI methods record only the threshold value of the appearance of the signal even if this energy level is highly excited and poorly filled. That is, if the instrument sensitivity is increased, then the AE of the EI and appearance potential (AP) of the PI processes (any bonds and molecules) will be shifted towards lower energies. The temperature also has an influence on the vibration level filling in that an increase in the temperature will also shift the AE of the EI process towards lower energies. For example, see Figure 5 [12] and 6 [13]. Because the peak intensity is changed of the temperature (vibrational states are filled), but is not changed peak positions.

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[3] The $W(CO)_6$ molecule is an octahedron such that all W-CO bonds are of an equivalent length.[11]

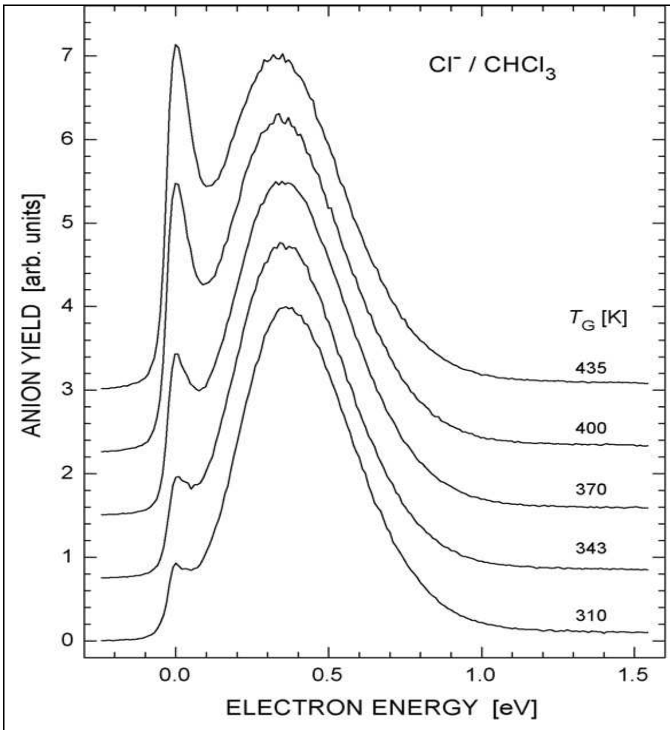

**Figure 5.** Dependence of the Cl$^-$ yield due to DEA to CHCl3 (measured with the HEM-QMS setup, resolution about 80 meV) on the gas temperature over the range $T_G$ = 310–435K; the respective anion yields were normalized to the same value at the higher energy peak and are shifted by adding a constant offset to each subsequent spectrum for clarity.Reproduced with permission from Kopyra *et al*. *Int. J. Mass Spectrom*. **2008** 277, 130 © 2008 Elsivier.

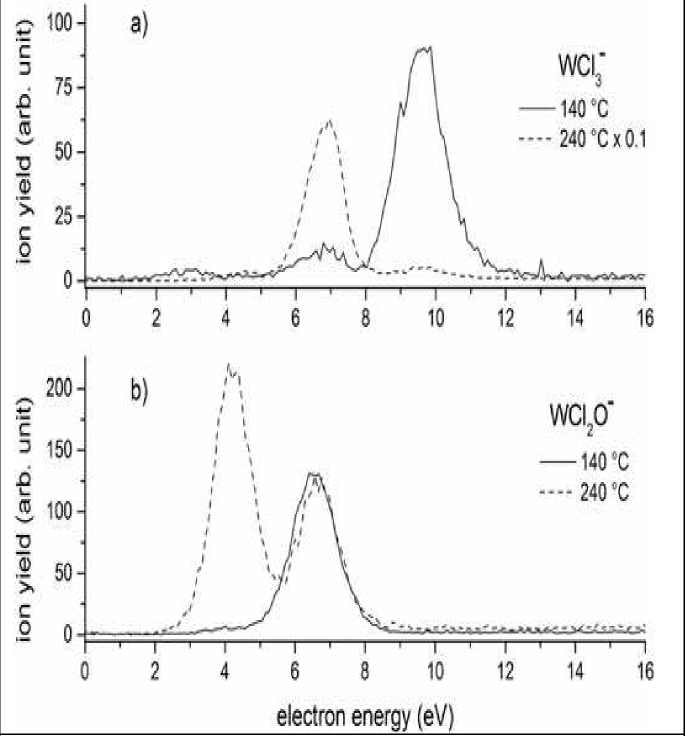

**Figure 6.** Comparison of the energy scans of WCl$_3^-$ (a) and WCl$_2$O$^-$ (b) obtained at ion source temperatures of 140 °C and 240 °C, respectively. Reproduced with permission from Neustetter *et al*. *Rapid Commun. Mass Spectrom*. **2016**, 30, 1139 © 2016 John Wiley & Sons.

A combination of these two factors will permit the whole vibration level spectrum to be obtained. As the vibrational levels are discrete energy levels, any change in the AE of the EI process will be abrupt. The instrument can also output average values between neighbouring energy levels, but this will depend on the built-in signal processing algorithm. It is possible to compare data from the EI method with only those data from the PI method that are unambiguously identified as pertaining to the main (not photoexcited) state. The difference in the energies of the vibrational levels can be observed experimentally using infrared spectroscopy.

The electronic-vibrational excited states are the result of moving one of the 2p electrons of oxygen to a vacant molecular orbital. This process simulates the addition of an electron in the electron attachment[4], and thus, the BDE values corresponding to a number of values for the BDEs of the PI processes must occur in the DEA process, i.e. 4.03 eV, 3.46 eV, 2.13 eV, 1.31 eV, and 1.07 eV. The DEA process obtained a series of energies of 4.65 eV, 3.15 eV, 2.15 eV, 1.55 eV, 1.05 eV. This is a very good match with the discrepancies caused by the difference in the vibrational levels.

If using experimental values, i.e. 4.03 eV, 3.46 eV, 2.13 eV, 1.31 eV, and 1.07 eV, of the BDE(W-CO), obtained by the PI processes[3] and the electron affinity equal 2.15eV[1], according to the equation (5b) to calculate the energy of the ion appearance (AE) in the DEA process, i.e. 1.88eV, 1.31eV, ~0eV, -0.84eV, and -1.08eV, some values will be negative, i.e. -1.08 eV, -0.84eV. Surprisingly, it is these “negative” kinetic energy of an electron observed experimentally, as show in Fig.2. The “negative” kinetic energy of an electron (AE<0) is the

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[4] This is a consequence of the identity of elementary particles.

result of quantum tunnelling through a potential wall, which creates a repelling electrode. There is a direct analogy in the case of the DEA process, namely, the threshold values of $^{239}_{94}Pu$, $^{233}_{92}U$, and $^{235}_{92}U$ fission under the effect of thermal neutrons with a negative kinetic energy. The equivalent neutron energies at the centre of the first threshold are as follows: -1.61 MeV for $^{239}_{94}Pu$, -1.47 MeV for $^{233}_{92}U$, and -0.60 MeV for $^{235}_{92}U$. The second thresholds are observable only for the first two: -0.72 MeV for $^{239}_{94}Pu$ and -0.72 MeV for $^{233}_{92}U$.[14] However, a detailed treatment of this issue is beyond the scope of the paper. The problem discussed in detail in the textbook of Mukhin[15]. However, we note that such an anomalous electron capture may be important for catalytic processes and for biological systems.

If the BDE values are converted to per-unit values by taking 4.65 eV as one then we see that the series of relative units corresponds to a series formed by a combination of two of the three numbers 1, 2/3, and 1/3. Series of relative units BDE(W-CO) is calculated from the "negative" value of the kinetic energy (AE <0). However, the entire series of six members at AE ≥ 0 experimentally observed Engmann *et al.*[5] in the decay hexafluoroacetylacetone using dissociative electron attachment. It is resonances at 0, 1.0, 3.0, 5.4, 7.0, and 10 eV.

Table 2 lists the results of the calculations for the DEA. For the production of the $W(CO)_3^-$ ion with a loss of three CO groups, the BDE(W−CO) of the first and second resonances are 1.68 and 1.98 eV, respectively. A calculation using Eqn. (13), in agreement with the experiment, was performed for the case where the value of $t_1$ changes from −2 (1.54 and 2.15eV) to −3 (1.66eV) and −1 (1.98eV) for the first and second resonances, respectively. It is likely that in this case there is a redistribution of the energy between the vibrational levels in the TNI. To do this, we make use of Eqn. (5a) and take a constant EA value of 2.15 eV. We can assume a constant value because on the right-hand side of Eqn. (5b) a stable EA value for one and the same ion is more likely than a stable BDE value in the same ion. We also estimate the AE values from Fig. 1 and Fig. 2[5].

**Table 2. Calculation of BDE(W−CO) for several CO group losses via DEA and PI**

| **BDE[a] (*AE*[b]) [eV] (DEA)** | | | | **BDE [eV] calculation** | $z_1 \cdot z_2$ | **BDE[eV] (PI)** | **BDE [eV] calculation** |
|---|---|---|---|---|---|---|---|
| $W(CO)_5^-$ | $W(CO)_4^-$ | $W(CO)_3^-$ | $W(CO)_2^-$ | | | | |
| 4.65 (*2.5*) | 4.57 *(7)* | —[c] | —[c] | 4.61 ($t_1$ = −2) | *e·e* | 4.03 | 4.08 ($t_1$ = 0) |
| 3.15 (*1*) | ?[d] | 3.08 *(7.1)* | —[c] | 3.14 ($t_1$ = −2) | *e·g* | 3.46 | 3.47 ($t_1$ = −3) |
| **2.15** (0) | **2.18** *(2.2)* | **1.98** *(3.8)* | **2.16** (6.5) | 2.15 ($t_1$ = −2)<br>1.98 ($t_1$ = −1) | *g·g* | 2.13<br>1.80 | 2.15 ($t_1$ = −2)<br>1.84 ($t_1$ = 0) |
| 1.55 (*−0.6*) | 1.53 (0.9) | 1.68 (2.9) | —[c] | 1.54 ($t_1$ = −2)<br>1.66 ($t_1$ = −3) | *e·q* | 1.31 | 1.36 ($t_1$ =0) |
| 1.05 (*−1.1*) | —[c] | —[c] | —[c] | 1.05 ($t_1$ = −2) | *g·q* | 1.03 | 1.07 ($t_1$ = −2) |

[a] The most intense resonances are shown in bold text.

[b] Estimated AE values are italicized.

[c] The energies in these ranges overlapped with those of production processes for other ions.

[d] For the production of the $W(CO)_4^-$ ion, Fig. 1 shows a shoulder (indicated by the arrow) possibly for the resonance with AE ~ 4.15 eV.

Engmann *et al.* [5] all the calculations made using as a basis BDE(O-H) at (hfac) equal 4,3эв. This BDE(O-H) is typical of saturated alcohols. However, this energy is less at enols. For vinyl alcohol BDE(O-H) is 3.65 eV[16]. The bond length O-H at (hfac) is $0,988 \cdot 10^{-10}$ m[17]. Table 3

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[5] For the dissociation process of the W-CO bond, the particular place this occurs in the instrument is of little consequence; it does not matter where it occurs be it in the gaseous or liquid phase, from the neutral molecule or from a metastable molecule, or a parent or a daughter ion. None of these factors alter the essence of the process, i.e. the disruption of the W-CO bond, but they influence the efforts that are necessary to achieve the desired result. It is the absolute values of these energies that are of interest here.

lists the results of the calculations BDE(O-H) for the hexafluoroacetylacetone. The results obtained using Eqn. (12) to calculate BDE(O-H), values of $\lambda_H = 5.284 \cdot 10^{-11} m$ , $k_O = 6$, $t_0 = 0$, $t_1 = 0$ and $t_2 = 0$. Only the $z_i$ charge combinations were varied.

**Table 3. Calculation of BDE(H−O) and AE of the dehydrogenated (hfac) radical**

| | **Calculation Eqn.12** | | **Resonances [eV][5]** |
|---|---|---|---|
| $z_1 \cdot z_2$ | **BDE [eV]** | **AE[eV]** | |
| *e·e* | 11.02 | 9.62 | 10 |
| *e·g* | 7.40 | 6.0 | 7.0 |
| *g·g* | 4.97 | 3.57 | 5.4 |
| ***e·q*** | **3.67** | **2.27** | **3.0** |
| *g·q* | 2.47 (2.13[a]) | 1.07 (0.73[a]) | 1.0 |
| *q ·q* | 1.22 | -0.18 | 0 |

[a] calculation at $t_1 = 1$

Calculated value of BDE(O-H) is 3.67 eV, at $z_1 \cdot z_2 = e \cdot q$, agree with the experimental date BDE(O-H) is 3.65 eV. This corresponds to a resonance 3.0 eV and appearance energy equal 2.27 eV. Consequently, electron affinity of the dehydrogenated (hfac) radical is 1,40 eV. This corresponds to typical values of electron affinity of the alcohol radical equal to ~ 1.5eV[8]. Electron affinity of the dehydrogenated (hfac) radical is 4.3 eV[5] incorrectly.

Table 4 lists the results of the calculations BDE(Pd-O) for the bishexafluoroacetylacetonate palladium(II), Pd(hfac)$_2$. The results obtained using Eqn. (12) to calculate BDE(Pd-O), values of $k_{Pd} = 12$, $t_0 = 0$, $t_1 = 0$ and $t_2 = 0$. $R_{Pd-O} = 1.982 \times 10^{-10} m$ ,[18] , $\lambda_{Pd} = 3.81410^{-11} m$ .Only the $z_i$ charge combinations were varied.

**Table 4. Calculation of BDE(Pd−O) bishexafluoroacetylacetonate palladium(II) and AE of the dehydrogenated (hfac) radical**

| | **Calculation Eqn.12** | | **Resonances [eV][5]** |
|---|---|---|---|
| $z_1 \cdot z_2$ | **BDE [eV]** | **AE[eV]** | |
| *e·e* | 4.86 | 8.33 | - |
| *e·g* | 3.27 | 5.14 | 6.5 |
| *g·g* | 2.20 | 2.99 | 3.9 |
| ***e·q*** | **1.62[a]** | **1.84** | **2.4** |
| *g·q* | 1.09 | 0.78 | 1.30 |
| *e·e* | 0.54 | -0.32 | - |

[a] The experimental date is 1.55±0.08 eV [19] .

Table 5 lists the results of the calculations BDE(Cu-O) for the bishexafluoroacetylacetonate Copper(II), Cu(hfac)$_2$. The results obtained using Eqn. (12) to calculate BDE(Cu-O), values of $k_{Cu} = 8$, $t_0 = 0$, $t_1 = 1$ and $t_2 = 0$. $R_{Cu-O} = 1.913 \times 10^{-10} m$ [20], $\lambda_{Cu} = 3.695 \cdot 10^{-11} m$ . Electron affinity of the dehydrogenated (hfac) radical is 1,40 eV. Only the $z_i$ charge combinations were varied.

**Table5. Calculation of BDE(Cu−O) bishexafluoroacetylacetonate Copper(II) and AE of the dehydrogenated (hfac) radical**

| | **Calculation Eqn.12** | | **Resonances [eV][5]** |
|---|---|---|---|
| $z_1 \cdot z_2$ | **BDE [eV]** | **AE[eV]** | |
| *e·e* | 3.80 | 6.19 | - |
| *e·g* | 2.55 | 3.70 | 6.5 |
| ***g·g*** | **1.72[a]** | **2.03** | **3.2** |
| *e·q* | 1.27 | 1.13 | 2.1 |
| *g·q* | 0.85 | 0.30 | 1.3 |
| *e·e* | 0.42 | -0.56 | 0 |

[a] The experimental date is 1.65±0.09eV [21].

Resonances in Ref 5 explains the excited states of the system, using a variety of virtual orbitals. However, the excited states may be described using a quasiparticle [6]

Thus, to obtain the BDE values are listed in Tables 2-5 as a result of the electron attachment process, the following processes must be taking place:

$$g + {}^{1}\!/_{3}\, e \rightarrow e \qquad (19)$$

$$g - {}^{1}\!/_{3}\, e \rightarrow q \,. \qquad (20)$$

Evidence that these processes do indeed occur is provided by the accurate agreement between the calculated and observed BDE values for the DEA and PI methods presented in Tables 2-5.

To date, the only experimental observation of fractional charges (disregarding quarks) has been the fractional quantum Hall effect (FQHE),[22] which has been observed in two-dimensional structures at temperatures close to 0 K and in large magnetic fields of up to 30 T. Electrons under such conditions turn into a new state of matter − the Laughlin liquid, a state consisting of strongly interacting electrons in which the motion of an individual electron loses its meaning. One of the properties of this liquid is that on addition of an extra electron the liquid turns into an excited state to give birth to fractionally charged quasi-particles. It is thought that quasi-particles are comprised of an electron and several quanta of the captured magnetic field flux. FQHE has been observed in graphene,[23,24] and a spherical ball of graphene is an approximate model of a spherical layer of the valence electrons of tungsten. This layer contains correlated electrons, and by adding one electron to the layer gives rise to quasi-particles with a charge of ⅓*e*. But, there is no external magnetic field in this case! This result in the absence of an external magnetic field implies localization, specifically localization of the quasi-particles on the atoms. However, without an external magnetic field, the structure of these quasi-particles is unclear.

Conservation of charge requires that Eqns. (19) and (20) occur simultaneously, but no localization conditions for the excitations on the atoms of a single bond are imposed. Thus, if the *e*•*g* combination rather than the *g*•*g* combination is observed, then the *g*•*q* combination must also be detected. For the metastable $W(CO)_5^-$ ion, a small resonance is seen in Fig. 2 (indicated by the arrow), which corresponds to

$$e \cdot g + {}^{1}\!/_{3}\, e \rightarrow e \cdot e \qquad (21)$$

and in accordance with charge conservation, the following process must also occur:

$$e \cdot g - {}^{1}\!/_{3}\, e \rightarrow e \cdot q \,. \qquad (22)$$

The AE value of −0.6 eV corresponds to the *e*•*q* combination, and it is this energy that is observed for the main peak of the metastable ion. The disagreement between intensities is accounted for by the fact that the resonance overlaps the regions of the *g*•*g* (AE = 0 eV) and *e*•*g* (AE = 1 eV) states; the *g*•*g* state is the main channel of disintegration. The transition from the *g*•*g* state to the *e*•*e* state proceeds in two steps,

$$g \cdot g \xrightarrow{+{}^{1}\!/_{3} e} e \cdot g \xrightarrow{+{}^{1}\!/_{3} e} e \cdot e \,, \qquad (23)$$

---

[6] This is a consequence of wave-particle duality.

while the transition from the *g•g* state to the *e•q* state can occur in a single step, depending on the localization of the quasi-particles:

$$g\cdot g+\left(+\tfrac{1}{3}e-\tfrac{1}{3}e\right)\rightarrow e\cdot q \quad . \tag{24}$$

The fact that the most intense resonances of the DEA correspond to the BDE(W–CO) values of $W(CO)_6$ suggests that the main process is a direct “knocking-out” of a certain number of CO groups without producing a TNI. In cases in which the TNI is produced, Laughlin “quasi-particles” carrying fractional charge appear.

## CONCLUSIONS

The solution to the problem dependency of forces of interaction on the distance between interacting objects is fundamental laws of nature. Accordingly, the exact analytical solution to the problem of dependency of chemical bond energy on bond’s length is fundamental law of nature, such as Coulomb’s law or Newton’s law of universal gravitation. Description and application of this law we have done in this paper. We showed how about half of all possible states of chemical bond (without triplet states) can be calculated in a few minutes without venturing off elementary mathematics. Analysis of experimental data showed unusual events, such as the resonance capture an electron with "negative" kinetic energy and the formation of fractionally charged quasi-particles. An anomalous electron capture may be important for catalytic processes and for biological systems. As an experimental technique, mass spectrometry ranks next to (FQHE) in which fractional values of the charge quantization are observed. In mass spectrometry, unlike FQHE, fractionally charged quasi-particles are observed in the absence of a strong external magnetic field.

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