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Phenomenological Theory of the Activation Energy of
Hydrocarbon Reactions on Catalytic Stepped Platinum Surfaces⁺

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We present a phenomenological theory which allows us to calculate the heat of formation and activation energy of C-H, C-C and H-H bond scission processes on stepped platinum surfaces. The dependence of these energies on the location of the active platinum atoms shows trends

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which are those found experimentally. The catalytic properties of steps and kinks can therefore be attributed to the local field properties of the platinum d-electrons. Results are presented in tabular form.

I. INTRODUCTION

Surfaces of crystals characterized by high Miller indices consist of terraces of low index planes separated by steps often one atom in height. To date, experiments to study the correlation between the catalytic activity of Pt surfaces and their atomic surface structure seem to identify these atomic height steps and "kinks" in steps to be distinct catalytic sites where H-H, C-H and C-C bond scissions occur during the reactions of hydrocarbons. Three representative Pt single crystal surfaces which are distinguishable by their reactivities are shown schematically in Fig. 1. Fig. 1a is the low Miller index Pt ($\bar{1}11$) surface, all the surface sites S are equivalent with 9 nearest neighbors (i.e., coordination number equals 9). The high Miller index ($\bar{5}57$) surface is characterized by terraces of surface atoms S and the step corner atoms C_1 and C_2 along the monoatomic steps. Their coordination numbers are 7 and 11 respectively. The ($\bar{6}79$) surface in Fig. 1 c has, in addition to terraces and steps, also kinks in the steps; this surface is characterized by surface sites S, step corner sites C_1 and C_2 as well as kink sites K_1 (8 nearest neighbors), K_2 (6 nearest neighbors) and K_3 (10 nearest neighbors). Molecular beam scattering experiments¹ indicate the reaction probability for $H_2 - D_2$ exchange increases by four orders of magnitude on a highly stepped Pt surface similar to that shown schematically in Fig. 1b than on the Pt ($\bar{1}11$) surface. It is also found that the dehydrogenation of cyclohexane and cyclohexene to benzene occurs at an appreciable rate only on stepped Pt surfaces,^{2,3}

the rate is almost an order of magnitude lower on a Pt ($\bar{1}11$) surface. These experimental data point to the plausible conclusion that step corner sites such as C_1 and C_2 are sites for breaking H-H and C-H bonds. Other catalytic reactions of hydrocarbons, carried out on Pt surfaces, indicate the rate of cyclohexane hydrogenolysis to n-hexane⁴ increases slowly with step density and rapidly with surface kink density. The rates of n-hexane production per kink is almost an order of magnitude higher than that per step. Since the formation of n-hexane must be the result of C-C bond scissions, it seems that kinks are effective in breaking C-C bonds as well as C-H and H-H bonds.

In this paper, we construct a workable theoretical model corresponding to these catalytic bond-breaking reactions on Pt surfaces and present calculations which yield results consistent with the above experimental findings. The picture one has in mind for a typical H-H bond-breaking reaction at the Pt surface is as follows: a molecule approaches the Pt surface, at a certain distance X from the surface, it becomes energetically favorable to break the H-H bond and form two surface Pt-H bonds instead at catalytic sites on the Pt surface. Our theoretical calculations give the activation energy E_A required for such a reaction to occur at each of the distinct surface binding sites shown in Fig. 1: the sites S, C_1 , C_2 , K_1 , K_2 and K_3 . Fig. 2 is an energy diagram which describes such a reaction schematically. The initial state of the reaction when the H-H bond is still intact is described by a parabolic potential well of the H_2 molecule; the final state of the reaction after the H-H bond is broken and two surface

Pt-H bonds are formed is represented by another parabolic potential well. The centers of the two potential wells are separated by a generalized reactant distance X (which we assume for the time being known). The reaction occurs because there is a net lowering of energy with the breaking of one H-H bond and the formation of two Pt-H surface bonds. The energy difference of the initial and final states ($E_f - E_i$) is then represented by the relative energy coordinates of the centers of the two potential wells, it is equal to the H-H bond energy minus two Pt-H surface bond energies, as denoted by $E_{H-H} - 2 E_{Pt-H}$ in the Figure. Now one has a situation where the initial and the final states of the chemical reaction are well defined; not much is known about the actual reaction path except that it should be close to the energetically most favorable path. Here we make the plausible assumption that if a smooth curve is allowed to pass through the two potential wells such that it fits the bottom of the potential wells exactly, i.e., it should match the slope and curvature of the two respective potential wells at their respective positions, then the maximum energy barrier thus obtained for the transition from initial to final state should approximate the actual activation energy E_A of such a reaction. A fifth order polynomial fits beautifully such a curve with the six boundary conditions (positions, first derivatives and second derivatives of the bottom of the two potential wells). The activation energies thus determined for different surface sites are listed in Table 3. Lower activation energies are generally obtained for final binding on the step corner and kink sites than on

the (111) surface sites S. Before discussing the results, we turn now to outline the actual theoretical calculations involved in arriving at the desired results.

II. FORMULATION

The theoretical model used in the calculation of the activation energies E_A for catalytic reactions on different surface sites involves the following:

(1) The typical bond energies of C-C bonds, C-H bonds and H-H bonds are assumed to be their respective diatomic molecular dissociation energies taken out of Herzberg.⁵ These values are comparable to experimentally determined values⁶ for specific hydrocarbons involved in the surface catalytic reactions; yet their choice allows us to treat the reaction in the context of a bond scission in a simple diatomic molecule rather than that of a complicated hydrocarbon.

(2) In the neighborhood of the equilibrium separation r_e (bond length) of a diatomic molecule, the potential curve U is well represented by the parabola

$$U = (1/2)k (r - r_e)^2 \quad (1)$$

where k is the spring constant responsible for the vibronic modes of the diatomic molecule. The curvature of the potential wells shown in Fig. 2 can then be derived from the spectroscopic data⁵ of the ground states of diatomic molecules: H_2^1 , C_2^{12} and $C^{12}H^1$. No spectroscopic data are tabulated for Pt-H and Pt-C; to approximate the curvature for this potential well, we use the average of the values derived from spectroscopic data for NiH ($k = 13.5 \text{ ev/\AA}^2$) and CuH ($k = 13.7 \text{ ev/\AA}^2$).

The mean value $\underline{k} = 13.6 \text{ ev/\AA}^2$ for Pt-H and Pt-C is probably a good approximation since (i) the three transition metals Ni, Pt, Cu have proximal d electron occupation — Ni ($3d^8$), Pt ($5d^9$) and Cu ($3d^{10}$) and (ii) the bond energies of NiH, CuH, Pt-H, Pt-C are quite comparable. The dissociation energies of NiH and CuH are 3.1 ev and 2.9 ev respectively; $\sqrt[5]{\text{bond energy bond length calculations}}$ $\sqrt[7]{\text{of Pt-H and Pt-C bond on a (111) surface}}$ yields the values 2.9 ev and 2.7 ev respectively.

(3) The parameter X in Fig. 2 is an unknown. It is supposed to represent the separation of, say, the Pt-H₂ and (PtH)-H systems along the reaction path. A reasonable guess is that it should be comparable to the bond lengths of the molecules involved in the reaction. Intuitively, the larger the separation of the two potential wells X in Fig. 2, the higher the resultant activation energy will be, provided all other parameters are fixed. However, X should play very little role in determining the variation of the reaction activation energies from one specific geometric surface site to another, which is the main effect we seek to calculate. For the purpose of this calculation, we simply treat X as a phenomenological parameter, two values are chosen for the calculation, one is the H-H bond length — 0.74Å; the other the geometric mean of the H-H and Ni-H bond lengths — 1.04Å. At this point, one has all the data required to calculate the activation energy required for the bond scission to occur on a Pt(111) surface site (i.e., S). The data that have been discussed so far are summarized in Table 1.

(4) Bond energies of Pt-H and Pt-C on a Pt(111) surface have been estimated by bond energy bond length calculations.^{7/} On a Pt(111) surface, only the surface site S is available for binding to a C or H atom. Since it is the localized d electrons on the surface Pt ion that form the bonding orbitals, it is to be expected that the d electrons, subject to different local fields on distinct surface, step and kink sites with varying coordination number, may form very different bonding orbitals. That the stereochemistry of a transition metal changes with different local geometries in a transition metal stepped surface has been demonstrated in previous calculations.^{8/} (hereafter referred to as I). One major step in the present calculation is to obtain quantitatively a value for the bond energies $E_{\text{Pt-H}}$ and $E_{\text{Pt-C}}$ on each distinct site (C_1, C_2, K_1, K_2, K_3); these values will crucially affect the resultant activation energy E_A . One starts by retracing the formulation described in paper I. The conduction band of the Pt metal is assumed to be constituted by the free-electron-like s electrons. The d electrons are assumed to be atomic like and localized on the Pt metal ions at the lattice sites. At the Pt surface, the local field is different depending on the position of the ion: on the planar surface, in a step corner or at a step kink. This local field has two major effects. The first one is to produce a sizeable d electron transfer to or from a surface metal ion with the conduction band serving as a reservoir for such transfers. The electronic configuration of atomic Pt is $(\text{Xe}) 5s^2 5p^6 5d^9 6s$, the possible electronic charge transfer at the surface implies that the d electron

configuration of a surface metal ion may range from $\text{Pt}^{++}(\text{5d}^8)$ to $\text{Pt}(\text{5d}^{10})$. Kesmodel and Falicov⁹ have investigated the problem of electron charge transfer for a 2-dimensional corner geometry. To extend that calculation to actual 3-dimensional surface geometries is too formidable a task. Hence, the actual d electron configuration on each surface site is not known. However, an adequate physical picture emerges if the bond energies $E_{\text{Pt-H}}$, $E_{\text{Pt-C}}$ on all surface sites are calculated for the two limiting cases: $\text{Pt}^{++}(\text{5d}^8)$ and $\text{Pt}^+(\text{5d}^9)$; the $\text{Pt}(\text{5d}^{10})$ case is ruled out since a filled d shell is inert as far as bonding is concerned. The second effect of the local field is to produce level splittings of the many electron configurations. In the absence of local field, the electronic ground state, ψ_0 , determined by Hunds' rule for the free metal ion is ^2D for $\text{Pt}^+(\text{5d}^9)$ and ^3F for $\text{Pt}^{++}(\text{5d}^8)$. These states have an orbital degeneracy of order $(2L + 1)$ so the D state is five-fold orbital-degenerate and the F state has a seven-fold orbital degeneracy. Once the Pt metal ion is placed in the local crystal field $V(x)$ of the different surface sites, the ground state degeneracies are partially or completely lifted. To calculate the ground state splitting at each site one diagonalizes the matrix $\langle \psi_0 | V(x) | \psi_0 \rangle$. The interested reader is referred to paper I for the method of crystal field calculation. Relevant formulas and parameters for $V(x)$ particular to this calculation are presented in Appendix A.

After obtaining the energies and the wavefunctions of the d level splittings of the Pt metal ion at each distinct surface site, we proceed to relate them to the different bond energies of Pt-C and Pt-H. The theoretical model constructed for this purpose is as follows:

(a) For each distinct surface site, a vector $\hat{d}$ is defined as the direction pointing furthestmost away from all its non-missing nearest neighbors. A Pt ion in the bulk has 12 nearest neighbors, one can represent each nearest neighbor site by a vector originating from the reference ion. At a surface site, the coordination number is less than 12, for example, for the K_1 site, the coordination number is only 8, 4 nearest neighbors are missing, the vector sum of these 4 missing nearest neighbors define the desired direction $\hat{d}$.

(b) A directed orbital ψ_d is defined to be the atomic d orbital having the symmetry of the spherical harmonic $Y_{20}(\theta, \phi)$, angles θ and ϕ defined with respect to $\hat{d}$. Such a directed orbital is then assumed to be the energetically most favorable bonding orbital at the particular surface site for molecules approaching the metal surface.

(c) Now the crystal field calculation described earlier splits the free ion ground state of Pt^+ and Pt^{++} into levels that span an energy range of many electron volts. These wave functions have various symmetries compatible with the local environment. The ideal state for bonding is one which presents its electronic charge directly facing the preferential direction $\hat{d}$. Such state can be made by combining the various local-field states, and in general it requires the admixture of excited states. It therefore has an average energy such that it is higher than the ground state energy by an amount E .

This energy, which we call the directed valence energy, can be calculated with the aid of Clebsch-Gordon coefficients and rotation matrices¹⁴ of the second¹⁵ and third rank.¹⁶ It is tabulated for each position in Table 2. These $\bar{E}_t$ ($t = S, C_1, C_2, K_1, K_2, K_3$) are a direct measure of the surface bond energies of Pt-H and Pt-C on different surface sites. The lower the $\bar{E}_t$, the larger is the binding energy of Pt-H or Pt-C on the particular site. Using these values of $\bar{E}_t$ in conjunction with the bond energies of Pt-C and Pt-H for the particular (111) surface site S (these are tabulated in Table 1; they serve as the reference values of $E_{\text{Pt-H}}$ and $E_{\text{Pt-C}}$ for all the other sites), one obtains the important parameter ($E_f - E_i$), separation in energy of the two potential wells in Fig. 2 for every geometrical site. In cases where ($E_f - E_i$) becomes positive, the reaction will not take place in the framework of our theoretical model. This completes the set up for the calculation of the activation energies E_A for the bond scission of C-H, H-H and C-C for all the distinct surface sites, in the two cases $\text{Pt}^{++}(\text{5d}^8)$ and $\text{Pt}^+(\text{5d}^9)$ with two values of the generalized reactant distance X . The calculated E_A 's are tabulated in Table 3.

III. RESULTS AND DISCUSSION

The results tabulated in Table 3 are very encouraging. Each column in the table spans all the six surface sites and lists the activation energies for a particular bond breaking reaction, with a given general reactant distance parameter X . In discussing the results, it is necessary to consider the pair of adjacent columns for the $\text{Pt}^{++}(5d^8)$ and $\text{Pt}^+(5d^9)$ together because these are the two relevant components of the same system at a surface site, the exact number of localized d electrons on a surface Pt ion being, quantum mechanically, not well defined. Using the S site as the reference, we note that for each pair of columns the activation energy E_A is considerably lowered at the C_2 site for the $\text{Pt}^+(5d^9)$ ion; it is drastically lowered at the K_2 site for both configurations and slightly lowered at the K_1 site for the $\text{Pt}^{++}(5d^8)$ ion. Fig. 1 shows that a simple Pt (111) surface consists of only S sites; a stepped surface (557) is characterized by terraces of S sites and step corner atoms C_1 and C_2 ; and a kinked surface Pt (679) contains sites K_1 , K_2 , K_3 as well as S, C_1 and C_2 . The common trend of the lowering of E_A in corner sites and kink sites in each pair of columns in Table 3 plainly identify the step corner site C_2 and kink sites K_1 and K_2 as catalytic sites.

The variation of the value of E_A from column to column depends on the properties of the incoming molecule: (i) bond energy and (ii) vibronic spring constant k of the incoming molecule. Higher bonding energy and stiffer spring constant result in larger activation energy.

We have already discussed the fact that increasing the parameter X — the generalized reactant distance — has the effect of raising the calculated value of the activation energy.

The activation energy enters into the reaction rate in a Boltzmann exponential: $\exp(-E_A/k_B T)$. In Table 4, we tabulate the values of this exponential factor at room temperature ($T = 20^\circ\text{C}$) for all the three bonds considered: C-H, H-H and C-C, using the particular parameter $X = 0.74\text{\AA}$. For C-H, the exponential factor is small for the S site, it is one order of magnitude larger in both the corner and kink sites. For H-H, the exponential factor is again small at S — it is about 400 times larger on the corner and kink sites. Therefore, the corner and kink sites definitely have the property of increasing the rate of C-H, H-H bond breaking surface reactions. With the identical set of parameters X and T , the calculated exponential factor at S for C-C is at least two orders of magnitude smaller than the corresponding values at S for C-H and H-H. If under this set of experimental conditions the bond-breaking reactions of C-H and H-H are barely observable, then the much smaller value of the exponential at the S site for C-C implies that the C-C bond breaking should be negligible. The fact that the values of this exponential factor at C_2 and K_2 become comparable to those found for the reactions involving C-H and H-H implies that the kink surface can catalyze the C-C bond scission reactions to an experimentally observable rate.

In conclusion, by making drastic assumptions and resorting to empirical parameters, we have been able to construct a workable theoretical model which allows us to estimate activation energies. Our results confirm experimental evidence which identify atomic steps and kinks on Pt surfaces to be distinct catalytic sites. Our method has capabilities of calculating similar properties for other configurations, other metals and other reactions.

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FIGURE CAPTIONS

Fig. 1. Schematic representations of three representative Pt single crystal catalyst surfaces:

(a) Pt ($\bar{1}11$), (b) Pt ($\bar{5}57$), (c) Pt ($\bar{6}79$).

Fig. 2. Schematic energy diagram of a typical bond breaking surface reaction (H-H bond on Pt surface).

Table 1. Parameters needed for calculation of activation energy.

Molecular bond energies (from diatomic molecular dissociation energies)

C-H
3.47evH-H
4.47evC-C
3.6ev

Pt surface bond energies (site S in particular)

Pt-C
2.71evPt-H
2.91evVibronic spring constants k (ev/ $\text{\AA}^2$)C-H
27.93 ev/ $\text{\AA}^2$ H-H
35.73 ev/ $\text{\AA}^2$ C-C
-59.31 ev/ $\text{\AA}^2$ Pt-H or Pt-C
13.6 ev/ $\text{\AA}^2$ $(E_f - E_i)$ for the bond scission with final state on the S sitesC-H
-2.15evH-H
-1.35evC-C
-1.82ev

Table 2. Directed valence energies $\bar{E}_t$, where $t = S, C_1, C_2, K_1, K_2$ and K_3 .

Surface Site	S	C_1	C_2	K_1	K_2	K_3
$\bar{E}(\text{ev})$ for $\text{Pt}^{++}(\text{5d}^8)$	3.74	3.99	4.37	2.49	0.78	4.79
$\bar{E}(\text{ev})$ for $\text{Pt}^+(\text{5d}^9)$	6.10	8.08	1.33	6.38	0.42	6.40

Table 3. Activation energies E_A for the bond scissions: C-H, H-H and C-C at different surface sites.

Surface Site	$E_A(\text{ev})$ for C-H scission				$E_A(\text{ev})$ for H-H scission				$E_A(\text{ev})$ for C-C scission			
	X = 0.74Å		X = 1.04Å		X = 0.74Å		X = 1.04Å		X = 0.74Å		X = 1.04Å	
	Pt ⁺⁺ (5d ⁸)	Pt ⁺ (5d ⁹)	Pt ⁺⁺ (5d ⁸)	Pt ⁺ (5d ⁹)	Pt ⁺⁺ (5d ⁸)	Pt ⁺ (5d ⁹)	Pt ⁺⁺ (5d ⁸)	Pt ⁺ (5d ⁹)	Pt ⁺⁺ (5d ⁸)	Pt ⁺ (5d ⁹)	Pt ⁺⁺ (5d ⁸)	Pt ⁺ (5d ⁹)
S	0.059	0.059	0.240	0.240	0.151	0.151	0.476	0.476	0.273	0.273	0.797	0.797
C ₁	0.080	-	0.299	-	0.213	-	0.584	-	0.336	-	0.902	-
C ₂	0.144	0.004	0.432	0.026	0.398	0.009	0.818	0.054	0.482	0.031	1.101	0.166
K ₁	0.019	0.084	0.103	0.307	0.046	0.222	0.210	0.599	0.120	0.345	0.467	0.916
K ₂	0.008	0.003	0.047	0.020	0.017	0.006	0.097	0.042	0.056	0.024	0.265	0.135
K ₃	-	0.086	-	0.313	-	0.229	-	0.609	-	0.352	-	0.925

Table 4. The exponential factor $\exp(-E_A/k_B T)$ for $X = 0.74\text{\AA}$ and $T = 20^\circ\text{C}$.

Surface Sites	C-H		H-H		C-C	
	$\text{Pt}^{++}(5d^8)$	$\text{Pt}^+(5d^9)$	$\text{Pt}^{++}(5d^8)$	$\text{Pt}^+(5d^9)$	$\text{Pt}^{++}(5d^8)$	$\text{Pt}^+(5d^9)$
S	0.09	0.09	0.002	0.002	2×10^{-5}	2×10^{-5}
C_1	0.04	-	0.0002	-	1×10^{-6}	-
C_2	0.003	0.85	10^{-7}	0.7	4×10^{-9}	0.29
K_1	0.46	0.03	0.16	10^{-4}	8×10^{-3}	10^{-6}
K_2	0.73	0.89	0.51	0.79	0.11	0.38
K_3	-	0.03	-	10^{-4}	-	8×10^{-7}

APPENDIX A

The expressions for crystal field Potential V at sites S , C_1 , C_2 , K_1 , K_2 and K_3 are given in the same notations as are used in Paper I.⁸ These notations are:

q - net charge on each nearest neighbor metal ion

a - nearest neighbor distance = 5.2398 a.u.

$\langle r^2 \rangle, \langle r^4 \rangle$ - computed radial averages of Pt 5d atomic orbitals, the atomic wavefunctions are taken out from Herman and Skillman,⁹ their values are 13.44 a.u., 77.13 a.u.

$\tilde{O}_{\ell m}$ - Racah operator equivalents, angular momentum operators which transform in the same way as the spherical tensors

$$\left(\frac{4\pi}{2\ell+1} \right)^{1/2} Y_{\ell m}(\theta, \phi)$$

α_J, β_J - numerical factors which arise as the crystal field potential are transformed into "operator equivalents," they are specific to the angular momentum and spin quantum numbers of the free ion ground state.¹⁰ For $Pt^+(5d^9)$, $\alpha_J = 2/21$, $\beta_J = -2/63$. For $Pt^{++}(5d^8)$, $\alpha_J = 2/105$, $\beta_J = 2/315$.

We introduce the additional

$$\begin{aligned} \tilde{O}_{\ell m}^+ &= \tilde{O}_{\ell m} + \tilde{O}_{\ell m} \\ \tilde{O}_{\ell m}^- &= \tilde{O}_{\ell m} - \tilde{O}_{\ell m} \end{aligned}$$

to simplify the following expressions of the crystal field potentials.

$$\begin{aligned}
 v_S(x) = & \frac{9q}{a} + \frac{q}{a} \frac{\langle r^2 \rangle}{a^2} \alpha_J \left[\frac{\sqrt{6}}{4} (\tilde{O}_{21}^- + i \tilde{O}_{21}^+) \right] \\
 & + \frac{q}{a} \frac{\langle r^4 \rangle}{a^4} \beta_J \left[\frac{-21}{16} \tilde{O}_{40} + \frac{\sqrt{5}}{16} (\tilde{O}_{41}^- + i \tilde{O}_{41}^+) \right. \\
 & \left. + \frac{i\sqrt{10}}{8} \tilde{O}_{42}^- + \frac{\sqrt{35}}{16} (\tilde{O}_{43}^- - i \tilde{O}_{43}^+) - \frac{3\sqrt{70}}{32} \tilde{O}_{44}^+ \right] \quad (A1)
 \end{aligned}$$

$$\begin{aligned}
 v_{C_1}(x) = & \frac{7q}{a} + \frac{q}{a} \frac{\langle r^2 \rangle}{a^2} \alpha_J \left[\frac{1}{4} \tilde{O}_{20} + \frac{\sqrt{6}}{4} \tilde{O}_{21}^- + \frac{5\sqrt{6}}{8} \tilde{O}_{22}^+ \right] \\
 & + \frac{q}{a} \frac{\langle r^4 \rangle}{a^4} \beta_J \left[\frac{-41}{32} \tilde{O}_{40} + \frac{\sqrt{5}}{16} \tilde{O}_{41}^- - \frac{\sqrt{10}}{12} \tilde{O}_{42}^+ + \frac{\sqrt{35}}{16} (\tilde{O}_{43}^-) - \frac{3\sqrt{70}}{64} \tilde{O}_{44}^+ \right] \quad (A2)
 \end{aligned}$$

$$\begin{aligned}
 v_{C_2} = & 11 \frac{q}{a} + \frac{q}{a} \frac{\langle r^2 \rangle}{a^2} \alpha_J \left[-1/4 \tilde{O}_{20} + \frac{\sqrt{6}}{4} \tilde{O}_{21}^- - \frac{\sqrt{6}}{8} \tilde{O}_{22}^+ \right] \\
 & + \frac{q}{a} \frac{\langle r^4 \rangle}{a^4} \beta_J \left[\frac{-139}{32} \tilde{O}_{40} + \frac{\sqrt{5}}{16} \tilde{O}_{41}^- - \frac{5\sqrt{10}}{32} \tilde{O}_{42}^+ + \frac{\sqrt{35}}{16} \tilde{O}_{43}^- - \frac{9\sqrt{70}}{64} \tilde{O}_{44}^+ \right] \quad (A3)
 \end{aligned}$$

$$\begin{aligned}
 v_{K_1} = & 8 \frac{q}{a} + \frac{q}{a} \frac{\langle r^2 \rangle}{a^2} \alpha_J \left[-\frac{1}{4} \tilde{O}_{20} + \frac{\sqrt{6}}{4} \tilde{O}_{21}^- + \frac{\sqrt{6}}{8} \tilde{O}_{22}^+ - i \frac{\sqrt{6}}{4} \tilde{O}_{22}^- \right] \\
 & + \frac{q}{a} \frac{\langle r^4 \rangle}{a^4} \alpha_J \left[-\frac{29}{32} \tilde{O}_{40} + \frac{\sqrt{5}}{16} \tilde{O}_{41}^- + \frac{5\sqrt{10}}{32} \tilde{O}_{42}^+ + i \frac{\sqrt{10}}{8} \tilde{O}_{42}^- + \frac{\sqrt{35}}{16} \tilde{O}_{43}^- \right. \\
 & \left. - \frac{7\sqrt{70}}{64} \tilde{O}_{44}^+ \right] \quad (A4)
 \end{aligned}$$

$$v_{K_2} = 6 \frac{q}{a} + \frac{q}{a} \frac{\langle r^4 \rangle}{a^4} \beta_J \left[-\frac{7}{8} \tilde{O}_{40} - \frac{\sqrt{70}}{16} \tilde{O}_{44}^+ \right] \quad (A5)$$

$$\begin{aligned}
 v_{K_3} = & 10 \frac{q}{a} + \frac{q}{a} \frac{\langle r^2 \rangle}{a^2} \alpha_J \left[-\frac{1}{2} \tilde{O}_{20} + \frac{\sqrt{6}}{4} (\tilde{O}_{21}^- + i \tilde{O}_{21}^+) \right] \\
 & + \frac{q}{a} \frac{\langle r^4 \rangle}{a^4} \beta_J \left[-\frac{63}{16} \tilde{O}_{40} + \frac{\sqrt{5}}{16} (\tilde{O}_{41}^- + i \tilde{O}_{41}^+) + \frac{\sqrt{35}}{16} (\tilde{O}_{43}^- - i \tilde{O}_{43}^+) \right. \\
 & \left. - \frac{5\sqrt{70}}{32} \tilde{O}_{44}^+ \right] \quad (A6)
 \end{aligned}$$

Diagonalization of $\langle \psi_0 | V(v) | \psi_0 \rangle$ gives the d level splittings, their actual values are generally obtained in terms of the experimentally measurable cubic crystal field parameter $10 Dq$ by the following relationship:

$$\text{For the D ground state (Pt}^+), Dq = \frac{|q|}{a} \left(\frac{21}{8}\right) \frac{\langle r^4 \rangle}{a^4} \beta_J, \quad (A7)$$

$$\text{for the F ground state (Pt}^{++}), Dq = 5 \frac{|q|}{a} \left(\frac{21}{8}\right) \frac{\langle r^4 \rangle}{a^4} \beta_J. \quad (A8)$$

Experimental values of the crystal field parameter $10 Dq$ are available in the literature¹¹ for all the ions with outer 3d electrons.

That for Pt is obtained by scaling the electronic band structures^{12,13} of Ni and Pt at Γ point, namely, the d gap $\Gamma_{12} - \Gamma_{25}$. The scaled value is 1.738ev for $10 Dq$ in Pt.

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Fig. 1

Fig. 2

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