DISSOCIATION ENERGY AND DISSOCIATION PRODUCTS FOR THE GROUND AND FIRST EXCITED STATES OF MONO-OXIDE AND CARBIDE OF PLATINUM

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Experimental potential energy curves have been computed for the ground and first excited states of PtO and PtC using the Rydberg–Klein–Rees (RKR) method as modified by Vanderslice et al. A curve fitting has been made between the experimental potential energy curve and the three-parameter Lippincott potential function to estimate the dissociation energy and the result thus obtained has been compared with earlier results. Further, the dissociation products have been correlated for the above mentioned states of PtO and PtC molecules in accordance with the Wigner–Witmer rules. It has been found that, in the PtC molecule, the same dissociation products correspond to the ground as well as to the first excited state.

1. Introduction

Spectral study on the diatomic carbides, especially, of metals is very scarce. This is because its excitation is quite tedious. However, during the last two decades after the advent of the various sophisticated techniques of excitation like flash discharge, matrix isolation technique, condensed discharge and laser induced excitation, people got interested in the more intricate problems of excitation. One such group of molcules which received major attention was the study of diatomic oxides and carbides of the transition metals as well as those of the elements from the Actinide and Lanthanide series. In a series of such investigations the high resolution spectra of PtO and PtC was studied by Nilsson et al. [1] and Scullman and Yttermo [2], respectively. The dissociation energy of these two molecules was disputed due to a large amount of divergence noticed among the various results. The dissociation products were also discussed for PtO and PtC molecules by these authors [1, 2] and especially for the first excited state in these molecules the products

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were predicted in a questionable manner. It was, therefore, thought worthwhile to determine
the dissociation limit in the ground and the first excited electronic states of PtO and PtC
by the method of comparing an empirical potential function with the true potential energy
curve. It was also worthwhile to see whether a result thus obtained can help in deciding
among the various results for the dissociation energy and also in either refuting or accepting
the prediction for dissociation products in different states.

2. Computational procedure

For molecules with simple electronic structure, it becomes possible to obtain the
numerical values of the binding energy by the (SCF-LCAO) and (SCF-MO) methods,
as one can easily make simplified assumptions for the electronic orbits. But this is not
the case in general with heavy molecules. In addition to these fundamental calculations
some advances have also been made in the derivation of dissociation energy using empirical
potential functions. One of the most widely used and applicable potential energy functions
for diatomic molecules is that given by Lippincott et al. [3] and modified by Steele [4, 5]
using three parameters and given as below

$$U(r) = D_e \left[1 - \exp\left(\frac{-n(r-r_e)^2}{2r} \right) \right] \left[1 - a \left(\frac{b^2 n}{2r} \right)^{1/2} (r-r_e) \exp\left\{ - \left(\frac{b^2 n}{2r_e} \right)^{1/2} (r-r_e) \right\} \right].$$

$$(1)$$

The above potential function is basically a five parameter function. However, b is
a constant having the value 1.065 for nearly all the diatomic molecules, thus the parameters
may be reduced to four, D_e, n, r_e and a. Among these, r_e is the equilibrium internuclear
distance and D_e is the dissociation energy. The other two parameters viz., n and a are
related to the vibrational frequency ω_e, the anharmonicity $\omega_e x_e$, rotational constant B_e,
and the vibrational rotational coupling constant α_e through equations

$$n = (k_e r_e)/D_e, \quad \text{where} \quad k_e = 4\Pi^2 c^2 \omega_e^2 \mu,$$

$$a = F/(b\Delta^{1/2}), \quad \text{where} \quad F = \alpha_e \omega_e/6B_e^2, \quad \Delta = k_e r_e^2/2D_e.$$

Additional relationship,

$$a = F/(1 + 5F/4)$$

have been given by Steele and Lippincott [4] which reduces the Lippincott function to
a three-parameter function. The "r" appearing in equation (1) refers to r_{min} and r_{max} cor-
responding to different vibrations.

This method, though, suffers from a drawback because it does not take into account
the electronegativity of atoms and several other factors which could play a vital role in
ascertaining the dissociation energy of the molecule. But it has an added advantage that
it can be applied to the excited electronic states too, and thereby in estimating the D_e using
equation (1) for different electronic states, which in turn may help in deciding among the

various alternative dissociation products with the Wigner-Witmer rule. This method has been found to be fairly successful in many such studies conduced in our laboratory [6–8].

The above potential function was, therefore, employed to estimate the D_e in various electronic states of the PtO and PtC. The true potential energy curves for comparison were calculated using the method of Rydberg [9] — Klien [10] — Rees [11] as it stands after modification by Vanderslice et al. [12]. The explicit expression to evaluate the classical turning points are given below

$$r_{min} = [(f/g)+f^2]^{1/2}-f, \tag{2}$$

$$r_{max} = [(f/g)+f^2]^{1/2}+f, \tag{3}$$

where f and g are originally two integrals. For discrete vibrational levels, they will be replaced by following summations:

$$f = \left(\frac{8\Pi^2 \mu c}{h}\right)^{-1/2} \sum_{i=1}^{n} (\omega x)_i^{-1/2} \ln W_i$$

and

$$g = \left(\frac{2\pi^2 \mu c}{h}\right)^{1/2} \sum_{i=1}^{n} \{2\alpha_i(\omega x)_i^{-1}[(U_n-U_{i-1})^{1/2}-(U_n-U_i)^{1/2}]$$

$$+(\omega x)_i^{-1/2}[2B_i-\alpha_i(\omega x)_i^{-1}\omega_i] \ln W_i\},$$

where

$$W_i = \left| \frac{[\omega_i^2-4(\omega x)_i U_i^{1/2}]-2(\omega x)_i^{1/2}(U_n-U_i)^{1/2}}{[\omega_i^2-4(\omega x)_i U_{i-1}^{1/2}]-2(\omega x)_i^{1/2}(U_n-U_{i-1})^{1/2}} \right|,$$

where the symbols ω, ωx, B, α and U stand for vibrational frequency, anharmonicity constant, rotational constant, vibration-rotation interaction constant and term value above the potential minimum, respectively. The suffix i refers to i^{th} vibrational level. The suffix n refers to quantum number of the vibrational level under consideration and i takes the values from 1 to n.

TABLE I

Molecular constants (in cm^{-1}) of PtO and PtC

Mole-cule	State	T_e	ω_e	$\omega_e x_e$	B_e	α_e	$r_e(\text{Å})$	F^*	a^*	n
PtO	$A^1\Sigma$	16995.11	727.07	5.42	0.35386	0.00291	1.79462	2.8163	0.6230	2.5835×10^9
	$X^1\Sigma$	0.0	851.09	4.97	0.38223	0.00283	1.72670	2.7476	0.6195	2.5829×10^9
PtC	$A^1\Pi$	18626.60	818.80	5.50	0.4802	0.0041	1.76236	2.4264	0.6017	2.094×10^9
	$X^1\Sigma^+$	0.0	1051.18	4.87	0.5303	0.0033	1.67705	2.0559	0.5759	1.724×10^9

* Dimensionless quantity.

TABLE II

True potential energy curves for the ground and excited states of PtO and PtC

Molecule	Molecular state	v	$U(r)$ cm^{-1}	r_{min} Å	r_{max} Å	$T_e + U(r)$ cm^{-1}
PtO	A$^1\Sigma$	0	362.18	1.7706	1.8351	17357.29
		1	1078.41	1.7370	1.8970	18073.52
		2	1783.80	1.7155	1.9432	18778.91
		3	3478.35	1.7014	1.9822	19473.46
		4	3162.06	1.6912	2.0175	20157.17
		5	3834.93	1.6836	2.0508	20830.04
		6	4496.96	1.6777	2.0827	21492.07
		7	5148.15	1.6732	2.1137	22143.26
		8	5788.50	1.6699	2.1441	22783.61
		9	6418.01	1.6675	2.1740	23413.12
		10	7036.68	1.6659	2.2036	24031.79
		11	7644.51	1.6650	2.2331	24639.62
		12	8241.50	1.6647	2.2625	25236.61
	X$^1\Sigma$	0	424.30	1.7039	1.7634	424.30
		1	1265.45	1.6723	1.8199	1265.45
		2	2096.66	1.6520	1.8617	2096.66
		3	2917.93	1.6385	1.8967	2917.93
		4	3729.26	1.6286	1.9282	3729.26
		5	4530.65	1.6211	1.9578	4530.65
		6	5322.10	1.6152	1.9860	5322.10
		7	6103.61	1.6106	2.0132	6103.61
		8	6875.18	1.6070	2.0397	6875.18
		9	7636.81	1.6044	2.0658	7636.81
		10	8388.50	1.6024	2.0914	8388.50
		11	9130.25	1.6012	2.1168	9130.25
		12	9862.06	1.6005	2.1421	9862.06
		13	10583.93	1.6003	2.1672	10583.93
PtC	A$^1\Pi$	0	408.03	1.7354	1.8048	19034.63
		1	1215.83	1.6988	1.8711	19842.43
		2	2012.63	1.6754	1.9204	20639.23
		3	2798.43	1.6599	1.9618	21425.03
		4	3573.23	1.6487	1.9993	22199.83
		5	4337.03	1.6402	2.0345	22963.63
		6	5089.83	1.6337	2.0682	23716.43
		7	5831.63	1.6286	2.1009	24458.23
		8	6562.43	1.6248	2.1329	25189.03
		9	7282.23	1.6221	2.1643	25908.83
		10	7991.03	1.6202	2.1954	26617.63
		11	8688.83	1.6191	2.2263	27315.43
		12	9375.63	1.6187	2.2570	28002.23
	X$^1\Sigma^+$	0	524.37	1.6521	1.7129	524.37
		1	1565.81	1.6171	1.7688	1565.81
		2	2597.51	1.5944	1.8097	2597.51

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TABLE II. (continued)

Molecule	Molecular state	v	$U(r)$ cm^{-1}	r_{min} Å	r_{max} Å	$T_e + U(r)$ cm^{-1}
		3	3619.47	1.5788	1.8435	3619.47
		4	4631.69	1.5669	1.8738	4631.69
		5	5634.17	1.5574	1.9019	5634.17
		6	6626.91	1.5496	1.9285	6626.91
		7	7609.91	1.5431	1.9540	7609.91
		8	8583.17	1.5376	1.9787	8583.17
		9	9546.69	1.5330	2.0028	9546.69
		10	10500.47	1.5291	2.0264	10500.47
		11	11444.51	1.5258	2.0496	11444.51
		12	12378.81	1.5231	2.0726	12378.81
		13	13303.37	1.5209	2.0953	13303.37
		14	14218.19	1.5192	2.1178	14218.19
		15	15123.27	1.5178	2.1402	15123.27
		16	16018.61	1.5169	2.1626	16018.61

TABLE III

Dissociation energy and dissociation products for the ground and excited states of PtO and PtC

Molecule	State	D_e value in eV	$T_e + D_e$ in eV	Dissociation products
PtO	$X^1\Sigma$	3.30	3.30	$Pt\ (^3D_g) + 0\ (^3P_g)$
	$A^1\Sigma$	2.50	4.61	$Pt*(^3D_g) + 0\ (^3P_g)$
PtC	$X^1\Sigma^+$	5.30	5.30	$Pt\ (^3D_g) + C(^3P_g)$
	$A^1\Pi$	2.90	5.20	$Pt\ (^3D_g) + C(^3P_g)$

* This refers to excited state of Pt, which is of the same type (^3D_g) as the ground state.

The details of mathematics involved in computations are given elsewhere [12]. The RKRV method was used to evaluate the true potential energy curve as it is now the most accepted method. Of course, some minor corrections are going on which only improve the accuracy after three or four places of decimal in $r(Å)$ values.

The data used for computations is given in Table I and the results obtained are listed in Tables II and III.

3. Dissociation energy and dissociation products for PtO

Since the spectra of PtO has only been recently studied [1], the data on its dissociation energy is not known using various techniques. Due to a certain amount of preciseness in the spectroscopic data, they become much more important in determining the dissociation energy. Such a determination is also fairly good because of the fact that the spectro-

scopic data like ω_e, $\omega_e x_e$ etc. are directly related to the separation between successive vibrational energy levels of molecule.

In the first approximation, to estimate the dissociation energy from the above data, the Morse potential is appreciably good and according to this function

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}.$$

Using the above equation, the dissociation energy of PtO was found to be 3.85 eV [1]. However, the present value comes out to be 3.30 eV. Further, using the same equation, the D_e value for $A^1\Sigma$ state was found to be 3.22 eV, whereas the same value as determined in the present study is 2.50 eV. Further, Nilsson et al. [1] conjectured that the ground state corresponds to atomic products having both the atoms Pt and O in their respective ground state $[Pt(^3D_g)+O(^3P_g)]$. They further contended that if the A state is also a $^1\Sigma^+$ state, the ground state pair of atoms cannot lead to a second $^1\Sigma^+$ state. Moreover, the possibility of Pt being in ^1S_g state and the O in ground state ^3P_g was also excluded by them on the grounds that the combination of these two atomic states cannot result in a singlet molecular state according to the Wigner–Witmer rule. Now the second excited state of Pt is ^3P_g, whereas the first excited state of O is ^1D. Thus the excited state $A^1\Sigma$ of PtO could have both the products:

(I) $Pt(^1S_g)+O(^1D)$, (II) $Pt(^3D_g)+O(^3P_g)$.

Though Nilsson et al. [1] have guessed the latter to be the real product, the final criterion deciding among these two products would be the energy consideration. It is obvious from the values listed in Table III that the latter one would be the real products for the $A^1\Sigma$ state, as the corresponding excitation energy (~ 10132 cm^{-1}) is very near to the value that we obtain from the equation

$$E = T_e + D_e' - D_e'' \quad (\sim 10546 \text{ cm}^{-1}).$$

Thus it is rather established that the dissociation products for the $A^1\Sigma$ state are Pt $(^3D_g)+O(^3P_g)$.

4. Dissociation energy and dissociation products for PtC

The dissociation energy of a diatomic molecule is closely related to the ionicity of the bond in question. As the electronegativity of Pt (2.2 eV) does not differ much from that of C (2.5 eV), the PtC molecule would have only a small amount of ionic character. The Birge-Sponer extrapolation produces fairly good results for a large number of molecules. Its reliability is increased when more vibrational quanta are observed. However, for the ground state of PtC, extrapolation was made only from four vibrational levels and therefore the result obtained ($\simeq 7.0$ eV) should be a bit higher as the convergence of higher vibrational levels is at a slower rate in comparison to lower vibrational levels. Thus our result (5.3 eV) is well within the range of the value recommended by Gaydon [13], which is 6.5 ± 1 eV.

The lowest electronic states of Pt and C atoms are correlated with the molecular states of PtC according to the following:

$$Pt(^3D_g) + C(^3P_g) \rightarrow PtC[\Sigma^+, \Sigma^-(2), \Pi(3), \Delta(2), \Phi],$$
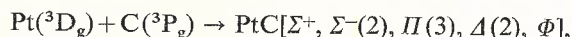
with multiplicities, singlets, triplets and quintets. Further, for the united atom PtC, the lowest electron configuration is given as

$$KLMNO_{sp}(6s\sigma)^2 (6p\sigma)^2 (6p\pi)^2,$$
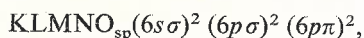
which can give rise to three types of molecular states namely $^1\Sigma^+$, $^3\Sigma^-$ and $^1\Delta$. Thus the observed ground state $^1\Sigma^+$ arises from the lowest electron configuration. But $A^1\Pi$ may result when an electron either from $(5d\delta)$ or $(6p\sigma)^2$ goes to $(6p\pi)$ orbital.

To discuss the atomic products in the ground and the first excited state of PtC, one would have to look into the D_e values for both the states, i. e., $A^1\Pi$ and $X^1\Sigma^+$ and the T_e value for the A–X system. It is obvious from Table III that $(T_e + D_e')$ has the value which is very near to $D_e'' = 5.3$ eV. Thus our results lead to the conclusion that both the states $X^1\Sigma^+$ and $A^1\Pi$ correspond to the same dissociation products $Pt(^3D_g) + C(^3P_g)$, i.e., normal dissociation products.

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