Notes

On the Calculation of Ionization Potentials of Hydrocarbons in the Pariser-Parr-Pople Method

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It has been shown that when the coulomb integral parameter in the Pariser-Parr-Pople theory is chosen to conform to the symmetrically orthogonal nature of the basis set, significant improvement in the calculated ionization potential values is achieved for hydrocarbons.

A PECULIAR feature of parametrization scheme in Pariser-Parr-Pople (PPP) method is that a particular set of parameters do not simultaneously fit spectral and ionization potential data[1,2]. It is the purpose of this note to show that this discrepancy arises because the value commonly assigned to the coulomb integral parameter appears to be inconsistent with the nature of the basis set assumed in the PPP model. The discussion given below illustrates this point with reference to hydrocarbons.

As is well known, the zero differential overlap assumption invoked in the PPP theory implies that the basis set is symmetrically orthogonal[3]. It is pertinent therefore to analyse whether or not the parametrization of various integrals is in conformity with the nature of the basis set. The analysis for different integrals can be done as follows:

(i) *Resonance integral* (β) — It has been shown that Linderberg's relation[4] (1)

$$\beta = \frac{1}{R}\frac{dS}{dR} \qquad \dots (1)$$

where S is the overlap integral in the non-orthogonal basis and R the distance between the orbital centres, yields β in symmetrically orthogonal basis[5]. Now the above relation results in a β value in the vicinity of -2.5 eV for hydrocarbon like distances. Since most PPP calculations on hydrocarbons employ a value in this neighbourhood, it can be concluded that the commonly chosen values of the resonance integral parameter are consistent with the requirement that the basis set be symmetrically orthogonal.

(ii) *Electron repulsion integrals* — An unambiguous analysis is difficult in these cases. However, even if it is argued that the Pariser approximation for the one-centre integral and the Nishimoto-Mataga formula for the two-centre integral are more appropriate for a non-orthogonal basis, this does not cause serious discrepancy. This happens because the values of these integrals do not change drastically on transformation to an orthogonal basis[3]. Further, the value of one-centre integral is slightly larger while that of the two centre one is slightly smaller, in the non-orthogonal basis. Therefore, some cancellation would result in those expressions where both these integrals are present together. Also, since these integrals occur with multiplicative factors which are less than unity, their influence on the final result is not appreciable.

(iii) *Coulomb integral* (α) — Here the situation is quite different. In the commonly used Goeppert-Mayer-Sklar approximation, the expression for this integral is given by Eq. (2)

$$\alpha = <\phi_p| -\tfrac{1}{2}\Delta^2 - V_p|\phi_p> -\sum_{q\neq p}<\phi_p|V_q|\phi_p> \qquad \dots(2)$$

where the symbols have standard meaning. Now the first integral on the right hand side is normally set equal to the valence state ionization potential, W on the assumption that Eq. (3)

$$-\tfrac{1}{2}\Delta^2 - V_p|\phi_p> \; = W_i\phi_p> \qquad \dots(3)$$

is valid. But such a step is justifiable only if ϕ_p is an atomic eigenfunction, i.e. ϕ_p belongs to the non-orthogonal basis. In an orthogonal basis, the equation is clearly invalid. The evaluation of α using valence state ionization potential is, therefore, inconsistent with the assumption of orthogonal basis set.

This inconsistency can, however, be easily removed by utilizing the relation between the coulomb integrals in the two basis sets. It can be shown that for a two-centre case, the integral (α) in the orthogonal basis is related to the integral ($\bar{\alpha}$) in the non-orthogonal basis by Eq. (3)

$$\alpha = \bar{\alpha} - \beta \qquad \dots(4)$$

For an atom with n neighbours, we therefore have

$$\alpha \approx \bar{\alpha} - nS\beta \qquad \dots(5)$$

Since $\bar{\alpha}$ can be determined from the valence state data and β from the Linderberg relation, α is easily

TABLE 1 — IONIZATION POTENTIALS (eV) OF HYDROCARBONS

Molecule	Calc.		Expl
	Using α	Using $\bar\alpha$	
Benzene	10.22	9.12	9.25[6]
Naphthalene	9.12	8.04	8.12[7,8], 8.26[8]
Anthracene	8.48	7.39	7.55[8]
Naphthacene	8.09	6.99	6.95[9], 7.00[10]
Pentacene	7.83	6.73	—
Phenanthrene	9.03	7.89	8.03[8]
Chrysene	8.75	7.59	7.71[11]
Pyrene	8.48	7.34	7.55[10]
Azulene	8.84	7.29	7.43[12], 7.50[13]
Coronene	8.68	7.42	7.44[14]
Perylene	8.19	7.04	7.13[11], 7.15[10]
Styrene	9.59	8.53	8.55[10], 8.86[15]
t-Stilbene	9.13	7.97	7.95[10]

estimated. This value was used in the PPP scheme to calculate the ionization potentials of hydrocarbons, and the results are presented in Table 1. Also given are the values obtained with the $\bar{\alpha}$ parameter. It is obvious that striking improvement occurs when $\bar{\alpha}$ is replaced by α. The spectral transitions are of course unaffected by this replacement. Thus we are led to the conclusion that simultaneous agreement in transition energies and ionization potential can be obtained, if a value of coulomb integral is used which is consistent with the basis set assumed in the PPP model.

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Physicochemical Properties of Sodium Molybdate Catalyst

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Thermal characteristics of sodium molybdate ($Na_2MoO_4.2H_2O$) have been studied and the various transition products characterized by chemical analysis, IR, X-ray diffraction, surface acidities, magnetic susceptibilities and surface area measurements. Sodium molybdate dihydrate undergoes endothermic changes at 150°, 470°, 643° and 689°. The endothermic transitions at 150° are due to dehydration, at 470° and 643° account for crystal transformation and at 689° are due to melting. This compound contains acid sites in the pk_a range, $+6.8$ to -3.0. Medium acid sites ($pk_a = +3.3$) are reduced at 510° whereas weak acid sites ($pk_a \geqslant +5.0$) are increased at 660° and above. The strong acid sites ($pk_a \leqslant +2.0$) however, remain

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almost unchanged till melting. The pure molybdate as well as its thermal transition products are diamagnetic. Surface area of the compounds decreases consistently as a function of calcination temperature. This decrease is suggested to be due to enlargement of micropores formed in individual sodium molybdate crystallites due to sintering.

IT appears from a literature survey that catalytic activity of sodium molybdate[1-6] has some dependence on its calcination temperature. However, the systematic studies on the thermal properties of this molybdate are meagre. The present note deals with the differential thermal analysis (DTA), thermogravimetry (TG), infrared (IR), X-ray diffraction (XRD), surface acidity, magnetic susceptibility and surface area of pure as well as various thermal transition products of sodium molybdate.

DTA and TG of sodium molybdate were carried out by the methods reported earlier[7]. For characterization of the thermal transitions sodium molybdate was calcined at 230°, 510°, 660° and 710° in air for 2 hr in each case. IR spectra and XRD patterns of the pure as well as of the calcined samples were obtained at room temperature by the methods described elsewhere[8]. The surface acidic strength distribution in the above samples was measured by indicator-titration method using n-butylamine and indicators of various pk_a values[9]. Magnetic susceptibilities of the samples were determined by Faraday method at 24° using $Hg[Co(NCS)_4]$ as calibrant. Surface areas of the samples were measured by low temperature nitrogen adsorption BET method. The composition of sodium molybdate, as reported is $Na_2MoO_4.2H_2O$.

The DTA curve (not included) records a sharp endothermic peak at 150° followed by three sharp endothermal changes at 470°, 643° and 689°. The TG curve (not included) registers a total weight loss amounting to 15.1% in the temperature range 90-360°. The weight loss (14.3%) in the temperature range 110-60° corresponds to the removal of two molecules of water from the molybdate. Thus, the endothermic peak at 150° is due to the dehydration of sodium molybdate dihydrate. However, after 160°, the weight loss registered in the TG curve is almost negligible (0.8%) which probably accounts for the removal of adsorbed traces of water.

The bands observed in the IR spectrum of pure sample at 3260 and 2220 cm^{-1} are characteristic of symmetric and antisymmetric $\nu O-H$ and $\delta H-O-H$ of lattice water[10-12]. The bands at 900 and 800 cm^{-1} are due to $\nu Mo-O$ characteristic of normal molybdates[13]. The spectrum also reveals the presence of bands at 1800, 1692, 1680 cm^{-1} which are probably due to overtone and combination bands. In the spectra of the samples preheated at 230° and above (up to 700°) a strong band at 830 cm^{-1} is assigned to ν_3 (ref. 14) and that at 1680 cm^{-1} is attributed to first overtone of the band at 830 cm^{-1}. These bands are characteristic of pure Na_2MoO_4 (ref. 14). XRD pattern of the pure sample is reasonably distinct with the characteristic lines having $d = 6.829$, 3.171, 3.050, 3.0, 2.1456, 1.666 Å, etc., which compare excellently with those