

## Adsorption of Lawrencium on Metal Surfaces. An Approach to the Determination of the Influence of Relativistic Effects on the Electronic Ground State Configuration

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### Abstract

Relativistic effects can determine the adsorption behaviour of lawrencium on a metal surface. For 20 adsorbent metals adsorption enthalpies were calculated by an empirical model assuming a  $7s^27p$  (Lr(p)) and a  $7s^26d$  (Lr(d)) configuration. Pt, Pd, Au, Mo, W and Fe are recommended as adsorbent metal columns in gas adsorption chromatography experiments designed to reveal the true electronic configuration.

### Introduction

The predicted ground state configuration for Lr is  $5f^{14}7s^26d^1$  based on its analogy to lutetium. However, in 1971 Brewer [1] calculated by a semi-empirical method a configuration of  $5f^{14}7s^27p^1$ . Later calculations [2, 3] led to controversial results. The newest calculations [4, 5], taking into account electron correlation and relativistic effects, show that the Lr  $s^2p$   $J = 1/2$  state is energetically more favoured than the  $s^2d$   $J = 3/2$  state.

The relativistic effects are due to the relativistic mass increase of the electrons which are strongly accelerated in the vicinity of a highly charged nucleus. These relativistic effects are most pronounced with the spherical  $s$ - and the  $p_{1/2}$ -orbitals which have high electron densities near the nucleus [6].

The experimental determination of the Lr ground state is pending. The possibility of testing the precision of the configuration calculations and thus furthering the knowledge of the element Lr have caused great interest in this question. The result could demonstrate the magnitude of the influence of the relativistic effect and lead to basically new insights into the periodicity of the chemical properties of the

heaviest elements. Last, but not least, it would provide a key to further investigations of the transactinide elements.

Keller [7] recently published a review on the experimental methods used to investigate the chemical properties of heavy actinides and transactinides. Hulet [8] proposed a Stern–Gerlach experiment to directly determine the ground state configuration of Lr.

This work describes a gas chromatography experiment which could yield information on the ground state configuration of Lr. Such techniques – in the form of on-line and off-line thermochromatography and isothermal gas chromatography in metal columns – have already been applied to the lanthanides, the actinides Am [9], Cf, Es, Fm, Md [10] and No [11], and also to short-lived nuclides of other heavy elements [12–18].

The basis of our working hypothesis is the experimentally determined correlations between the adsorption behaviour and the electronic configurations of the adsorbed species, using a model to calculate the partial molar adsorption enthalpy of a gaseous metal on a metal surface at zero coverage [19–21]. The two possible ground state configurations of Lr have distinctly different adsorption properties, which gives us the possibility of determining the ground state configuration by measuring the adsorption properties.

We model the adsorption behaviour of Lr as a typical member of the trivalent actinide elements with an  $s^2d$  configuration (in the following Lr(d)) as well as that of a hypothetical p-element of the third group with a  $s^2p$  configuration (Lr(p)).

The adsorption enthalpy of Lr(d) on several metal surfaces has already been published [22]. An analogous calculation for Lr(p) requires the prediction of some properties of this metal as a p-element. For this purpose we employ extrapolations with empirical functions for the p-metals of the third group.

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A critical discussion of this approach is given, together with a discussion of the results and the requirements for a gas chemical experiment to determine the ground state configuration of Lr.

### Methods and Parameters

The model for the calculation of the partial molar adsorption enthalpies of gaseous metals on the surface of a metal at zero coverage has been discussed extensively in refs. 19–21. Here we restrict ourselves to the evaluation of the necessary parameters for Lr(p): the electron density at the Wigner–Seitz cell boundary of the solid metal, the electronegativity parameter, the atomic volume of the pure solid metal, the desublimation enthalpy and the hybridization energy depending on the adsorbent metal surface.

#### Electron Density ( $n_{ws}$ ) and Atomic Volume ( $V$ )

In order to calculate the electron density ( $n_{ws}$ ), we use its relation [20] to the standard entropy of the pure solid metal  $S_{298}^{\circ}$ :

$$n_{ws} = 6.3874 \times 10^{-3} \beta^{1/3} V^{-2/3} A^{1/2} \exp(7.03 - S_{298}^{\circ}/3R) \quad (1)$$

where  $\beta$  is the structural factor,  $A$  the atomic weight and  $R$  the gas constant. The atomic volume ( $V$ ) and the standard entropy ( $S_{298}^{\circ}$ ) were determined by extrapolation of the properties of the solid p-metals of the third group. Figure 1 shows the correlations of the standard entropy versus the log of the atomic volume (I), the atomic number (II) and the atomic weight (III), respectively. All three functions give a linear correlation with values for the correlation

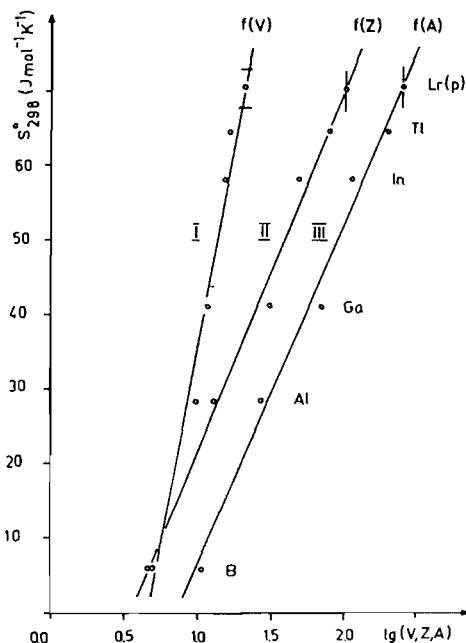


Fig. 1. Standard entropy of solid p-metals of the third group as a function of the atomic volume (I), the atomic number (II) and the atomic weight (III) [23].

coefficient  $r \geq 0.98$ . The two extrapolations for Lr(p) with the atomic number ( $Z = 103$ ) and the atomic weight ( $A = 260$ ) give the standard entropy value which is listed in Table I. This value was used on the graph (I, Fig. 1) to estimate the atomic volume of Lr(p) (Table I). For the structural factor we take  $\beta^{1/3} = 1.1224$ , which represents the hexagonal close-packed structure. With these values substituted in eqn. (1) we calculated the electron density at the Wigner–Seitz cell boundary for Lr(p) (Table I).

TABLE I. Atomic Volumes  $V$ , Electron Density  $n_{ws}$ , Electronegativity Parameter  $\Phi^*$ , Standard Entropy  $S_{298}^{\circ}$ , Structural Factor  $\beta^{1/3}$ , Desublimation Enthalpy  $\Delta H_D^0$  and Hybridization Term  $R/P$  for Different Adsorbent Metals of Lr(d) and Lr(p)

	Lr(d)		Lr(p)	
	Value	Reference	Value	Reference
$V$ (cm <sup>3</sup> )	18.00	22	21.14	a
$n_{ws}$ (density units)	2.039	22	1.030	a
$\Phi^*$ (V)	3.26	22	3.74	a
$S_{298}^{\circ}$ (JK <sup>-1</sup> mol <sup>-1</sup> )	55.22	24	70.4 ± 0.2	a
$\beta^{1/3}$	1.1021	22	1.1224	a
$\Delta H_D^0$ (kJ mol <sup>-1</sup> )	-352	24	-132 ± 7	a
	-410	25	-135	7
$R/P$ (eV <sup>2</sup> )				
Transition metals	0.0	26, 27	1.9	26, 27
Cu, Au	0.0	26, 27	0.57	26, 27
Ag	0.0	26, 27	0.29	26, 27
Ca	0.0	26, 27	0.75	26, 27

<sup>a</sup>This work.

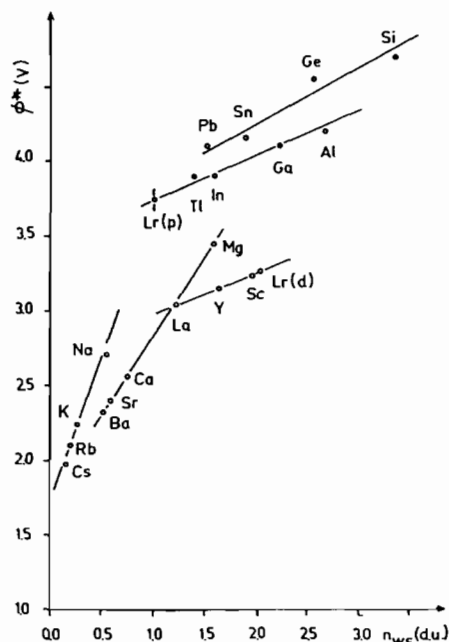


Fig. 2. Comparison of the electronegativity parameter  $\Phi^*$  and the electron density  $n_{ws}$  at the Wigner-Seitz cell boundary of some metals [26, 27, 29].

#### Electronegativity Parameter ( $\Phi^*$ )

Figure 2 shows the relation between the electron density and the electronegativity parameter for some metals. As shown in ref. 28 there exist linear relationships for these two values within the elements of a group. The value of  $\Phi^*$  for Lr(p) was extrapolated on the line of the p-metals of the third group using the  $n_{ws}$  value from above (Table I). For comparison, a similarly calculated value for Lr(d) [22] is shown in Fig. 2 on the line of the rare earth elements. Both the electron density  $n_{ws}$  and the electronegativity parameter  $\Phi^*$  for Lr(d) are very similar to those predicted for Lu [28].

#### Desublimation Enthalpy ( $H_D^0$ )

There are published values available for  $\Delta H_D^0$  of Lr(d) (Table I). Figure 3 shows the extrapolation of  $\Delta H_D^0$  ( $= \Delta H_S^0$ , the sublimation enthalpy) for Lr(p). A linear relationship is found for the p-metals Al, Ga, In and Tl with  $\Delta H_S^0 = 2.06Z + 343.98$ . From this relation we determined the desublimation enthalpy of Lr(p). Our value is in agreement with an extrapolation made by Keller [7] (Table I).

#### Hybridization Term ( $R/P$ )

The hybridization parameter (see refs. 26, 27) is dependent on the combination of the adsorbed species and the adsorbing surface. In a combination of Lr(d) with transition metals, earth alkaline metals, and Cu, Ag and Au we adopted, in agreement with refs. 26 and 27, an  $R/P$  value of zero. However, for

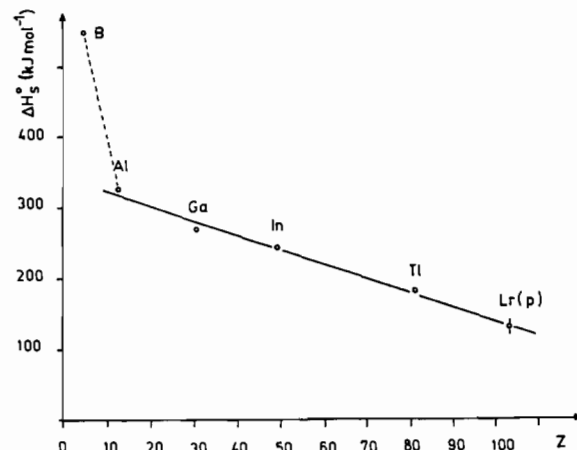


Fig. 3. Standard sublimation enthalpy ( $\Delta H_S^0$ ) of the p-metals of the third group vs. the atomic number.

Lr(p) combined with one of the above-mentioned adsorbents, the hybridization term makes a significant contribution to the interaction. We then used the values proposed by Miedema *et al.* [26, 27] (Table I).

#### Results and Discussion

For comparison, the calculated adsorption enthalpy ( $\Delta \bar{H}_a$ ) of Lr(p), the enthalpy of solution in the solid adsorbent metal ( $\Delta \bar{H}_{SL}$ ) and the corresponding values for Lr(d) are given in Table II. The indices (1) and (2) distinguish two possible types of adsorption [19]: (1) stands for adsorption on the surface and (2) for adsorption by substituting adsorbent atoms in the surface layer. Due to the higher volatility of Lr(p) we expect a weaker adsorption than for Lr(d). This higher volatility is not compensated for by the different metal-metal interaction.

The tendency to go into solid solution or to form intermetallic compounds (compare  $\Delta \bar{H}_{SL}$  in Table II) is lower for Lr(p) and therefore also the tendency for adsorption of type (2) (see ref. 19). There is a remarkable shift for the range of adsorption enthalpies from Lr(d) (minimum value for Ca:  $-352$  kJ/mol; maximum value for Pt:  $-749$  kJ/mol) to Lr(p) (minimum value for Ti:  $-179$  kJ/mol; maximum value for Ta:  $-337$  kJ/mol). Most remarkable are the low values of the adsorption enthalpy for Lr(p) on the surface of the platinum metals and gold and silver, as well as the strong adsorption on calcium.

This effect can be explained by the change in the electron density between Lr(d) and Lr(p) which results in a weakening of the interaction with metals having a high electron density (Pd, Pt, etc.) and a strengthening for metals with a low electron density (e.g. Ca).

TABLE II. Partial Molar Adsorption Enthalpies  $\Delta\bar{H}_a$  (kJ mol<sup>-1</sup>) of Lr on (1) or in (2) Metal Surfaces at Zero Coverage (see text) and Partial Molar Solution Enthalpies  $\Delta\bar{H}_{SL}$  (kJ mol<sup>-1</sup>) in the Solid Adsorbent Metals

Adsorbent	Lr(d)			Lr(p)		
	$\Delta\bar{H}_{SL}$	$-\Delta\bar{H}_{a(1)}$	$-\Delta\bar{H}_{a(2)}$	$\Delta\bar{H}_{SL}$	$-\Delta\bar{H}_{a(1)}$	$-\Delta\bar{H}_{a(2)}$
Ca	+66	352		-170		299
Ti	+30		369	+9		178
V	+42		378	+179	278	
Cr	+10		414	+242	269	
Mn	-40		437	+109	260	
Fe	-53		457	+235	219	
Ni	-196		577	+121	282	
Cu	-155		542	+81	267	
Zr	+15		377	-75		247
Nb	+81	484		+177	250	
Mo	+57	550		+307	236	
Rh	-281		662	+68	319	
Pd	-390		745	-76		253
Ag	-151		514	+59	205	
Ta	+80	560		+186	337	
W	+51	611		+339	288	
Re	-161		578	+233	319	
Ir	-279		667	+123	322	
Pt	-390		749	+3		187
Au	-322		656	-98		239

The big differences in the adsorption properties of the two hypothetical configurations of Lr make gas adsorption chromatography an ideal tool to determine the true configuration. Due to the decay properties and the low production rates of the Lr-isotopes [7, 30], on-line isothermal gas chromatography [11, 15] is most suitable.

The retention temperature of Lr(d) for transportation in the gaseous phase through a metal column is for all mentioned metals higher than 1800 K [15]. At these temperatures losses by diffusion cannot be ruled out. We therefore propose an experiment based on the calculated – relatively low – adsorption enthalpies of Lr(p) to search for Lr in the hypothetical p-metallic state. As stationary phase we suggest a metal with an adsorption enthalpy as low as possible for Lr(p) and a difference as high as possible in the enthalpies for Lr(p) and Lr(d) (Table II). These conditions are met by the metals Pt, Pd, Au, Ag, Mo, W and Fe. The retention temperature for Lr(p) in columns of all these metals should be approximately 500 K lower than for Lr(d). With this temperature difference the possibility of any transport of Lr(d) can be excluded, even taking into account the uncertainties of our extrapolations.

The experiment requires the absence of oxygen in both the gas phase and as oxide cover on the surface of the metal column. This condition can be met by using a noble metal column. With Mo, W or Fe a reducing component in the carrier gas is necessary.

Finally, we would like to discuss some possible sources of systematic errors. The relativistic effects do not only influence the configuration Lr(d)  $\rightarrow$  Lr(p) but also other properties. Lr(p) has a filled 5f<sup>14</sup> shell, whereas p-elements of the third group have filled d<sup>10</sup> shells. Discrepancies from the properties predicted for Lr(p) by simple extrapolations within the elements of the third group could arise from this fact [7]. The linear extrapolation of the atomic volume and the standard entropy (Fig. 1) give probably upper limits for these parameters. The true electron density could therefore be higher than the value calculated in this paper.

While the relativistic decrease in the p-orbital radius gives an overall increase in the electron density, it can also lead to a steeper radial gradient in the outer regions. Miedema and Boom [29] discussed the volatility of a metal as a function of these two effects, *i.e.* the magnitude of the electron density and of the orbital overlap. Since these two effects have an opposite influence on the bond strength, a higher volatility can result than predicted by the linear extrapolation [31]. The sublimation enthalpy of Lr(p) in Table I is therefore probably an upper limit. The adsorption properties of Lr(p) are influenced by the electron density and the volatility of the adsorbed species in opposite directions, so that changes of these parameters due to relativistic effects may partially cancel out. It seems to be acceptable to take only the change of the configuration Lr(d)  $\rightarrow$  Lr(p)

into account and to ignore possible relativistic effects within the p-elements.

Depending on the nature of the adsorbent material it is also possible that structural changes in the electron shells can be induced by the adsorption process which could be different from those of the p-elements of the third group; e.g. by promotion to other valence states. However, the aim of this work is only to model the adsorption behaviour of Lr(p) as an element similar to Tl.

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