The calculation of Van der Waals interaction energy in the crystallites of metal β-diketonates (metal= Al, Cr, Fe and Ir)

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Abstract. The ability of metal beta-diketonates to pass into gas phase without decomposition is widely used in the processes involving the deposition of various coatings by CVD. In order to optimize the CVD method (e.g. the choice of the precursors etc.) the study of volatility of metal-beta-diketonates are needed. In this work the acetylacet onates of III-valent metals: Al(Acac)₃, Cr(Acac)₃, Fe(Acac)₃, and Ir(Acac)₃, were chosen for calculation of sublimation enthalpy in the atom-atomic molecular mechanics approximation. The different types of interaction potential is considered: the Buckingham potential (6-exp), the Lennard-Johns potential (6-12) and modified Buckingham potential (M-6-exp), the last two potentials are used in a UFF framework. The most reliable one is found to be the Buckingham potential (6-exp).

1. Introduction

Much attention is given to the investigation of such an important property as volatility, which is necessary to optimize the parameters of coating deposition, to choose the precursors and to getting the materials with adjusted properties. In our work modeling of volatility of the molecular complexes of metal with organic ligandes including calculation of enthalpy in range atom-atomic approximation was carried.

In order to accomplish this task selection of interaction potential the most reliable to describe these metal organic systems was accomplished. All these complexes are crystallize in the molecular type lattice and for this reason intermolecular interaction energy are essentially low than intramolecular bond energy. This fact allow to transfere of these complexes in gaseous state at relatively low temperatures.

The investigated metal beta-diketonates have the same molecular structure: the central metal atom have slightly strained octahedral coordination by six oxygen atoms that are form the part of three acetylacetonate ligands.

Essential distinction of these compoundes from customary organic compoundes are specifical intra-molecular distribution of electron density, where significant positive charge are located on the central metal atom, and negative charge are located on the atoms of ligands. For this reason some difficulties in using of standart potentials for these specific compounds to take place.

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2. Calculation part

The calculation was carry out in the framework of atom-atomic approximation. To investigate the molecular crystals of metal β-diketonates we have used the following semi-empirical potentials:

a) Buckingham potential (6-exp):
The form of potential and the basis set of parameters for light atoms were taking from the paper Kitaigorodsky et al.[1]. But parameters for metal-metal interactions were estimated from \( \varepsilon_0(r_0) = f(N) \) dependence (where \( N \) is the number of metal), that was plotted by known parameters of noble gases.

b) Lennard-Johns potential (6-12), that have used in the framework UFF potential [2]

c) Modified Buckingham potential (M-6-exp) that have used in the framework UFF potential [2]:

\[
E_{VDW} = \left[ D_y \left( \frac{6}{\zeta - 6} \right) e^{\frac{\zeta}{\zeta - 6}} \right] - \left[ D_y \left( \frac{\zeta}{\zeta - 6} \right) x^6_y \right] / x^6
\]

where \( D_y \) is the well depth, \( x_y \) is the van der Waals bond lenght and \( \zeta \) is the shape parameter.

3. Results and discussion

During our investigation was established that the one of important problem in modeling these complicated metal organic systems is calculation of metal contribution in intermolecular interactions. All obtained enthalpy data that was calculated to diferent potentials are overestimated in comparison with experimental data.

The results of van der Waals energy calculations and experimental data for beta-diketonates of Al, Cr, Fe and Ir are given in table I. The situated in table I experimental data was obtained by graphical averaging of the series of experimental data.

As can see from table I, better agreement of calculation results with the results of experiments in the case of using the Buckingham potential (6-exp) are observed. In the case of using Lennard-Johns potential (6-12) and Modified Buckingham potential (M-6-exp) values of interaction energy are overestimated.

The potential curves for elements that are included in beta-diketonates of Al, Cr, Fe and Ir are plotted in figure 2. There are curves of standart Buckingham potential and Lennard-Johns potential (the curve
of modified Buckingham potential are not present because as can see from [2] there using the same tabulated values and for this reason the results of calculation are very similar and these curves are overlapped).

As can see from figure 2 in the case of light atoms (H, O, C) potential curves are similarly and ordered one under another. But as we compare the potential curves for metal, we can see that for the most part of these metals (Cr, Fe, Ir) the well depth for 6-exp potential are significantly deep and are shifted to the right. However, for the most of light elements from this series (Al) the opposite event are observed.

Table 1. The results of calculation of Van-der-Vaals interaction energy in the crystals of metal β-diketonates (metal= Al, Cr, Fe and Ir).

| Complex name in CSDB | 6-exp | 6-exp-6-12 | -6-exp | 6-12 | Experimental values of ΔH (kJ/mol) |
|----------------------|-------|------------|--------|------|----------------------------------|
| Al(aa) | *-113 | -131 | -171 | -169 | -104 |
| ALACAC11 | **-113 | -131 | -171 | -173 | -104 |
| Cr(aa) | -117 | -108 | -148 | -133 | -120 |
| ACACCR02 | -120 | -106 | -151 | -150 | -120 |
| Fe(aa) | -154 | -113 | -156 | -156 | -124 |
| FEACAC03 | -121 | -112 | -152 | -153 | -124 |
| Ir(aa) | QQQCXJ01 | -139 | -116 | -135 | -126 | -128 |

*Calculated with experimental H coordinates
**Calculated with fitted H coordinates

Figure 2a. The comparison of the Buckingham potential and Lennard-Johns potential for light atoms.
Figure 2b. The comparison of the Buckingham potential and Lennard-Johns potential for metal atoms.
In the course of our calculation the assumption that the inaccuracies in the structural data for hydrogen atoms are insert the significant contribution in the discrepancy of calculated and experimental free energy values was done. The calculation displayed that the interactions that are insert the significant contribution in the free energy are included of hydrogen atoms. Moreover, at the analyzing of the CSDB structural data for investigated complexes that fact that the coordinates of hydrogen atoms in structures either not determined or these coordinates have significantly discrepancy for same compound are observed.

With the purpose of more precise definition of our calculation we decide to change the CSDB structural data for hydrogen atoms on calculated values that was obtained by XPOW program complex. But in the case of acetylacetonate Ir (III) all the hydrogen data are calculated since the authors [3] do not determine them by experimentally.

As can see from table I these exchanges are give a good agreement in free energy values (6-exp calculations) with experimental data. However, in the case of using 6-12 and M-6-exp potentials that results are not observed. On the whole, as can see from table I the values of free energy that obtained by any of these three potentials are overestimated in different degree. Besides, we have assumed that the overestimation of free energy in the case of using 6-exp potential to take place because of the incorrect estimation of metal-metal and metal-light element interactions. Since the parameters for metal-metal interactions were estimated from \( \varepsilon(r_0) = f(N) \) dependence (where N is the number of metal), that was plotted by known parameters of noble gases.

As the solution of this problem we have take the parameters for metals from [2] and substitute them in 6-exp calculations (the parameters for light atoms stay the same). This mixed potential are designated that 6exp-6-12 in the table I. As can see from table I the values of free energy that was obtained by 6exp-6-12 potential are overestimated too.
4. Conclusion
As appears from the above, the problem of calculation of the metals contribution in the intermolecular interactions are one of the fundamental problems for the force fields that was developed for the standard organic compounds. However, calculations of these complicated compounds that used classical 6-exp potential give the most reliable agreement with experimental data.

References
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