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Effect of conformational correction to the enthalpy of formation calculated by G4 theory

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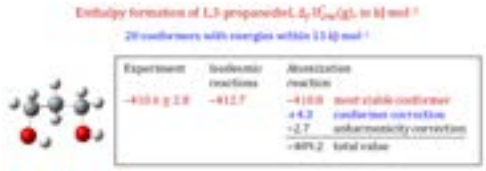
There is an important difference between the experimental gas-phase enthalpy of formation and that determined from theoretical computation. The calculated value is usually based on only one most stable conformer, while the experimental enthalpy of formation reflects a Boltzmann distribution of conformers which have statistically significant populations at 298.15 K. The gas-phase enthalpies of formation of four molecules with high flexibility (1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, and glycerol), which leads to the existence of a large number of low-energy conformers, were calculated with the G4 method to see whether the lowest energy conformer is sufficient to achieve high accuracy in the computed values. The calculated values were in good agreement with the experiment, whereas adding the correction for conformer distribution makes the agreement worse. The reason for this effect is a large anharmonicity of low-frequency torsional motions, which is ignored in the calculation of zero-point vibrational energy (ZPVE) and thermal enthalpy. In G4 theory, the ZPVEs and thermal contributions to enthalpy are calculated using B3LYP/6-31G(2df,p) harmonic frequencies, whereas these values calculated with anharmonic frequencies have lower values than those calculated using harmonic frequencies. For approximate treatment of molecules with low-frequency internal rotations, a free rotor model was used in this work. It was shown that the approximate correction for anharmonicity estimated using this model is of very similar magnitude compared with the conformer correction but has the opposite sign, and thus almost fully compensates for it. Thus, we can conclude that the enthalpy of formation calculated by G4 method for the lowest energy conformer gives a better estimate of the gas-phase enthalpy of formation than that calculated taking into account the presence of the higher energy conformers. Therefore, the common practice of adding only the conformer correction is not without problems.



Recent Publications:

1. Dorofeeva O V and Suchkova TA (2018) Theoretical calculation of enthalpy of formation of multiconformational molecules: 1,2-ethanediol, propanediols, and glycerol. Chemical Physics Letters. 698:218-222. Doi:10.1016/j.cplett.2018.03.029.
2. Dorofeeva O V, Ryzhova O N and Suchkova T A (2017) Enthalpies of formation of hydrazine and its derivatives. Journal of Physical Chemistry A. 121(28):5361-5370. Doi:10.1021/acs.jpca.7b04914.
3. Suntsova M A and Dorofeeva O V (2017) Prediction of enthalpies of sublimation of high-nitrogen energetic compounds: modified Politzer model. Journal of Molecular Graphics and Modelling. 72:220-228. Doi: 1016/j.jmgm.2017.01.013.
4. Dorofeeva O V and Ryzhova O N (2016) Enthalpy of formation and O-H bond dissociation enthalpy of phenol. Journal of Physical Chemistry A. 120(15):2471-2479. Doi: 10.1021/acs.jpca.6b02233.
5. Suntsova M A and Dorofeeva O V (2016) Use of G4 theory for the assessment of inaccuracies in experimental enthalpies of formation of aromatic nitro compounds. Journal of Chemical and Engineering Data. 61(1):313-329. Doi: 10.1021/acs.jced.5b00558.

Biography

Taisiya A Suchkova is currently pursuing her studies at the Faculty of Chemistry of the Lomonosov Moscow State University, Russia. She has done research and is interested in the fields of chemistry such as computational quantum chemistry and chemical thermodynamics. She has participated in several grants dealing with estimation of mutually consistent thermodynamic properties of nitrogen-containing compounds and their derivatives. She has co-authored a few papers in theoretical calculation of enthalpies of formation. She was awarded a Diploma for her work at the International Conference for Students and Young Scientists "Lomonosov" in 2017. She has demonstrated excellence in learning physical and computational chemistry.

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