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Predictions of the ideal gas properties of refrigerant molecules

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ABSTRACT

The knowledge of ideal gas properties of refrigerant molecules is crucial for the design and optimization of refrigerant production processes and the simulation of energetic systems. In this work, the ideal gas properties of chlorinated and fluorinated hydrocarbons have been predicted by using different methods based on quantum calculations. Enthalpies of formation have been predicted by using semi-empirical methods such as PM3, PM6 and PM7, as well as the procedure of Osmont et al. [Combustion and Flame, 151 (2007) 262–273]. We obtain a good agreement between the enthalpies reported in databases and the predictions from *ab initio* calculations, for most refrigerant molecules. The ideal gas heat capacities of refrigerants can be accurately predicted by using MP2-DGTZVP and B3LYP/6-31G(d,p) *ab initio* calculations, and rescaling the vibrational temperatures by a factor of about 0.98. The method is extended to hydrofluoroolefins (HFO) and excellent predictions of heat capacities are obtained.

Prévisions des propriétés des gaz parfaits des molécules de frigorigènes

Mots clés : Gaz idéal ; Puissance de chauffage ; Enthalpie de formation ; Frigorigène ; HFO

1. Introduction

The refrigerant industry must constantly develop new refrigerant fluids that have lower impacts on the global warming of Earth and on the ozone layer. According to the European directive 2006/40/EC all mobile air-conditioning systems (MACS) should contain refrigerants that have a Global Warming Potential (GWP) lower than 150. Besides the safety and environmental constraints, these alternative fluids must have proper thermodynamic properties in order to be considered as efficient refrigerants, and their energetic properties should be equivalent to the previous fluids in order to avoid important modifications of the system and heavy investment costs. Hydrofluoroolefins (HFO) and hydrochlorofluoroolefins (HCFO) have recently been considered as possible alternative to hydrofluorocarbons (HFC) and hydrochlorofluorocarbons (HCFC) as their GWP is much lower and below 10. However, there are few experimental data available in the literature concerning HFOs, in particular for ideal gas properties. Predictive tools that can evaluate the thermodynamic properties of refrigerants are then of great interest for the refrigerant industry, either to

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Nomenclature

q	partition function
$\Delta_f H^0_{298.15K(g)}$	ideal gas enthalpy of formation at 298.15 K [kJ·mol^{-1}]
E	absolute electronic energy [Hartree per molecule]
ΔH_{corr}	thermal corrections [Hartree per molecule]
c_i	contribution of atom i to the formation enthalpy [Hartree per atom]
α_i	number of atoms of type i on the molecule [dimensionless]
C_p^{ideal}	ideal gas heat capacity [J·mol^{-1}·K^{-1}]
R	ideal gas constant [J·mol^{-1}·K^{-1}]
T	temperature [K]
$\Theta_{i,gaussian}$	vibrational temperature predicted with Gaussian
Θ_i	scaled vibrational temperature
f_Θ	scaling factor

Subscripts and superscripts

trans	translational
rot	rotational
vib	vibrational
elec	electronic
nucl	nuclear
ideal	ideal gas

estimate the efficiency and feasibility of a given refrigerant molecule for a particular application, or to design and optimize the production processes. Thermochemical properties are also valuable for the prediction of the chemical behavior and the lifetime of refrigerants released in the atmosphere.

Thermodynamic properties are usually computed as the sum of an ideal part and a residual part. For a gas the residual part is negligible and it is particularly important to have accurate values for the ideal contribution. Ideal gas properties of polyatomic molecules are commonly predicted by using expressions derived from statistical mechanics, which are based on the assumption that the vibration modes of molecules are harmonic oscillators. Quantum (*ab initio*) calculations are then performed to determine all the required information used in these expressions, such as the vibrational temperatures of the normal modes. Several levels of theory as well as basis sets can then be considered and compared, and more accurate results are expected by using a very high level of theory combined with an extensive basis set. The Gaussian n-procedures developed by Pople et al. (1989) and Curtiss et al. (1991, 1998, 1999) are procedures for accurate calculation of various properties such as enthalpy of formation. The reader is directed to excellent books (Jensen, 2001; Leach, 2001; Sandler, 2003) for an introduction to quantum calculations and an overview of the most common *ab initio* methods used in thermochemistry. The most accurate methods available at the moment are G3 and G4. G4 involves MP4 and couple cluster methods. The main drawbacks of these methods are the computational time, especially for large molecules. Besides, systematic errors are usually found between theoretical predictions and the experimental data when an *ab initio* method of moderate level of theory combined with an average basis set is used. As a result, it can be useful to propose simple empirical corrections for such an *ab initio* method in order to develop a predictive method with low average deviation and computational time. Osmont et al. (2007, 2008) proposed such a method for the predictions of formation enthalpies.

Several studies dealing with the predictions of the thermochemical properties of refrigerant fluids can be found in the literature: Berry and co-workers have compared different *ab initio* methods (MP2, BAC-MP4, G2, G2(MP2), etc.) to predict the formation enthalpies of fluoromethanes (Berry et al., 1995), chloromethanes (Berry et al., 1996a), and fluoroethane (Berry et al., 1996b). Smith and Tufts (1996) used group contribution methods to predict the properties of HFC refrigerants. One can refer to other theoretical studies of fluorinated compounds (Bond, 2007; Duncan et al., 2010; Haworth et al., 2000; Lazarou et al., 2002; Li et al., 2011; Mulero et al., 2013; Nagy et al., 2014; Speis et al., 2000, 2001; Wang et al., 2015; Zhang et al., 2010). Concerning HFO and HCFO refrigerants, the modeling studies of ideal gas properties are rather scare and we are only aware of the work of Raabe and Maginn (2010b), who predicted the ideal gas heat capacity of HFO-1234yf by using different *ab initio* methods. However, these predictions are below the experimental data as shown later in this paper. The aim of this work is to evaluate the predictive capabilities of different methods based on *ab initio* calculations and then to provide reliable predictive tools for the properties of HFOs and HCFO.

2. Predictive methods

Ideal gas properties can be predicted from a combination of statistical thermodynamics and quantum calculations, and are calculated from the partition function q of an isolated molecule, which is expressed as the product of different contributions (McQuarrie, 2000) (translational, rotational, vibrational, electronic and nuclear),

$$q = q_{trans} q_{rot} q_{vib} q_{elec} q_{nucl} \quad (1)$$

To compute ideal gas properties of refrigerants, we only consider the most stable conformation of the molecules, corresponding to the lowest ground state energy at 0 K, and assume that the contributions due to the other conformations are negligible. The most stable conformation of the studied molecules is obtained from the minimization of the ground state energy, after checking that all vibrational frequencies are positive. The entropies and heat capacities are calculated following the harmonic oscillator approximation. This approximation is the one generally used for the predictions of thermochemical properties. Heat capacities and entropies corrected for anharmonic molecular motions, in particular internal rotations, are seen to be approximately equal to uncorrected predicted values (Osmont et al., 2007, 2008).

2.1. *Ideal gas standard enthalpy of formation*

In this work, we use the procedure proposed by Osmont et al. (2007, 2008) to predict the ideal gas heat of formation of organic