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Internal rotation for predicting conformational population of 1,2-difluorethane and 1,2-dichloroethane

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ABSTRACT

The contribution of internal rotation to the thermal correction of Gibbs free energy (ΔG) is estimated using the quantum pendulum model (QPM) to solve the characteristic Schrödinger equation. The procedure is applied to theoretical prediction of conformational population of 1,2-difluorethane (1,2-DFE) and 1,2-dichloroethane (1,2-DCE) molecules. The predicted population for the *anti* form was 37% and 75%, for 1,2-DFE and 1,2-DCE respectively, in excellent agreement with experimental gas phase data available, 37 ± 5% and 78 ± 5%. These results provide great support to the use of the QPM model to account for the low vibrational frequency modes effect on the calculation of thermodynamic properties.

1. Introduction

Statistical thermodynamics is a very useful tool to obtain macroscopic information of a certain system from microscopic data. Through the development of computational chemistry some models based on simple quantum–mechanical systems have been used with success. The most common models are the particle in a potential well for translational motion, rigid-rotor, for rotational motion, and harmonic oscillator for vibrational motion. However, those models do not work very well in some cases. If we consider, for example, large amplitude movements, it is expected large deviations from observed data.

There are seven coordinates allowed for describing large amplitude movements: the three coordinates of center of mass, the Euler angles θ, φ and χ and the angle of internal rotation (α) [1]. The internal rotation was classified by Wilson [2] in three possible groups: the completely hindered rotation (such as C=C), the free internal rotation (where the potential energy is lower than kT, k is the Boltzmann constant and T absolute temperature and may be neglected) and the moderate ones, governed by intermediate potentials. The latter were extensively studied by Pitzer [3], who built several tables, from which was possible to obtain thermodynamic data for some types of rotors. However, those tables were not designed for all kinds of system. Nonetheless, since then, several works have been reported in the literature using the internal rotation approximations and developments to compute thermal properties of different types of systems, such as transition states, molecular clusters and many others. The most popular models are those of Pitzer–Gwinn [4], Truhlar [5] and Ayala–Schlegel [6]. The latter one is implemented in Gaussian-03 package [7].

Despite the success attained of those models cited above, some systems require a more detailed treatment when the major interest is related to the thermodynamic properties. This necessity of a refined treatment is due to the fact that, although the majority of conformers are likely to prefer the *anti* conformation, some molecules present themselves with the *gauche* conformer as a more stable state. This is known as *gauche* effect and a good example of it is the 1,2-difluoroethane (1,2-DFE). Gauche effect has been largely attributed to hyper conjugation factors. However, a recent study suggests that the gauche effect is mainly guided by attractive electrostatic interactions in some haloethanes, including 1,2-DFE [8].

In this work, the main goal was the correct calculation of the thermal properties of the more stable conformer by including the internal rotation effects and the temperature influence in these properties. However, is important to point out that for systems in which two possible conformers are likely to exist, it is

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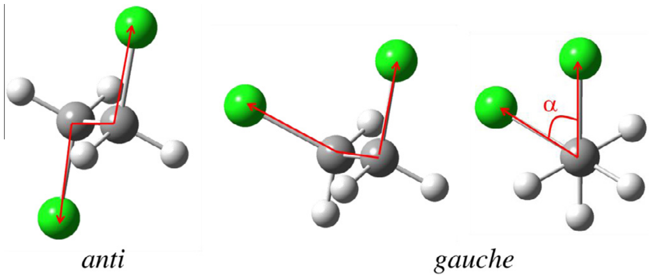

Fig. 1. Schematic representation of *anti* and *gauche* conformers for 1,2-disubstituted ethane. The dihedral angle α is defined.

interesting to understand this competition and quantify the populations of the two conformers: *anti* and *gauche*. The present work has as the main goal to study the internal rotation and quantify the relative populations of *anti* and *gauche* conformers in two substituted ethanes, 1,2-difluorethane (1,2-DFE) and 1,2-dichloroethane (1,2-DCE), shown in Fig. 1, through the quantum pendulum model (QPM) [9]. The motivation for this study came from our previous work [10] where the applied procedures to correct the partition functions were not successful to predict the conformer's population of 1,2-DFE. Here, a numerical procedure was used to calculate the eigenvalues of the Schrödinger equation for internal rotation and, thereby evaluate the corresponding thermal contribution to the Gibbs free energy (ΔG) for each conformer. The results are in excellent agreement with experimental conformation population [11,12].

2. Theoretical background and methods

The choice of QPM [9] to solve the internal rotation problem is based in the following principle: assuming that the dihedral angle (α) specified in Fig. 1 varies with the movement of the two vectors along the C–X bond, it is possible to write the Schrödinger equation as:

$$\left\{-\frac{\hbar^2}{2I_{red}}\frac{d^2}{d\alpha^2}+Q(\alpha)\right\}\psi_k(\alpha)=\varepsilon_k\psi_k(\alpha) \tag{1}$$

where I_{red} is the reduced moment of inertia of the rotating part, $Q(\alpha)$ is the periodic potential of internal rotation, with the property $Q(\alpha) = Q(\alpha + 2\pi)$, and $\hbar$ is the reduced Planck constant. These types of equations are known as Hill Equations [13] and can be solved numerically as described in the next paragraphs.

The reduced moment of inertia represents the difficulty of a group to perform a rotation around a single bond. There are two main ways to calculate it: the Eckart effective moment of inertia and the Pitzer reduced moment of inertia [14]. The difference between them is that the Eckart effective moment of inertia may be applied in any case, in such way that the rotating group is not required to be symmetrical to the reference group; which are a condition to Pitzer's reduced moment of inertia to be required. Wong et al. [14] also showed that the reduced moment of inertia may be different for different conformers, such as *anti* and *gauche*. Therefore, solving the Schrödinger equation, two different values of I_{red} are required to calculate conformational data. Later on Wong et al. [15] developed an algorithm to obtain the correct moment of inertia for molecules with asymmetric internal rotors and obtained its thermodynamic properties relative to the internal rotation for 1,2-dihaloethanes.

Although the two conformers of the substituted ethanes studied here are located in the same PES, the calculation of the individual thermodynamic properties due to internal rotation must be carried out carefully using different PES, chosen as described below. Fig. 2 shows a hypothetical PES where the *anti* conformer is more stable than the *gauche* conformation (1,2-DCE results). In Fig. 2a the 180° torsion angle value is taken as reference for ΔE evaluation for the *anti* form and ±60° used as reference for the *gauche* form in Fig. 2b. From this, it is possible to assume that the excited states of internal rotation of *anti* conformer are able to access all states located above its ground state (global minimum). Similarly, the accessible excited states of internal rotation of *gauche* conformer are only those whose energy is higher than the ground state of *gauche* conformation (local minimum). It is important to mention that Eq. (1) must be solved for a periodic potential of internal rotation that accommodates both *anti* and *gauche* forms of substituted ethanes, so the cutting off procedure indicated in Fig. 2b has to be applied. In this paper the substituted ethanes studied were 1,2-DFE and 1,2-DCE. The latter follows the example described above while the former has the *gauche* conformer as the global minimum and the same reasoning applies.

Once the eigenvalues of internal rotation are known it is possible to obtain the partition function of the system and, consequently, the thermal properties. According to [16] the entropy is given by,

$$S=\left(lnQ+\frac{Q_S}{Q}-ln\sigma\right) \quad \therefore \sigma = \text{symmetry number} \tag{2}$$

where,

$$Q=\sum_{i=0}^{n}g_i exp\left(-\frac{\varepsilon_i-\varepsilon_0}{k_BT}\right) \quad \therefore g_i = \text{degree of degeneracy} \tag{3}$$

$$Q_S=\sum_{i=0}^{n}g_i\left[-\frac{\varepsilon_i-\varepsilon_0}{k_BT}\right]exp\left(-\frac{\varepsilon_i-\varepsilon_0}{k_BT}\right) \tag{4}$$

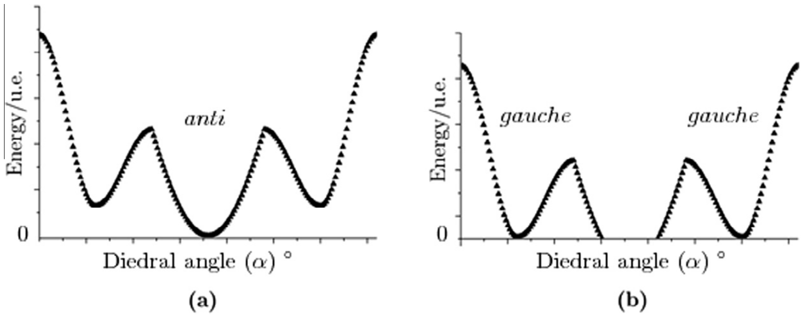

Fig. 2. CCSD(T)/6-311++G(3df,3pd)//MP2/6-311++G(3df,3pd) torsional potential energy surface (PES) for (a) *anti* conformer and (b) *gauche* conformer of substituted ethane (1,2-DCE curve is shown). The 180° and ±60° torsion angle values are used as reference for ΔE evaluation for *anti* (a) and *gauche* (b) conformers respectively. The visible part of the curves accounts for the allowed states which can be accessed by each conformer.