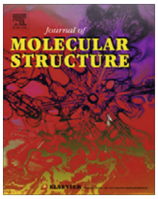
Journal of Molecular Structure 1009 (2012) 89–95

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



A group increment scheme for infrared absorption intensities of greenhouse gases

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ARTICLE INFO

Article history:
Available online 7 December 2011

Keywords:
IR intensities
ab initio calculations
Additivity models
Global warming molecules
Hydrofluorocarbons
Hydrofluoroethers

ABSTRACT

A molecule's absorption in the atmospheric infrared (IR) window (IRW) is an indicator of its efficiency as a greenhouse gas. A model for estimating the absorption of a fluorinated molecule within the IRW was developed to assess its radiative impact. This model will be useful in comparing different hydrofluorocarbons and hydrofluoroethers contribution to global warming. The absorption of radiation by greenhouse gases, in particular hydrofluoroethers and hydrofluorocarbons, was investigated using *ab initio* quantum mechanical methods. Least squares regression techniques were used to create a model based on this data. The placement and number of fluorines in the molecule were found to affect the absorption in the IR window and were incorporated into the model. Several group increment models are discussed. An additive model based on one-carbon groups is found to work satisfactorily in predicting the *ab initio* calculated vibrational intensities.

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1. Introduction

Greenhouse gases (GHGs), such as chlorofluorocarbons (CFCs), perfluorocarbons (PFCs), and hydrofluorocarbons (HFCs) can contribute significantly to climate change [1]. Since the Montreal Protocol and the initial IPCC assessment, the Environmental Protection Agency (EPA) has investigated the use of HFCs and hydrofluoroethers (HFEs) as possible replacements for CFCs [2]. Although the industrial use of CFCs has been phased out, PFCs and HFCs are currently used heavily in the air conditioning, carpeting, drug, and the electronics industries [3,4]. In addition, they are used as tracers in atmospheric studies and have some medical applications [5,6]. These greenhouse gases (HFCs, PFCs), which possess carbon–fluorine bonds, are known to absorb heavily in the atmospheric infrared (IR) window. The relative climate impact of these gases, as expressed by the global warming potential (GWP), is sometimes thousands of times that of CO_2 due to their inherent ability to absorb radiation within the Earth's atmospheric IR window (IRW). The GWP is defined as the ratio of the time-integrated radiative forcing from the instantaneous release of one kilogram of a trace substance relative to that of one kilogram of a reference gas, which is usually taken to be CO_2 [1,7]. The radiative forcing of a molecule has been shown to depend on its radiative efficiency and atmospheric abundance [7]. A large molecular radiative efficiency has been shown by Bera et al. to arise when a molecule exhibits a large infrared absorption intensity within the IR window due to large dipole derivatives of highly polar bonds [8]. Moreover, HFCs and especially PFCs, tend to possess long atmospheric lifetimes since carbon–fluorine bonds are generally not very reactive with hydroxyl radicals in the atmosphere. All of these factors lead to a large global warming potential. Finally, based on the analysis of the molecular origin of the strong absorption of radiation within the atmospheric IR window [8], design strategies were devised to minimize an industrial molecule's radiative efficiency [9].

Due to the relatively shorter atmospheric lifetimes, HFEs have been recommended as alternatives for PFCs and HFCs [10,11]. HFEs generally have an increased reactivity with hydroxyl radicals, which decreases their atmospheric lifetimes [12]. However, they absorb IR radiation very efficiently in the Earth's atmospheric window wavelength range [9,13]. The carbon–oxygen stretches fall within the atmospheric IRW and have a large IR intensity due to the polarity of the C–O bond. This in combination with the carbon–fluorine vibrational stretch, which also occurs within the atmospheric IRW, makes perfluoroethers (PFEs) and HFEs very effective greenhouse gases [8,9,12,14–18].

For fluorinated hydrocarbons and ethers, molecular structure greatly impacts its ability to absorb IR radiation [9]. It has been shown that by strategic distribution of fluorine atoms along the carbon framework, the infrared radiation absorption capacity can be reduced by a factor of two [8,9]. Based on this knowledge, a group increment scheme for absorption intensities is proposed and investigated in the present study. The idea of a group increment scheme is analogous to Benson's work with molecular thermodynamic

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doi:10.1016/j.molstruc.2011.11.048

properties. Benson approached the idea of describing thermodynamic properties by distinguishing different groups within a molecule and applying additivity rules [19]. With the different groups and their corresponding thermodynamic quantities, one can simply add the values of the different groups within a given molecule and estimate one of several thermodynamic properties. In a similar manner, PFCs, HFCs, PFEs, and HFEs can be characterized by different groups present in them, such as CF_3, CF_2, CHF_2, CH_2F, CH_2, and CHF–O etc, in order to estimate the integrated infrared absorption intensity for a given molecule. Each group has a 'base value', which is determined by a specific model. Each groups' effective contribution, i.e. 'base value' towards the total infrared absorption, is then estimated using a regression analysis of infrared intensities on a test set of over 350 fluorocarbons that included hydrofluorocarbons, perfluorocarbons, hydrofluoroethers and perfluoroethers in this work. Due to the nature of groups present in the partially or fully fluorinated hydrocarbons as opposed to partially and fully fluorinated ethers, two sets of base values are estimated for similar groups, or in other words, we develop a model for fluorocarbons and a separate model for fluoroethers. These 'base values' are expected to greatly simplify the process of estimating infrared absorption intensities and thus molecular radiative efficiencies for PFCs, HFCs, PFEs, and HFEs. Also, while the exact definition of the Earth's IR window has varied from one work to another, for purposes of the present study we define the window as 775–1425 cm^{-1} in order to be inclusive. We realize that this is a relatively large defined IRW, but we note that the vibrational frequencies we use are harmonic, and inclusion of anharmonic contributions would lower the stretching modes, in particular, by 15–30 cm^{-1}.

Before proceeding, we point out that there has been some discussion in the literature recently concerning a molecule's radiative efficiency (RE) versus its integrated IR absorption intensity within the Earth's IRW [20,21]. Firstly, we note that the term RE has been used inconsistently in the literature, and in some cases RE is used in a fashion in which it is essentially the integrated IR intensity. However, the most commonly used definition for RE is related to the molecule's integrated IR intensity, but also is multiplied by the Planck function (usually using a narrow band model – see Refs. [22,23]), and can also take into account IR absorption by other molecules in the atmosphere. Essentially, the RE defined in this way is part of the radiative transfer model used as part of a climate model. One concern, however, that we have with this approach is that it does not take into account the number of photons that can be processed per second by a single molecule (i.e., the model lacks details from molecular physics). In any case, we plan to explore this further in the future, but this is beyond the scope of the present study. Hence for the present investigation we limit the group increment scheme to the integrated IR intensity within the IRW, knowing full well that one could adapt this method for REs (computed using the narrow band model Planck function, etc.) and expect similar results.

In the next two sections the methods for obtaining the 'base values' for the groups and their use in obtaining total absorption intensities are explained.

2. Theoretical methods

The molecular geometries were optimized using the second-order Møller–Plesset perturbation theory (MP2) along with a double zeta plus polarization one-particle basis set, denoted DZP++, which includes diffuse functions on hydrogen atoms as well as the heavy atoms [24–26]. The MP2 method was chosen rather than a density functional theory (DFT) approach, for example B3LYP, because while the B3LYP method may fortuitously yield harmonic frequencies that are closer to the experimental fundamental vibrational frequency compared to MP2, it is our experience that MP2 is superior in predicting the IR intensities [27,28]. This is explained by the well known fact that DFT methods generally do not describe the diffuse part of wave functions reliably, and electrical properties such as the dipole moment, dipole derivatives, and polarizabilities, all depend significantly on the diffuse part of the wave function. All *ab initio* electronic structure calculations were performed using the Q-Chem3.1 quantum chemistry program [29]. Harmonic vibrational frequencies and IR intensities were computed at the same level of theory (MP2/DZP++). The IR intensities were computed under the double harmonic approximation, meaning the harmonic oscillator approximation was utilized in the mechanical and electrical framework. With this approximation, the IR vibrational intensities are proportional to the square of the dipole derivatives [30]. From comparison with experimental data, the IR intensities computed at the MP2/DZP++ level of theory are expected to be between 5% and 20% larger than experimental values [31]. For determining whether this type of model can work for IR intensities, the MP2/DZP++ level of theory is adequate. Linear least squares regression models were determined using Minitab 15 Statistical Software (2007) [32]. R^2 values, residuals, and fitted intensity values were computed using Minitab 15.

3. Statistical background

The residual is defined as the difference between the intensity calculated by *ab initio* methods and the intensity predicted by the model,

$$e_i = y_1 - \hat{y}_1 \tag{1}$$

The fitted intensities matrix that minimizes the sum of squares is given by the following formula where X represents the matrix that has n molecules as rows and m columns of x-variables. $\hat{\beta}$ denotes the matrix consisting of the fitted parameters, and y represents the column matrix consisting of all *ab initio* calculated intensities.

$$\hat{\beta} = (X^T X)^{-1} X^T y \tag{2}$$

$$\hat{y} = X\hat{\beta} = X(X^T X)^{-1} X^T y \tag{3}$$

The coefficient of determination for a model with n molecules is used to assess the fit of the model. It is given in Eq. (4) below where $\bar{y}$ represents the mean of the *ab initio* calculated intensities.

$$R^2 = 1 - \frac{\sum_{i=1}^{n} e_i^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2} \tag{4}$$

e is the residual, y the *ab initio* calculated IR absorption intensity, $\hat{y}$ the IR absorption intensity predicted by model, X the matrix consisting of all input data for molecules, $\hat{\beta}$ the matrix consisting of least squares fitted parameters, and R^2 is the coefficient of determination.

A summary of the linear regression analysis that we have used is contained in Ref. [33].

4. Results and discussion

4.1. Hydrofluorocarbon and perfluorocarbon models

We have used *ab initio* quantum chemical methods to calculate the harmonic vibrational frequencies and intensities for IR absorption for partially and fully fluorinated two carbon, three carbon, four carbon molecules and partially fluorinated five-carbon molecules. For the two, three, and four carbon molecules, we started with singly fluorinated species and included all possible arrangements through molecules saturated with fluorine. From the *ab initio* computed intensities several model hydrocarbon and perfluorocarbons, shown in Table 1, were created.

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