Theoretical Study of the Anthropogenic Greenhouse Gas (SF_5CF_3).

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Palavras Chave: *Anthropogenic Greenhouse Gas, QCISD(T), Pseudopotential.*

Introdução

SF_5CF_3 was recently detected in the earth's atmosphere. This has lead to various experimental and theoretical studies aimed at establishing the properties of this molecule (and its analogous molecules, from which to understand how it is formed, and how it may impact on the atmosphere (it is a powerful greenhouse gas)[1]. The dissociation energy of the S-C bond: $SF_5^{\cdots}CF_3 = SF_5 + CF_3$, is a particularly important thermo chemical quantity, and the knowledge of this value may help to establish how SF_5CF_3 can be destroyed in the atmosphere. If the bond is relatively weak, then it may be possible to destroy the molecule in the stratosphere by either photo dissociation or neutral-neutral reactions. If the bond is somewhat stronger, then molecules of SF_5CF_3 will not be destroyed until they reach the mesosphere, where they will be removed by electron attachment. Existing values for the S-C bond dissociation energy in SF_5CF_3 span a wide range, from estimates of about 200 kJ.mol^{-1}, obtained from theoretical calculations on SF_5CF_3 using the G2 and G3 protocols, to 390 ± 45 kJ.mol-1 derived from experimental studies of the photo ionization of SF_5CF_3. The latter value is similar to that for S-F in SF_6, and as such seems rather high, since the theoretical calculations show an equilibrium geometry with a relatively long S-C bond (the result of repulsions between the relatively bulky CF_3 and SF_4...F).

Resultados e Discussão

In theoretical calculations the number of electrons to be described is reduced using pseudo potential. To make use of these effective core potentials the basis set for the outer electrons has to be optimized to match the core. This is done using the generator coordinate method (GCM), to give the best match to a number of experimentally known properties of the atom, and molecules containing the atom. Two basis sets were constructed for each atom, a small basis set (labeled B0), and a larger basis set (labeled B1) containing additional more diffuse functions[2]. To molecular systems the calculations of the energies required five steps. In the first step, Hartree-Fock calculations of the energy are made with basis B0, and used to produce an optimized (minimum energy) geometry. Vibrational frequencies are calculated at this (HF/B0) level of theory. The HF/B0 optimized geometry is used as the starting point for a second stage of geometry optimization, using MP2/B0 energies, commencing with vibrational force constants obtained from the HF/B0 vibrational frequency step. The MP2/B0 optimized geometry was used in the two subsequent steps - the calculation of a QCISD(T)/B0 energy and a MP2/B1 energy. For molecules, an estimate of the QCISD(T)/B1 energy is obtained from Eq. (1). Thus the 'best' energy obtained may be designated as QCISD(T)/B1//MP2/B0, meaning an estimate of the QCISD(T)/B1 (or QCISD(T)/ECP+GCM) energy at the MP2/B0 optimized geometry.

$$E[QCISD(T)/B1//MP2/B0] = E[QCISD(T)/B0//MP2/B0] + E[MP2/B1//MP2/B0] - E[MP2/B0//MP2/B0] + ZPE//HF/B0 \qquad (2)$$

All calculations used the Gaussian/03 quantum chemistry package. An MP2/B0 optimized structure was found for SF_5CF_3, which is a good match to the structure found in the G2 and G3 calculations on SF_5CF_3. In addition to these orbital-based computations, the MP2/B0 optimized geometry shows a relatively long S-C bond. At the QCISD(T)/B1//MP2/B0 level, with scaled HF/B0//HF/B0 zero point energies, the dissociation energy is 275 kJ.mol^{-1}, and the experience gained through the calculations of the dissociation energies of $SF_n^{-\cdots}F$ suggests that QCISD(T)/B1//MP2/B0 energies (Eq. 1) tend to give low bond dissociation energies. This suggests that the S-C bond dissociation in SF_5CF_3 could be greater than 275 kJ.mol^{-1}. However, it is not known if the conclusions of the bond dissociation energy tests for SF_n molecules are transferrable to other molecules. Also the G2 and G3 protocols have been specifically developed to give good values for thermochemical properties such as bond dissociation energies. In the case of SF_n molecules, G2 enthalpies of formation perform extremely well in comparison to the values recently obtained by Bauschlicher and Ricca from higher level calculations[3].

Conclusões

SF_5CF_3 is chemically very inert, and is not destroyed in the troposhere. Theoretical calculations using effective core potential (ECP) based on high level methods - QCISD(T), were performed for molecular systems related to SF_5CF_3. Existing values for the S-C bond dissociation energy in SF_5CF_3 span a wide range, from estimates of about 200 to 300 kJ.mol^{-1}, obtained from theoretical calculations on SF_5CF_3 using the DFT, G2 and G3 protocols, to 390 ± 45 kJ.mol^{-1} derived from experimental studies of the photo ionization of SF_5CF_3. At the QCISD(T)/ECP+GCM level, the dissociation energy - $D^o(0K, SF_5\text{-}CF_3)$, is 274.66 kJ.mol^{-1}.

Agradecimentos

I would like to thank the computational facilities of Chemistry Institute at UNICAMP and the financial support from CNPq and FAPESP.

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