

Infrared and Raman spectra and vibrational analyses calculated with Moeller-Plesset perturbation theory of second order of nitrosoethylene and its chloro-derivatives. Forner, Wolfgang; Badawi, Hassan M.. Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. *Journal of Molecular Modeling* (2005), 11(6), 542-550.

Abstract

The conformational and structural stabilities of nitrosoethylene $\text{CH}_2=\text{CH}-\text{N}=\text{O}$, chloronitrosoethylene $\text{CH}_2=\text{CCl}-\text{N}=\text{O}$, and dichloronitrosoethylene $\text{CCl}_2=\text{CH}-\text{N}=\text{O}$ were investigated by ab initio Moeller-Plesset perturbation theory of second order (MP2) calcns. using the 6-311 + G** basis set to include electron correlation. From the calcns. all three were predicted to exist predominantly in the planar trans structure (C = C and N = O bonds are trans to each other) with high trans-cis rotational barriers of about 9 kcal mol⁻¹ as a result of pronounced conjugation between C = C and N = O bonds. The vibrational frequencies were computed for the three mols., and also the d1 and d2 deuterated variants for the parent mol. at the MP2 level. Normal coordinate analyses were carried out and the potential energy distributions (PED), among the symmetry coordinates of the normal modes of the mol. were computed. Complete vibrational assignments were made on the basis of normal coordinate analyses for the mols. The two chlorinated derivs. of nitrosoethylene were also investigated in the same way. As expected, we then find high Raman and IR intensities in all modes that contain a high content of chlorine movements because vibrations of C-Cl bonds lead to large changes in polarizability, as well as to a large change in dipole moment. However, modes involving double bonds also have quite large intensities. An appreciable no. of modes in these mols. are more or less pure symmetry coordinates.