Protonated N-Nitrosodimethylamine: a comparative MR-CISD and NEVPT2 study

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INTRODUCTION

Nitrosamines are considered carcinogenic and have been detected even in drinking water[1]. The photolysis is a technique that can be used to treat or even remove these substances.[2] In high acid concentration N-nitrosodimethylamine (NDMA) become protonated (Figura 1) and will not undergo photolysis. Thus, the protonated nitrosamine is a key species in the study of NDMA photostability.

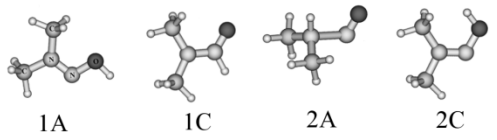

Figura 1: Ground state conformations of protonated NDMA.

The main photochemical reactions of NDMA in acid solution are shown in:

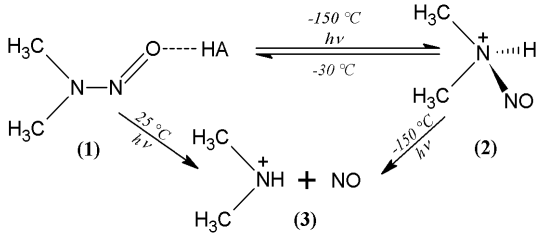

Figura 2: Main photochemical reactions of NDMA in acid solution (adapted from[3]).

METHODS

The CASSCF, MR-CISD and NEVPT2 [4] methods with the aug-cc-pVDZ basis set have been used in the calculations. COLUMBUS [5] and ORCA [6] softwares have been used for the first two and for the last method, respectively. The active space consists of the following set of orbitals: $2s_O$, $2s_N$, σ_{XH}, σ_{NN}, π_{NO}, σ_{NO}, np_X, π^*_{NO}, σ^*_{NN}, σ^*_{NO}, σ_{XH}^*, where X = N or O.

RESULTS AND DISCUSSION

Tabela 1 shows the relative energies of the four tautomers of NDMA. The energies shown have been obtained at the CASSCF, MR-CISD and NEVPT2 levels based on CASSCF (14,11) geometries optimized with the aug-cc-pVDZ basis set. As can be seen from this Table there is good agreement between MR-CISD and NEVPT2 results. Figura 3 shows the energies of the first four singlet electronic states of protonated NDMA obtained from a relaxed scan along the N-N distance.

Tabela 1: CASSCF, MR-CISD and NEVPT2 with aug-cc-pVDZ energies (in kcal/mol) of the four tautomers NDMA.

Structures	CASSCF[7]	MR-CISD[7]	NEVPT2
1A	0,00	0,00	0,00
1C	11,10	11,34	12,15
2A	-15,41	2,54	1,35
2C	10,92	14,47	15,72

As can be seen from this plot there is very good agreement between the results obtained at the MR-CISD and NEVPT2 levels.

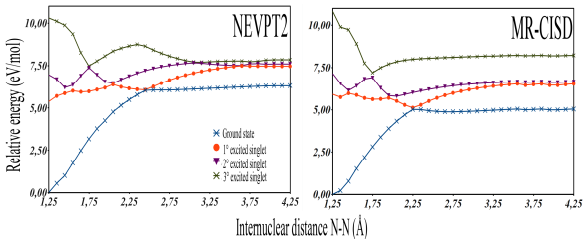

Figura 3: Potential energies curves for the first four singlet electronic states of protonated NDMA obtained at the NEVPT2 and MR-CISD levels along the N-N bond distance of structure 1A. The energies shown have been obtained from a relaxed scan.

CONCLUSIONS

The very good agreement between the MR-CISD and NEVPT2 results suggests the use of the latter method (which has a much lower computational cost) for larger nitrosamines of varied photostability.[8] Besides, solvent effects (with continuum solvent models) can also be included at the latter level.

ACKNOWLEDGMENTS

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