

Theoretical Study of the effects of solvents on energy components of Picric acid.

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Abstract: Quantum mechanical calculations of different energies components of Picric acid in ground and excited state were carried out by HatreeFock method , in isolated state and in various solvents to study the effects of solvents on various energy components. The solvation energy, chemical potential, hardness, electrophilicity of picric acid were calculated with the help of computed HOMO-LUMO gap of picric acid in different solvents in both ground and excited state. The plots of energy components and thermodynamic parameters against the dielectric constant of the corresponding solvents were found to be polynomial of higher order. The 3D plot of HOMO-LUMO of Picric acid and dielectric constants of various solvents in ground state and excited state reveals that LUMO of picric acid is more affected than that of HOMO by change in the dielectric constant of the solvent

Keyword: Ground state, Excited state, picric acid, HF-method, energy components, HOMO, LUMO, solvation energy, dielectric constants.

Introduction

Physical and chemical property of a molecule depends on the structure and the various kinds of energies of the molecule. Chemical reaction of a molecule in solution is affected by the nature of the solvent; solvent affects not only the energies of HOMO and LUMO of the molecule, but also other kinds of energies. Energy of a molecule may be considered to have various energy components such as reaction field energy, total zero-electron terms, Nuclear-nuclear, Nuclear-solvent, total one-electron terms, Electron-nuclear, Electron-solvent, Kinetic, total two-electron terms, Electronic energy, total quantum mech. energy, Gas phase energy, Solution phase energy, total solute energy, total solvent energy, Solute cavity energy, Reorganization energy, Solvation energy total internal energy , total enthalpy, total Gibbs free energy, and zero point energy. Picric acid is a yellow crystalline, bitter[1-2], toxic[3-5], explosive solid[6] which is widely used in the identification of activated compounds in the labs[7], preparation of Charge transfer complexes[8-12] of various utilities etc. It has been used as an explosive [6], dyes [13] and antiseptic [14]. Keeping in view the utility of picric acid various kinds of energies of picric acid in the

ground as well as excited states in gaseous phase and in different kinds of solvents have been theoretically calculated in this paper.

Computational methods

The initial structure of Picric acid was built with Chem-Draw ultra8.0 and the structure was optimized on Chem3D ultra 8.0. The structure was exported to Maestro 9.3 of Schrodinger 2012 version. The optimization of the structure was done on the Jaguar panel of the Maestro 9. The HF-B3LYP method of theory was chosen. 6-31g^{##} basis set was selected and 255 basis functions were created for calculation. The molecule was assigned net zero charge and singlet multiplicity. In the solvent menu of the jaguar panel PBF solver was used for optimization of the structure in both the gaseous and solution phase. The optimization the gaseous state and in the different solutions were done both ground states and the excited states of the molecule. The thermochemical data were determined with the help of vibrational frequency determination.

Geometry optimization

for perform a geometry optimization one needs to guess at the geometry and the direction in which to search, a set of co-ordinates to optimize, and some criteria for when to optimization is complete. The search direction is obtained from the gradient of the energy and the initial Hessian. An initial Hessian(second derivative matrix or force constant matrix) and the gradient are used to define search direction that should result in lowering of energy. The choice if co-ordinate systems have a substantial impact on the convergence of the optimization. The ideal set of Co-ordinate is one in which the energy change along each co-ordinate is maximized, and the coupling between co-ordinates is minimized. Jaguar chooses the coordinate system by default. It has two options Cartesian and z-matrix that produces an efficient optimization requires an understanding of the coupling between simple internal co-ordinates

For optimization to minimum energy structures, the convergence criterion for SCF calculation is chosen to assure accurate analyses gradients. For these jobs, a wave function is considered converged when the root mean square (RMS) change in density matrix element is less than the RMS density matrix element change criterion, whose default value is 5.0×10^{-6} . The geometry is considered to have converged when the energy of successive geometries and the elements of analyze gradients of the energy and the displacement has met convergence criteria. For optimization in solution, the default criteria are multiplied by a factor of three, and a higher priority is given to the energy convergence criterion. Thus if the energy change criterion is met before the gradient and displacement criteria have been met, the geometry is considered converged. The optimized geometry may not have a local minimization energy i.e it may have reside on a saddle. To know whether it is global minimization we look for the value of vibrational frequencies. If all the vibrational frequencies are real (i.e +ve) then it represents global minimum, but if any of the vibrational frequencies is negative (i.e imaginary) then it is local minimum.

Performing a solvation calculation

It involves several iterations in which the wave functions for the molecule in the gas phase are calculated. The program ch performs electrostatic potential fitting, which represents the wave function as a set of point charges on the atomic centers. The interactions between the molecule and the solvent are evaluated by Jaguar's Poisson-Boltzmann solver [15-16], which fits the field produced by the solvent dielectric continuum to another set of point charges. These charges are passed back to scf, which performs a new calculation of the wave function for the molecule in the field produced by the solvent point charges. Electrostatic potential fitting is performed on the new wave function, the solvent-molecule interactions are reevaluated by the Poisson-Boltzmann solver, and so on, until the solvation free energy for the molecule converges.

For solvation calculations on neutral systems in water the program pre evaluates the Lewis dot structure for the molecule or system and assigns atomic van der Waals radii accordingly. The van der Waals radii are used to form the boundary between the solvent dielectric continuum and the solute molecule. The Lewis dot structure and van der Waals radii information both appear in the output from the program pre. The radii are listed under the heading "vdw2" in the table of atomic information below the listing of non-default options. After the pre output,

the usual output appears for the first, gas-phase calculation, except that the energy breakdown for the scf output also describes the electron-nuclear and kinetic contributions to the total one-electron terms in the energy, as well as the virial ratio $-V/T$, where V is the potential energy and T is the kinetic energy. This ratio should be -2 if the calculation satisfies the virial theorem. After the first scf output, the output from the first run of the program *ch* appears. Since performing a solvation calculation enables electrostatic potential fitting to atomic centers, the usual output for that option is included every time output from the program *ch* appears in the output file. The post program writes out the necessary input files for the Poisson-Boltzmann solver; this step is noted in the output file. The next output section comes from the Poisson-Boltzmann solver. The output includes information on the area (in \AA^2) of the molecular surface formed from the intersection of spheres with the van der Waals radii centered on the various atoms; the reaction field energy in kT (where $T = 298$ K), which is the energy of the interaction of the atom-centered charges with the solvent; the solvent-accessible surface area (in \AA^2), which reflects the surface formed from the points whose closest distance from the molecular surface is equal to the probe radius of the solvent; and the cavity energy in kT , which is computed to be the solvation energy of a nonpolar solute whose size and shape are the same as those of the actual solute molecule. The output from the program *sol* follows the Poisson-Boltzmann solver results, giving the number of point charges provided by the solver to model the solvent, the sum of the surface charges, the nuclear repulsion energy already calculated by Jaguar, the nuclear-point charge energy representing the energy of interaction between the molecule's nuclei and the solvent point charges, and the point-charge repulsion energy, which is calculated but not used because it is irrelevant to the desired solvation results. After this output, the output for the second solvation iteration begins. The output from *scf* comes first, giving the results for the molecule-and-solvent-point-charges system. Total quantum mech. energy corresponds to the final energy from the *scf* energy table for that iteration, and includes the entire energies for the molecule-solvent interactions. The output next includes the gas phase and the solution phase energies for the molecule, since these terms are, of course, necessary for solvation energy calculations. The first solution phase energy component is the total solute energy, which includes the nuclear-nuclear, electronuclear, kinetic, and two-electron terms, but no terms involving the solvent directly. The second component of the solution phase energy is the total solvent energy, which is computed as half of the total of the nuclear-solvent and electron-solvent terms, since some of its effect has already changed the solute energy. Third, a solute cavity term, which computes the solvation energy of a nonpolar solute of identical size and shape to the actual solute molecule, as described in reference [15], is included. This is only done for water as solvent. The last solution phase energy component (shown only if it is nonzero) is term (T), the first shell correction factor, which depends on the functional groups in the molecule, with atoms near the surface contributing most heavily. Finally, the list ends with the reorganization energy and the solvation energy. The reorganization energy is the difference between the total solute energy and the gas phase energy, and does not explicitly contain solvent terms. The final solvation energy is calculated as the solution phase energy described above minus the gas phase energy. The solvation energy is listed in Hartrees and in kcal/mol,

Chemical potential (μ) [17]

HOMO as ionization energy (IE) and LUMO as electron affinity (EA) have been used for calculating the electronic chemical potential (μ) which is half of the energy of HOMO and LUMO.

$$\mu = (E_{\text{HOMO}} + E_{\text{LUMO}}) / 2$$

Hardness (η) [18]

The hardness (η) as half of the gap energy of HOMO and LUMO has been calculated using the following equation

$$\text{Gap} = E_{\text{HOMO}} - E_{\text{LUMO}}$$

$$\eta = \text{Gap} / 2$$

Electrophilicity (ω) [19]

The electrophilicity (ω) has been calculated using equation-

$$\omega = \mu^2 / 2 \eta$$

Reaction field energy (in KT)

This gives us the energy of the interactions of atom centred charges with the solvent; Solvent accessible surface area (SASA in A^0^2) reflects the surface formed from the points whose closest distance from the molecular surface is equal to the probe radius of the solvent.

Cavity energy (in KT)

This is solvation energy of a non-polar solute whose size and shape are the same as those of actual solute molecule.

Quantum mechanical energy

This term corresponds to the entire energies for the molecule solvent interaction and is equal to the sum of total zero electron terms and electronic energy.

Reorganisation energy

This is the difference between the total solute energy and the gas phase energy, and does not explicitly contain solvent terms.

Calculations for excited states

The energy parameters in excited states for closed shell Hatree-Fock reference wave function have been calculated by configuration interaction singles (CIS) method on Jaguar panel of Maestro9.3.

Thermochemical Properties

Thermochemical calculations of the constant volume heat capacity (C_v), internal energy (U) entropy (S), enthalpy (H) and Gibbs Free energy are calculated at standard temperature and pressure by calculating vibrational frequencies with the help of rotational symmetry numbers, which identify the number of orientation of a molecule which can be obtained from each other by rotation, and zero point energies are also computed.

Results and discussion

Solvent parameters:

Table-1 summarizes the solvent parameters such as dielectric constants, molecular weight, density and polarity of the solvents used for the present theoretical study by Poisson-Boltzmann solver. In table-3 the energy components calculated by Hatree-Fock method on Jaguar panel of the Maestro 9.3 with 6-31g^{##} basis set utilizing 255 basis functions for Picric acid in the ground state have been incorporated. In table 4 the values of same parameters for picric acid in the excited state calculated by the CIP method appears. The pictures of HOMO and LUMO of picric acid in gaseous state, in most stabilizing solvents has been shown in fig.8.

An electron acceptor represents the ability to obtain an electron in the LUMO and HOMO represents the ability to donate electron.

The ($E_{HOMO}-E_{LUMO}$) gap is an important scale of stability [23] and compounds with large ($E_{HOMO}-E_{LUMO}$) gap value tend to have higher stability. The perusal of the table-3 indicates the stability of picric acid increases in the solvents in the ground and excited state in the order; gas>acetone>nitrile>dmf>methanol>dichloromethane >THF> chloroform> water>carbontetrachloride> benzene>cyclohexane and acetone>nitrile>dmf> methanol> dichloromethane >THF> chloroform> water> gas>carbontetrachloride> benzene>cyclohexane respectively.

Table1: Physical parameters of various solvents

Solvents	M.W	Density	Dielectric constant	Probe radius
	g/mol	g/ml		A ^o
1.Acetonitrile	37.5	0.777	37.5	2.19
2.Benzene	78.12	0.87865	2.284	2.6
3.Carbontetrachloride	153.82	1.594	2.238	2.67
4.Chloroform	119.38	1.4832	4.806	2.52
5.Cyclohexane	84.16	0.77855	2.023	2.78
6.Dichloromethane	84.93	1.3266	8.93	2.33
7.DMF	73.09	0.944	36.7	2.49
8.methanol	32.04	0.7914	33.62	2
9.THF	72.11	0.8892	7.6	2.52
10.Water	18.02	0.99823	80.37	1.4

Table: 2

job name		HOMO	LUMO	Gap	$\mu = E_{\text{HOMO}} + E_{\text{LUMO}}/2$	$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2$	Electrophilicity $\omega = \mu^2/2\eta$
1	Gas (GS)	-0.40811	0.0025	-0.41061	-0.202805	0.205305	0.004222084
	Gas (ES)	-0.40809	0.0024	-0.41049	-0.202845	0.205245	0.004222515
2	acetonitrile(GS)	-0.384175	0.02435	-0.408525	-0.1799125	0.2042625	0.003305836
	acetonitrile(ES)	-0.384128	0.024407	-0.408535	-0.1798605	0.2042675	0.003304006
3	benzene(GS)	-0.39758	0.012733	-0.410313	-0.1924235	0.2051565	0.003798145
	benzene(ES)	-0.39754	0.012646	-0.410186	-0.192447	0.205093	0.003797897
4	carbontetrachloride(GS)	-0.397804	0.012367	-0.410171	-0.1927185	0.2050855	0.003808481
	carbontetrachloride(ES)	-0.397804	0.012367	-0.410171	-0.1927185	0.2050855	0.003808481
5	chloroform(GS)	-0.391053	0.018444	-0.409497	-0.1863045	0.2047485	0.003553345
	chloroformexcited(ES)	-0.391056	0.018421	-0.409477	-0.1863175	0.2047385	0.003553668
6	cyclohexan(GS)	-0.398972	0.011423	-0.410395	-0.1937745	0.2051975	0.003852435
	cyclohexane(ES)	-0.398958	0.011448	-0.410406	-0.193755	0.205203	0.003851763
7	dichlormethane(GS)	-0.387654	0.02142	-0.409074	-0.183117	0.204537	0.003429251
	dichlormethane(ES)	-0.387654	0.02142	-0.409074	-0.183117	0.204537	0.003429251
8	dmf (GS)	-0.384524	0.024194	-0.408718	-0.180165	0.204359	0.003316688
	dmfexcited(ES)	-0.384328	0.024311	-0.408639	-0.1800085	0.2043195	0.003310289
9	methanol(GS)	-0.384105	0.024625	-0.40873	-0.17974	0.204365	0.003301156
	methanol(ES)	-0.384105	0.024625	-0.40873	-0.17974	0.204365	0.003301156
10	THF(GS)	-0.38841	0.020805	-0.409215	-0.1838025	0.2046075	0.003456164
	THF(ES)	-0.388387	0.02084	-0.409227	-0.1837735	0.2046135	0.003455175
11	Water(GS)	-0.38495	0.02469	-0.40964	-0.18013	0.20482	0.003322879
	Water(ES)	-0.384914	0.024636	-0.40955	-0.180139	0.204775	0.00332248

Table.3 : Energy components of Picric acid in the Ground state in gas phase and various solvents.

Energy components , in hartrees	Gas-phase	Acetonitrile	Benzene	Carbon tetrachloride	Chloroform	Cyclohexane	Dichloro methane	dmf	methanol	THF	Water
(A)Total zero electron terms		1117.88	1119.97	1120.08	1119.05	1120.22	1118.45	1117.84	1117.96	1118.67	1118.19
(B)Nuclear-nuclear/nuclear repulsion	1121.69	1120.33	1121.03	1121.11	1120.77	1121.13	1120.53	1120.24	1120.39	1120.64	1120.55
(C)Nuclear-solvent		-2.44	-1.06	-1.03	-1.72	-0.92	-2.07	-2.40	-2.44	-1.98	-2.36
(E)Total one electron terms	-3481.02	-3475.23	-3478.38	-3478.59	-3477.04	-3478.77	-3476.10	-3475.11	-3475.37	-3476.46	-3476.01
(F)Electron-nuclear		-4391.50	-4393.41	-4393.59	-4392.66	-4393.67	-4392.03	-4391.33	-4391.63	-4392.31	-4392.28
(G)Electron-solvent		2.36	1.03	1.00	1.66	0.89	2.01	2.32	2.36	1.91	2.31
(H)Kinetic		913.90	914.00	914.00	913.95	914.01	913.93	913.90	913.90	913.94	913.95
(I)Total two electron terms	1443.37	1441.31	1442.42	1442.52	1441.97	1442.57	1441.62	1441.23	1441.38	1441.77	1441.82
(L)Electronic energy (E+I)	-2037.65	-2033.92	-2035.96	-2036.07	-2035.07	-2036.21	-2034.48	-2033.88	-2033.99	-2034.69	-2034.20
(N)Total quantum mechanical energy(A+L)	-915.96	-916.04	-915.99	-915.99	-916.01	-915.99	-916.02	-916.03	-916.04	-916.02	-916.01
(O)Gas phase energy		-915.96	-915.96	-915.96	-915.96	-915.96	-915.96	-915.96	-915.96	-915.96	-915.96
(P)Solution phase energy(Q+R+S)		-915.99	-915.98	-915.98	-915.98	-915.97	-915.99	-915.99	-915.99	-915.99	-915.98
(Q)Total solute energy(N-C-G)		-915.95	-915.96	-915.96	-915.96	-915.96	-915.96	-915.95	-915.95	-915.96	-915.96
(R)Total solvent energyC/2+G/2)		-0.04100	-0.01631	-0.01589	-0.02762	-0.01397	-0.03401	-0.04011	-0.04079	-0.03227	-0.02644
(S)Solute cavity energy		0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00502
(U)Reorganization energy(Q-O)		0.06000	0.00072	0.00066	0.00271	0.00041	0.00417	0.00582	0.00581	0.00374	0.00295
(V)solvation energy(P-O)		-0.03500	-0.01558	-0.01523	-0.02491	-0.01355	-0.02984	-0.03429	-0.03498	-0.02853	-0.01934
Reaction Field Energy (kT)		-43.63791	-17.38373	-16.92319	-29.47034	-14.88405	-36.2714	-42.8392	-43.4540	-34.4478	-28.11175

Table4 : Energy components of Picric acid in the excited state in gas phase and various solvents.

Energy components , in hartrees	Gas-phase	Acetonitrile	Benzene	Carbon tetrachloride	Chloroform	Cyclohexane	Dichloro methane	dmf	methanol	THF	Water
(A)Total zero electron terms		1117.88	1120.06	1120.08	1119.05	1120.22	1118.45	1117.99	1117.96	1118.66	1118.13
(B)Nuclear-nuclear/nuclear repulsion	1121.69	1120.33	1121.11	1121.11	1120.77	1121.13	1120.53	1120.39	1120.39	1120.64	1120.50
(C)Nuclear-solvent		-2.45	-1.06	-1.03	-1.72	-0.92	-2.07	-2.40	-2.44	-1.98	-2.38
(E)Total one electron terms	-3481.02	-3475.23	-3478.56	-3478.59	-3477.04	-3478.77	-3476.10	-3475.42	-3475.37	-3476.46	-3475.90
(F)Electron-nuclear		-4391.50	-4393.58	-4393.59	-4392.66	-4393.67	-4392.03	-4391.64	-4391.63	-4392.30	-4392.17
(G)Electron-solvent		2.37	1.03	1.00	1.66	0.89	2.01	2.32	2.36	1.91	2.32
(H)Kinetic		913.90	914.00	914.00	913.95	914.01	913.93	913.91	913.90	913.93	913.95
(I)Total two electron terms	1443.37	1441.31	1442.51	1442.52	1441.97	1442.57	1441.62	1441.39	1441.38	1441.77	1441.77
(L)Electronic energy (E+I)	-2037.65	-2033.92	-2036.05	-2036.07	-2035.07	-2036.21	-2034.48	-2034.03	-2033.99	-2034.69	-2034.14
(N)Total quantum mechanical energy(A+L)	-915.96	-916.04	-915.99	-915.99	-916.01	-915.99	-916.02	-916.03	-916.04	-916.02	-916.01
(O)Gas phase energy		-915.96	-915.96	-915.96	-915.96	-915.96	-915.96	-915.96	-915.96	-915.96	-915.96
(P)Solution phase energy(Q+R+S)		-916.00	-915.98	-915.98	-915.98	-915.97	-915.99	-915.99	-915.99	-915.99	-915.98
(Q)Total solute energy(N-C-G)		-915.95	-915.96	-915.96	-915.96	-915.96	-915.96	-915.95	-915.95	-915.96	-915.96
(R)Total solvent energy(C/2+G/2)		-0.04098	-0.01631	-0.01589	-0.02760	-0.01398	-0.03401	-0.04011	-0.04079	-0.03230	-0.02657
(S)Solute cavity energy		0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00502
(U)Reorganization energy(Q-O)		0.00597	0.00072	0.00066	0.00270	0.00042	0.00417	0.00574	0.00581	0.00376	0.00300
(V)solvation energy(P-O)		-0.03500	-0.01560	-0.01523	-0.02490	-0.01356	-0.02984	-0.03437	-0.03498	-0.02854	-0.01943
Reaction field energy (kT)		-43.7310	-17.3812	-16.92319	-29.4448	-14.9102	-36.2714	-42.854	-43.4540	-34.5070	-28.0616

The plot of the energy gap between HOMO and LUMO versus dielectric constant of solvents in ground state and excited state have been shown in the fig 1a and 1b respectively. The dependence of the energy gap (y) on dielectric constant (x) in ground and excited state follows the equation $y = 2E-10x^5 - 4E-08x^4 + 2E-06x^3 - 6E-05x^2 + 0.0006x - 0.4114$ ($R^2 = 0.9913$) and $y = 2E-10x^5 - 4E-08x^4 + 2E-06x^3 - 6E-05x^2 + 0.0006x - 0.4113$ ($R^2 = 0.9943$) respectively.

The Picric acid molecule has been found to be stabilized in the ground state in gas, acetonitrile, THF, and cyclohexane in the order; gas> acetonitrile> THF> cyclohexane than their corresponding excited states whereas, the excited state is more stabilized in chloroform, water, benzene and gaseous state, the order being chloroform>water>benzene>gaseous state. Therefore, if it is desired to stabilize picric acid in the ground state then out of ten solvents studied acetonitrile is the best. On the other hand, chloroform is the best choice for the stabilization of picric acid in the excited state than its ground state. However, methanol, carbontetrachloride and dichloromethane stabilizes the ground state and excited state to the same extent; the order of stabilization being methanol> dichloromethane>carbontetrachloride.

The 3D plots of HOMO-LUMO and dielectric constant shown in figure 7a and 7b reveals that LUMO of picric acid is more effected than HOMO in both the ground and excited state by change in the dielectric constant of the solvent.

The chemical potentials (μ) of picric acid in the ground state and excited state are in the following order; methanol>gas> acetonitrile>water>dmf> dichloromethane>THF> chloroform>benzene> carbontetra chloride> cyclohexane>gas and methanol> acetonitrile>gas>dmf> water> dichloromethane> THF>chloroform> benzene> carbontetrachloride> cyclohexane respectively and same in carbontetra chloride, dichloromethane, methanol. The chemical potentials of picric acid in methanol, carbontetrachloride and dichloromethane are identical in both the ground and excited states.

The plot of the chemical potential versus dielectric constant of solvents in ground state and excited state have been shown in the fig2a and 2b. The dependence of the chemical potential (y) on dielectric constant(x) follows the equation

The Picric acid molecule has been found to possess higher chemical potential in the ground state in benzene, chloroform, gas, methanol, water in the order; methanol>gas>water> chloroform>benzene>, whereas, the excited state has higher chemical potential in acetonitrile, carbontetrachloride, cyclohexane, dichloromethane, dmf and THF, the order being; acetonitrile>dmf> dichloromethane> THF>carbontetrachloride>cyclohexane. Therefore, if it is desired to have highest chemical potential, picric acid in the ground state, then out of ten solvents studied methanol is the best. However, chemical potential of picric acid in methanol, carbontetrachloride and dichloromethane in the ground state and excited state are same; the order being; methanol>dichloromethane >carbontetrachloride.

The hardness(η) of picric acid increases in the ground and excited state in the following order; cyclohexane> benzene>carbontetrachloride> water> chloroform> THF> dichloromethane> methanol> dmf> acetonitrile> gas and cyclohexane>benzene>carbontetrachloride> gas> water> chloroform>THF > dichloromethane> methanol>dmf> acetonitrile respectively. The hardness in carbontetrachloride, dichloromethane, methanol, is same in both the ground and excited states.

The plot of hardness versus dielectric constant of solvents in the ground state and excited state have been shown in the fig3a and 3b respectively. The dependence of hardness (y) on dielectric constant(x) follows the $y = -1E-10x^5 + 2E-08x^4 - 1E-06x^3 + 3E-05x^2 - 0.0003x + 0.2057$, ($R^2 = 0.9913$) and $y = -1E-10x^5 + 2E-08x^4 - 1E-06x^3 + 3E-05x^2 - 0.0003x + 0.2057$ ($R^2 = 0.9943$) in the ground and excited state respectively.

The Picric acid molecule has been found to be hardest in cyclohexane in both the ground and excited states; the hardness. Therefore, if it is desired to increased hardness of picric acid to largest extent in the ground state then out of ten solvents studied cyclohexane is the best.

The electrophilicity (ω) of picric acid increases in ground and excited state in the following order cyclohexane>carbontetrachloride>benzene>chloroform>THF>dichloromethane>water>dmf>acetonitrile> methanol> gas and cyclohexane>carbontetrachloride>benzene> chloroform> THF> dichloromethane> water> gas>dmf> acetonitrile> methanol. The electrophilicity of picric acid is identical in both the ground and excited state in methanol, carbontetrachloride, and dichloromethane.

The plot of electrophilicity (y) versus dielectric constant(x) of solvents in ground state and excited state have been shown in the fig4a and 4b respectively. The dependence of the electrophilicity on dielectric constant follows the $y = 8E-12x^6 - 1E-09x^5 + 9E-08x^4 - 3E-06x^3 + 4E-05x^2 - 0.0003x + 0.0043$ ($R^2 = 0.9998$) and $y = 6E-12x^6 - 1E-09x^5 + 8E-08x^4 - 2E-06x^3 + 4E-05x^2 - 0.0003x + 0.0043$ ($R^2 = 0.9999$) in the ground and excited state respectively.

The Picric acid molecule has been found to possess high electrophilicity in the ground in cyclohexane. Therefore, if it is desired to increase electrophilicity of picric acid to larger extent in the ground state, then out of ten solvents studied cyclohexane is the best. However, methanol, carbontetrachloride and dichloromethane stabilizes the ground state and excited state to the same extent; the order of stabilization being; carbontetrachloride> dichloromethane> methanol.

The Solvation energy of picric acid in the ground state and excited state are in the following order; acetonitrile> methanol>dmf>dichloromethane>THF>chloroform> water>benzene>carbontetrachloride>cyclohexane .

The plot of the solvation energy versus dielectric constant of solvents in ground state and excited state have been shown in the fig5a and 5b respectively. The dependence of the solvation energy(y) on dielectric constant(x) follows the equation $y = 4E-10x^6 - 7E-08x^5 + 4E-06x^4 - 0.0001x^3 + 0.0017x^2 - 0.0116x + 0.0037$ ($R^2 = 0.9996$) and $y = 3E-10x^6 - 6E-08x^5 + 4E-06x^4 - 0.0001x^3 + 0.0016x^2 - 0.0114x + 0.0035$ ($R^2 = 0.9997$) in the ground and excited state respectively.

Picric acid is solvated more in the excited state than the ground state in benzene, dmf, THF water and cyclohexane, whereas the ground state is solvated more than excited state in only chloroform. The rest four solvents namely acetonitrile, carbontetrachloride, dichlormethane, and methanol have same influence on both the ground and excited states.

The reaction field energy in kT (where $T=29K$) increases in the order both in the ground state and excited state cyclohexane>carbontetrachloride>benzene> water> chloroform> THF>dichlormethane> DMF> methanol> acetonitrile and cyclohexane>carbontetrachloride>benzene> water>chloroform>THF> dichlormethane> DMF> methanol> acetonitrile respectively. and same in methanol, dichloromethane, carbontetrachloride.

The values of various thermodynamic quantities of picric acid in gaseous phase and ten different solvents appear in Table 5 and 6. The data are self-explanatory.

Thermodynamic parameters: An examination of table 5 and 6 gives an idea about different thermodynamic parameter.

Entropy:

The excited state of picric acid becomes ordered in different solvents in the order benzene> water> DMF> acetonitrile> THF>. In carbontetrachloride, cyclohexane, dichloromethane and methanol, the ground state and excited states have same ordered states. In chloroform and gaseous state the ground state is more ordered .

Enthalpy:

The solvation of excited states of picric acid is exothermic in acetonitrile, benzene, cyclohexane, dmf, and THF, while it is endothermic in chloroform and water. Carbontetrachloride, dichloromethane and methanol have some influence on both ground and excited states of picric acid.

Change in Gibbs free energy:

The excited state is more favored in acetonitrile, THF, and cyclohexane. The order being acetonitrile> THF> cyclohexane.

Figure 1a. Effect of dielectric constant on the HOMO-LUMO gap of picric acid in the GS

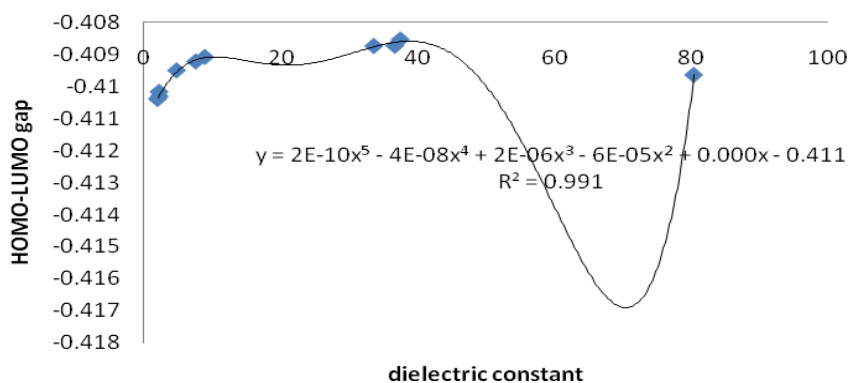


Figure 1b. Effect of dielectric constant on the HOMO-LUMO gap of picric acid in the ES

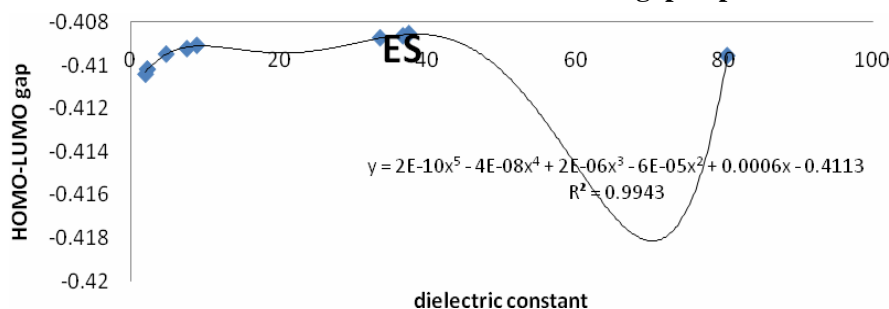


Figure 2a. Effect of dielectric constant on the chemical potential of picric acid in the GS

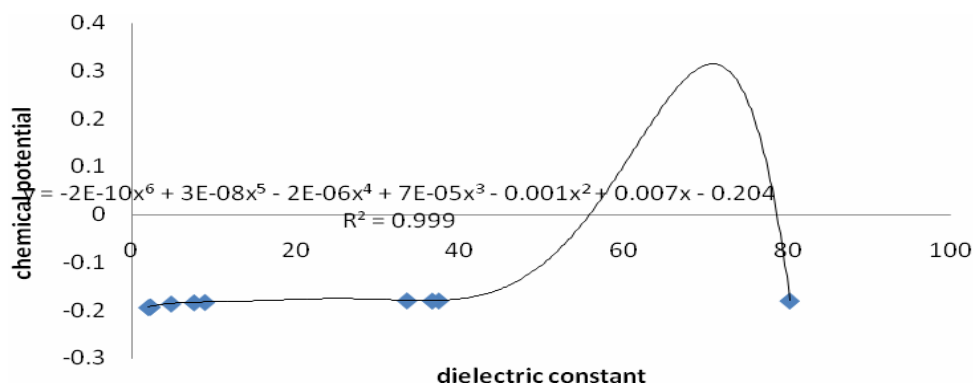


Figure 2b.Effect of dielectric contant on the HOMO-LUMO gap of picric acid in the ES

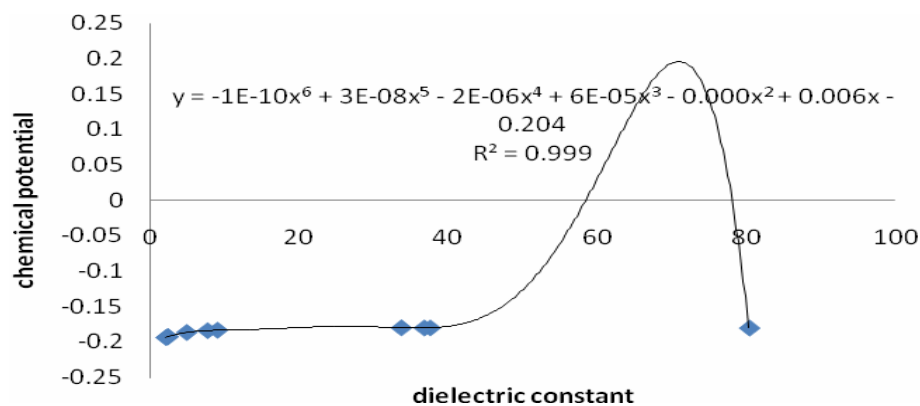


Figure 3a.Effect of dielectric contant on the hardness of picric acid in the GS

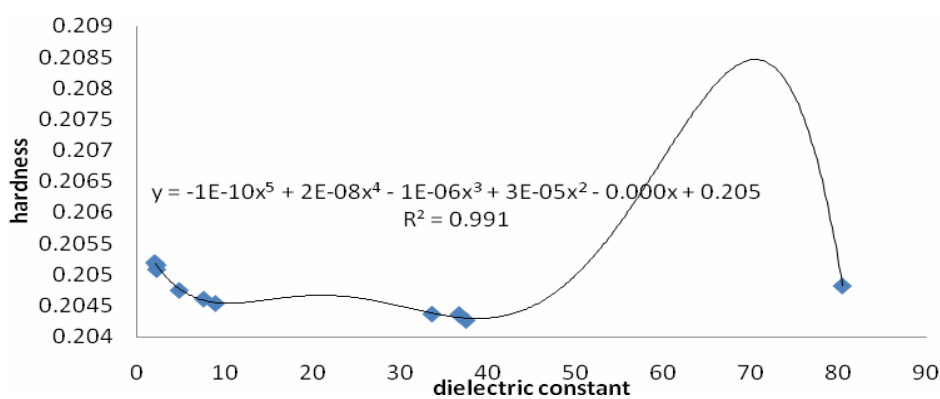


Figure 3b.Effect of dielectric contant on the hardness of picric acid in the ES

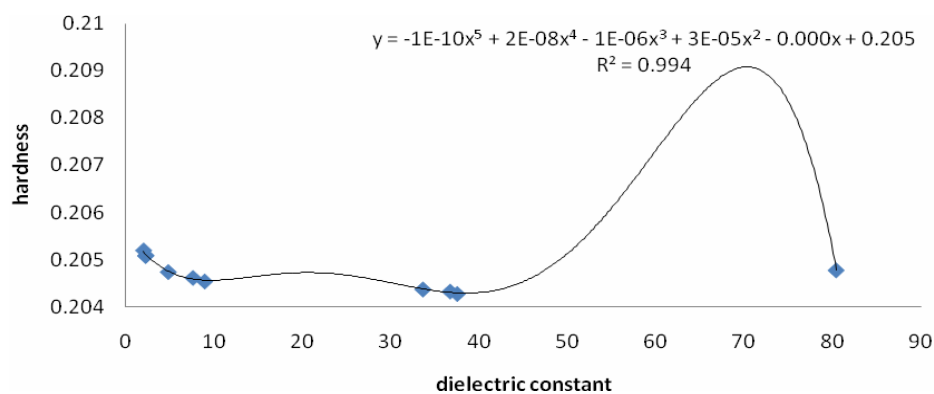


Figure 4a.Effect of dielectric contant on the electrophilicity of picric acid in the GS

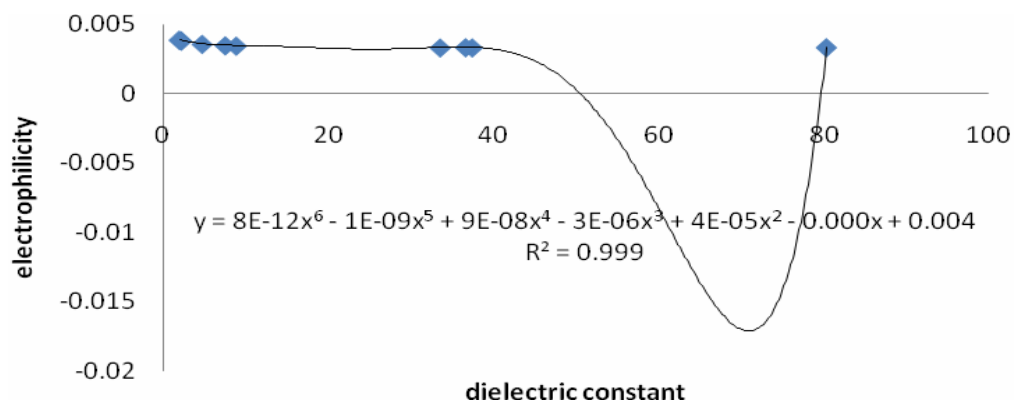


Figure 4b.Effect of dielectric contant on the electrophilicity of picric acid in the ES

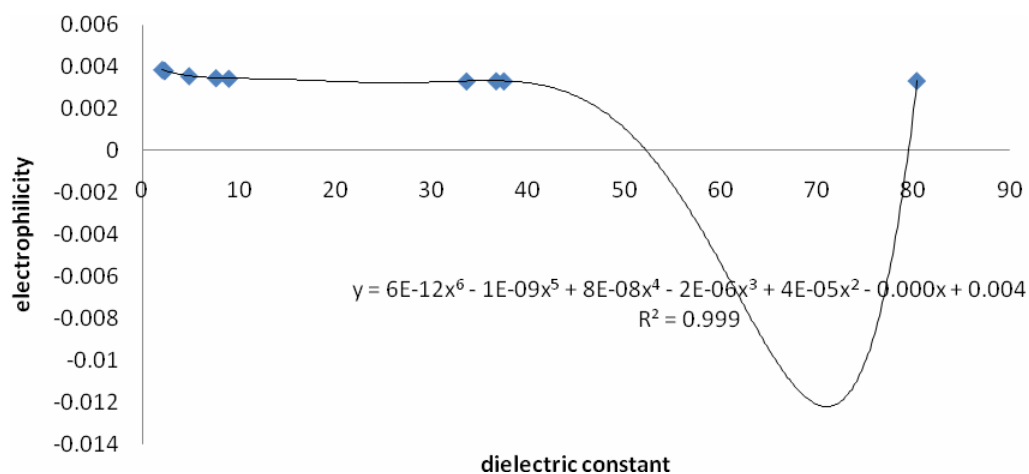


Figure 5a.Effect of dielectriccontant on the solvation energy of picric acid in the GS

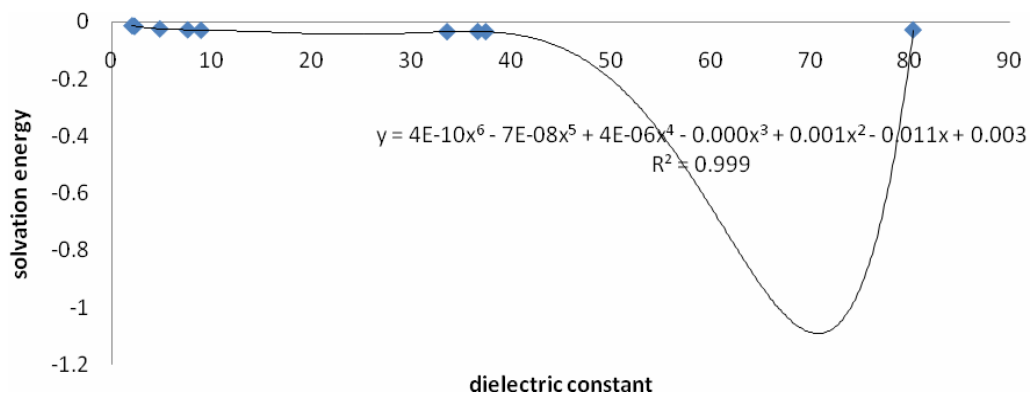


Figure 5b.Effect of dielectric contant on the solvation of picric acid in the ES

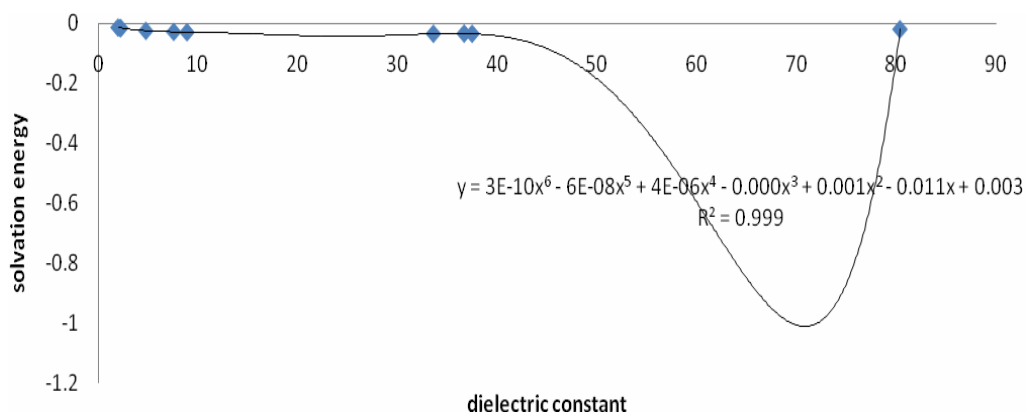


Figure 6a.Effect of dielectric contant on the reaction field of picric acid in the GS

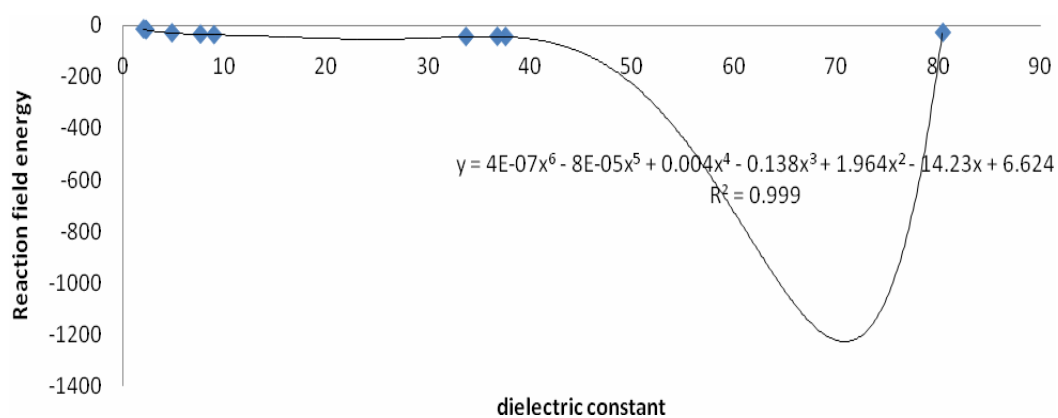


Figure 6b.Effect of dielectric contant on the reaction field of picric acid in the GS

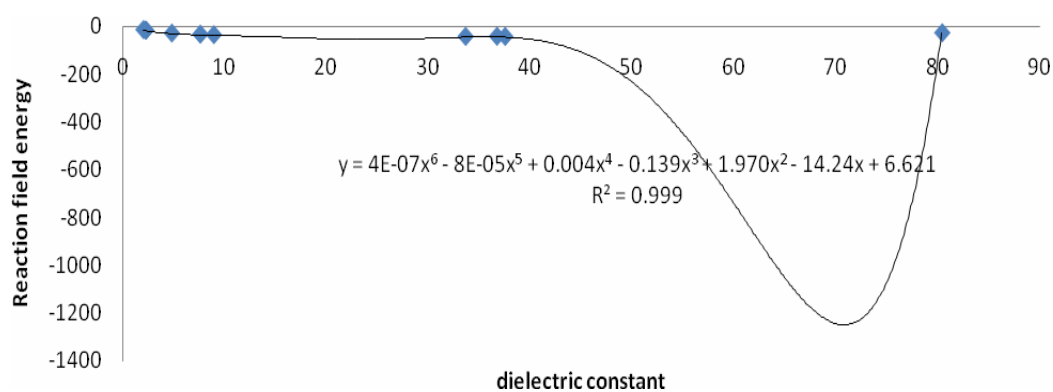


Figure7a. 3D plot of HOMO-LUMO-dielectric constant to study the effect on HOMO and LUMO of picric acid with the change in the dielectric constant of solvents in GS

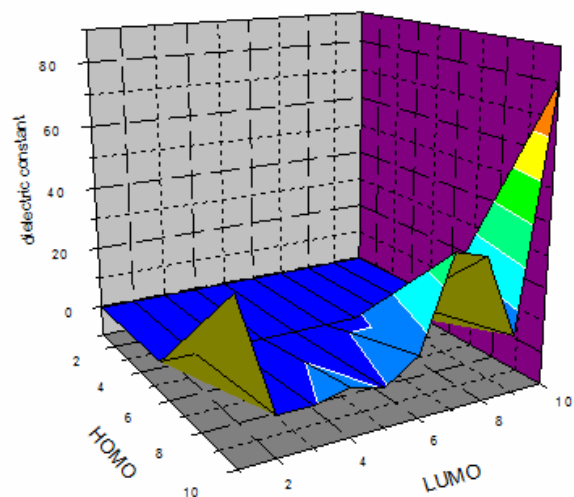


Figure7b. Figure 3D plot of HOMO-LUMO-dielectric constant to study the effect on HOMO and LUMO of picric acid with the change in the dielectric constant of solvents in ES

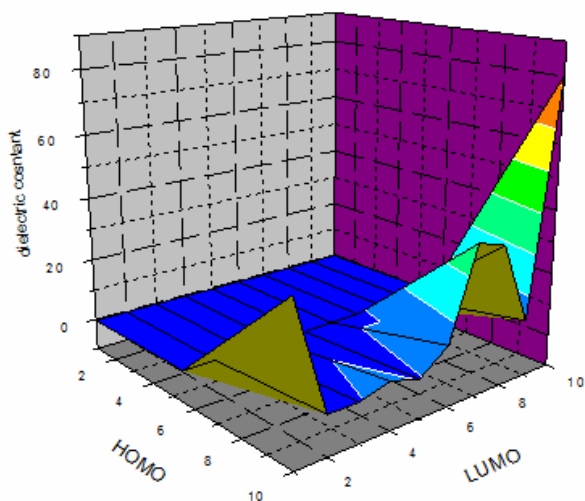


Figure 8. Picture of HOMO and LUMO in gaseous state, most stabilizing solvents and least stabilizing solvents in ground and excited state.

(cyclohexane* methanol** water***)

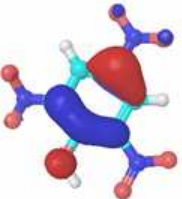
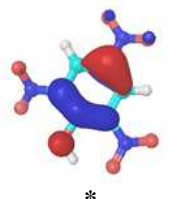
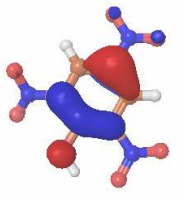
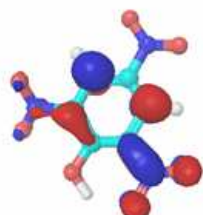
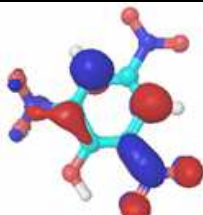
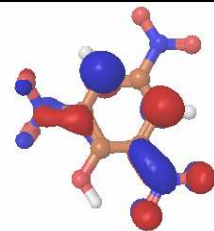

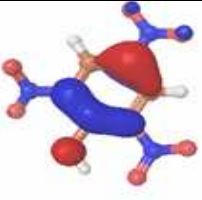
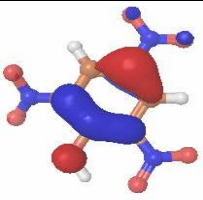
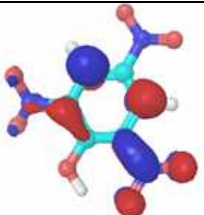
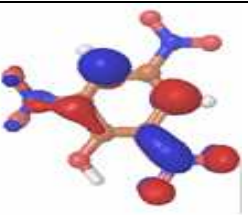
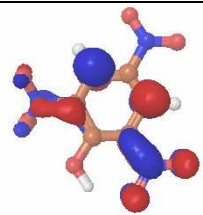
	Gaseous state	In most stabilizing solvent	In least stabilizing solvent
HOMO (GS)		 *	 **
LUMO (GS)		 *	 ***
HOMO(ES)		 *	 **
LUMO(ES)		 *	 ***

Table 5 :Thermochemical results of the constant volume heat capacity (C_v), internal energy (U), entropy (S), enthalpy (H) and Gibbs Free energy

	U	C_v	S	H	G	lnQ	Utotal (SCFE + ZPE + U) cal/mol	Htotal (Utot + pV) cal/mol	Gtotal (Htot - T*S) cal/mol
Gas-phase(GS)	7.37000	43.10000	108.82300	7.96200	-24.48300	41.32289	-1820.01388	-1820.01201	-1820.11476
Gas-phase(ES)	7.46000	43.18400	110.35700	8.05300	-24.85100	41.94288	-1819.98284	-1819.98096	-1820.08516
Acetonitrile(GS)	7.36400	43.08300	108.75100	7.95600	-24.46800	41.29738	-1820.01397	-1820.01210	-1820.11478
Acetonitrile(ES)	7.36300	43.08200	108.73600	7.95500	-24.46400	41.29120	-1820.01404	-1820.01216	-1820.11483
Benzene(GS)	7.45400	43.14800	110.27100	8.04600	-24.83100	41.91032	-1819.97490	-1819.97303	-1820.07714
Benzene(ES)	7.43600	43.11100	110.00200	8.02900	-24.76800	41.80403	-1819.97497	-1819.97309	-1820.07695
Carbontetrachloride(GS)	7.43800	43.11200	110.03400	8.03100	-24.77600	41.81742	-1819.97424	-1819.97236	-1820.07625
Carbontetrachloride(ES)	7.43800	43.11200	110.03400	8.03100	-24.77600	41.81742	-1819.97424	-1819.97236	-1820.07625
Chloroform(GS)	7.39500	43.08200	109.28800	7.98800	-24.59600	41.51382	-1819.99370	-1819.99183	-1820.09502
Chloroform(ES)	7.39600	43.08200	109.30100	7.98900	-24.59900	41.51896	-1819.99368	-1819.99181	-1820.09501
Cyclohexane(GS)	7.45800	43.13900	110.36600	8.05000	-24.85500	41.95106	-1819.97084	-1819.96896	-1820.07317
Cylohexane(ES)	7.45800	43.13800	110.36600	8.05000	-24.85500	41.95118	-1819.97086	-1819.96898	-1820.07318
Dichloromethane(GS)	7.38300	43.08900	109.05300	7.97500	-24.53900	41.41683	-1820.00362	-1820.00174	-1820.10471
Dichloromethane(ES)	7.38300	43.08900	109.05300	7.97500	-24.53900	41.41683	-1820.00362	-1820.00174	-1820.10471
DMF(GS)	7.37300	43.09600	108.87600	7.96500	-24.49600	41.34480	-1820.01263	-1820.01075	-1820.11355
DMF(ES)	7.36400	43.08700	108.73900	7.95700	-24.46300	41.28959	-1820.01275	-1820.01087	-1820.11354
Methanol(GS)	7.36400	43.09000	108.73100	7.95700	-24.46100	41.28612	-1820.01395	-1820.01208	-1820.11474
Methanol(ES)	7.36400	43.09000	108.73100	7.95700	-24.46100	41.28612	-1820.01395	-1820.01208	-1820.11474
THF(GS)	7.39000	43.10100	109.08100	7.97800	-24.54400	41.42542	-1820.00095	-1819.99908	-1820.10207
THF(ES)	7.38600	43.10100	109.08000	7.97800	-24.54400	41.42513	-1820.00100	-1819.99912	-1820.10211
Water(GS)	7.46100	43.18500	110.41800	8.05300	-24.86800	41.97242	-1819.98306	-1819.98118	-1820.08544
Water(ES)	7.45300	43.18000	110.24800	8.04500	-24.82500	41.90019	-1819.98303	-1819.98116	-1820.08525

Table 6: Thermochemical results of the constant volume heat capacity (C_v), internal energy (U) entropy (S), enthalpy (H) and Gibbs Free energy

	ΔU	ΔH	ΔG	ΔS
Gas-phase(ES-GS)	0.03105	0.03105	0.02960	1.53400
Acetonitrile (ES-GS)	-0.00007	-0.00007	-0.00005	-0.01500
Benzene (ES-GS)	-0.00007	-0.00006	0.00019	-0.26900
Carbontetrachloride(ES-GS)	0.00000	0.00000	0.00000	0.00000
Chloroform(ES-GS)	0.00002	0.00002	0.00001	0.01300
Cyclohexane(ES-GS)	-0.00002	-0.00002	-0.00002	0.00000
Dichloromethane(ES-GS)	0.00000	0.00000	0.00000	0.00000
DMF(ES-GS)	-0.00012	-0.00012	0.00001	-0.13700
Methanol(ES-GS)	0.00000	0.00000	0.00000	0.000000
THF(ES-GS)	-0.00004	-0.00004	-0.00004	-0.00100
Water(ES-GS)	0.00003	0.00003	0.00019	-0.17000

Conclusion:

The present study on solvation of picric acid by ten different solvents has lead us to conclude that the three categories of solvents one which stabilizes the ground state more than the excited state of picric acid, the other category has just opposite influences the third category has equal preferences for both ground and excited state. Out of the studied solvents chloroform belongs to first category; cyclohexane, benzene, water, THF, DMF belong to the second category and rest belongs to the third category.

The *hardness* of picric acid in ground and excited state is found to be highest in cyclohexane and lowest in acetonitrile. The electrophilicity of picric acid is found to be highest in cyclohexane and lowest in methanol while chemical potential is highest in methanol and lowest in cyclohexane.

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