

Theoretical approach to study the formation of $C_2H_4O_2$ isomers in interstellar medium through reaction between interstellar formaldehyde molecules ^{*}

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Abstract The three isomers of $C_2H_4O_2$, viz., glycolaldehyde ($HCOCH_2OH$), acetic acid (CH_3COOH) and methyl formate ($HCOOCH_3$), have been detected in copious amounts in the interstellar medium (ISM). The possibility for formation of these molecules through interstellar formaldehyde ($HCHO$) has been explored by using the quantum chemical approach described by density functional theory (DFT) and second order Moller-Plesset perturbation (MP2) theory with a 6–311G(d,p) basis set in the gas phase as well as in icy grains. The associated molecule-molecule interactions have been discussed to study the formation of isomers of $C_2H_4O_2$ in ISM. The reactions of two formaldehyde molecules exhibit a considerable potential barrier but due to quantum tunneling, these reactions could be possible in ISM. The chemical pathway is exothermic, which gives rise to a high probability for the formation of all three isomers, viz. glycolaldehyde, methyl formate and acetic acid, in interstellar space. Anharmonic rotational vibration, centrifugal distortion constants and coupling constants are also calculated and results suggest that the vibrations are harmonic in nature.

Key words: ISM: molecules — astrochemistry — astrobiology — abundances

1 INTRODUCTION

The isomers of $C_2H_4O_2$ i.e., glycolaldehyde ($HCOCH_2OH$), acetic acid (CH_3COOH) and methyl formate ($HCOOCH_3$), have significant astrobiological importance. These molecules can provide information about the potential of associated interstellar chemistry which is responsible for extraterrestrial life and the formation of life on new planets through organic prebiotic chemistry (Snyder 2006).

Glycolaldehyde plays an important role in study of the origin of life as it is one of the simplest monosaccharide sugars, since sugars participate in the formation of the sugar phosphate backbone of DNA and RNA. It has been identified around the Galactic center and dust cloud Sagittarius B2 (Sgr B2) (N), and has been confirmed by several subsequent detections (Hollis et al. 2000; Hollis et al. 2004; Halfen et al. 2006).

Acetic acid (CH_3COOH) is the second isomer of $C_2H_4O_2$, which also has significant astrobiological relevance because it plays a vital role in the formation of the

amino acid glycine (Sorrell 2001). Acetic acid was first observed in space in the hot molecular core Sgr B2 (N-LMH) (Mehring et al. 1997). It has also been detected in several other regions like high-mass star forming regions (Remijan et al. 2004) in the low-mass protostars and also hot molecular cores (Remijan et al. 2002, 2003) in IRAS 16293.2422 (Cazaux et al. 2003), and toward the proto-planetary nebula CRL 618 (Remijan et al. 2005). It has also been found within the Murchison meteorite, and suggested in comet Hale-Bopp (Huang et al. 2005; Despois et al. 2005). Recently, the column density of acetic acid was reported as 6.1×10^{15} molecules cm^{-2} (Remijan et al. 2002).

Methyl formate ($HCOOCH_3$) is the most abundant isomer of $C_2H_4O_2$ in hot cores. Methyl formate may be connected to acetic acid (CH_3COOH) and even to glycine (NH_2CH_2COOH), the simplest amino acid. Brown et al. (1975) suggested the first detection of interstellar methyl formate towards the star-forming region Sgr B2. After that, it was also detected in several hot cores (three hot corinos). The hot corinos were identified as due to the nearest surroundings of low-mass protostars in which proto-stellar radiation and shock waves heated the gas and dust

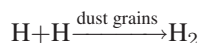
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(Torrente et al. 2007) and in comets (Despois et al. 2005; Remijan & Hollis 2006). It has also been observed in Orion A (Eller et al. 1980), G34.3+0.15 (MacDonald et al. 1996), G327.3_0.6 (Gibb et al. 2004) and the low-mass star-forming region IRAS 16293_2422 (Remijan & Hollis 2006) and also toward the proto-planetary nebula CRL 618 (Remijan et al. 2005). All these detections suggest that methyl formate may be widely distributed in the Galaxy. The column density of methyl formate is 1.1×10^{17} molecules cm⁻² in Sgr B2 at 25 K (Turner 1991).

Several theoretical models have already been proposed for the formation of glycolaldehyde, acetic acid and methyl formate from various interstellar molecules (Sorrell 2001). Experimental analysis has been proposed for the formation of interstellar methyl formate after cosmic ion irradiation on icy grains containing CO and CH₃OH (Modica & Palumbo 2010). Bennett & Kaiser (2007) suggested the formation of glycolaldehyde, methyl formate and acetic acid in the interstellar medium (ISM) through a binary mixture of CH₃OH and CO at 10 K in the presence of cosmic ray particles. Hollis et al. (2000) also hinted at the formation of glycolaldehyde through the formose reaction catalyzed by base, clay or radiation.

In the present manuscript, bond formation via dust grain catalyzed reaction (neutral and ionic) is discussed. Dust grain chemistry is hard to analyze. However, the mechanisms available for dust grains to catalyze reactions in space must be similar to those involved in surface catalysis on Earth. A reaction of vital importance in the ISM which is known to occur almost exclusively on the surface of dust grains is the formation of H₂ from the absorbance of two H atoms to the surface.



Organic synthesis is also thought to occur on the surface of dust grains.

So, it can be concluded that reactions that occur in the gas phase can be catalyzed by dust particles or dust grains. Reactions in the gas phase efficiently occur on the surfaces of dust grains. Hence, the associated reaction of two formaldehyde molecules can take place efficiently due to the presence of dust grains.

2 COMPUTATIONAL DETAILS

To gain insight into the mechanistic pathway of C₂H₄O₂ isomers, the electronic structures of these molecules, reaction complex (RC), transition state (TS) and final products involved in the proposed reaction paths were optimized at the B3LYP/6–311G(d,p) (Scott & Radom 1996) and MP2/6–311G(d,p) (Cramer 2013; Glaser et al. 2007)

level in the gas phase. Optimizations were carried out thorough frequency calculations at the same level of theory to investigate the nature of the stationary point as minima (no negative frequency) or TS structure (only one imaginary frequency with the normal mode of vibration). The same set of frequency calculations has been also used to compute the zero point vibrational energy (ZPVE) corrections. Calculations for intrinsic reaction coordinates (Fukui 1981, Dykstra et al. 2005) have been performed to check if TS connects reactants and product. Since organic synthesis also occurs on the surface of dust grains, the Polarizable Continuum Model (PCM) (Miertuš et al. 1981) has been applied to simulate the effect of these icy dust grains (of water) on the reaction energetics. All the calculations were performed using Gaussian09 software (Frisch et al. 2009). The employed chemical model, viz. DFT-B3LYP/MP2/DFT-D-B3LYP, in conjugation with the 6–311G(d,p) basis set succeeded in reproducing experimental data with high reliability so that it is widely employed in computational chemistry (Cramer 2013; Glaser et al. 2007). Dispersion-corrected density functional theory (DFT-D) can validate the data. Moller-Plesset perturbation (MP2) optimized to describe dispersion interactions cannot be used to describe the quantum part. The conventional density functional theory (DFT) approaches poorly simulate weak dispersion interactions. DFT-D methods are specially optimized to describe dispersion interactions and enable us to successfully simulate Van der Waals systems containing inert gas atoms (Ar) and aromatic systems (Andriichenko & Ermilov 2013). The anharmonic constants, rotational constant, and Nielsen's and Wilson's constants (Kivelson & Bright Wilson 1952) are calculated for analyzing the deformation in the geometry of molecules from their equilibrium geometry. These constants are also utilized to check the nature of vibrational spectra and to test the stability of isomers of C₂H₄O₂. With the help of Koopmans' theorem (Parr & Yang 1989) the global softness, hardness and global electrophilicity index are determined using the energy of frontier molecular orbitals E_{HOMO} and E_{LUMO}.

The rate constants for proposed reactions have been calculated by the temperature independent semi-empirical formula given by Bates (1983) (Eq. (1)). If the rate coefficients calculated by Equation (1) exceed the limit then the value calculated by the "Langevin equation" (Eq. (2)), the Langevin limit, should be adopted, which is also temperature independent (Herbst 2001).

$$K = 1 \times 10^{-21} A_r (6E_0 + N - 2)^{3N-7} / (3N - 7)! \text{ cm}^3 \text{ s}^{-1}. \quad (1)$$

Here E₀ is the association energy in eV, N is the number of nuclei in the complex and A_r is the transition probability in s⁻¹, which is taken as 100 as suggested by Bates (1983).

$$K = 7.41 \times 10^{-10} \alpha^{1/2} (10/\mu)^{1/2} \text{ cm}^3 \text{ s}^{-1}, \quad (2)$$

where α is the polarizability in Å³ and μ is the reduced mass of the reaction expressed in 12C amu.

In the present work, the molecules are considered to have an evenly distributed charge, therefore an isotropic polarizability (α) is applied. In the present work, quantum chemical techniques were employed to explore the formation of isomers of C₂H₄O₂ in ISM. The efficiency of the proposed reaction pathway has been estimated by rate constant calculations and energetic considerations.

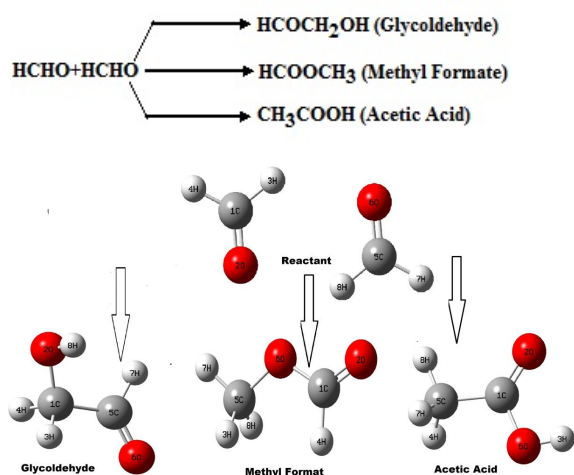
3 RESULTS AND DISCUSSION

Unimolecular and bimolecular reactions are involved in the formation of various interstellar molecules. A wide variety of reaction mechanisms operate within the ISM. These can be categorized into bond formation, bond breaking and rearrangement reactions. In the present work, the formation of isomers of C₂H₄O₂ has been studied in the gas phase and in the icy grains.

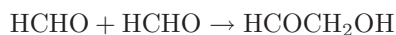
In the proposed reaction path, the formation of isomers of C₂H₄O₂ has been discussed through the reaction of two formaldehyde molecules in the ISM. The single step reaction path has been considered for the formation of glycolaldehyde, methyl formate and acetic acid by the molecules of interstellar formaldehyde. Total energy (TE), ZPVE and electronic energy (EE) of glycolaldehyde, methyl formate and acetic acid were calculated and are expressed in Tables 1, 2 and 3. The energy curves of all reaction paths are displayed in Figures 3, 6 and 9.

The different orientations of RCs yield the required products, illustrated as follows.

Reaction Path



3.1 Glycolaldehyde Formation from Interstellar Formaldehyde Molecules



The proposed reaction for the formation of glycolaldehyde with two molecules of interstellar formaldehyde is a single step reaction. To obtain glycolaldehyde, the molecules of formaldehyde (HCHO) are arranged as shown in Figure 1. Initially, the RC is obtained at the bond length 3.57 Å between atoms 1C and 5C, and the associated dihedral angle is almost zero degrees.

The required product (glycolaldehyde) has been formed via TS located at 72.16 Kcal mol^{−1} with respect to RC in the gas phase. In TS the hydrogen atom 8H (partial charge 0.241 e.s.u.) gets attached to the oxygen atom 2O (0.387 e.s.u.) of the formaldehyde molecule and is optimized at a bond length of 2.72 Å between atoms 1C and 5C, having bond angles 102.85° (1C-2O-8H) and 116.76° (6O-5C-7H) with one imaginary frequency at −479.59 cm^{−1}. Finally, the glycolaldehyde forms with a bond length of 1.522 Å (1C-5C) and bond angles of 108.37° (1C-2O-8H) and 122.33° (6O-5C-7H). The EE, ZPVE and TE of reactant, RC, TS and product at B3LYP/6–311G(d,p) in gas phase and PCM are provided in Table 1. The DFT calculations indicate that the reaction energy of the proposed reaction is −11.78 Kcal mol^{−1} and −5.54 Kcal mol^{−1} in the gas phase and PCM respectively. This reaction path involves the potential barrier of 72.16 Kcal mol^{−1} in the gas phase and 72.22 Kcal mol^{−1} in PCM. The increase of potential barrier in PCM signifies the lesser reactivity of formaldehyde in a polar solvent medium or in icy grains for the glycolaldehyde formation. The optimized geometries of the reactants, RC, TS and product involved in the reaction are schematically shown in Figure 2.

The formation of glycolaldehyde has also been studied with MP2/6–311G(d,p) theory. The RC has been optimized with 1C-5C at a distance of 3.573 Å. The TS has been optimized with single imaginary frequency of −822.47 cm^{−1}. Atoms 1C-5C become attached at a distance of 2.729 Å but the 8H atom detaches from the atom 5C and attaches to the atom 2O, in TS, having bond length for 1C-5C of 1.522 Å and bond angle for 2O-1C-5C of 112.573°. The glycolaldehyde has been formed after crossing the activation barrier of 94.25 Kcal mol^{−1} and 90.36 Kcal mol^{−1} at MP2/6–311G(d,p) in the gas phase and PCM respectively. The reaction energy of glycolaldehyde formation is obtained as −13.14 Kcal mol^{−1} and −16.97 Kcal mol^{−1} in the gas phase and PCM respectively in MP2/6–311G(d,p) theory (see Table 1). The higher values of rate coefficient in icy grains than in the gas phase signify the higher feasi-

Table 1 EE, ZPVE and TE of molecules, using B3LYP/6–311G(d,p) and MP2/6–311G(d,p) in gas phase and PCM. Energies are in a.u.

B3LYP/6–311G(d,p)						
Gas phase				PCM		
Molecule	EE	ZPVE	TE	EE	ZPVE	TE
HCHO	–114.5364	0.0265	–114.5099	–114.5410	0.0266	–114.5144
HCHO+HCHO	–229.0728	0.0530	–229.0198	–229.0820	0.0532	–229.0288
RC	–229.0796	0.0551	–229.0245	–229.0856	0.0550	–229.0307
TS	–228.9643	0.0548	–228.9095	–228.9699	0.0543	–228.9156
Glycolaldehyde	–229.1048	0.0606	–229.0442	–229.1134	0.0605	–229.0530

MP2/6–311G(d,p)						
Gas phase				PCM		
Molecule	EE	ZPVE	TE	EE	ZPVE	TE
HCHO	–114.2350	0.0270	–114.2080	–114.2390	0.0271	–114.2117
HCHO+HCHO	–228.4700	0.0540	–228.4160	–228.4780	0.0542	–228.4234
RC	–228.4772	0.0560	–228.4212	–228.4821	0.0561	–228.4260
TS	–228.3311	0.0541	–228.2770	–228.3365	0.0545	–228.2820
Glycolaldehyde	–228.5041	0.0617	–228.4424	–228.5116	0.0615	–228.4501

DFT-D/B3LYP/6–311G(d,p)						
Gas phase				PCM		
Molecule	EE	ZPVE	TE	EE	ZPVE	TE
HCHO	–114.5369	0.0264	–114.5105	–114.5415	0.0265	–114.5150
HCHO+HCHO	–229.0738	0.0528	–229.0210	–229.0830	0.0530	–229.0300
RC	–229.0834	0.0553	–229.0282	–229.0896	0.0554	–229.0342
TS	–229.9835	0.0558	–228.9278	–229.0352	0.0509	–228.9843
Glycolaldehyde	–229.1086	0.0604	–229.0482	–229.1173	0.0603	–229.0570

Table 2 EE, ZPVE and TE of molecules, using B3LYP/6–311G(d,p) and MP2/6–311G(d,p) in gas phase and PCM. Energies are in a.u.

B3LYP/6–311G(d,p)						
Gas phase				PCM		
Molecule	EE	ZPVE	TE	EE	ZPVE	TE
HCHO	–114.5364	0.0265	–114.5099	–114.5410	0.0266	–114.5144
HCHO+HCHO	–229.0728	0.0530	–229.0198	–229.0820	0.0532	–229.0288
RC	–229.0796	0.0551	–229.0250	–229.0856	0.0550	–229.0306
TS	–229.0061	0.0550	–228.9511	–229.0153	0.0549	–228.9604
Methyl formate	–229.1225	0.0609	–229.0616	–229.1315	0.0610	–229.0705

MP2/6–311G(d,p)						
Gas phase				PCM		
Molecule	EE	ZPVE	TE	EE	ZPVE	TE
HCHO	–114.2350	0.0270	–114.2080	–114.2390	0.0271	–114.2117
HCHO+HCHO	–228.4700	0.0540	–228.4160	–228.4780	0.0542	–228.4234
RC	–228.5190	0.0020	–228.4212	–228.4821	0.0564	–228.4256
TS	–228.3972	0.0559	–228.3413	–228.4047	0.0559	–228.3488
Methyl Formate	–228.5187	0.0619	–228.4568	–228.5116	0.0615	–228.4607

DFT-D/B3LYP/6–311G(d,p)						
Gas phase				PCM		
Molecule	EE	ZPVE	TE	EE	ZPVE	TE
HCHO	–114.5369	0.0264	–114.5105	–114.5415	0.0265	–114.5150
HCHO+HCHO	–229.0738	0.0528	–229.0210	–229.0830	0.0530	–229.0300
RC	–229.0791	0.0539	–229.0252	–229.0896	0.0554	–229.0342
TS	–229.0680	0.0450	–229.0230	–229.0680	0.0449	–229.0230
Methyl Formate	–229.1264	0.0609	–229.0656	–229.1356	0.0610	–229.0746

bility of formation of glycolaldehyde at the surface of icy grains in comparison to dust grains. The reaction energy calculated with MP2 theory is less than that calculated with DFT, hence demonstrating the high feasibility of glycolaldehyde formation under MP2 calculations. The energy curve of glycolaldehyde formation at B3LYP/6–311G(d,p)

and MP2/6–311G(d,p) is displayed in Figure 3 in both the gas phase and PCM.

The global and local reactivity descriptors of glycolaldehyde are calculated at B3LYP/6–311G(d,p) and displayed in Table 4. The global and local descriptors are very helpful and reliable tools for analyzing reaction mechanisms, and behavior of reactants and products in any or-

Table 3 EE, ZPVE and TE of molecules, using B3LYP/6–311G(d,p) and MP2/6–311G(d,p) in gas phase and PCM. Energies are in a.u.

B3LYP/6–311G(d,p)						
Gas phase				PCM		
Molecule	EE	ZPVE	TE	EE	ZPVE	TE
HCHO	–114.5364	0.0265	–114.5099	–114.5410	0.0266	–114.5144
HCHO+HCHO	–229.0728	0.0530	–229.0198	–229.0820	0.0532	–229.0288
RC	–229.07956	0.05552	–229.02404	–229.08561	0.05552	–229.03029
TS	–229.00610	0.05496	–228.95114	–229.01532	0.05489	–228.96043
Acetic Acid	–229.15643	0.06166	–229.09477	–229.16314	0.06139	–229.10175

MP2/6–311G(d,p)						
Gas phase				PCM		
Molecule	EE	ZPVE	TE	EE	ZPVE	TE
HCHO	–114.2350	0.0270	–114.2080	–114.2390	0.0271	–114.2117
HCHO+HCHO	–228.4700	0.0540	–228.4160	–228.4780	0.0542	–228.4234
RC	–228.47729	0.05638	–228.42089	–228.48233	0.05655	–228.42578
TS	–228.39715	0.05598	–228.34117	–228.40464	0.05594	–228.34487
Acetic Acid	–228.55667	0.06254	–228.49481	–228.56270	0.06300	–228.50040

DFT-D/B3LYP/6–311G(d,p)						
Gas phase				PCM		
Molecule	EE	ZPVE	TE	EE	ZPVE	TE
HCHO	–114.5369	0.0264	–114.5105	–114.5415	0.0265	–114.5150
HCHO+HCHO	–229.0738	0.0528	–229.0210	–229.0830	0.0530	–229.0300
RC	–229.0839	0.0556	–229.0283	–229.0896	0.0554	–229.0342
TS	–229.0298	0.0508	–228.9790	–229.0840	0.0539	–229.0301
Acetic Acid	–229.1598	0.0614	–229.0983	–229.1625	0.0611	–229.1014

ganic reaction. In this regard, global electronegativity (χ), chemical potential (μ), global hardness (η), global softness (S) and electrophilicity index (ω) are highly successful in predicting the feasibility and polarity in the reaction. With the help of Koopmans' theorem (Parr & Yang 1989), the global softness and global electrophilicity index are determined using the energy of frontier molecular orbitals E_{HOMO} and E_{LUMO} (Parr & Pearson 1983; Parr et al. 1999; Chattaraj & Giri 2007). To explore the local reactivity, chemical reactivity and site selectivity associated with the addition of two HCHO, the Fukui function and local electrophilicity/nucleophilicity have been used. By these calculations, it is observed that glycolaldehyde is formed with the soft-soft interaction of HCHO and HCHO. The 8H and 5C atoms of HCHO molecules contain higher electrophilicity than other hydrogen and carbon atoms. By global and local descriptors, the values of 2O and 8H atoms demonstrate that atom 2O would be the most favorable reaction site and atom 8H atom preferably attacks atom 2O and, as a further step, 1C and 5C (highly electropositive) get attached, to form glycolaldehyde. The reaction mechanism of this reaction path is depicted in Figure 4.

3.2 Methyl Formate Formation through Interstellar Formaldehyde Molecules



Methyl formate has been formed through two molecules of HCHO by the arrangement exhibited in

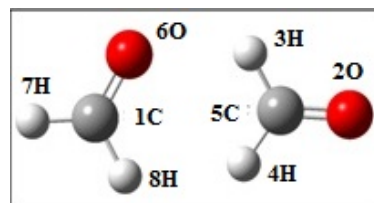
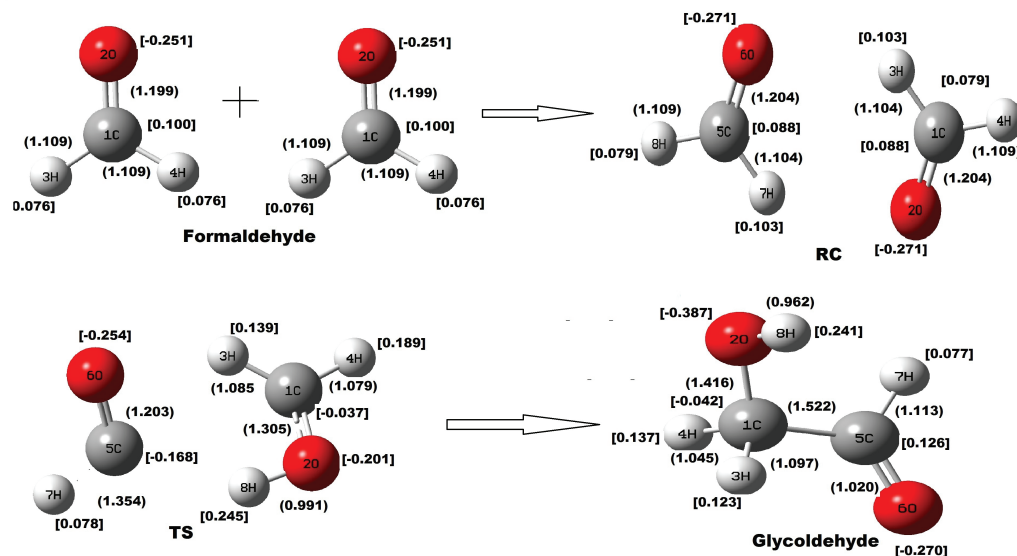


Fig. 1 Schematic arrangement of molecules (HCOOH) for the formation of glycolaldehyde (HCOCH₂OH). Red, gray and white spheres represent oxygen, carbon and hydrogen atoms, respectively. Each atom is also labeled with a sequential number and element symbol.

Figure 5. This reaction path involves the same reactants (formaldehyde) as those involved in the formation and are illustrated in Figure 5. Initially, both the reacting molecules have been optimized at a 1C–5C distance of 3.57 Å. They form the product via TS. In TS, one 3H atom detaches from the 1C atom and is optimized at the 3H–1C distance of 1.37 Å. The angles 5C–3H–1C and 4H–1C–2O are optimized at 96.07° and 137.97°, respectively, in TS. This has reaction energy of $-0.89 \text{ Kcal mol}^{-1}$ and $-5.42 \text{ Kcal mol}^{-1}$ in the gas phase and PCM, respectively. The required product of methyl formate has been formed by crossing the potential barrier of 45.11 and 44.05 Kcal mol^{-1} in the gas phase and in PCM respectively in B3LYP/6–311G(d,p) theory. The bond length (6O–1C) and bond angle (5C–6O–1C) are 1.35 Å and 116.54° respectively in the optimized product. All the optimized geometries of the reactants, RC, TS and products involved in the above reaction are schematically il-

Table 4 Calculated Global and Local Reactivity Descriptors for Glycolaldehyde (eV) Using the DFT Method

Molecule/Atom	Global descriptor			Local descriptor			
	Hardness (η)	Softness (S)	Global philicity (ω)	f_0^k	S_0^k	η_0^k	ω_0^k
HCHO	0.11175	4.26548	0.110654				
1C				0.2229	0.9508	0.0249	0.0247
2O				0.3514	1.4988	0.0393	0.0389
3H				0.2129	0.9081	0.0238	0.0235
4H				0.2129	0.9081	0.0238	0.0235
HCHO-HCHO(RC)	0.10515	4.75480	0.113551				
1C				0.1200	0.5706	0.0126	0.0136
2O				0.1649	0.7841	0.0173	0.0187
3H				0.0731	0.3475	0.0077	0.0083
4H				0.1421	0.6756	0.0149	0.0162
5C				0.2200	0.5706	0.0126	0.0136
6O				0.1649	0.7841	0.0173	0.0187
7H				0.0731	0.3475	0.0077	0.0083
8H				0.1421	0.6756	0.0149	0.0136
HCOCH ₂ OH(P)	0.10865	4.60193	0.10867				
1C				-0.0419	0.1928	0.0045	0.0045
2O				0.0954	0.4390	0.0104	0.0104
3H				0.0984	0.4528	0.0107	0.0106
4H				0.1204	0.5541	0.0131	0.0014
5C				0.1652	0.7602	0.0179	0.0179
6O				0.2549	1.1730	0.0276	0.0276
7H				0.1625	0.7478	0.0176	0.0176
8H				0.1452	0.6682	0.0158	0.0158

**Fig. 2** Geometries of reactants, TS and product in the formation of glycolaldehyde in B3LYP/6–311G(d,p) theory. The charge densities are shown in parentheses. Bond lengths are in Å and shown in parentheses. Charge densities are shown in square brackets.

illustrated in Figure 6. EE, ZPVE and TE of all the reactants, RC, TS and product in MP2 and DFT level of theory are given in Table 2. In MP2 also, the one molecule of HCHO reacts with the other molecule of HCHO and forms methyl formate with reaction energy $-3.34 \text{ Kcal mol}^{-1}$ and $-16.47 \text{ Kcal mol}^{-1}$ in the gas and PCM phase respectively. Also, the potential barrier in MP2 theory is $49.94 \text{ Kcal mol}^{-1}$ and $50.75 \text{ Kcal mol}^{-1}$ respectively. The rate coefficient in icy grains is higher than that in the gas

phase in both DFT and MP2 theory (Table 7). This indicates there is a higher probability of formation of methyl formate with the PCM model in comparison to the gas phase. The energy curves of methyl formate formation at B3LYP/6–311G(d,p) and MP2/6–311G(d,p), respectively, are drawn in Figure 7(a) and 7(b), in gas phase and PCM.

The energy values suggest that the final product of every reaction step has lower energy than the RC, and TS is formed after crossing the potential barrier. All the calcu-

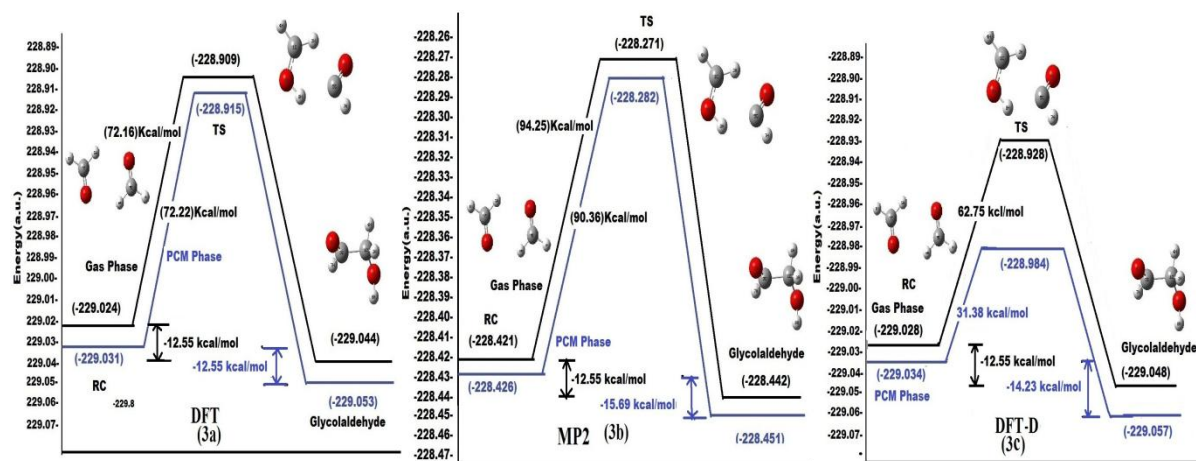


Fig. 3 Energy diagram showing the geometries of reactant, TSs and products involved in the reaction steps for glycolaldehyde formation in (a) B3LYP/6–311G(d,p) (DFT), (b) MP2/6–311G(d,p) and (c) B3LYP/6–311G(d,p) (DFT-D). The blue lines represent the reactions in solvent (PCM) and the black lines signify the gas phase reactions. The reaction energies are also listed.

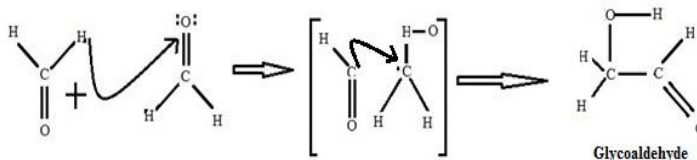


Fig. 4 The reaction mechanism of formation for glycolaldehyde. The first step of the mechanism is breaking of C=O by attack from a hydrogen atom and formation of free electrons on both carbon atoms. The next step is bond formation between carbon atoms (C-C) via radical-radical mechanism.

lations suggest the high feasibility of methyl formate formation in the ISM. The calculations for global and local reactivity descriptor are performed at B3LYP/6–311G(d,p) and expressed in Table 5. By these values, methyl formate has been formed through the soft-soft interaction of formaldehyde. The value of Fukui function (Table 5) signifies that the initial favorable reaction sites are 3H and 5C, and further the highest Fukui function containing atom 6O preferably reacts with atom 1C with high f_0^k values and also due to the electronegative and electropositive character of both atoms respectively. The reaction mechanism of formation for the methyl formate reaction path is displayed in Figure 8.

3.3 Acetic Acid Formation through Interstellar Formaldehyde Molecules



Acetic acid has been formed through two molecules of HCHO by the arrangement illustrated in Figure 9. It is a single step reaction with two formaldehyde molecules so that the required product can be formed. In the process of acetic acid formation, initially, both reactants

form the RC with C-C distance of 3.17 Å, then they react with each other and form the product via TS. In TS, atom 4H becomes detached from atom 5C and optimized at bond lengths of 1.374 Å and 1.392 Å for 4H-1C and 4H-5C respectively. The imaginary frequency of TS is found at -1183.77 cm^{-1} . The potential barrier of $41.62 \text{ Kcal mol}^{-1}$ has been observed at the B3LYP/6–311G(d,p) level of theory in this reaction. Further, in the final product in which atom 4H gets attached to 5C, 6O attaches to atoms 3H and 1C, and 5C attaches to 1C at a bond length of 1.506 Å. The reaction energy is $-19.84 \text{ Kcal mol}^{-1}$ and $-11.63 \text{ Kcal mol}^{-1}$ in the gas phase and PCM respectively. The EE, ZPVE and TE of all the reactants, product, RC and TSs are given in Table 3.

The formation of acetic acid is also studied with MP2 theory. The MP2 calculations give reaction energy $-49.32 \text{ Kcal mol}^{-1}$ and $-48.13 \text{ Kcal mol}^{-1}$ in the gas phase and PCM respectively. The EE, ZPVE and TE of all molecules, at MP2/6–311G(d,p), are provided in Table 3. The potential barrier in MP2 theory is $49.94 \text{ Kcal mol}^{-1}$ and $50.76 \text{ Kcal mol}^{-1}$ in the gas phase and PCM respectively. Hence, the height of the barrier in MP2 theory is higher than that in DFT theory. The rate coefficient in icy

Table 5 Calculated Global and Local Reactivity Descriptors for Methyl Formate (eV) Using DFT Method

Molecule/Atom	Global descriptor			Local descriptor			
	Hardness (η)	Softness (S)	Global philicity (ω)	f_0^k	S_0^k	η_0^k	ω_0^k
HCHO	0.11175	4.26548	0.110654				
1C				0.2229	0.9508	0.0249	0.0247
2O				0.3514	1.4988	0.0393	0.0389
3H				0.2129	0.9081	0.0238	0.0235
4H				0.2129	0.9081	0.0238	0.0235
HCHO-HCHO(RC)	0.10515	4.69461	0.113551				
1C				0.1200	0.5706	0.0126	0.0136
2O				0.1649	0.7841	0.0173	0.0187
3H				0.0731	0.3475	0.0077	0.0083
4H				0.1421	0.6756	0.0149	0.0162
5C				0.1200	0.5706	0.0126	0.0136
6O				0.2649	0.7841	0.0173	0.0187
7H				0.0731	0.3475	0.0077	0.0083
8H				0.1421	0.6756	0.0149	0.0136
HCOOCH ₃ (P)	0.13929	3.58963	0.07933				
1C				0.1835	0.65869	0.0555	0.0145
2O				0.2932	1.05248	0.04093	0.0232
3H				0.0673	0.24337	0.00944	0.0053
4H				0.1664	0.59731	0.02317	0.0132
5C				0.0975	0.34998	0.01358	0.0077
6O				0.0728	0.26132	0.01014	0.0057
7H				0.1100	0.39485	0.01532	0.0087
8H				0.2038	0.73156	0.02838	0.0161

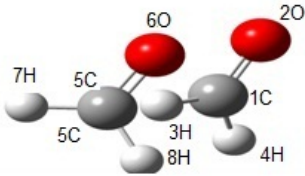


Fig. 5 Schematic representation of molecules (HCOOH) involved in the formation of methyl formate (HCOOCH₃). Red, gray and white spheres represent oxygen, carbon and hydrogen atoms, respectively. Each atom is also labeled with a sequential number and element symbol.

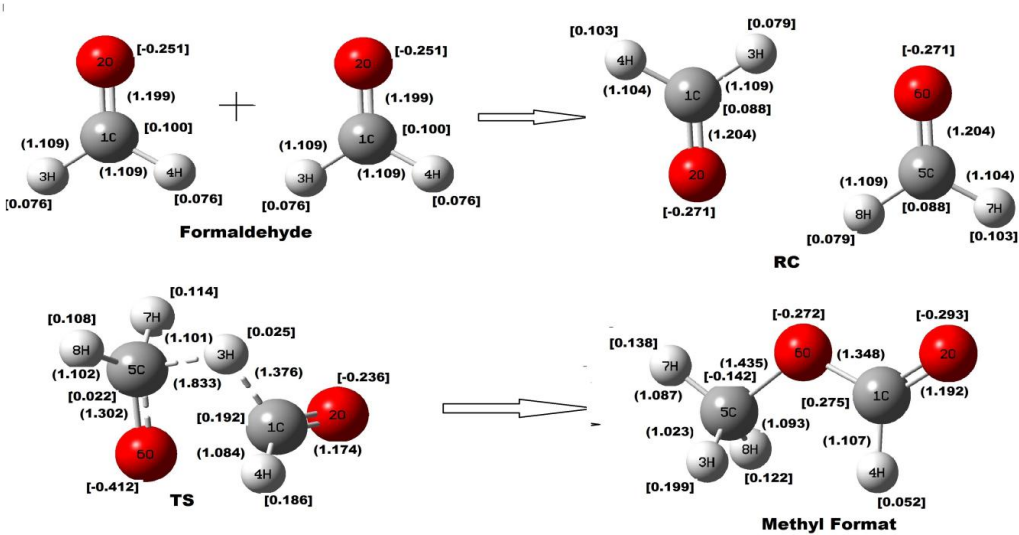


Fig. 6 Geometries of reactants, TS and product in the formation of methyl formate in B3LYP/6–311G(d,p) theory. The charge densities are written in parentheses. Bond lengths are in Å and expressed in *parentheses*. Charge densities are provided in *square brackets*.

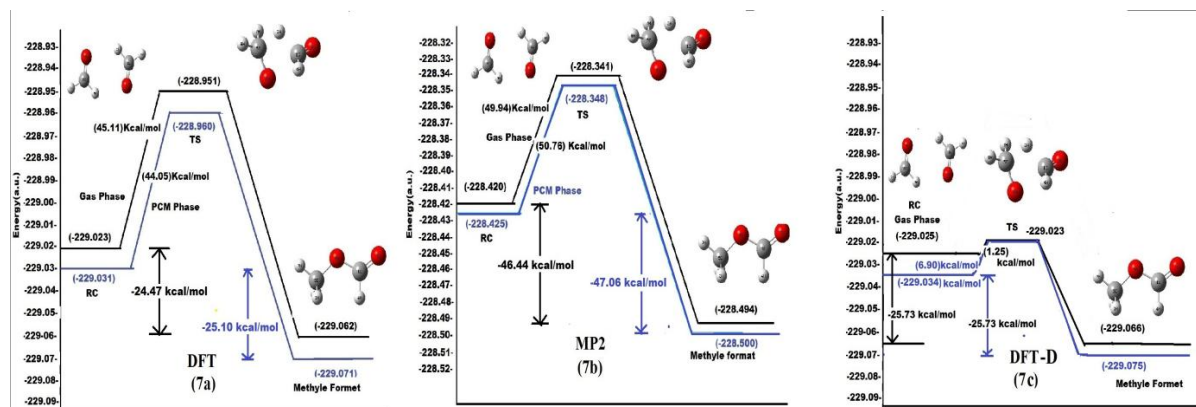


Fig. 7 Energy diagram showing the geometries of reactant, TSs and products involved in the reaction steps of methyl formate formation at (a) B3LYP/6–311G(d,p) (DFT), (b) MP2/6–311G(d,p) and (c) B3LYP/6–311G(d,p) (DFT-D). The reaction energies are also provided in the figure.

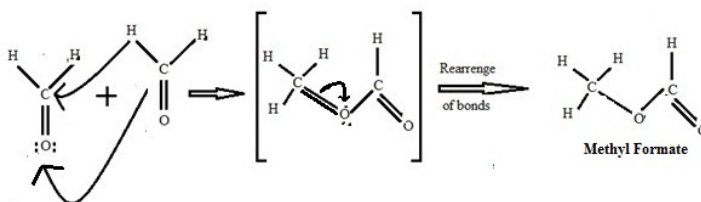


Fig. 8 The reaction mechanism of formation for methyl formate. In this mechanism, carbon and hydrogen atoms of one formaldehyde molecule attack oxygen and carbon atoms of the other formaldehyde molecule due to the presence of a lone pair of electrons on an oxygen atom. Then through the rearrangement of bonds, methyl formate has been formed.

grains is higher than that in gas phase for both DFT and MP2 theory, which indicates the higher probability of formation for acetic acid with PCM in comparison to the gas phase.

Acetic acid formation at DFT level theory yields more favorable results in comparison to the one obtained at the MP2 level. The calculated reaction energy in B3LYP theory is less than that calculated with MP2 and hence points to the high feasibility of acetic acid formation under B3LYP calculations. The optimized geometries of the reactants, products and TSs involved in the reaction are displayed in Figure 10. The energy curves of acetic acid formation at B3LYP/6–311G(d,p) and MP2/6–311G(d,p) level are shown in Figure 11(a) and 11(b) in gas phase.

The global and local reactivity descriptors are calculated at B3LYP/6–311G(d,p) and expressed in Table 6. 6O and 3H are the most favorable reaction sites due to the higher value of Fukui function (f_0^k). Further, 5C will be reacting with 1C due to the presence of an OH group with atom 1C. The reaction mechanism for formation of the acetic acid reaction path is given in Figure 12.

The rate constants calculated by the Langevin and Arrhenius Equations are listed in Table 7.

All the three reaction mechanisms associated with the formation of glycolaldehyde, methyl formate and acetic

acid have also been studied through DFT-D theory with B3LYP/6–311G(d,p) functional. The values of energies obtained through DFT-D theory show higher stability and less energy in comparison to DFT and MP2 theories.

4 ANHARMONIC SPECTROSCOPIC CONSTANTS

A_0 , B_0 and C_0 represent the ground state vibrational constants including zero-point vibrations and distortions. In the equilibrium geometry, the rotational constants of the molecule are calculated at B3LYP/6–311G(d,p) levels. Molecules having anharmonic vibrations represent more or less deformation from their equilibrium configuration. Some distortion in the molecules is generated because of centrifugal force and these quartic centrifugal distortions are computed by Kivelson-Wilson formalism (Kivelson & Bright Wilson 1952). These distortions are calculated and listed in Table 8.

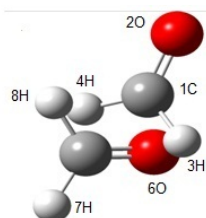
The rotational constants (Table 8(a)) of glycolaldehyde are very low, therefore glycolaldehyde is much less deformed from its equilibrium position in comparison to methyl formate and acetic acid. The rotational-vibrational coupling constants (α) are generated by applying B3LYP theory with the 6–311G(d,p) basis set and shown in Table 9.

Table 6 Calculated Global and Local Reactivity Descriptors for Acetic Acid (eV) Using DFT Method

Molecule/Atom	Global descriptor			Local descriptor			
	Hardness (η)	Softness (S)	Global philicity (ω)	f_0^k	S_0^k	η_0^k	ω_0^k
HCHO	0.11175	4.26548	0.110654				
1C				0.2229	0.9508	0.0249	0.0247
2O				0.3514	1.4988	0.0393	0.0389
3H				0.2129	0.9081	0.0238	0.0235
4H				0.2129	0.9081	0.0238	0.0235
HCHO-HCHO(RC)	0.10275	4.8659	0.0.123054				
1C				0.0546	0.0546	0.0056	0.0067
2O				0.1832	0.8914	0.0188	0.0225
3H				0.2246	0.6063	0.0128	0.0153
4H				0.1261	0.6136	0.0129	0.0155
5C				0.1361	0.6622	0.0139	0.0167
6O				0.1478	0.7192	0.0152	0.0182
7H				0.1391	0.6768	0.0142	0.0171
8H				0.0885	0.4310	0.0091	0.0108
CH ₃ COOH	0.14068	3.55403	0.073078				
1C				0.1377	0.4893	0.01937	0.01006
2O				0.3038	1.0797	0.04274	0.02221
3H				0.0815	0.2896	0.01146	0.00595
4H				0.1374	0.4883	0.01933	0.01004
5C				0.0004	0.0014	0.00005	0.00002
6O				0.1219	0.4332	0.01714	0.00890
7H				0.1378	0.4897	0.01938	0.01007
8H				0.0795	0.2825	0.01118	0.00580

Table 7 Rate Coefficients of All Involved Reactions of Formation in Isomers of C₂H₄O₂

Molecules	By Langevin Equation		By Arrhenius Equation	
	Gas phase	PCM	Gas Phase	PCM
Glycolaldehyde	3.238410 ^{−9}	3.530210 ^{−9}	2.0338210 ^{−10}	1.8584210 ^{−10}
Methyl Formate	3.234710 ^{−9}	3.524210 ^{−9}	3.9615610 ^{−13}	1.3244710 ^{−13}
Acetic Acid	3.218310 ^{−9}	3.513510 ^{−9}	3.8957110 ^{−13}	1.3244110 ^{−13}

**Fig. 9** Schematic arrangement of molecules (HCOOH) for the formation of acetic acid (CH₃COOH). Red, gray and white spheres represent oxygen, carbon and hydrogen atoms, respectively. Each atom is also labeled with a sequential number and element symbol.

The small magnitudes of the rotation-vibration coupling constants and Wilson's and Nielsen's centrifugal distortion constants indicates that the molecular vibrations of isomers of C₂H₄O₂ are almost harmonic in nature.

5 LOCAL AND GLOBAL ELECTRONIC DESCRIPTORS

DFT has been rising as a significant and computationally economical quantum chemical tool for studying different chemical problems. Applying DFT is useful to define and justify concepts of chemical reactivity. DFT based global and local reactivity descriptors and condensed Fukui function ($f_k(r)$, $s_k(r)$, $\omega_k(r)$) have now been widely utilized

for rationalization and explanation of diverse aspects of chemical binding, reaction mechanisms and reactive centers. In this work, an attempt has been made to explore the uses of DFT descriptors to investigate the reaction sites of two reactants. A rigorous theoretical basis for the descriptors of global and local reactivity indices has been provided by the conceptual DFT. Nowadays, these indices have been extensively employed for interpreting diverse aspects of chemical binding and reaction mechanism. The quantitative definition of global reactivity descriptors such as electronegativity χ , chemical potential μ , global hardness η , global softness (S) and global electrophilicity index ω for a system of N electrons associated with EE, within the field

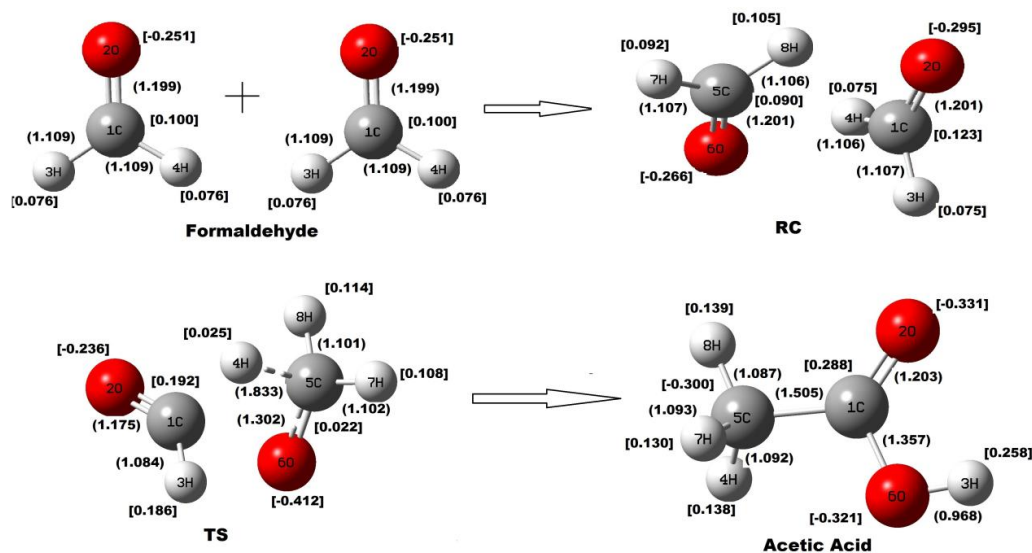


Fig. 10 Geometries of reactants, TSs and product in the formation of acetic acid in B3LYP/6–311G(d,p) theory. Charge densities are in square bracket and bond lengths are in parentheses.

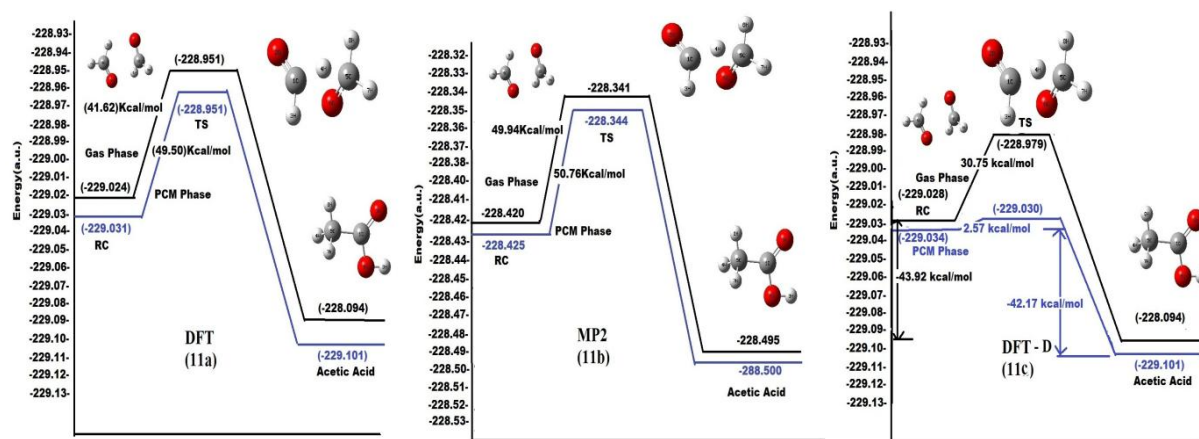


Fig. 11 Energy diagram depicting the geometries of reactants, TSs and products involved in the reaction steps associated with the formation of acetic acid in (a) B3LYP/6–311G(d,p) (DFT) and (b) MP2/6–311G(d,p) and B3LYP/6–311G(d,p) (DFT-D). The reaction energies are also expressed in the figure.

of one more fixed nuclei which generate an external potential $V(r)$ are defined by equations: $\chi = -(\partial E/\partial N)_{(V(r))}$

$$\mu = (\partial E/\partial N)_{(V(r))}$$

$$\eta = 1/2((\partial^2 E/\partial N^2))_{(V(r))} = 1/2(\partial \mu/\partial N)_{(V(r))}$$

$$S = (\partial N/\partial \mu)_{(V(r))}$$

The electrophilicity index (ω) is given by an equation $\omega = \mu^2/2\eta$, where $\mu = -1/2(IP + EA)$ and $\eta = 1/2(IP - EA)$ are the electronic chemical potential and chemical hardness, respectively, in terms of the vertical ionization potential (IP) and electron affinity (EA). On the basis of Koopman's theorem (Parr & Yang 1989), in the finite difference approximation the IP and EA can be replaced by the HOMO and LUMO energies, respectively, i.e., $IP \approx -E_{HOMO}$, and $EA \approx -E_{LUMO}$. The global reactivity

descriptors such as electronegativity (χ), chemical potential (μ), global hardness (η), global softness (S) and global electrophilicity index (ω) are calculated using the energies of frontier molecular orbitals E_{HOMO} , E_{LUMO} and given by equations (Parr & Yang 1989; Padmanabhan et al. 2006; Parr & Pearson 1983; Parr et al. 1999; Chattaraj & Giri 2007; Padmanabhan et al. 2007).

$$\chi = -1/2(E_{HOMO} + E_{LUMO})$$

$$\mu = -\chi = 1/2(E_{LUMO} + E_{HOMO})$$

$$\eta = 1/2(E_{LUMO} - E_{HOMO})$$

$$S = 1/2\eta$$

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

The energies of frontier molecular orbitals (E_{HOMO} , E_{LUMO}), energy gap ($E_{LUMO} - E_{HOMO}$), electronegativ-

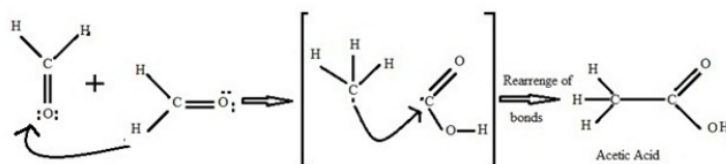


Fig. 12 The reaction mechanism involved in the formation of acetic acid. Initially, the hydrogen atom of one formaldehyde molecule attacks an oxygen atom of the other formaldehyde molecule and two radicals CH₃ and COOH are formed. Then through the radical-radical reaction mechanism, both the carbon atoms get bonded (C-C) and produce acetic acid.

Table 8 Rotational Constants (cm⁻¹) including Terms Due to the Quadratic Centrifugal Distortion Constant and Nielsens and Wilsons Centrifugal Distortion Constants (10⁻⁶cm⁻¹) of Isomers of C₂H₄O₂ Using B3LYP/ 6–311G (d,p)

Isomers of C ₂ H ₄ O ₂	Rotational Constant		Centrifugal distortion constants	Nielsens constants	Wilsons constants
Glycolaldehyde	A _e	1.619084	DJ	0.037505	0.036519
	B _e	0.155295	DJK	−1.064954	−0.025419
	C _e	0.145625	DK	13.330255	0.036522
	A ₀	1.597649	R5	0.058886	
	B ₀	0.154226	R6×10 ^{−6}	0.022856	
	C ₀	0.144704	δJ × 10 ^{−6}	0.002776	
Methyl Formate	A _e	0.378172	DJ	0.344064	0.356148
	B _e	0.315479	DJK	−0.416713	−0.611347
	C _e	0.177657	DK	−0.100727	0.286276
	A ₀	0.375638	R5	0.054723	
	B ₀	0.313214	R6×10 ^{−6}	0.016671	
	C ₀	0.176224	δJ × 10 ^{−6}	0.021214	
Acetic Acid	A _e	1.206252	DJ	0.062227	0.070209
	B _e	0.143760	DJK	−1.786907	−0.022704
	C _e	0.135164	DK	46.288325	0.008984
	A ₀	1.230969	R5	−0.185553	
	B ₀	0.142329	R6×10 ^{−6}	−0.000562	
	C ₀	0.133167	δJ × 10 ^{−6}	−0.0034298	

Table 9 Rotational- Vibrational Coupling Constant of Isomers of C₂H₄O₂ Using B3LYP/6–311G(d,p) Having in Unit 10⁻⁴cm

	Glycolaldehyde			Methyl Formate			Acetic Acid		
	a	b	c	a	b	c	a	b	c
α ₁	59.0	0.1	-0.4	5.2	0.2	-0.2	-1.1	3.1	0.6
α ₂	1.9	0.1	-0.2	39.1	-0.2	-0.3	1.5	2.5	0.9
α ₃	-15.2	0.6	1.0	41.7	0.2	0.1	2.4	0.6	0.4
α ₄	-43.2	1.3	2.8	28.8	0.5	0.5	2.9	1.5	0.4
α ₅	7.5	4.4	3.7	-2.5	4.9	4.3	12.0	7.2	4.3
α ₆	-38.3	0.2	-2.1	-287.5	-3.1	-7.2	-152.0	-17.8	-0.5
α ₇	58.8	-6.0	5.1	-1071.4	-52.9	-13.0	155.3	-2.1	-6.4
α ₈	-0.2	7.1	0.3	1380.8	57.3	21.4	2.4	16.9	8.8
α ₉	-3.3	0.7	3.5	-12.4	-0.2	0.7	5.0	4.9	3.9
α ₁₀	11.0	0.8	-0.8	-25.8	3.9	3.3	6.5	-0.7	4.6
α ₁₁	14.3	1.4	-3.6	-21.6	2.3	2.0	2.5	6.8	0.6
α ₁₂	-7.1	3.4	3.8	175.9	5.0	5.2	3.5	5.4	3.4
α ₁₃	46.1	7.1	12.8	-581.5	1.6	0.5	3.2	13.4	5.3
α ₁₄	-267.9	7.3	10.6	635.4	5.3	5.1	12.9	-3.3	0.3
α ₁₅	72.5	0.2	-1.1	-36.6	2.0	2.1	2.2	-4.2	-1.3
α ₁₆	169.0	1.9	5.1	-483.6	2.2	2.6	0.0	4.6	-1.3
α ₁₇	263.5	2.5	5.3	406.9	-2.0	-3.1	-4.5	-2.0	5.0
α ₁₈	162.9	-4.1	-5.8	237.8	-5.1	-5.7	-3.9	7.1	-0.2

ity (χ), chemical potential (μ), global hardness (η), global softness (S) and global electrophilicity index (ω) for reactants and products are listed in Tables 4, 5 and 6.

6 CONCLUSIONS

The possibility of formation of an isomer of C₂H₄O₂ such as glycolaldehyde, acetic acid and methyl formate from

an interstellar molecule, viz. HCHO, has been explored using quantum chemical methods. The quantum chemical calculations at B3LYP and MP2 level theory indicate the high probability of their formation through the proposed reaction mechanism. The proposed reaction paths have high potential barrier but due to quantum tunneling or thermal hopping, it is possible for reactants to cross

through the barriers. Woon (2002) has also justified the feasibility of interstellar reactions having potential barrier $>60 \text{ Kcal mol}^{-1}$. The study reveals that the formation of isomers of C₂H₄O₂ such as glycolaldehyde, methyl formate and acetic acid is efficient in the gas phase as well as in icy grains in the ISM. The observed potential barrier in the formation of glycolaldehyde, methyl formate and acetic acid is low enough to be penetrable when some energy is available from cosmic and ultraviolet rays in the hot core of Sgr B2. Therefore, there is a large probability for the formation of an isomer of C₂H₄O₂ in ISM. The small values of Wilson's and Nielsen's centrifugal distortion constants indicate that the molecular vibrations of the isomer of C₂H₄O₂ are almost harmonic in nature.

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References

- Andriichenko, N. N., & Ermilov, A. Y. 2013, Russian Journal of Physical Chemistry A, 87, 1342
- Bates, D. R. 1983, ApJ, 270, 564
- Bennett, C. J., & Kaiser, R. I. 2007, ApJ, 661, 899
- Brown, R. D., Crofts, J. G., Gardner, F. F., et al. 1975, ApJ, 197, L29
- Cazaux, S., Tielens, A. G. G. M., Ceccarelli, C., et al. 2003, ApJ, 593, L51
- Chattaraj, P. K., & Giri, S. 2007, Journal of Physical Chemistry A, 111, 11116
- Cramer, C. 2013, Essentials of Computational Chemistry: Theories and Models (Wiley)
- Despois, D., Biver, N., Bockelée-Morvan, D., & Crovisier, J. 2005, in IAU Symposium, Vol. 231, Astrochemistry: Recent Successes and Current Challenges, ed. D. C. Lis, G. A. Blake, & E. Herbst, 469
- Dykstra, C., Frenking, G., Kim, K., & Scuseria, G. 2005, Theory and Applications of Computational Chemistry: The First Forty Years (Elsevier Science)
- Ellder, J., Friberg, P., Hjalmarsen, A., et al. 1980, ApJ, 242, L93
- Frisch, M. J. and, T. G. W., Schlegel, H. B., Scuseria, G. E., et al. 2009, Gaussian09 Revision E.01, Gaussian Inc. Wallingford CT 2009
- Fukui, P. K. 1981, Accounts of chemical research, 14, 363
- Gibb, E. L., Whittet, D. C. B., Boogert, A. C. A., & Tielens, A. G. G. M. 2004, ApJS, 151, 35
- Glaser, R., Hodgen, B., Farrelly, D., & McKee, E. 2007, Astrobiology, 7, 455
- Halfen, D. T., Apponi, A. J., Woolf, N., Polt, R., & Ziurys, L. M. 2006, ApJ, 639, 237
- Herbst, E. 2001, Chemical Society Reviews, 30, 168
- Hollis, J. M., Jewell, P. R., Lovas, F. J., & Remijan, A. 2004, ApJ, 613, L45
- Hollis, J. M., Lovas, F. J., & Jewell, P. R. 2000, ApJ, 540, L107
- Huang, Y., Wang, Y., Alexandre, M. R., et al. 2005, Geochim. Cosmochim. Acta, 69, 1073
- Kivelson, D., & Bright Wilson, E., J. 1952, J. Chem. Phys., 20, 1575
- MacDonald, G. H., Gibb, A. G., Habing, R. J., & Millar, T. J. 1996, A&AS, 119, 333
- Mehring, D. M., Snyder, L. E., Miao, Y., & Lovas, F. J. 1997, ApJ, 480, L71
- Miertuš, S., Scrocco, E., & Tomasi, J. 1981, Chemical Physics, 55, 117
- Modica, P., & Palumbo, M. E. 2010, A&A, 519, A22
- Padmanabhan, J., Parthasarathi, R., Subramanian, V., & Chattaraj, P. K. 2006, Journal of Physical Chemistry A, 110, 2739
- Padmanabhan, J., Parthasarathi, R., Subramanian, V., & Chattaraj, P. K. 2007, Journal of Physical Chemistry A, 111, 1358
- Parr, R. G., & Pearson, R. G. 1983, Journal of the American Chemical Society, 105, 7512
- Parr, R. G., Szentpály, L. v., & Liu, S. 1999, Journal of the American Chemical Society, 121, 1922
- Parr, R. G., & Yang, W. T. 1989, Density-Functional Theory of Atoms and Molecules, International Series of Monographs on Chemistry (Oxford Univ. Press)
- Remijan, A., Snyder, L. E., Liu, S. Y., Mehring, D., & Kuan, Y. J. 2002, ApJ, 576, 264
- Remijan, A., Snyder, L. E., Friedel, D. N., Liu, S.-Y., & Shah, R. Y. 2003, ApJ, 590, 314
- Remijan, A., Shiao, Y.-S., Friedel, D. N., Meier, D. S., & Snyder, L. E. 2004, ApJ, 617, 384
- Remijan, A. J., Wyrowski, F., Friedel, D. N., Meier, D. S., & Snyder, L. E. 2005, ApJ, 626, 233
- Remijan, A. J., & Hollis, J. M. 2006, ApJ, 640, 842
- Scott, A. P., & Radom, L. 1996, The Journal of Physical Chemistry, 100, 16502
- Snyder, L. E. 2006, Proceedings of the National Academy of Science, 103, 12243
- Sorrell, W. H. 2001, ApJ, 555, L129
- Torrente, Y., Belicchi, M., Marchesi, C., et al. 2007, Cell Transplantation, 16, 563
- Turner, B. E. 1991, ApJS, 76, 617
- Woon, D. E. 2002, International Journal of Quantum Chemistry, 88, 226