

Reaction Between CH₂ and HCCN: A Theoretical Approach to Acrylonitrile Formation in the Interstellar Medium

Shivani · Alka Misra · Poonam Tandon

Received: 27 June 2014 / Accepted: 26 October 2014
© Springer Science+Business Media Dordrecht 2014

Abstract Acrylonitrile (CH₂CHCN) was first detected in dense molecular cloud SgrB2. The synthesis of this interstellar molecule is reported to be quite difficult. Therefore, in the present work an attempt has been made to explore the possibility of formation of acrylonitrile from some simple molecules and radicals detected in interstellar space by radical-radical interaction scheme, both in the gas phase and in the icy grains. All calculations are performed using quantum chemical methods with density functional theory (DFT) at the B3LYP/6-311G (d,p) level and Møller–Plesset perturbation theory at the MP2/6-311G (d,p) level. In the discussed chemical pathway, the reaction is found to be totally exothermic and barrier less giving rise to a high probability of acrylonitrile formation in Interstellar space.

Keywords Reaction mechanism · Density functional theory · Gas phase & grains · Interstellar grains · Acrylonitrile

Introduction

The discoveries of complex molecules in the interstellar clouds have provided valuable new tools for the study of physical conditions in these regions. The molecules are generally believed to be formed on the surfaces of the dust grains in the clouds (Cuppen and Herbst 2007; Das and Chakrabarti 2011). The great variety of molecules are found in the densest clouds, particularly in the regions of the galactic center and the Orion nebula. The physical and chemical conditions—including density, temperature, ultraviolet radiation and energetic particles—determine reaction pathways and the complexity of organic molecules in different space environments (Ehrenfreund et al. 2002).

Excluding diatomic molecules, ~30 % of all interstellar molecules have observed isomeric counterparts. These isomers are easily detectable in a number of interstellar environments and readily seen in the spectra of several molecular line surveys.

Shivani · A. Misra (✉)

Department of Mathematics & Astronomy, University of Lucknow, Lucknow, India
e-mail: alkamisra99@gmail.com

Shivani · P. Tandon

Department of Physics, University of Lucknow, Lucknow, India

Molecules with $C=C$ belong to olefins, which are known to be very reactive. Acrylonitrile (2-propenenitrile or vinyl cyanide) is one of the interstellar molecules belonging to olefin group and detected spectroscopically (Jung et al. 2011). It might conceivably undergo reactions like isomerizations to form an isocyanide or a ketenimine, eliminations of HCN or H_2 , and conversion to HCCCN. Acrylonitrile (CH_2CHCN) was first detected in the dense molecular cloud SgrB2 (by Gardner and Winnewisser 1975) and later in TMC1 (Matthews and Sears 1983). Agúndez et al. (2008) observed vinyl cyanide in circumstellar shell of IRC + 10216, and Muller et al. (2008) measured the spectra of ^{13}C isotope to identify its presence in Sgr B2(N). The microwave spectrum of vinyl cyanide is discussed in detail by Gardner and Winnewisser (1975). Snyder (2006) also verified the presence of acrylonitrile in the hot molecular core is named the Large Molecule Heimat source, or Sgr B2(N-LMH) by the Interferometric observations (Jobst et al. 2008).

The detection of acrylonitrile or vinyl cyanide (CH_2CHCN) shows the possibility of formation of cyanopolynes such as cyanoallene (CH_2CCHCN), cyanoacetylene (HCCCN), by the addition of C atom and depletion of H atom respectively, in interstellar space (Singh et al. 2014). Its detection also strengthens the probability of presence of ethylene, the simplest olefin (Gardner and Winnewisser 1975). The formation of cyanopolynes and other carbon chain molecules give the possibility of carbon based chemistry in the universe like earth. However, nitriles can be easily converted to acids by heating in liquid H_2O (hydrolysis). Liquid H_2O is thought to have been at least briefly present in the asteroidal parent bodies of certain meteorites (Robert and Epstein 1982), and this hydrolysis is a step in various proposed parent body reactions that may lead to amino acids (Ehrenfreund et al. 2001; Bernstein et al. 2004) which are one of the building blocks of proteins - in interstellar dust clouds in our galaxy. The study of prebiotic chemistry for RNA, DNA bases (adenine etc.) and formation of bases, amino acids (such as serine, glycine, alanine etc.) in interstellar medium and molecular clouds has profound implications for understanding the origin of life (Orgel 2004, Chakrabarti and Chakrabarti 2000; Abelson 1966; Glaser et al. 2007). The possibility of formation of above all mentioned molecules give rise to carbon based extraterrestrial life.

The gas phase ion chemistry of acrylonitrile has been studied using several experimental and theoretical methods. The ion-molecule reactions related with acrylonitrile have been investigated by several groups (Jung et al. 2011; Petrie et al. 1992; Hollis et al. 1995; Ervasti et al. 2007, 2009; Gluch et al. 2008; Winnewisser and Gerry 1973; Sun et al. 1993; Jobst et al. 2008). On the surfaces and mantles of dust grains, CH_2CHCN , CH_3CN , HC_2CN and CH_3CH_2CN are formed as a result of H-addition reactions, thus depleting HC_2CN .

Terlouw and co-workers (Ervasti et al. 2007, 2009; Jobst et al. 2008) and Takagi et al. (1999) carried out theoretical studies related to the acrylonitrile radical cation ($CH_2=CH-C\equiv N^{+}$). Different experimental techniques like electron attachment (Heni and Illenberger 1986), electron impact ionization (Gluch et al. 2008), charge exchange ionization (Youn et al. (2003), and tandem mass spectrometry (Ervasti et al. 2007, 2009; Jobst et al. 2008; Ichihashi et al. 1995) are used for the characterization of acrylonitrile. A theoretical study of isomerization and dissociation of the acrylonitrile radical cation has also been carried out by Jung et al. (2011) through quantum chemical methods. Petrie et al. (1992) reported the ion molecule reactions of acrylonitrile involving ions relevant to the interstellar cloud chemistry. Youn et al. (2003) have studied the stability of different radicals in interstellar space along with acrylonitrile and found that the radiative life time of acrylonitrile is 970 μ sec. The protonated form of the molecule has been argued to exist in high abundances in the upper atmosphere of Titan based on a strong signal at $m/z = 54$ recorded by the ion-neutral-mass spectrometer (INMS) on board the *Cassini* spacecraft (Vuitton et al. 2006; Vigren et al. 2009).

Simulation of the formation and reactions of molecules and their precursors in the interstellar medium is a difficult task and it is necessary to propose the reactions that can occur at extremely low densities and temperatures. There is a rapidly growing interest for the use of the computational chemistry to study chemical mechanisms and interstellar organic reactions which are difficult to be detected and identified experimentally. It is not an easy task to find thermodynamically feasible step by step reaction mechanisms that can account for formation of acrylonitrile or various other molecules in interstellar medium.

In the present work the quantum chemical calculations are performed to explore the possibility of formation of acrylonitrile in interstellar medium via some detected interstellar molecules such as HCCN and CH₂. The free HCCN was first studied by electron spin resonance and UV/IR spectroscopy (Guelin and Cernicharo 1991; Dendramis and Leroi 1977; Merer and Travis 1965). The HCCN is found to be abundant in circumstellar envelop+IRC10216 with column density $1.2 \times 10^{13} \text{ cm}^{-2}$ (Breinhmin et al. 1965). The cyanocarbene (HCCN) is known to exist in high concentration in space and has been identified as the precursor for the formation of the pre-biotic molecules which dictate the reaction pathways for the formation of interstellar prebiotic molecules (Majumdar et al. 2012; Gupta et al. 2011). The CH₂ is detected in Orion-KL and W51 M molecular cloud through spectral line detection with column density 10^{15} and 10^{14} cm^{-2} respectively. It is also detected in SgrB2 and W49 N with its low excitation rotational lines in the interstellar medium by far infrared spectroscopy. The column density of CH₂ is observed $(7.5 \pm 1.1) \times 10^{14} \text{ cm}^{-2}$ (Hollis et al. 1995; Polehampton et al. 2005). As such both CH₂ and HCCN are well detected and abundant molecules in interstellar medium.

Several studies related to the coupled hydro-chemical model are also present in the literature. These studies explore the possibility of formation of several complex molecules in different regions of the molecular cloud (Das et al. 2008; Majumdar et al. 2013). The grain surface chemistry explored provides insights into the influence that photo dissociation-driven reactions have on the organic chemistry of the interstellar medium. Consider two types of interstellar chemical reactions: 1) grain-surface reactions. 2) gas-phase reactions. In a grain-surface mechanism on cold grains (10 K), simple molecules are formed in ices by single-atom addition reactions because heavier molecules are not mobile. The simple molecules in the ice are photodissociated to form radicals. Upon warming, these radicals become mobile on the ice surface and react via recombination reactions to form larger organic species. Eventually, as the temperature reaches 200–300 K, the ices are evaporated and some gas-phase molecules become ionized (Laas et al. 2011; Garrod et al. 2008; Garrod and Herbst 2006; Hasegawa et al. 1992; Herbst and Leung 1989; Herbst and Klemberer 1973).

Radical-radical reaction mechanism is proposed in this reaction path in gas phase and in icy grains. Using quantum chemical techniques, formation of acrylonitrile has been explored in a single step. In this step of the reaction we have computed the potential energy curve which is barrierless in the present case signifying the possibility of formation of acrylonitrile through this reaction path in interstellar space. The reported reaction path is barrier less and exothermic in both gas phase and ice mental.

Computational Details

The geometries of the different species involved in the reaction pathway have been obtained at the B3LYP and MP2 level of the theory including all the electrons in the calculations. The B3LYP functional is composed of Becke's three-parameter hybrid exchange functional (B3) and the correlation functional of Lee, Yang, and Parr (LYP) yields good results in calculations of molecular structure and energetic. In these optimizations 6-311G (d,p) basis set has been

employed. Each optimized structure was verified to be a satisfactory point by vibrational analysis carried out at the same level [B3LYP/6-311G (d,p) and MP2/6-311G(d,p)] of theory. Of all hybrid DFT methods, the B3LYP functional is the most widely used (Scott and Radom 1996). MP2/6-311G (d,p) method has been well established over many years because it succeeds in reproducing experimental data with high reliability (Lee et al. 1988; Parr and Yang 1989; Becke 1993). All calculations reported in this work were carried out with the Gaussian03W program package. The chemical analysis calculates the energy requirement for the predicted reaction path; all calculations are performed at room temperature and atmospheric pressure. All the stable geometries were optimized, and confirmed by the vibrational analysis where no imaginary frequency was found. The reaction involved in the present study is exothermic and barrierless and as such do not follow the temperature dependent Arrhenius expression (Bates 1983). The rate coefficient of the proposed reaction is calculated by the Langevin expression which is efficient for the ion-molecule reactions:

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

where α is the polarizability (isotropic polarizability because we are considering the whole molecule having an evenly distributed charge) in \AA^3 and μ is the reduced mass of the reactants on ^{12}C amu scale, as suggested by Bates (1983). This expression for the rate coefficient is totally independent of temperature and based on the strong ion-induced dipole long range force. It can be derived by the simple assumption that all collisions leading to capture or orbiting are reactive in nature. The validity of Langevin expression from room temperature and above down to temperatures below 10 K has already been confirmed by experiments (Herbst 2001). Several workers use the “Multiwell program” for calculating the temperature and pressure dependence of reaction rates (Woon and Park 2009; Woon 2006). Their results also indicate that the order of rate constant is not much affected by the temperature variation in the range 10–300 K. There is only a small variation in the magnitude of rate constant. The PCM (Polarization Continuum Model) as implemented in Gaussian03W program has been used to include the bulk solvation effect. Harmonic and anharmonic frequency calculations were also conducted to identify the stable states.

Result and Discussion

The reactions performed in interstellar space are due to the charge transfer process. Observed data is interpreted on the basis of exoergicity rule, which states that an energy resonant or exoergic ($\Delta E \leq 0$) charge exchange occurs efficiently at low collision energy while endoergic one ($\Delta E \geq 0$) is hardly observable. In the present work the possibility of formation of acrylonitrile, from HCCN and CH_2 radicals, is explored using quantum chemical calculations.



The optimized geometries of the reactants and product involved in the reaction are schematically shown in Fig. 1 for ground state and excited state respectively and the electronic energies, ZPVE and total energies of all the molecules, radicals at B3LYP/6-311G (d,p) are given in Table 1 for both ground state and excited state.

As the quantum chemical calculations show, HCCN reacts with CH_2 (carbene like structure) and forms CH_2CHCN with a reaction energy of -0.14836×10^2 eV with ZPVE correction in gas phase. ZPE is a much larger piece of energy pie for this molecule. ZPE is also more sensitive to the details of molecular structure than other kinds of corrections so ΔZPE can

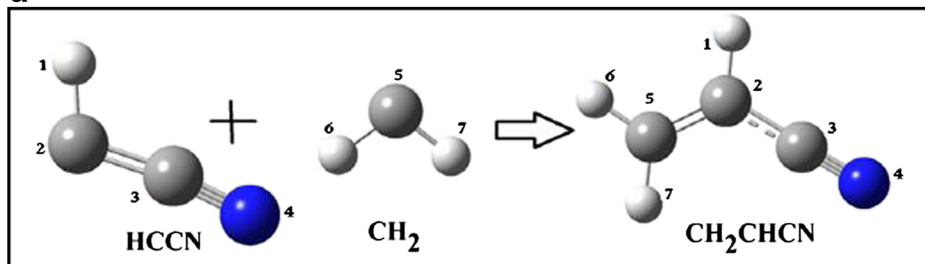
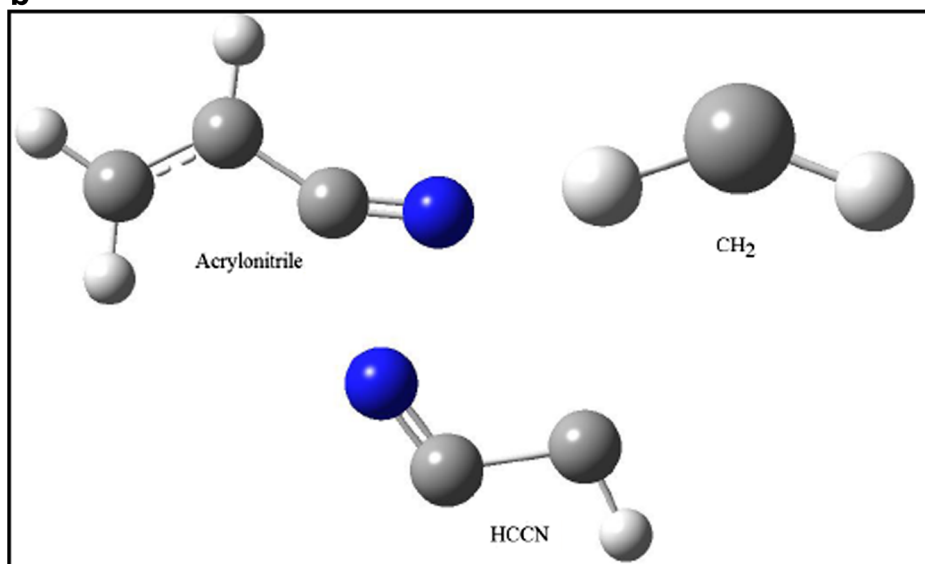
a**b**

Fig. 1 **a** Optimized geometries of reactants, product involve in the formation of acrylonitrile in reaction path at B3LYP/6-311G (d,p). **b** Optimized geometries of reactants, product involve in the destruction of acrylonitrile in reaction path at B3LYP/6-311G (d,p)

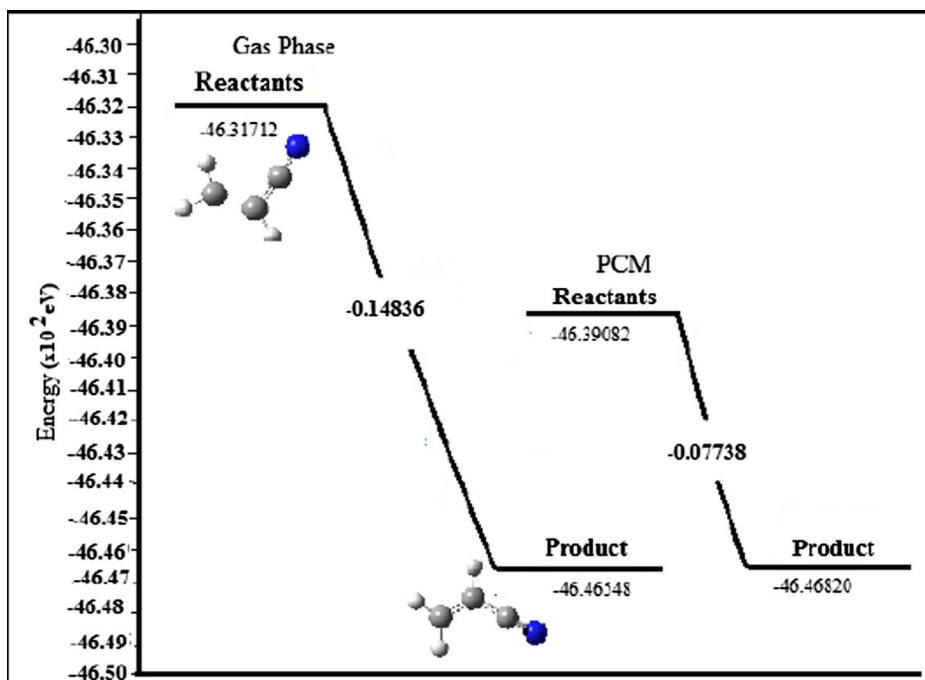
really affect reaction energies and barriers. Other energy corrections have much smaller effects. Mulliken population analysis of molecule in gas phase show that atomic charge on C (of CH_2) atom is -0.149 e.s.u., C (of HCCN) atoms are -0.100 e.s.u., 0.055 e.s.u., and N atom (of HCCN) is -0.226 e.s.u. These atoms can have an electrostatic force of attraction and leads to the formation of CH_2CHCN radical in gas phase with energy -46.46548×10^2 eV. The calculated dipole moment of the acrylonitrile is 3.9037D which compares well with the experimental value 3.68D reported by Gerry et al. (1979). The rate coefficient of this reaction in gas phase is calculated to be $1.68 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

In PCM also, the HCCN reacts with CH_2 and forms CH_2CHCN with reaction energy -0.284583 a.u. incorporating ZPVE correction. The electronic energies, ZPVE and total energies of all the molecules, radicals at B3LYP/6-311G (d,p) are given in Table 1. Mulliken population analysis of molecules in PCM or icy grains show that atomic charge on C (of CH_2) atom is -0.162 e.s.u., and C (of HCCN) atoms are -0.123 e.s.u., 0.088 e.s.u., and N atom (of HCCN) is -0.311 e.s.u., which are lower than the gas phase. These atoms can have stronger

Table 1 Electronic (EE), Zero Point Vibration (ZPVE) and total energies of molecules and radicals using B3LYP/6-311G (d,p) theory

Formation of Acrylonitrile						
Molecules	Energies in gas phase ($\times 10^2$ eV)			Energies in PCM ($\times 10^2$ eV)		
	E.E.	ZPVE	Total	E.E.	ZPVE	Total
HCCN	-35.74966	0.00494	-35.74452	-35.75180	0.00489	-35.74691
CH ₂	-10.57740	0.00480	-10.57260	-10.64853	0.00462	-10.64391
HCCN+CH ₂	-46.32706	0.00974	-46.31712	-46.40033	0.00951	-46.39082
CH ₂ CHCN	-46.47926	0.01378	-46.46548	-46.48188	0.01368	-46.46820
Destruction of Acrylonitrile						
HCCN	-35.65465	0.00372	-35.65093	-35.65912	0.00399	-35.65513
CH ₂	-10.48968	0.00460	-10.48508	-10.48951	0.00456	-10.48495
HCCN+CH ₂	-46.14433	0.00832	-46.13601	-46.14863	0.00855	-46.14008
CH ₂ CHCN	-46.39007	0.01229	-46.37778	-46.38851	0.01041	-46.37810

electrostatic force of attraction in comparison to gas phase and leads to the formation of more stable CH₂CHCN radical in icy grains with energy -46.46820×10^2 eV. The rate coefficient of the reaction in icy grains is calculated to be $1.86 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ which is higher than the calculated value in gas phase. This indicates that the higher probability of formation of acrylonitrile with PC model in comparison to the gas phase. The Energy curve of acrylonitrile formation at B3LYP/6-311G (d,p) shown in Fig. 2 in both gas phase and icy phase.

**Fig. 2** Energy level diagram for reaction path (for gas phase & PCM) at B3LYP/6-311G (d,p)

Acrylonitrile formation studied at MP2 level theory gives more accurate results in comparison to the one obtained at B3LYP level. In this theory CH₂CHCN forms in gas phase with the reaction energy of -0.08427×10^2 eV with ZPVE correction. The reaction energy calculated at MP2 theory is less than calculated with B3LYP and hence it shows that the high feasibility of acrylonitrile formation under MP2 calculations.

The electronic energies, ZPVE and total energies of all the molecules, radicals for gas phase at MP2/6-311G (d,p) are given in Table 2. Mulliken charge distribution analysis of reactants in gas phase at MP2 theory gives an atomic charge on C (of CH₂) atom is -0.179 e.s.u., and C (of HCCN) atoms are 0.039 e.s.u., 0.087 e.s.u., and N atom (of HCCN) is -0.280 e.s.u. As stated earlier, due to electrostatic force of attraction these molecules react and form CH₂CHCN radical in gas phase with energy -46.32899×10^2 eV.

With MP2 theory the acrylonitrile forms with the reaction energy -0.303335 a.u. with ZPVE correction. The electronic energies, ZPVE and total energies of all the molecules, radicals for PCM at MP2/6-311G (d,p) level are given in Table 2. The Charge distribution analysis of atoms in molecules involved in the reaction in PCM show an atomic charge on C (of CH₂) atom is -0.230 e.s.u., and C (of HCCN) atoms are 0.029 e.s.u., 0.122 e.s.u., and N atom (of HCCN) is -0.341 e.s.u. The negative charge on C5 and positive on C2 generate electrostatic force between both atoms and results the bonding of C5-C2 for acrylonitrile formation with energy -46.33064×10^2 eV in PCM at MP2 level of theory. The energy surface for the formation of acrylonitrile at MP2/6-311G (d,p) level in both gas phase and icy phase is shown in Fig. 3.

The calculation of global and local reactivity descriptors are performed at B3LYP/6-311G (d,p) and shown in Table 3. The global and local descriptors are very useful and reliable tools for the predication of reaction mechanisms. Thus exploration of global and local reactivity descriptors to understand the mechanistic aspects for the reaction is important. In this context, several reactivity descriptors have been proposed and used to analyse chemical reactivity and site selectivity. Global and local reactivity descriptors evaluated using DFT are very useful in explaining the behavior of reactant and products in an organic reaction. In this regard global electrophilicity, chemical potential, global hardness, global softness, and nucleophilicity are highly successful in predicting the feasibility and polarity of studied reactions

On the basis of Koopman's theorem (Parr and Yang 1989) global hardness (η), global softness (S) and global electrophilicity index (ω) are calculated using the energies of frontier molecular orbitals: E_{HOMO} , E_{LUMO} (Parr and Yang 1989; Parr and Pearson 1983; Geerlings et al. 2003; Parr et al. 1999; Chattaraj and Giri 2007). Fukui functions (f_k^+ , f_k^- , f_k^0) local softness (s_k^+ , s_k^- , s_k^0) and local electrophilicity indices (ω_k^+ , ω_k^- , ω_k^0) have been described earlier in literature (Parr et al. 1999; Chattaraj and Giri 2007). Using Hirshfeld population analyses of neutral, cation and anion state of molecule, Fukui functions are calculated and are shown in

Table 2 Electronic (EE), Zero Point Vibration (ZPVE) and total energies of molecules, radicals and transition state using MP2/6-311G (d,p) theory

Molecules	Energies in gas phase ($\times 10^2$ eV)			Energies in PCM ($\times 10^2$ eV)		
	E.E.	ZPVE	Total	E.E.	ZPVE	Total
HCCN	-35.64538	0.00508	-35.64030	-35.64719	0.00509	-35.64210
CH ₂	-10.60915	0.00474	-10.60441	-10.61078	0.00474	-10.60604
HCCN+CH ₂	-46.25453	0.00982	-46.24471	-46.25797	0.00983	-46.24813
CH ₂ CHCN	-46.34269	0.01370	-46.32899	-46.34439	0.01375	-46.33064

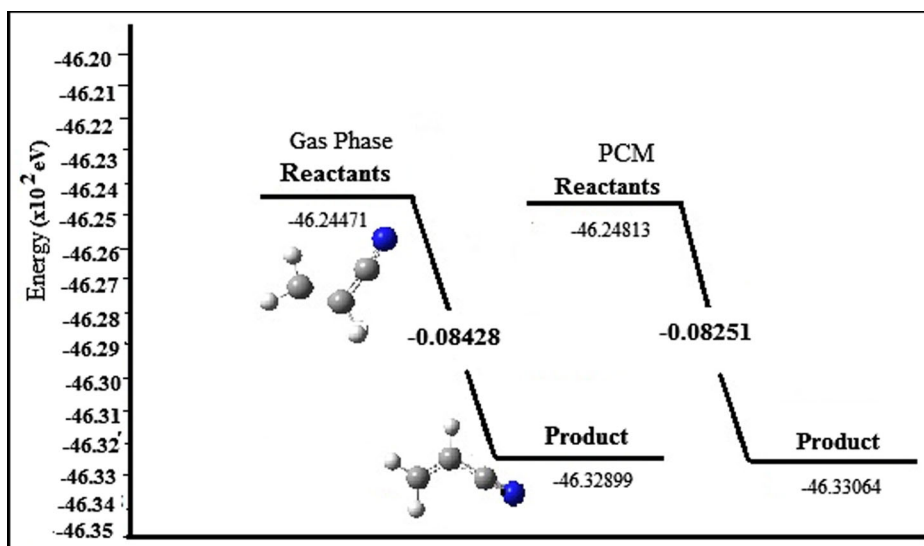


Fig. 3 Energy level diagram for reaction path (for gas phase & PCM) at MP2/6-311G (d,p)

Table 3. Fukui function and local electrophilicity/nucleophilicity are extensively applied to probe the local reactivity and site selectivity. Global and local descriptors such as chemical potential, molecular hardness and softness, electrophilicity and condensed Fukui functions have been helpful in predicting the chemical reactivity and regio-selectivity of the HCCN and

Table 3 Calculated Global and Local reactivity descriptors (eV)

Molecules/Atoms	Global Descriptors			Local Descriptors			
	Hardness(η)	Softness(S)	Philicity(ω)	f_k^0	η_k^0	S_k^0	ω_k^0
HCCN	1.2426	0.6213	2.4852				
1H				0.1207	0.1499	0.0750	0.2999
2C				0.4337	0.5389	0.3348	1.0778
3C				0.1418	0.1762	0.1079	0.3524
4N				0.3038	0.3775	0.2311	0.5743
CH ₂	6.1041	3.0520	1.6906				
5C				0.6616	4.0385	2.0192	1.1185
6H				0.1692	1.0328	0.5164	0.2861
7H				0.1692	1.0328	0.5614	0.2861
CH ₂ CHCN	3.1662	1.5831	6.3323				
1H				0.0723	0.2289	0.1145	0.4578
2C				0.1687	0.5341	0.8455	1.0683
3C				0.1202	0.3806	0.6025	0.7611
4N				0.2399	0.7596	1.2025	1.5191
5C				0.2329	0.7374	1.1674	1.4748
6H				0.0869	0.2751	0.4355	0.5503
7H				0.0792	0.2508	0.3970	0.5015

CH₂ radical additions. All the local and global descriptors have been calculated with the well known formulas with the help of “Atoms in Molecule” and “Multiwfn” Softwares. All the formulae are summarized in the paper of Singh et al. 2013

As may be clear from the Table 3 that acrylonitrile is formed with the soft-soft interaction of CH₂ and HCCN. The carbon atom (C5) in CH₂ has higher philicity than hydrogen atom and the carbon atom (C2) in HCCN contains higher philicity than hydrogen, carbon (C3) and nitrogen atoms. And also C5 atom of CH₂ can preferably attack C2 atom of HCCN with Fukui function (f_k^0) value 0.6616. As such the most favorable reacting site for acrylonitrile formation will be C2-C5 than any other site.

The proposed reaction path has other possible products which are shown in Fig. 4. But the required product acrylonitrile has the minimum energy among all possible products. The calculated IR spectrum is also shown in Fig. 5 which is agreed well with the observed data (<http://www.chemanalytical.com/ft-ir-spectra/Acrylonitrile> and also the NTP TR report 2001).

Results obtained with both the level of theories indicate that the acrylonitrile formation under solvent effect is more spontaneous than in gas phase.

All the bond angles and bond lengths (Table 4) of acrylonitrile agree well with observed data of Gerry et al. (1979). Potential energy curve for acrylonitrile has also been shown for its different energy isomers in Fig. 5.

Anharmonic Spectroscopic Constants

The rotational constants of cyanoallene at same level of theory are given in Table 5 & 6. The constants A₀, B₀ and C₀ for the ground vibrational state include the affects of zero-point vibrations and distortions. The rotational constants at the equilibrium geometry of the molecule were calculated at B3LYP/6-311G(d,p) and MP2/6-311G(d,p) levels. Generally due to the anharmonic vibrations the molecule deformed more or less from the equilibrium configuration. The centrifugal force due to the overall rotation acts on component atoms to shift their average positions away from the centre of gravity of the molecule. This force generates some distortions in the molecule and these distortions were calculated by Wilson and developed by Nielsen. The quartic centrifugal distortion constants based on Kivelson-Wilson formalism (Kivelson and Wilson 1952) for acrylonitrile are also given Table 5. The rotation-vibration coupling constants based on the second order perturbative approach (PT2) (Barone 2005) using B3LYP/6-311G (d,p) and MP2/6-311G (d,p) vibrational treatment are given in Table 6. The second order perturbation approximation, the constant α is obtained by taking the difference between the rotational constant in the first excited state of a normal vibration and that in the ground state. The constant α has two uses for molecular structure investigations: it is

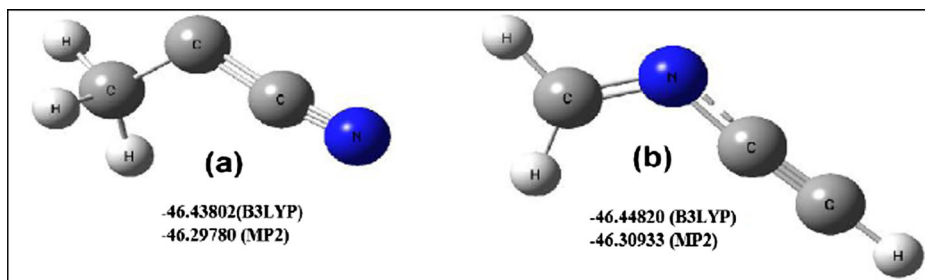


Fig. 4 Possible products of the reaction of CH₂ and HCOOH at B3LYP and MP2 (Energies in $\times 10^2$ eV)

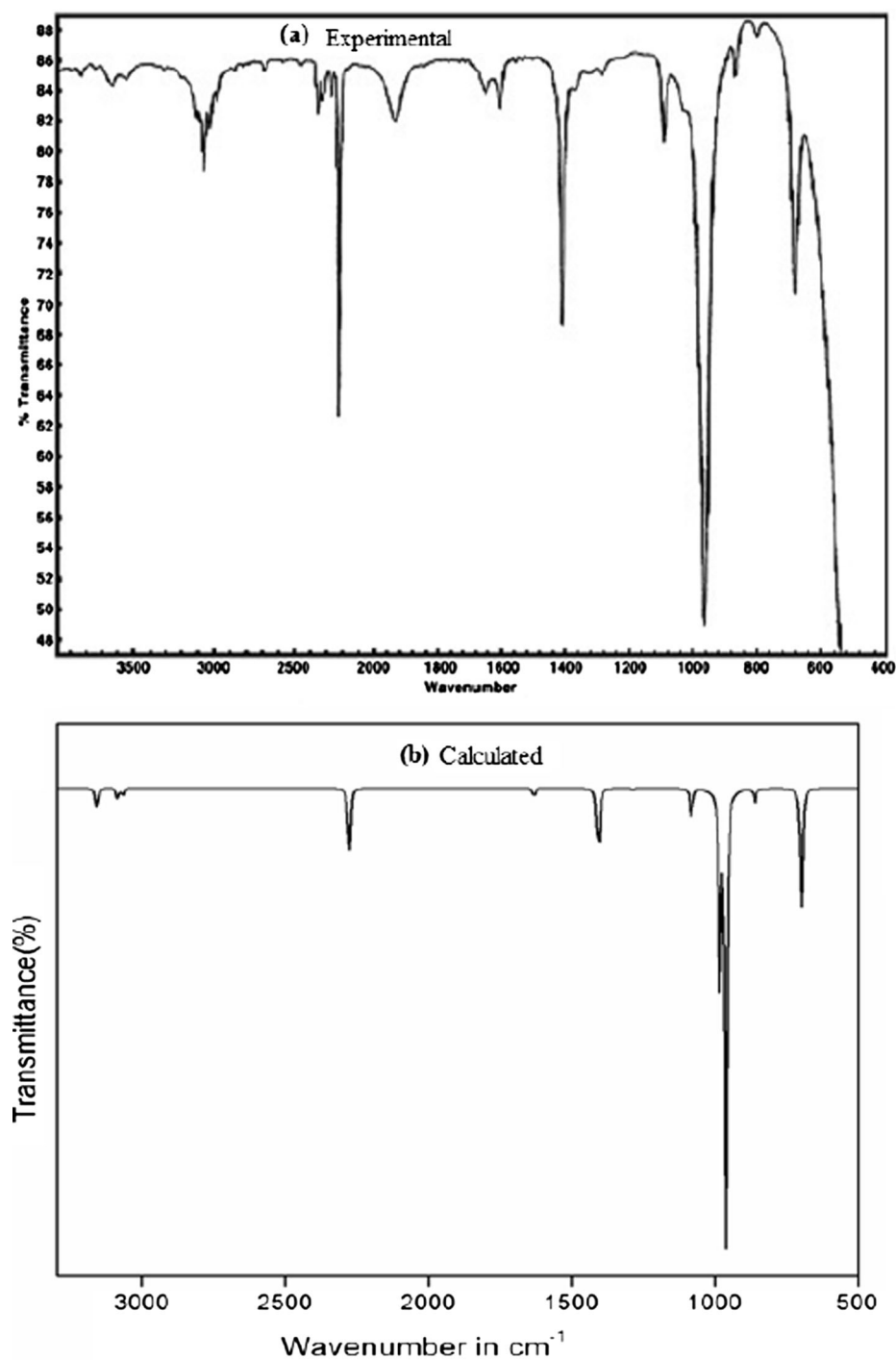


Fig. 5 a FT-IR spectra of Acrylonitrile. b Calculated IR spectra of Acrylonitrile

Table 4 Bond lengths and bond angles of all molecular species involved in proposed reaction path by using B3LYP/6-311G (d,p)

	Bond Lengths (Å)				
	C2H1	C2C3	C3N4	C2C5	C5H6
Reactants (HCCN+CH ₂)	1.09846	1.37179	1.17668	1.41000	1.10215
Product (CH ₂ CHCN)	1.08506	1.42742	1.15517	1.33429	1.08287
	Bond Angles (degrees)				
	H1C2C3	C2C3N4	H6C5H7	H1C2C5	
Reactants (HCCN+CH ₂)	111.49828	172.08397	104.67152	141.55780	
Product (CH ₂ CHCN)	115.70008	178.88360	117.64597	121.18048	

used for the evaluation of the cubic potential constants and for the determination of the equilibrium structure as already stated.

Very small magnitudes of the rotation-vibration constants and Wilson and Nielsen centrifugal distortion constants show that the molecular vibrations of acrylonitrile are almost harmonic in nature.

Vibrational Analysis

A complete vibrational analysis for the molecule has been attempted on the basis of harmonic and anharmonic frequency calculations using the B3LYP/6-311G(d,p) theory. No scaling is needed for the anharmonic frequencies. Vibrational frequencies were scaled by the single scaling factor given by Andersson and Uvdal (2005).

The calculated values have been compared with the experimental frequencies of acrylonitrile Assignments of the vibrational modes have been made on the basis of potential energy distribution (PED) over internal coordinates for the rb3lyp/6-311G(d,p) method. The PED was calculated by using software GAR2PED (Martin and Van Alsenoy 1995). The results are given in Table 7. The following discussion is, therefore, based on B3LYP/6-311G(d,p) calculations.

C-H Vibrations

In the exp IR spectrum of acrylonitrile, CH stretching is observed at 3050 cm⁻¹ which corroborates with the calculated wave number at 3048 cm⁻¹. The rocking mode of CH in

Table 5 Rotational constants (cm⁻¹) including terms due to quartic centrifugal distortion constant and Nielsen's-Wilson's centrifugal distortion constants ($\times 10^{-6}$ cm⁻¹) of acrylonitrile using B3LYP/6-311G (d,p) and MP2/6-311G (d,p).

Rotational Constants				Nielsen's Constants		Wilson's Constants	
B3LYP		MP2		B3LYP	MP2	B3LYP	MP2
A _e	1.7053598	1.644031	DJ	0.066794	0.069592	0.041316	0.042425
B _e	0.1655115	0.164118	DJK	-2.839217	-28.833504	0.040186	0.042701
C _e	0.1508691	0.149222	DK	91.736880	87.638806	0.014361	0.015511
A ₀	1.7042333	1.644174	R5	0.063022	0.068288	-	-
B ₀	0.1649767	0.163497	R6 ×10 ⁻⁶	-0.000898	-0.000969	-	-
C ₀	0.1502050	0.148501	ΔJ×10 ⁻⁶	0.013637	0.014553	-	-

Table 6 Rotational-vibrational coupling constants ($\times 10^{-4}$ cm $^{-1}$) of acrylonitrile

	B3LYP/6-311G(d,p)			MP2/6-311G(d,p)		
	a	b	C	a	b	C
α_1	42.1	0.80	0.9	44.9	0.6	0.8
α_2	-26.0	3.2	2.3	-19.2	3.3	2.5
α_3	42.4	0.7	0.9	46.3	0.4	0.8
α_4	21.7	6.9	5.9	20.7	8.4	7.1
α_5	12.07	1.4	2.7	110.3	1.3	2.6
α_6	-61.1	-0.9	0.6	-53.3	-0.7	0.7
α_7	31.4	-2.7	-0.3	22.2	-2.3	-0.1
α_8	-180.0	-3.2	2.0	-123.4	-3.5	1.8
α_9	152.2	2.5	-0.7	93.6	3.2	-0.6
α_{10}	124.7	2.3	-0.1	68.3	2.0	0.2
α_{11}	-92.2	5.9	4.3	-31.9	5.8	4.1
α_{12}	-157.9	-1.2	-1.7	-159.2	-0.9	-1.6
α_{13}	121.5	1.7	1.2	83.6	2.0	1.4
α_{14}	-290.8	-0.6	-2.5	-294.1	-1.0	-2.8
α_{15}	173.6	-0.6	-2.4	188.6	-6.1	-2.5

experimental band is observed at 1640, 1400 and 1082 cm $^{-1}$ which corresponds to the calculated vibrational band at 1612, 1390 and 1069 cm $^{-1}$ respectively. The out of plane wagging mode of CH in experimental data is observed at 681 cm $^{-1}$ which corroborates to the calculated wave number 689 cm $^{-1}$.

Table 7 Experimental and calculated infrared spectra of Acrylonitrile. Frequencies in cm $^{-1}$

Observed frequencies	Calculated Frequencies		Assignments (% ped)
	Unscaled	Scaled	
	3245	3121	ν (C5-H6) (51) + ν (C5-H7) (48)
3050	3169	3048	ν (C2-H1) (93) + ν (C5-H7) (5)
	3152	3032	ν (C5-H6) (48) + ν (C5-H7) (47) + ν (C2-H1) (4)
2230	2340	2251	ν (C2-N4) (88) + ν (C2-C3) (12)
1640	1676	1612	ν (C2-C5) (67) + δ_{sciss} (CH $_2$) (18) + ρ (C2- H1) (9) + ν (C2-C3)(5)
1400	1445	1390	δ_{sciss} (CH $_2$) (74) + ρ (C2- H1) (14) + ν (C2-C5) (6) + ν (C2-C3) (5)
	1319	1269	ρ (C2- H1) (64) + ν (C2-C5) (14) + ρ (CH $_2$) (13)+ δ_{sciss} .(CH $_2$) (5)
1082	1111	1069	ρ (CH $_2$) (51) + ρ (C2- H1)(19) + ν (C2-C3)(16) + δ (C5-C2-C3)(10)
	1008	970	τ (C2-C5) (63) + ω (C2- H1) (35)
960	988	950	ω (C5-C2)(98)
	883	849	ν (C2-C3)(61) + ρ (CH $_2$) (26)+ ν (C2-N4)(7) + ν (C2-C5)(4)
681	716	689	ω (C2- H1)(52) + τ (C2-C5)(25)+ τ (C2-C3)(22)
-	584	562	δ (C5-C2-C3)(42) + δ (C2-C3-C4) (38) + ρ (CH $_2$) (12)

Types of Vibrations: ν – stretching, δ_{sciss} – scissoring, ρ – rocking, ω – wagging, δ – deformation, τ – torsion

The scissoring of CH₂ observed at experimental band of 1640 and 1400 cm⁻¹ and which corroborates with the calculated vibrational band at 1612 and 1390 cm⁻¹, respectively. The rocking mode of CH₂ in experimental band is observed at 1082 cm⁻¹ which corresponds to the calculated vibrational band at 1069 cm⁻¹ respectively.

C-N Vibrations

In the IR spectrum of acrylonitrile, the experimental band for the CN stretching is observed at 2230 cm⁻¹ which corroborates with the calculated band at 2251 cm⁻¹.

Conclusion

Acrylonitrile formation studies at B3LYP and MP2 level of quantum chemical calculations show high probability of its formation through proposed reaction mechanism. The MP2 level theory gives more accurate results in comparison to the one obtained at B3LYP level. The proposed reaction is found to be more feasible in icy grains than in gas phase. The reaction is exothermic and barrierless which increases the probability of feasibility of this reaction in interstellar space. It is also concluded that the proposed reaction, which is feasible and exothermic at room temperature and atmospheric pressure, can also have a high probability of the occurrence at the low temperature (<30 K) and pressure (≤1 atm) in interstellar space. In a dense molecular cloud, ices are estimated to receive both particle and photon doses on the order of a few eV/molecule⁻¹ during the cloud's lifetime. Although the results depend on the conditions of the environment such as radiation field, temperature and pressure, but our study gives qualitative indicators to the formation of acrylonitrile in ISM. Exothermic reaction pathway is most suitable for acrylonitrile formation. Anharmonic spectroscopic parameters such as rotational constants, rotation-vibration coupling constants, and centrifugal distortion constants have been also calculated.

Very small magnitudes of the rotation-vibration coupling constants and Wilson's and Nielsen's centrifugal distortion constants show that the molecular vibrations of acrylonitrile are almost harmonic in nature.

References

- Abelson PH (1966) Chemical events on the primitive earth. *Proc Natl Acad Sci* 55:1365–1372
- Agúndez M, Fonfría JP, Cernicharo J, Pardo JR, Guélin M (2008) Detection of circumstellar CH₂CHCN, CH₂CN, CH₂CCH, and H₂CS. *Astron Astrophys* 479:493–501
- Andersson MP, Uvdal P (2005) New scale factors for harmonic vibrational frequencies using the B3LYP density functional method with the triple- α basis Set 6–311+G(d, p). *J Phys Chem A* 109:2937–2941
- Barone V (2005) Anharmonic vibrational properties by a fully automated second-order perturbative approach. *J. Chem. Phys.*, 122:014108-1-014108-10
- Bates DR (1983) Theory of molecular formation by radiative association in interstellar clouds. *Astrophys J* 270: 564–577
- Becke AD (1993) Density-functional thermochemistry. III The Role of Exact Exchange. *J Chem Phys* 98:5648–5652
- Bernstein MP, Ashbourn SFM, Sandford SA, Allamandola LJ (2004) The lifetimes of nitriles (CN) and acids (COOH) during ultraviolet photolysis and their survival in space. *Astrophys J* 601:365–370
- Breinhmin RA, Kempf RJ, Gramas JV, Skell PS (1965) Electron paramagnetic resonance of triplet alternant methylenes. Propargylene and Homologs. *J Chem Phys* 43:196–200

- Chakrabarti S, Chakrabarti SK (2000) Can DNA bases be produced during molecular cloud collapse? *A&A* 354: L6–L8
- Chattaraj PK, Giri S (2007) Stability, reactivity and aromaticity of compounds of a multivalent superatom. *J Phys Chem A* 111:11116–11121
- Cuppen HM, Herbst E (2007) Simulation of the formation and morphology of Ice mantles on interstellar grains. *Astrophys J* 668:294–309
- Das A, Chakrabarti SK (2011) Composition and evolution of interstellar grain mantle under the effects of photodissociation. *MNRAS* 418:545–555
- Das A, Chakrabarti SK, Acharyya K, Chakrabarti S (2008) Time evolution of simple molecules during proto-star collapse. *NEWA* 13:457–467
- Dendramis A, Leroi GE (1977) Matrix isolation spectroscopic study of the free radical HCCN. *J Chem Phys* 66: 4334–4340
- Ehrenfreund P, Glavin DP, Botta O, Cooper G, Bada JL (2001) Extraterrestrial amino acids in Orgueil and Ivuna: tracing the parent body of CI type carbonaceous chondrites. *Proc Natl Acad Sci* 98:2138–2141
- Ehrenfreund P, Irvine W, Becker L, Blank J, Brucato JR, Colangeli L, Derenne S, Despois D, Dutrey A, Fraaije H, Lazcano A, Owen T, Robert F, an International Space Science Institute ISSI-Team (2002) Astrophysical and astrochemical insights into the origin of life. *Rep Prog Phys* 65:1427–1487
- Ervasti HK, Jobst KJ, Gerbaux P, Burgers PC, Ruttink PJA, Terlouw JK (2007) The acrylonitrile dimer ion: A study of its dissociation via self-catalysis, self-protonation and cyclization into the pyrimidine radical cation. *Int. J. Mass Spectrom* 262:88–100
- Ervasti HK, Jobst KJ, Gerbaux P, Burgers PC, Ruttink PJA, Terlouw JK (2009) The reaction of the acrylonitrile ion $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}^+$ with HCN: Proton-transport catalysis vs formation of ionized pyrimidine. *Chem Phys Let* 482:211–216
- Gardner FF, Winnewisser G (1975) The Detection of interstellar vinyl cyanide (Acrylonitrile). *Astrophys J* 195: L127–L130
- Garrod RT, Herbst E (2006) Formation of methyl formate and other organic species in the warm-Up phase of Hot molecular cores. *Astron Astrophys* 557:927–936
- Garrod RT, Widicus Weaver SL, Herbst E (2008) Complex chemistry in star-forming regions: an expanded Gas-grain warm-Up chemical model. *Astrophys J* 682:283–302
- Geerlings P, De Proft F, Langenaeker W (2003) Conceptual Density Functional Theory. *Chem Rev*, 103:1793–1873
- Gerry MCL, Yamada K, Winnewisser G (1979) Microwave spectra of molecules of astrophysical interest: XIV. Vinyl cyanide (acrylonitrile). *J Phys Chem Ref Data* 8:107–123
- Glaser R, Hodgen B, Farrelly D, McKee E (2007) Adenine synthesis in interstellar space: mechanisms of prebiotic pyrimidine-ring formation of monocyclic HCN-pentamers. *Astrobiology* 7:455–70
- Gluch K, Cytawa J, Michalak L (2008) Electron impact ionization of acrylonitrile. *Int J Mass Spectrom* 278:10–14
- Guelin M, Cernicharo J (1991) Astronomical detection of the HCCN radical. Towards a new family of carbon-chain molecules?. *ApJ*, 244:21–24
- Gupta VP, Tandon P, Rawat P, Singh RN, Singh A (2011) Quantum chemical study of a new reaction pathway for the adenine formation in the interstellar space. *Astron Astrophys* 528:A129–A134
- Hasegawa TI, Herbst E, Leung CH (1992) Models of gas-grain chemistry in dense interstellar clouds with complex organic molecules. *ApJS* 82:167–195
- Heni M, Illenberger E (1986) Electron attachment by saturated nitriles, acrylonitrile ($\text{C}_2\text{H}_3\text{CN}$), and benzonitrile ($\text{C}_6\text{H}_5\text{CN}$). *Int J Mass Spectrom* 73:127–144, Ion Processes
- Herbst E (2001) The Chemistry of Interstellar Space. *Chem Soc Rev* 30:168–176
- Herbst E, Klemm W (1973) The formation and depletion of molecules in dense interstellar clouds. *Astrophys J* 185:505–533
- Herbst E, Leung CM (1989) Gas-phase production of complex hydrocarbons, cyanopolyynes, and related compounds in dense interstellar clouds. *ApJS* 69:271–300
- Hollis JM, Jewell PR, Lovas FJ (1995) Confirmation of interstellar methylene. *Astrophys J* 438:259–264
- Ichihashi M, Tsukuda T, Nonose S, Kondow TJ (1995) Collision-induced dissociation of acrylonitrile cluster ions: geometrical structure of polymerized cluster anion. *Phys Chem* 99:17354–17358
- Jobst KJ, Hasan SA, Terlouw JK (2008) Does the ion-molecule reaction between $\text{HC}\equiv\text{CH}^+$ and HCN lead to $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}^+$? A computational and experimental study of the reverse process. *Chem Phys Let* 450: 243–247
- Jung SH, Lee G-H, Choe JC (2011) Isomerization and dissociation of the acrylonitrile radical cation: a theoretical study. *Bull Korean Chem Soc* 32:3873–3879
- Kivelson D, Wilson EB (1952) Approximate treatment of the effect of centrifugal distortion on the rotational energy levels of asymmetric-rotor molecules. *J Chem Phys* 20:1575–1579

- Laas JC, Garrod RT, Herbst E., Wicicus Weaver S. L. (2011) Contributions From Grain Surface And Gas Phase Chemistry To The Formation Of Methyl Formate And Its Structural Isomers. *ApJ*, 728(1):71(9 pp)
- Lee CT, Yang WT, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron-density. *Phys Rev* 37B:785–789
- Majumdar L, Das A, Chakrabarti SK, Chakrabarti S (2012) Hydro-chemical study of the evolution of interstellar pre-biotic molecules during the collapse of molecular clouds. *RAA* 12:1613–1624
- Majumdar L, Das A, Chakrabarti SK, Chakrabarti S (2013) Study of the chemical evolution and spectral signatures of some interstellar precursor molecules of adenine, glycine alanine. *NEWA* 20:15–23
- Martin JML, Van Alsenoy C (1995) GAR2PED. University of Antwerp, Computer Software
- Matthews HE, Sears TJ (1983) The detection of Vinyl Cyanide in TMC-1. *Astrophys J* 272:149–153
- Merer AJ, Travis DN (1965) Absorption spectrum of the CCN radical. *Can J Phys* 43(10):1795–1830
- Muller HSP, Belloche A, Menten KM, Comito C, Schilke P (2008) Rotational spectroscopy of isotopic vinyl cyanide, H₂CCHCN, in the laboratory and in space. *J Mol Spectrosc* 251:319–325
- Orgel LE (2004) Prebiotic chemistry and origin of the RNA world. *Biochem Mol Biol* 39:99–123
- Parr RG, Pearson RG (1983) Absolute hardness: comparison parameter to absolute electronegativity. *J Am Chem Soc* 105:7512–7516
- Parr RG, Yang W (1989) Density functional theory of atoms and molecules. Oxford University Press, Oxford
- Parr RG, Szentpaly L, Lui S (1999) Electrophilicity index. *J Am Chem Soc* 121:1922–1924
- Petrie R, Freeman CG, McEwan MJ (1992) The ion-molecule chemistry of acrylonitrile - Astrochemical implications. *Mon Not R Astr Soc* 257:438–444
- Polehampton ET, Menten KM, Brünken S, Winnewisser G, Baluteau J-P (2005) Far-infrared detection of methylene A&A 431:203–213
- Robert F, Epstein S (1982) The concentration and isotopic composition of hydrogen, carbon and nitrogen in carbonaceous meteorites *Geochim. Cosmochim Acta* 46:81–85
- Scott AP, Radom L (1996) Reported energies include zero-point energy corrections scaled by 0.9806. *J Phys Chem* 100:16502–16513
- Singh RN, Amit K, Tiwari RK, Poonam R, Rajiv M (2013) Synthesis, molecular structure, and spectral analyses of ethyl-4-[(2,4-dinitrophenyl)-hydrazonomethyl]-3,5-dimethyl-1H-pyrrole-2-carboxylate. *Struct Chem* 24: 713–724
- Singh A, Shivani MA, Tandon P (2014) Formation of cyanoallene (buta-2, 3-dienenitrile) in the interstellar medium: a quantum chemical and spectroscopic study. *RAA* 14:275–284
- Snyder LE (2006) Interferometric observations of large biologically interesting interstellar and cometary molecules. *PNAS* 103:12243–12248
- Sun J, Grützmacher HF, Lifshitz CJ (1993) Ion/molecule reactions of carbon cluster ions and acrylonitrile. *J Am Chem Soc* 115:8382–8388
- Takagi N, Fukuzawa K, Osamura Y, Schaefer HF III (1999) Ion-molecule reactions producing HC₃NH⁺ in interstellar space: forbiddenness of the reaction between cyclic C₃H₃⁺ and the N atom. *ApJ* 525:791–798
- NTP Technical Report (2001) Toxicology And Carcinogenesis Studies Of Acrylonitrile (CAS No.107-13-1), 1–197
- Vigren E, Hamberg M, Zhaunerchyk V, Kaminska M, Thomas RD, Larsson M, Millar TJ, Walsh C, Geppert WD (2009) The dissociative recombination of protonated acrylonitrile, Ch₂chenh⁺, with implications for the nitrile chemistry in dark molecular clouds and the upper atmosphere of titan. *Astrophys J* 695:317–324
- Vuitton V, Yelle RV, Anicich VG (2006) The nitrogen chemistry of Titan's upper atmosphere revealed. *ApJL* 647:175–178
- Winnewisser G, Gerry MCL (1973) Microwave spectrum and centrifugal distortion constants of vinyl cyanide. *J Mol Spectrosc* 48:1–16
- Woon DE (2006) Modeling chemical growth processes in Titan's atmosphere: theoretical rates for reactions between benzene and the ethynyl (C₂H) and cyano (CN) radicals at low temperature and pressure. *Chemphys* 331:67–76
- Woon DE, Park J-Y (2009) Modeling chemical growth processes in Titan's atmosphere 2. Theoretical study of reactions between C₂H and ethene, propene, 1-butene, 2-butene, isobutene, trimethylethene, and tetramethylethene. *ICARUS* 202:642–655
- Youn YY, Choe JC, Kim MS (2003) Discovery of long-lived excited electronic states of vinylchloride, vinylbromide, vinyliodide, and acrylonitrile cations. *Am Soc Mass Spectrom* 14:110–116