STUDY OF CYCLOPROPENYLIDENE CLUSTERS

A literature review submitted in partial fulfilment of requirements for the degree of

Master of science (M.Sc.) in chemistry

Physical Chemistry

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By

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DECLARATION

I declare that the literature review titled “STUDY OF CYCLOPROPENYLIDENE CLUSTERS” has been carried out by me in the Chemistry Department, School of Chemical Sciences, Goa university. The information derived from the literature has been duly acknowledged in the text and a list of references is provided.

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CONTENTS

INTRODUCTIONS

Cyclopropenylidene or CCPD is a partially aromatic molecule belonging to a highly reactive class of organic molecules known as carbenes. On Earth, cyclopropenylidene is only seen in the laboratory due to its reactivity. However, cyclopropenylidene is found in significant concentrations in the interstellar medium (ISM) and on Saturn's moon Titan. Its C2v symmetric isomer, propadienylidene (CCCH2) is also found in the interstellar medium (ISM), but with abundances about an order of magnitude lower. A third C2 symmetric isomer, propargylene (HCCCH), has not yet been detected in the ISM, most likely due to its low dipole moment.[1,2] The simplest cyclic conjugated carbene is generated by pyrolysis of the polycycle.[3] We carried out the crossed molecular beam reaction of ground state methylidyne radicals, CH, with acetylene, C2H2 at a nominal collision energy of 16.8 kJ/mol. Under single collision conditions, we identified both the atomic and molecular hydrogen loss pathways forming C3H2 and C3H isomers, respectively.[4]

Twenty-seven rotational lines of cyclo-C3 H2 were identified in the experiments or in astronomical sources, and the rotational and centrifugal distortion constants which were previously unobserved.[1] Nonempirical molecular electronic structure theory has been used to predict the geometries and energetics of the lowest singlet and triplet states of C-HC=CH. The closed-shell singlet ground state is predicted to lie about 70 kcal/mol below the lowest triplet state.[5] Propellane, methylenecyclopropane, cyclopropenylidene, and thiirene are discussed. A compilation of ab initio vibrational calculation is also included.[6] An improved complete basis set-quadratic CI/at. pair natural orbital (CBS-QCI/APNO) model is described in this paper.[7] A general-purpose implementation of analytic CCSD(T) 21nd derivs. is presented. Its applicability is demonstrated by calculations of vibration-rotation interaction consts. for the astrophys. important mol. cyclopropenylidene.[8] Experimental Investigation on the Formation of Carbon-Bearing Molecules in the Interstellar Medium via Neutral-Neutral Reactions.[9]

Photoionization mass spectrometry using tunable vacuum-ultraviolet synchrotron radiation is applied to the study of C 3 H 2 sampled from a rich cyclopentene flame. The photoionization efficiency has been measured between 8.5 eV and 11.0 eV. Franck-Condon factors for photoionization are calculated from B3LYP/ 6-311++G (d, p) characterizations of the neutral and cation of the two lowest-energy C 3 H 2 isomers, triplet propargylene (HCCCH, prop-2ynylidene) and singlet cyclopropenylidene (cyclo-HCCCH).[10] The gas-phase high-resolution absorption spectrum of the v6 band of cyclopropenylidene (c-C3H2) has been observed using a Fourier transform infrared spectrometer for the first time.[11]

To further reveal the reactivity of cyclopropenylidene with R-H compounds, mechanisms of four reactions between cyclopropenylidene and R-H (R=F, OH, NH2, CH3) have been systematically investigated employing the second-order Møller-Plesset perturbation theory (MP2) method.[12] OPB is the predicted to be the second-brightest transition, and it will be observed very close to 775 cm.[13] The spatial distribution of mols. Around starless cores are a powerful tool for studying the physics and chem. governing the earliest stages of star formation. Our aim is to study the chem. differentiation in starless cores to det. the influence of large-scale effects on the spatial distribution of mols. within the cores.[14]

We report the first detection on Titan of the small cyclic mol. cyclopropenylidene (c-C 3 H2) from high sensitivity spectroscopic observations made with the Atacama Large Millimeter/submillimeter Array.[15] Recent work on cyclopropenylidene, c-CH, sought to improve on past ab initio results with a complete basis set (CBS) quartic force field method capable of predicting fundamental bands to within 5 cm -1 accuracy of gas-phase spectroscopy expts. for semirigid mols.[16]

The recent detection of ethynyl-functionalized cyclopropenylidene (CPPD) has initiated the search for other functional forms of cyclopropenylidene (c-C 3 H 2) in space. There is existing gas-phase rotational spectroscopic data for cyano cyclopropenylidene (c-C 3 HCN), but the present work provides the first anharmonic vibrational spectral data for that mol., as well as the first full set of both rotational and vibrational spectroscopic data for fluoro- and chloro-cyclopropenylidenes (c-C 3 HF and c-C 3 HCl)[17]

The electronic structure and bonding of cyclopropenylidenes with different substituents at the olefinic position viz., -H (1), electron-withdrawing groups (-CHO (2) and -COOH (3)) and electron-donating groups (-N (CH 3) 2 (4) and -N(iPr) 2 (5)), have been explored at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory.[18]

THEORETICAL METHODS

1. Schrödinger Equation

The Schrödinger equation is a linear partial differential equation that describes the wave function of a quantum mechanical system. In theory it can exactly predict any property of a given atoms or molecule, but in practice, has been solved exactly only for one electron system. The general expression for the Schrödinger equation is expressed as

$$\hat{H}\Psi = E\,\Psi$$

Where H is the Hamiltonian Operator, E is the energy and ψ is the wavefunction. The electron and nuclear positions are a function of ψ. It describes the electron as a wave, but cannot predicts exactly where the electron is, since it follows a probabilistic approach. The wavefunction must be continuous, single-valued, normalisable and antisymmetric with respect to the exchange of electrons.

The Schrödinger equations is expressed as

$$\frac{-\hbar^2}{2m}\nabla^2\Psi + V\Psi = E\Psi$$

Where $\hbar = \frac{h}{2\pi}$, V=potential energy, E= total energy, and $\nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ called the Laplacian operator.

The Schrödinger equation is an eigen value equation wherein Ψ is the eigen function and E is the eigen value. Any property of a given molecule can be obtained once the wavefunction has been determine. This is done by taking the expectation value of the operator for that property, denoted with <> (angled brackets).

$$\langle E\rangle = \int \Psi^{¿}\hat{H}\Psi$$

Is called the average value or expectation value equation, often called variational energy as it is always greater than equal to the exact energy. Different observable properties can be obtained by substituting different operators.

Hellmann-Feynman theorem can be used to obtain molecular properties. This theorem states that the derivative of energy with respect to same property P is given by $\frac{dE}{dP} = \left\langle \frac{\partial \hat{H}}{\partial P} \right\rangle$

Varying the property P, we can obtain different molecular properties.[19,20]

1.2. Born Oppenheimer Approximation

In 1927 Born and Oppenheimer showed that to a very good approximation the nuclei in a molecule are stationary with respect to the electrons. This is a qualitative expression of the principle; mathematically the approximation states that the Schrödinger equation for a molecule may be separated into an electronic and a nuclear equation. To calculate the energy of a molecule we have to solve the electronic Schrödinger equation and then add electronic energy to the internuclear repulsion to get the total internal energy. A deeper consequence of Born Oppenheimer Approximation is that a molecule has a shape.

The nuclei see the electrons as a smeared-out cloud of negative charge which binds them in fixed relative positions (because of the mutual attraction between electrons and nuclei in the internuclear region) and which defines the surface of the molecule. Because of the rapid motion of the electron compared to the nuclei the “permanent” geometric parameters of the molecule are the nuclear coordinates. The energy (and other properties) of a molecule is a function of coordinates ($E=\Psi(x, y, z\,of\,each\,electron)$; but depends only parametrically on the nuclear coordinates, i.e., for each geometry 1,2……. There is particular energy:(E1 = Ψ (x, y, z…., (E2 = Ψ (x, y, z, ….; cf x^n which is the function of x but depends only on parametrically on **n**. the nuclei are not stationary, but execute vibrations of small amplitude about equilibrium positions; it is these equilibrium position that we mean by the “fixed” nuclear positions. Its is only because it is meaningful to speak of (almost) fixed nuclear coordinates that the concepts of molecular geometry or shape and of the PES (Potential Energy Surface) are valid. The nuclei are much more sluggish than the electrons because they are much more massive (a hydrogen nucleus is about 2000 times more massive than an electron)[21]

2. Density Function Theory (DFT)

DFT is based the on-electron probability or the electron density function, unlike Hatree-fock and ab -initio which are based on the wavefunction. No matter how bulky the molecule is, the complexity of the wavefunction increase with the number of electrons, the electron density remains a functional of 3 variables only the DFT Hamiltonian is represented as

$$\rho(r)=\sum_{i=1}^{n} Xi^{¿}(xi)\,Xi(xi)$$

Where Xi(xi) is the i th spin orbital in n-electron system.

The Kohn-Sham equation is given as

$$f_i^{KS}\,X_i^{KS}=\varepsilon_i^{KS}\,X_i^{KS}$$

Where f_i^{KS} = Kahn-Sham Operator, ε_i^{KS}= Kohn – Sham orbital energy and X_i^{KS} = Kohn-sham molecular orbital.

The DFT total energy is generally expressed as

$$E^{DFT}(\rho)=T_{exact}(\rho)+E_{ne}(\rho)+J(\rho)+E_{XC}(\rho)$$

Where the first and second terms denote the exact kinetic energy and the Coulomb interaction energy between atomic- nucleus and the electrons respectively; whereas the third and fourth term denote Coulomb interaction energy between electrons and exchange interactions energy between electrons respectively.

In the absence of correlation energy, the Hartree-Fock molecular orbital are identical to Kohn – sham molecular orbital. DFT can calculate the geometries and the relative energies with roughly the same time requirements as that of HF calculations. Since wavefunctions can be represented exactly by a slater determinant, energy of idealized system can be calculated exactly. DFT tends to be classified as an ab-initio method in a class by itself.[19,20]

RESULT AND DISSCUSSION

Table 1: Harmonic normal modes at ωB97xD/6-311++G(2d,2p) level of theory. ν indicate stretching, where δ indicate bending vibration, CPPD= Cyclopropenylidene, or c-C3H2, the values in table indicate frequency and in bracket(IR intensity, Raman intensity)

cm−1	H2O	CPPD	CPPD-dimer	CPPD-Trimer	1-H2O-CPPD	2-H2O-CPPD
ν(O-H) unsymm	4007(66,26)	---	---	---	95(122,0) 381(91,0) 660(93,1) 3643(728,246) 3969(67,51)	165(64,0) 245(97,0) 413(86,0) 423(76,0) 715(166,1) 797(87,0) 3531(721,211) 3638(535,68) 3961(77,56) 3972(65,74)
ν(O-H) symm	3903(9,75)	---	---	---		
δ(O-H)	1649(73,4)	---	---	---	1680(38,0)	1672(60,4) 1695(44,1)
ν(C-H) unsymm	---	917(3,5) 1005(0,0) 3249(1,55)	934(26,0) 936(0,11) 1022(0,0) 3233(50,0) 3234(0,52)	919(0,0) 923(21,7) 991(0,0) 994(14,5) 1058(0,0) 1062(0,0) 1116(0,0) 1120(70,24) 3123(0,278) 3134(400,138) 3133(401,137) 3265(5,84) 3265(4,134)		
ν(C-H) symm	---	804(19,0) 3285(0,120)	827(33,0) 830(0,0) 3275(10,0) 3276(0,308)	849(48,0) 857(0,0)	816(12,0) 3291(1,117)	841(20,0) 3281(12,140)
δ(C-H)	---	897(21,5)	902(0,7)	---	908(28,2)	912(51,5)

			912(76,0)			
ν(C=C)	---	1650(0,59)	1646(2,0) 1646(0,148)	1638(1,244) 1632(13,18) 1636(13,24)	1651(0,64)	1648(0,70)
δ(H-C=C-C-H) in plane bending	---	1318(50,6)	1325(0,7) 1327(81,0)	1339(47,2) 1335(0,9)	1344(42,8)	1346(32,5)
δ(H-C=C=C-H)	---	1120(12,10)	1104(0,21) 1105(47,0)	---	1123(14,9)	1118(26,12)

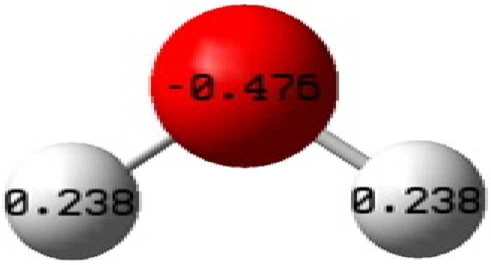
The above table tells us about the modes of vibration or degree of freedom which is calculated by formula 3N-5 for linear molecule and for nonlinear it is 3N-6 where N=number of atoms present. Three modes are been recorded in the above table symmetric stretching, unsymmetric stretching and bending, the frequency of different modes in cyclopropenylidene mol. Is done by using computer software

Computational details

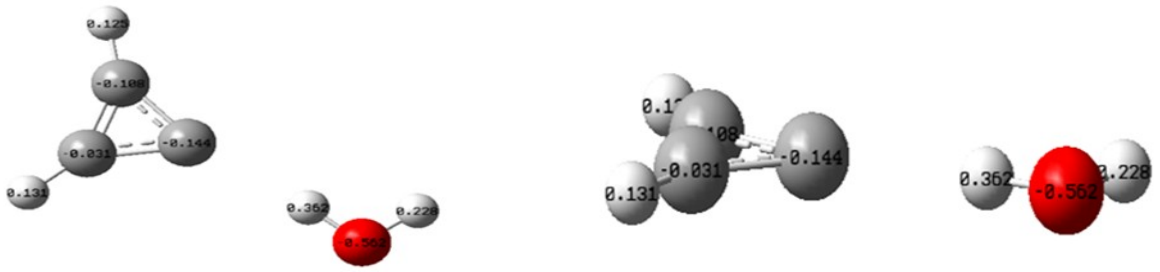
Initially, the geometry of cyclopropenylidene and its clusters as well as cluster with H2O molecules was generated using molecular modelling software Avogadro. Gas phase molecular calculations were carried out on these geometries. Subsequently, the geometry optimization of each structure was carried out using density functional theory (DFT). The compounds were optimized using the density functional theory incorporating the wB97xD exchange-correlation functional via Kohn-Sham self-consistent theory calculations employing the Gaussian 16 program.19 The 6-31+G** basis was used to represent the wavefunction on all atoms in the cyclopropenylidene clusters. Stationary point geometries of cyclopropenylidene structures thus obtained were characterized as local minima on potential energy surface from the frequencies of normal vibrations, all of which turn out all to be real. The fundamental vibration modes were assigned by visualizing displacements of nuclei around their equilibrium (mean) positions using the Avogadro program.

The harmonic vibrational frequencies at wB97xD/6-31+G** theory are scaled by value 0.9614 in order to account for unharmonic contributions. To understand electronic structure of these DFT simulations have been performed electrostatic nature of these compounds.

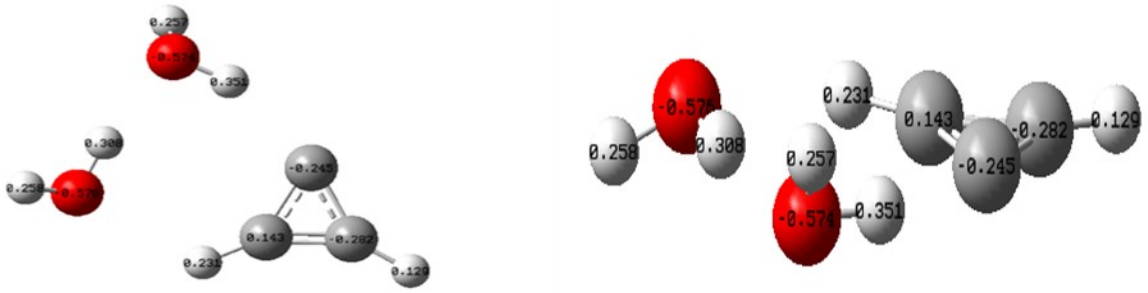
H2O



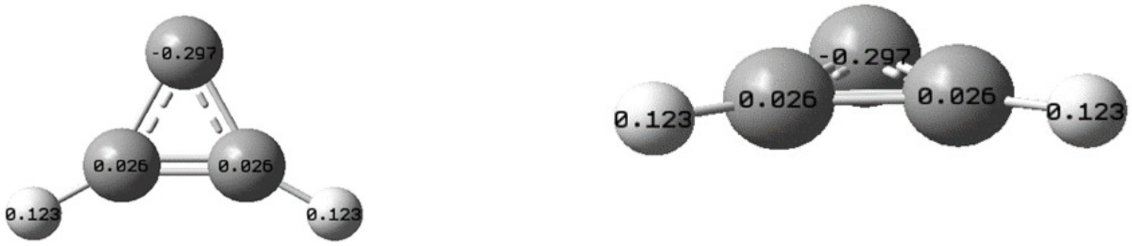
Cyclopropenylidene + H2O



Cyclopropenylidene +2H2O



Cyclopropenylidene



Dimer

Trimer

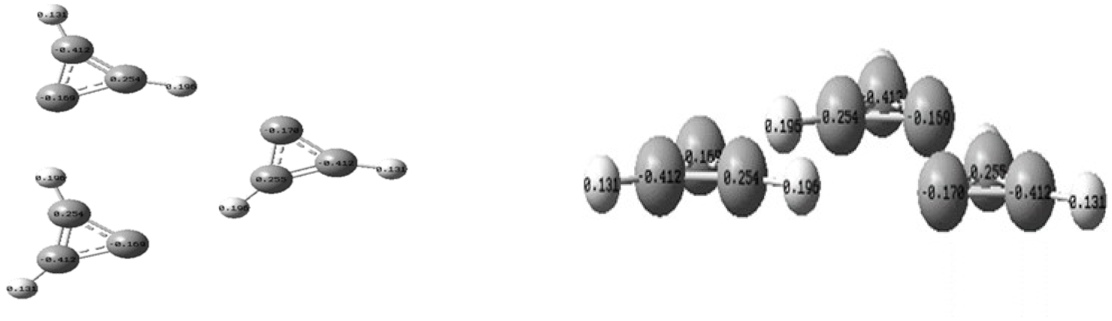


Figure 1: Planar and horizontal view of cyclopropenylidene and its clusters as well as cluster with H2O molecules

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