THEORETICAL INTERSTELLAR AND PREBIOTIC ORGANIC CHEMISTRY: A TENTATIVE METHODOLOGY

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Abstract. A theoretical methodology for the systematic study of the interstellar molecules is proposed.

Some examples, dealing with formaldehyde excited states, formyl radical and ion, reactivity of the excited states of formic acid, methyl cyanide and methyl acetylene, as well as the reaction path of formaldehyde photodecomposition are presented.

Quantum chemical methods appear to be a powerful tool to study the structure and behaviour of molecules related with interstellar space and the Origin of Life.

1. Introduction

Recently, an interesting experiment described by Khare and Sagan (1973) has initiated the field of Interstellar Organic Chemistry. The present study intends to follow the same line of thought from the theoretical standpoint.

The discovery of the first interstellar molecules by optical means took place during the 1937–49 period (Adams, 1948). In 1963 the OH radical was the first molecule identified by radio-astronomy (Weinreb *et al.,* 1963).

Actually, the list of identified structures is considerable (Buhl, 1973; Buhl, 1974; Snyder and Buhl, 1970; Solomon, 1973; Winnewisser *et al.,* 1974).

The most striking feature of interstellar molecules lies in the fact that some of them are very similar, if not identical, to the molecular structures found in prebiotic synthesis experiments. This similarity between two, apparently distant, experimental facts prove, without doubt, that Cosmochemistry and Prebiotic Chemistry should be considered as particular events of a number of elementary and, at the same time, general phenomena.

The physical conditions where this kind of chemical phenomena occur are most of them extremely adequate to permit a theoretical research, using the present powerful techniques of quantum Chemistry.

The theoretical study of the structure, properties, reactions, and interactions of interstellar and prebiotic molecules may be as interesting as a laboratory experiment and, in some aspects, may be more advantageous. Interstellar or prebiotic conditions (low gas densities and temperatures, for instance) are implicitly considered in calculations using the usual quantum chemical techniques, whereas a laboratory experiment, in order to be adequate to the required environment needs a reactor of galactic or planetary size (Khare and Sagan, 1973).

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Keeping these considerations in mind, a systematic and computationally coherent study of the most relevant interstellar molecules and related structures from a prebiotic point of view is being carried out in our laboratory.

The present paper is devoted to developing a methodological framework and to showing some practical results as a starting point and as an example of its application.

2. Outline of the Methodological Framework

We approach the study of interstellar molecules from a theoretical point of view through a set of four well defined steps:

(a) Wavefunction calculation of ground and first excited states, positive ions, radical fragments, ..., for each molecular structure.

(b) Evaluation of changes made in molecular parameters upon excitation and ionization (molecular geometry, charge density, dipole moment, ...).

(c) Study of the interaction between different molecular species.

(d) Study of photodecomposition and recombination reactions related to interstellar and prebiotic molecular structures.

In order to find examples of the above mentioned computational paths, we sketch below step (a); Section 3 contains an example of step (b); Sections 4 and 5 are devoted to the study of some cases of step (c); finally, Section 6 shows an analysis of formaldehyde photolysis, a typical problem associated with step (d).

In a first stage of this work, some relevant molecular wavefunctions have been calculated through SCF theory, following a generalized computational framework to solve Hartree-Fock equations, proposed by some of us (Caballol et al., 1974; Carbó et al., 1975). In order to open the way to more exact calculations, which are actually in a computational stage, the Fock matrices have been constructed in the INDO approximation level (Pople and Beveridge, 1970), using a STO-4G basis set of gaussian atomic orbitals (Steward, 1970). Molecular electrostatic potentials and interactions (Bonaccorsi et al., 1970) have been calculated, using a simple scheme also proposed by some of the authors of the present paper (Caballol et al., 1974; Caballol et al., 1974; Bertrán et al., 1975; Carbó and Martín, 1975).

In this manner the results we will present here have a formal coherence, which is not to be found in some isolated calculations, already made on this kind of molecules by various authors and in other contexts.

3. Molecular Properties

As a typical sample calculation, and owing to the fact that we will use, in the next sections some information presented here, in Table I are shown the results obtained for some molecular properties of the formaldehyde molecule. Ground (S_0), first excited singlet (S_1), and first triplet (T_1) states are studied as well as HCO and HCO^+. Geometries have been obtained from Herzberg (1966) and Kirby and Miller (1971) or have been optimized, as in the HCO and HCO^+ cases. The information in Table I gives first total energies, which permit one to evaluate the energetic gap between each pair of structures (for example: $T_1 - S_0$: 2.11 eV; $S_1 - S_0$:

2.40 eV; $S_1 - T_1$: 0.20 eV), which do not correspond to vertical transitions, due to the conformational changes used when calculations were performed. E(HOMO) and E(LUMO) provide information about the molecular orbital energies of the highest occupied and lowest unoccupied orbitals respectively, which in ground singlet states may be related to ionization potential and electron affinities. A third section for each structure and state shows the valence atomic orbital charges, ($S = 1s$ or $2s$; $X = 2p_x$; $Y = 2p_y$; $Z = 2p_z$) for each atom. The total charge on each atom is the sum of orbital charges, the effective charge corresponds to the excess (<0) or defect (>0) of electrons at the molecular centers. The dipole moments have been calculated by means of a point charge approach.

A rough inspection of Table I gives information about the electronic changes in the H_2CO molecule upon excitation. The most conspicuous phenomenon can be clearly seen when one examines the effective charges: electronic excitation produces a charge migration from the oxygen to the carbon atom, in good agreement with experimental evidence (Turro et al., 1972). This charge migration effect is well known and is a characteristic feature of carbonyl group photochemistry; for more details see Caballol et al., (1975).

The consequences of this charge redistribution in the chemical reactivity of formaldehyde excited states fall into a broad category of effects and will be studied in Section 5.

4. Electrostatic Molecular Potentials of Some Interstellar Molecules

Figure 1 represents some planes of the electrostatic molecular potentials of a sample formed by three well known interstellar molecules: formic acid, methylcyanide, and methylacetylene. For each molecular structure three states have been studied: ground state (S_0), first excited triplet (T_1), and singlet (S_1). The curves in the diagram correspond to equipotential lines whose energy is expressed in Kcal/mol. Each point represents the electrostatic interaction energy between the molecule and a point positive charge located at the same site.

The potential minimum for the formic acid ground state is found to be in the neighbourhood of the carbonyl group in the direction of the oxygen lone pairs. Geometry optimization performed on the excited states shows that the HC=O plane is not coplanar with the C—OH plane. This situation and the electronic redistribution due to the excitation, causes a transference of the potential well to a plane located at 3 a.u. above the C—OH plane, near the carbonyl oxygen. In the same manner, in T_1 and S_1, the oxygen in the hydroxyl group shows a deeper potential well compared with that of S_0. The stability and geometry of the $H^+...HCOOH$ complex will be completely different in the electronic molecular excited states.

Methylcyanide presents less pronounced changes because excitation has been calculated keeping ground state geometry. However, in the S_0 state the activated complex will be collinear with the C≡N bond, whereas in both excited states it will be triangular shaped with the cyano group forming one of the triangle sides. The ground state complex, as in formic acid, will be more stable than in excited states.

TABLE I

1. FORMALDEHYDE MOLECULAR PROPERTIES

(a) *Ground state*

(a1) Coordinates (a.u.)

Atom	x	y	z
H_1	1.7933879	0.0	−1.1097769
H_2	−1.7933879	0.0	−1.1097769
C	0.0	0.0	0.0
O	0.0	0.0	2.2825

(a2) Total Energy: −700.30535 eV
E(HOMO):   13.7 eV
E(LUMO):   −4.41 eV

(a3) Charges

Atom	s	x	y	z	Total	Effective
H_1 and H_2	1.05368				1.05368	−0.05368
C	1.09178	0.89943	0.80331	0.86560	3.66012	0.33988
O	1.76201	1.89891	1.19669	1.37491	6.23252	−0.23252

(a4) Dipole Moment: 1.05D

(b) *First triplet*

(b1) Coordinates (a.u.)

Atom	x	y	z
H_1	1.7797016	0.0	−1.0483243
H_2	−1.7797016	0.0	−1.0483343
C	0.0	0.0	0.0
O	0.0	1.4199375	2.0278810

(b2) Total Energy: −698.19040 eV

E(HOMO):   5.57 eV
E(LUMO):   −10.6 eV

(b3) Charges

Atom	s	x	y	z	Total	Effective
H_1 and H_2	0.97803				0.97803	0.02197
C	1.15888	0.92918	1.00878	0.85827	3.95509	0.04491
O	1.80421	1.05041	1.67818	1.55604	6.08884	−0.08884

(b4) Dipole moment: 0.66D

(c) *First Excited Singlet*

(c1) Coordinates (a.u.)

Atom	x	y	z
H_1	1.7797016	0.0	−1.0483243
H_2	−1.7797016	0.0	−1.0483243
C	0.0	0.0	0.0
O	0.0	1.2876737	2.1430489

(c2) Total Energy: -697.90470 eV

E(HOMO):	5.61 eV	
E(LUMO):	-3.35 eV	

(c3) Charges

Atom	s	x	y	z	Total	Effective
H_1 and H_2	0.97910				0.97910	0.02090
C	1.14391	0.93153	1.00648	0.84728	3.92919	0.07081
O	1.80929	1.03986	1.73902	1.52444	6.11261	-0.11261

(c4) Dipole moment: 0.81D

2. HCO FRAGMENT MOLECULAR PROPERTIES

(a) *HCO (Ground Doublet)*

(a1) Coordinates (a.u.)

Atom	x	y	z
H	-1.615581	-1.355624	0.
C	0.	0.	0.
O	2.2825	0.	0.

(a2) Total Energy: -674.88394 eV

E(HOMO):	5.38 eV	
E(LUMO):	-0.011 eV	

(a3) Charges

Atom	s	x	y	z	Total	Effective
H	0.99758				0.99758	0.00242
C	1.32744	0.86305	1.03021	0.64205	3.86092	0.13988
O	1.76267	1.40721	1.61183	1.35979	6.14151	-0.14151

(a4) Dipole Moment: 0.83D

(b) HCO^+ *(Ground Singlet)*

(b1) Coordinates (a.u.)

Atom	x	y	z
H	-2.10899	0.0	0.0
C	0.0	0.0	0.0
O	2.1825	0.0	0.0

(b2) Total Energy: -665.05930 eV

E(HOMO):	3.21 eV	
E(LUMO):	8.66 eV	

(b3) Charges

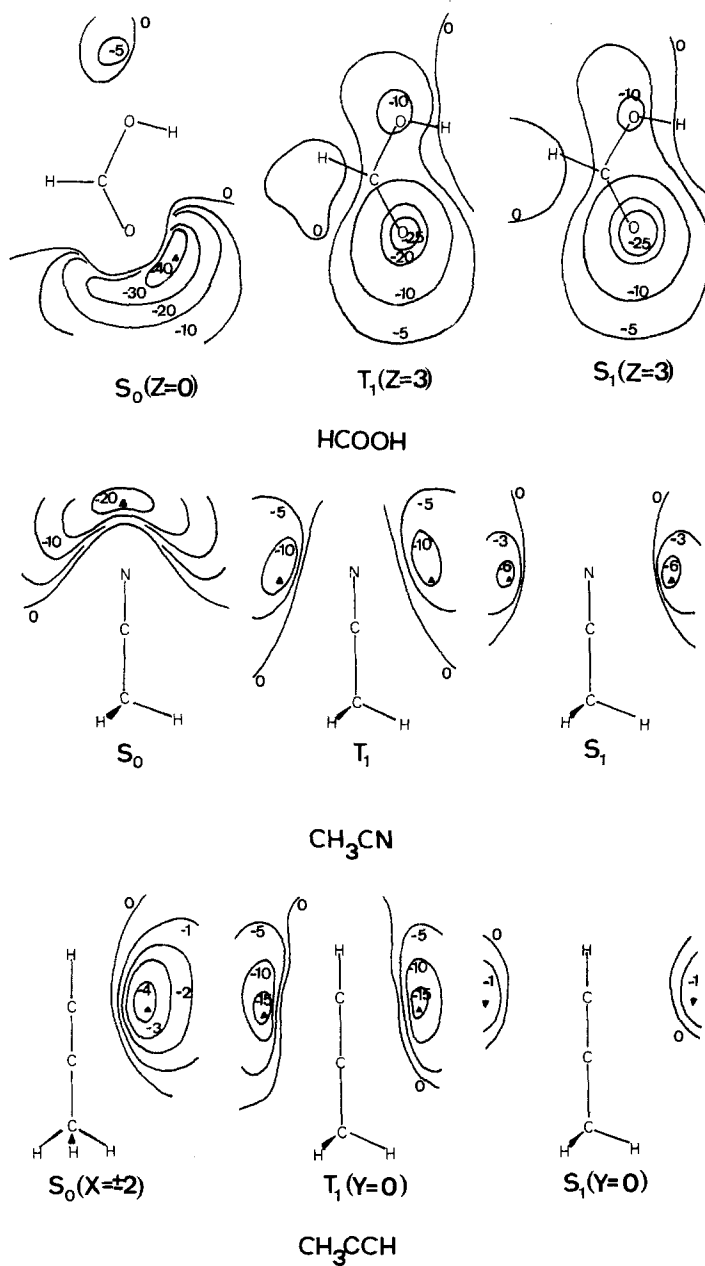| Atom	s	x	$y = z$	Total	Effective
H	0.77207			0.77207	0.22793
C	1.20928	0.88150	0.64751	3.39381	0.60619
O	1.76056	1.36859	1.35249	5.83412	0.16588

Fig. 1.   Electrostatic molecular potentials of three interstellar molecules. Isoenergetic curves in Kcal/mol.

Methylacetylene presents its own characteristics, among them the fact that, for a vertical transition, the stability ordering of the activated complexes will be $T_1 > S_0 \gg S_1$. The excited singlet state will behave, practically, in a repulsive manner toward a proton attack. Protonation will be favoured in the excited triplet; the ground state will have a small proton affinity as, in general, have hydrocarbons.

It is not difficult to see methylacetylene chemistry as a highly favoured triplet state chemistry.

5. Formaldehyde Electrostatic Interactions

Figure 2 shows three representative interactions chosen from among those which we have studied for formaldehyde. In order to study the changes produced by the excitation on the possible dimer formation, the interaction of two formaldehyde molecules is analyzed. In the figure, one of the molecules is supposed to be in the S_0 ground state, and the interactions $S_0 - S_0$, $T_1 - S_0$ and $S_1 - S_0$ are presented. Both molecules were arranged with the two CO bonds in opposite directions, the S_0 molecule having been placed with his own CO bond parallel to the axis which bisects the methylene group of the second molecule. This last axis has been chosen as rotational axis. The rotation angle $\gamma = 0$ corresponds to the position where the planes of both methylene groups are parallel (see in Figure 2 the diagrams for $S_0 - S_0$ and $S_1 - S_0$ interactions). The value $\gamma = 90$ corresponds to a situation with the methylene planes perpendicular (see the $T_1 - S_0$ interaction diagram of Figure 2). When $\gamma = 0$, both methylene planes are located at a distance of 6 a.u. For each interaction, three relative positions named E_1, E_2 and E_3 have been chosen, which are related to the alignment of both carbon atoms (E_2) or a translation along the rotation axis of the second molecule of 2.5 a.u. to the left (E_1) and to the right (E_3). The main reason for these displacements lies in the interest of studying the coincidence of the two CH_2 groups (E_1) or the two oxygen atoms (E_3).

The energy variation is shown in Kcal/mol. Results show that the most stable dimer in the $S_0 - S_0$ interaction corresponds to $\gamma = 90$, with a relative stability fairly superior to the $S_1 - S_0$ or $T_1 - S_0$ dimers. In this case the most stable position corresponds to E_2, and this result shows that hydrogen bond interaction between the two molecules is dominant.

This pattern varies completely when $T_1 - S_0$ or $S_1 - S_0$ interactions are studied. The principal new feature lies in the small interaction in the position E_1, due to the repulsive role of methylene groups. $T_1 - S_0$ gives stable minima at $\gamma = 0$, however the most stable situation is formed at $\gamma = 90$ and E_2; $S_1 - S_0$, on the other hand, gives E_3 and $\gamma = 0$ as the favoured molecular rearrangement. This result may be related to the possible formation of a cyclic dimer through an intermediate complex of this kind. In general, in the light of other results not shown here, it can be said that whereas the $S_0 - S_0$ interactions produce dimers with a great hydrogen bond contribution, cyclic formaldehyde dimers and polymer initiation may be produced in excited state interactions.

This result may be in agreement with a recent opinion (Wickramasinghe, 1974), which propounds that formaldehyde polymers may play an important role in the interstellar dust composition.
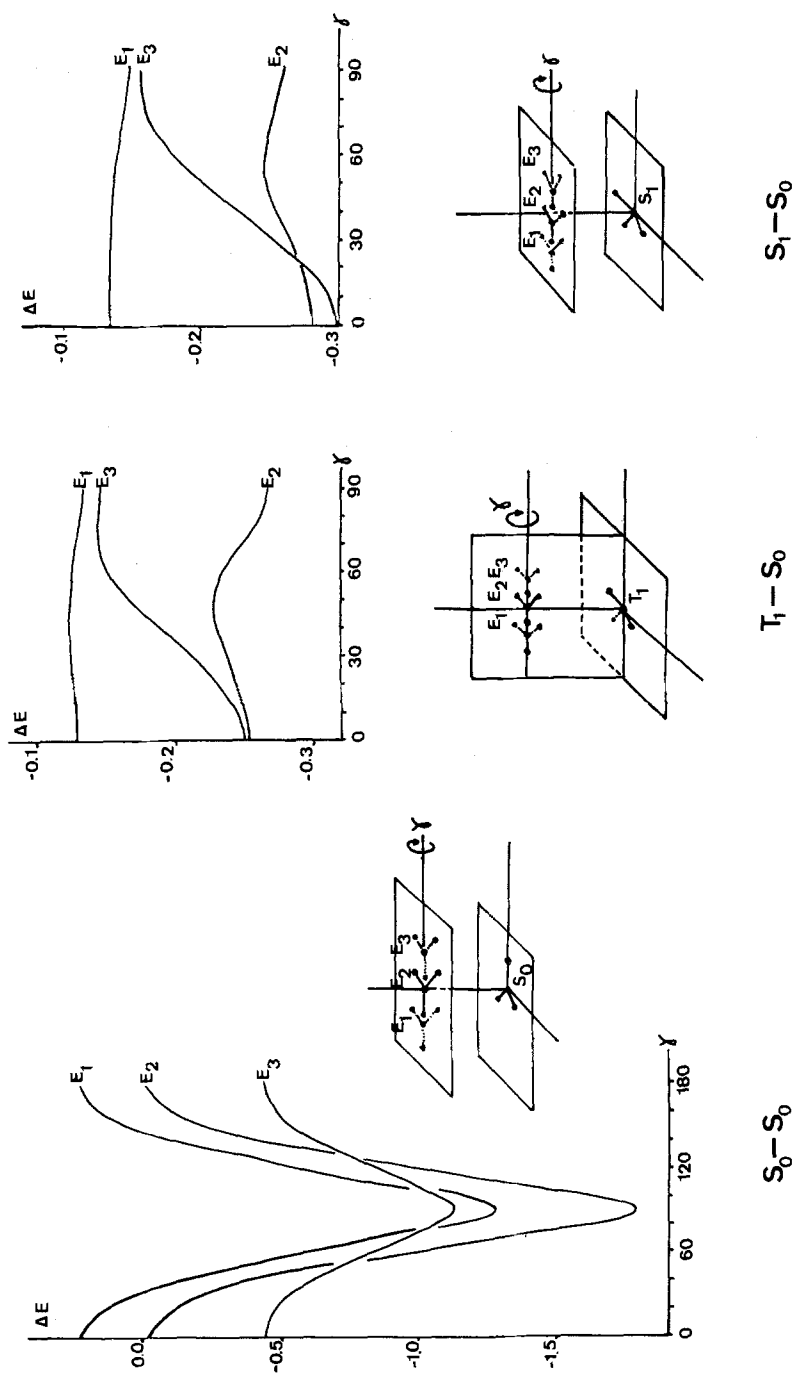
Fig. 2. Electrostatic interaction energy of two formaldehyde molecules in different excited states. Energies in Kcal/mol.

It is necessary to say, at this point that excited state interactions should only occur in interstellar cloud sites or planetary atmospheres, where molecular density and UV intensity are so well balanced as to make possible collisions in the short lifetime of excited states; in this kind of media such states can play a leading role.

6. Formaldehyde Photodecomposition

Photolysis of formaldehyde has an interesting position in interstellar and prebiotic chemistry as has been suggested by Khare and Sagan (1973) and by Dalgarno *et al.* (1973). The latter authors postulate that in diffuse interstellar clouds two photo-decomposition processes will be present:

$$H_2CO + h\nu \to H_2 + CO \tag{1}$$

$$H_2CO + h\nu \to H + HCO. \tag{2}$$

Both processes are competitive in the 3500-2500 Å region, the first being dominant at $\lambda > 3500$ Å, the second at $\lambda < 2500$ Å. Recently, Glicker and Stief (1971) pointed out that at $\lambda \sim 1400$ Å another decomposition will take place:

$$H_2CO + h\nu \to 2H + CO. \tag{3}$$

From an experimental point of view formaldehyde photochemistry has been widely studied by many authors, among whom one should mention Solomon *et al.* (1971) and Yeung and Moore (1973). On the theoretical side it is worth mentioning, among others, the work of Hayes and Morokuma (1972) and Jaffe *et al.* (1974). The theoretical analysis of these last references indicates that dissociation proceeds through the fundamental singlet, whereas a complete agreement is not found between experimentalists on a dissociative state S_0 or T_1. On the other hand, the α-breaking of ketone photochemistry may induce one to believe that dissociation occurs in a T_1 state (Turro *et al.*, 1972).

Figure 3 represents the energy evolution (in a.u.) calculated for the three processes above mentioned. In the first, and in accord with Morokuma's work, it is in the S_0 state where dissociation takes place. In both of the remaining cases the T_1 state is the leading one, in agreement with chemical intuition and the hypothesis of carbonyl group photochemistry. The energetic relationship calculated in all processes fits perfectly with experimental evidence: reaction (1) occurs in the lower energy zone, and (3) in the short wavelength regions.

Initial geometries used for the three reactions are the experimental ones, as shown in Table I; thus, energy differences in Figure 3 do not correspond to vertical transitions.

7. Conclusions

Although the analyzed examples cannot pretend to clarify any problem exhaustively, they are sufficiently representative in order to test the proposed methodological pathway and to show it can give a good deal of information on the structure, formation and evolution of interstellar and prebiotic molecules. It is, at present,
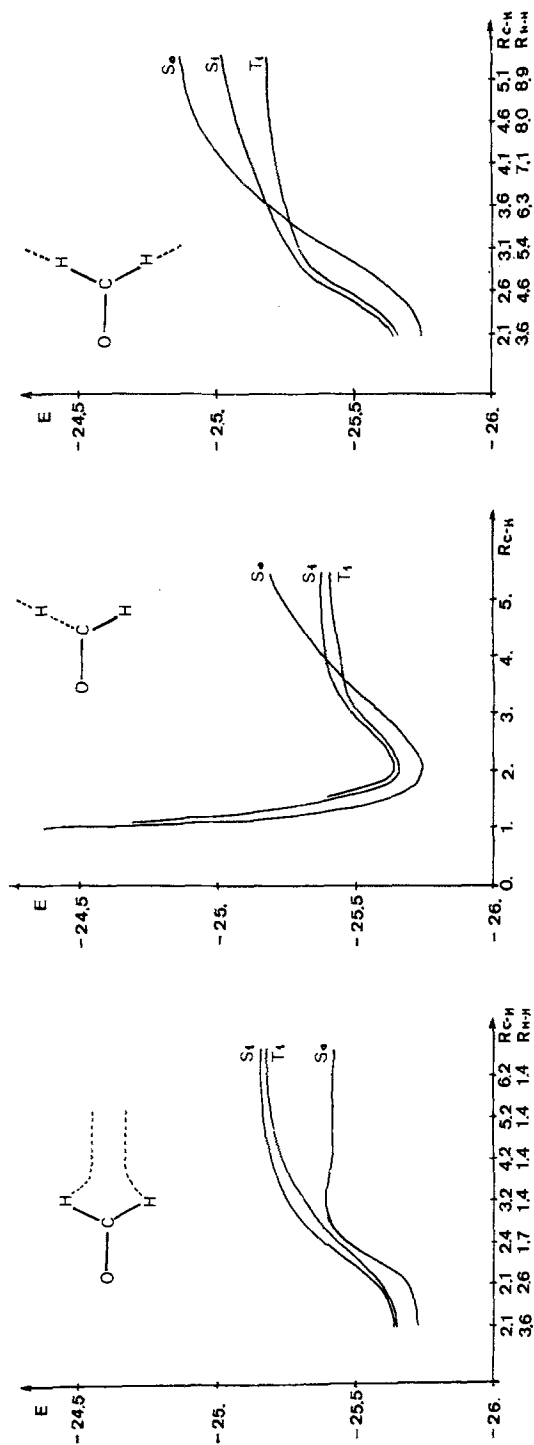
Fig. 3. Electronic energy (atomic units) versus carbon-hydrogen distances (atomic units) in the photo-chemical hydrogen abstraction of formaldehyde. See text for more details.

practically impossible to obtain in the laboratory some details which are given by theoretical computation; so quantum chemical calculations may be a considerable help toward knowing the nature of the reactions, the structure of new molecules, and the relationships between them.

A systematic and computationally coherent theoretical study of interstellar and prebiotic molecules may be a solid reference point for the future development of cosmic and prebiotic chemistry.

Acknowledgements

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