

LOOKING FOR MOLECULAR TITANIUM IN SPACE

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Abstract. This contribution looks at the possibility of astronomical detection of Titanium as part of molecular entities. The attention has been focused on the most stable species that can be formed with the [Ti,2C,2H] and [Ti,2C] sets of atoms. Density Functional Theory and post Hartree-Fock Coupled Cluster (CCSD) and multiconfigurational (CASSCF) ab initio calculations have been carried out. The lowest energy cyclic triplet states TiC₂ and TiC₂H₂ of C_{2v} symmetry, whose respective dipole moments of 3.3 and 11.3 Debye are large enough for radio detection, appear to be the best candidates.

1 Introduction

The hunt for new molecules is an increasingly difficult task as the number of molecules already identified in space covers the large majority of the important radio lines. It has become over the years a pluridisciplinary task relying on a complementary dialogue between astronomers, spectroscopists and quantum chemists.

Quantum Chemistry, indeed, is well adapted to Astrophysics as it refers for a large part to isolated systems and can be used to examine unstable species and chemical processes that are difficult, if not impossible, to study in the laboratory. It can support or even replace spectroscopy experiments

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by *a-priori* calculations of the spectral signatures without any restriction in the electronic spectrum (Radio, IR, Visible-UV). This ability can profitably be exploited for identification of a specific molecule in the laboratory, which has been generated in a mixture of transient species. The prediction of the spectral signatures of unknown molecules can also be an incentive for new observations or new experiments.

In this contribution we address the problem of finding new molecules containing metal atoms. Only a few of these species are known to exist, mainly in circumstellar environments. The metallic part is either an alkali metal (NaCl, NaCN, KCl) or an alkaline-earth metal (MgCN, MgNC) or Aluminium (AlF, AlNC, AlCl). An other class of organometallics is constituted of silicon containing molecules, the most important part of which is silicon carbides (SiC_n , $n=1-4$). Recently, laboratory experiments led to propose that Titanium carbide, TiC, could be the carrier of the enigmatic feature at $\sim 21\mu\text{m}$ in the infrared spectra of some protoplanetary nebulae (Von Helden et al. 2000). The spectrum reported in Figure 1 shows how promising the hypothesis is. These laboratory studies also have implications for models of dust nucleation. As in the laboratory, stable clusters of small dimensions may play an important role in the condensation of TiC dust in astrophysical settings (Cherchneff & Cau 1999). However, later studies suggested that there is not enough Titanium to form the TiC nanocrystals required to account for the observed intensities (Chigai et al. 2003, Li 2003).

On another hand, meteorites are known to contain micrometer sized graphite grains with embedded Titanium carbide cores which are believed to have served as heterogeneous centers for graphite grain condensation (Bernatowicz et al. 1996). Other interstellar grains with similar structures contain Silicon carbide cores.

More recently, Hony et al. (2003) proposed, that *“If TiC is the carrier of the $21\mu\text{m}$ feature, the TiC must be in grains or in polycrystalline domains smaller than a few hundred atoms”*. Then the question is: would it be possible to find the signatures of ancestors of these Ti-containing cores as small entities still accessible to radioastronomy?

When looking for the smallest possible clusters with Titanium, it is reasonable, by analogy with what is known for carbon and silicon molecules, to consider molecules with, as well as without, hydrogen atoms. The comparison of the three atoms, C, Si, Ti, is illustrated in Table 1.

The analogy and differences between these atoms relies on the structures of their valence shells. They all have 4 valence electrons and give the same

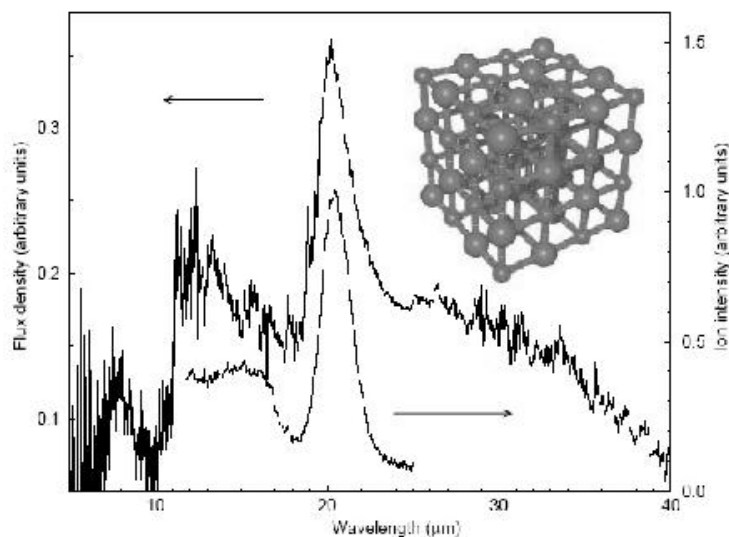


Fig. 1. The emission spectrum from the post-AGB object SAO 96709, taken by the ISO satellite (upper trace, left axis) and the wavelength spectrum of TiC nanocrystals recorded in the laboratory (lower trace, right axis). Embedded is the representation of a TiC nanocrystal. (Figure taken from Von Helden et al. 2000)

Table 1. Analogy between Carbon, Silicon and Titanium.

	C	Si	Ti
Dominant configurations	...2s ² 2p ²	...3s ² 3p ²	...4s ² 2d ²
Oxides	CO	SiO	TiO
Dioxides	CO ₂	SiO ₂	TiO ₂
Carbides	CC	SiC	TiC
Smallest stable systems	C ₃ H ₂	SiC ₂	TiC ₂ H ₂ ; TiC ₂

type of oxides and carbides. The difference is coming from the role played by d orbitals. For Carbon, they are high in energy, for Silicon, they are close to the valence shell and for Ti, they are the valence orbitals. The fact that Ti has a ...4s²2d² dominant configuration has the consequence to

favour high spin over low spin when electrons are not engaged in chemical bonds. Therefore, singlet as well as triplet states have to be considered.

2 Computational Methods

2.1 *Electronic Calculations*

The electronic calculations were performed by means of Density Functional Theory (DFT) and post-Hartree-Fock methods (Coupled Cluster CCSD and CASSCF) when necessary. The hybrid DFT/B3LYP method, associated with the 6-311G(d,p) basis set of triple-zeta quality with a set of polarization functions added on Titanium, Carbon and Hydrogen, was first employed because of its reliability and accuracy in the determination of molecular geometries (Cheikh & Pauzat 2001). In the case when a single determinant representation was not appropriate, CASSCF calculations were performed. Whatever the method used, all geometries were confirmed by vibrational analysis. All the calculations were performed using the methods and basis sets as implemented in the GAUSSIAN package.

2.2 *Rotational Constants Calculations*

Prediction of rotational constants with enough accuracy to make it possible to identify an unknown molecule with certainty is at the very limits of present computational chemistry. The major difficulty comes from the fact that the calculations are made within the rigid rotor approximation, thus leading to constants A_e , B_e and C_e at the equilibrium geometry, whereas the quantities needed to reproduce the radio signatures (Townes & Schawlow, 1975) are constants A_0 , B_0 and C_0 (taking into account the motion of the nuclei). This problem, however, is not without solutions.

It has been shown that the raw values given by quantum chemistry calculations, whose accuracy is on the order of $\sim 1\%$ can be corrected so as to obtain the $\sim 0.3\%$ precision that is generally considered as the upper limit required for a possible identification. All the calibration procedures rely on some combination of the calculated values with experimental data on well-known related compounds.

Different approaches are used according to whether the target molecule is the next member in a n -series or unique molecule (for more details see Dimur et al. 2001). In the latter case which is the one of interest here, the

calibration procedure is applied to the rotational constants themselves since the laboratory spectra of isovalent systems of comparable structures have already been determined. The conjecture is that, at a given level of theory, the ratio Q_{Theory}/Q_{Exp} , where Q may be any of the constants A , B or C , can be transferred between closely related species. This ratio is determined for a reference species and then applied to the target molecule.

3 Results and Discussion

3.1 The $[Ti,2C,2H]$ candidate

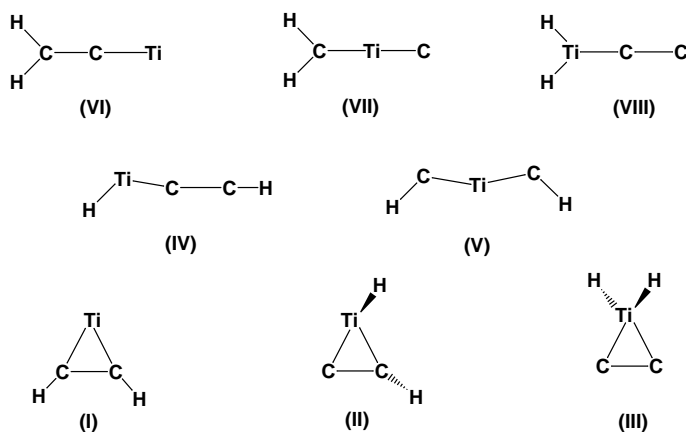


Fig. 2. The structures of TiC_2H_2 investigated

All the possible structures involving linear and cyclic arrangements displayed on Figure 2 have been optimized in the singlet and triplet spin states. A vibrational analysis has been carried out for each structure to verify that the stationary point found was effectively a minimum on the surface. The results of interest to the hunt for molecules are presented in Table 2 at the DFT/B3LYP level of theory.

The lowest energy structure is (I), a cyclic compound of C_{2v} symmetry. Contrary to cyclopropylidne C_3H_2 which is a singlet state (1A_1), TiC_2H_2 is a triplet ground state 3A_2 . This result is obtained for DFT calculations using B3LYP or BH&HLYP functionals, as well as for post-Hartree-Fock

Table 2. The lowest electronic state of TiC_2H_2 .

Structure	State	Relative Energy kcal/mol	A GHz	B GHz	C GHz	μ Debye
VI	$^1\text{A}_1$	35.6	292.640	4.0494	3.9941	4.05
IV	$^3\text{A}''$	10.6	292.577	3.6013	3.5575	3.41
I	$^3\text{A}_2$	0.0	34.485	8.0988	6.5585	3.27

Coupled Cluster (CCSD) calculations. The next isomer, ~ 11 kcal/mol higher on the energy scale (IV) is also a triplet state $^3\text{A}''$ with the Titanium atom inserted in the CH bond of an acetylene molecule. The first singlet state is found in third position at ~ 36 kcal/mol above the ground state. It is a ketene like molecule (VI) with Titanium at the extremity.

The calibration of the rotational constants is done at the DFT/B3LYP level of theory. For the reference molecule C_3H_2 , the calculated raw values are (GHz):

$$A_{\text{C}_3\text{H}_2}^{\text{Theo}} = 34.925 \quad B_{\text{C}_3\text{H}_2}^{\text{Theo}} = 32.330 \quad C_{\text{C}_3\text{H}_2}^{\text{Theo}} = 16.789$$

to be compared with the observed values (GHz):

$$A_{\text{C}_3\text{H}_2}^{\text{Obs}} = 35.093 \quad B_{\text{C}_3\text{H}_2}^{\text{Obs}} = 32.296 \quad C_{\text{C}_3\text{H}_2}^{\text{Obs}} = 16.746$$

It can be seen that the theoretical values are within $\sim 0.1 - 0.4\%$ of the experiment. Transferring the experimental to calculated ratio of the rotational constants of C_3H_2 to TiC_2H_2 one obtains a best estimate of (GHz):

$$A_{\text{TiC}_2\text{H}_2}^{\text{Estim}} = 34.318 \quad B_{\text{TiC}_2\text{H}_2}^{\text{Estim}} = 8.106 \quad C_{\text{TiC}_2\text{H}_2}^{\text{Estim}} = 6.571$$

that should be, in the average, within $\sim 0.3\%$ of the real values.

3.2 The $[\text{Ti}, 2\text{C}]$ candidate

The number of possibilities is limited here to an open chain structure, bent or linear, with the Titanium atom in between the two Carbons or at an extremity (CTiC or TiCC); the other possible structure is a triangular molecule. The energetical preference between linear and cyclic geometries is a well debated subject, and only the most sophisticated method can handle this type of questions. The closely related SiC_2 system is one of these examples. Comparison between the electronic spectra observed in carbon stars with laboratory experiments on C_2 suggested a linear structure, SiCC, but theoretical considerations were in favour of a triangular geometry. High

level post Hartee-Fock treatments were necessary (Grev & Schaefer 1984) to determine that the cyclic structure was effectively lower in energy (~ 5 kcal/mol) and that the linear structure did not present the spectroscopic constants corresponding to those observed (Pauzat & Ellinger 1984). Another carbide, CaC_2 , was also found as a cyclic structure (Redondo et al. 1991).

All DFT calculations using B3LYP, BH&HLYP and PW91 functionals show that the cyclic structure is lower in energy than any linear or slightly bent one. As shown previously, the Titanium containing compound TiC_2 is a triplet state, contrary to the Silicon analogue SiC_2 . However, the DFT calculation give a L-shape triangle with two different TiC bonds (TiC=2.18; 2.32 Å; CC=1.25 Å), slightly more stable than the isocle triangle (TiC=1.97 Å; CC=1.27 Å). Post Hartee-Fock Coupled Cluster treatments (CCSD) essentially yield a flat potential. It has taken a CASSCF treatment with 6 electrons distributed among the six most active orbitals to obtain the result that TiC_2 is a $^3\text{B}_1$ isocle triangle (TiC= 2.11 Å; CC= 1.27 Å). Although the symmetric structure is that of lowest energy, the energy difference with the L-shape is so small that very large amplitude motions are anticipated.

The calibration procedure is done here taking the results of an equivalent CASSCF calculation on SiC_2 as reference and the experimental values of Michalopoulos et al. 1984. The estimated rotational constants thus obtained are (GHz):

$$A_{\text{TiC}_2}^{\text{Estim}} = 51.83 \quad B_{\text{TiC}_2}^{\text{Estim}} = 8.061 \quad C_{\text{TiC}_2}^{\text{Estim}} = 6.919$$

Because of the “fluxional” character of the molecule, the above values are determined within a few percent, i.e. an order of magnitude less than for TiC_2H_2 . In all cases, with a dipole moment $\mu=11.3$ Debye, this small molecule appears as a good candidate for radio detection.

4 Conclusion

Small organometallic molecules including Titanium have been considered in order to provide useful information for their search in space. It has been shown that TiC_2H_2 ($^3\text{A}_2$) and TiC_2 ($^3\text{B}_1$) are the most stable systems that can be formed from the corresponding set of atoms. They are the Titanium analogues of ubiquitous C_3H_2 and SiC_2 , however singlet states. Precise rotational constants have been determined for TiC_2H_2 whose dipole moment of ~ 3.3 Debye makes it a reasonable candidate. Besides, TiC_2 with

a dipole moment $\mu \sim 11$ Debye appears more appealing for radiodetection. However it is a fluxional molecule whose ro-vibrational treatment remains to be done more precisely to obtain quantitative values.

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