

# A SUGGESTION FOR A SEARCH OF THE CYCLIC MOLECULE $c\text{-C}_7\text{H}_2$ IN COOL COSMIC OBJECTS

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Cyclic molecules of the general series  $c\text{-C}_n\text{H}_2$  ( $n$  odd), where three of the carbon atoms form a triangle, have been supposed to be important species in cool cosmic objects. Here, we investigate the particular case of  $n = 7$ , *i.e.*  $c\text{-C}_7\text{H}_2$ , with the aim to obtain information about the rotational transitions by which the molecule could be identified in cool interstellar environments. Since this molecular species, to our knowledge, has not yet been fully studied experimentally we obtained the necessary structural parameters using a density functional theoretical approach employing the gradient corrected exchange-correlation functional B3LYP in conjunction with the extended cc-pVTZ basis set. The electronic structure calculations showed that  $c\text{-C}_7\text{H}_2$  has at least nine stable isomers, the two lowest of which being energetically equal. The first one has  $C_{2v}$  and the other  $C_s$  symmetry. Of these two structures we suggest the symmetric one for a search in cool cosmic objects. At the chosen level of electronic structure theory we obtained the rotational constants  $A = 7852.8326$  MHz,  $B = 1565.0617$  MHz,  $C = 1304.9804$  MHz, and the electric dipole moment  $\mu = 3.853$  D. Though distortional effects might be significant they would not have a great influence on the qualitative behaviour of our investigation. We conclude that this molecule could be identified in cool interstellar environments by some of its rotational transitions  $4_{23} \rightarrow 5_{14}$ ,  $3_{22} \rightarrow 3_{13}$ ,  $1_{11} \rightarrow 2_{02}$ , and  $3_{21} \rightarrow 4_{14}$  at 3.0, 6.5, 0.5, and 9.1 GHz, respectively, in absorption against the CMB.

*Key words:* interstellar molecules, rotational transitions.

## 1. INTRODUCTION

To search for a certain molecule in interstellar space, at least the frequencies of the relevant rotational transitions are needed. It is very helpful to perform in addition NLTE radiative transfer calculations, from which follow the relative occupation numbers and the relative strengths of the different spectral

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lines in dependence of the physical conditions. For such calculations one needs to know the rotational energy level diagram, which can be obtained from the molecular constants, the Einstein  $A$ -coefficients, and the collisional rate coefficients. These molecular data can in principle either be measured in the laboratory or calculated theoretically.

The presence of cyclic molecules of the general composition  $c\text{-C}_n\text{H}_2$  ( $n$  odd), where three of the carbon atoms form a triangle, in cool cosmic objects has been widely discussed. The rotational transition  $2_{20} \rightarrow 2_{11}$  of  $c\text{-C}_3\text{H}_2$  has been found in absorption against the cosmic microwave background (CMB) in all observed objects [1, 2], except for the Planetary Nebula NGC 7027 where Cox *et al.* [3] found this transition in emission. For  $c\text{-C}_5\text{H}_2$  an upper limit on the column density was found in TMC-1 in emission by Dickens *et al.* [4]. Their investigation bore upon the unsymmetric  $C_s$  configuration of  $c\text{-C}_5\text{H}_2$  which in this case is the ground state and is shown in Fig. 1.  $c\text{-C}_5\text{H}_2$  was detected by Travers *et al.* [5] in the laboratory who determined the rotational constants, the distortional constants, and the dipole moment. From these data Chandra and Shinde [6] calculated the rotational energy levels belonging to the electronic and vibrational ground state and the Einstein  $A$ -coefficients. In addition, they estimated collisional rate coefficients. Based on NLTE radiative transfer calculations they predicted that the  $3_{13} \rightarrow 4_{04}$  transition at 4.314 GHz should show up in anomalous absorption against the CMB. The next larger probable candidate in this series is  $c\text{-C}_7\text{H}_2$ .

It has at least nine isomers [7] and the two energetically most stable ones are shown in Fig. 1. The unsymmetric ( $C_s$ ) isomer 1 has been observed in the laboratory by McCarthy *et al.* [8]. Based on their molecular data, Chandra *et al.* [9] carried out calculations similar to those for  $c\text{-C}_5\text{H}_2$ . They found that four transitions,  $4_{14} \rightarrow 5_{05}$ ,  $5_{15} \rightarrow 6_{06}$ ,  $6_{16} \rightarrow 7_{07}$  and  $7_{17} \rightarrow 8_{08}$  at 23.241, 21.105, 18.953 and 16.787 GHz, respectively, should show up in cool cosmic objects in absorption against the CMB.

For the symmetric ( $C_{2v}$ ) isomer 2 of comparable energy, which is the subject of the present investigation, to our knowledge no laboratory data are available in the literature. We therefore determined the molecular constants using a density functional theoretical approach. With these data we calculated the rotational energy levels of the electronic and vibrational ground state and the values of the Einstein  $A$ -coefficients. Using rough estimates (see Sec. 2.3.) of the collisional rate coefficients we then performed NLTE radiative transfer calculations. The results of these calculations indicate that four rotational transitions  $4_{23} \rightarrow 5_{14}$ ,  $3_{22} \rightarrow 4_{13}$ ,  $1_{11} \rightarrow 2_{20}$ , and  $3_{21} \rightarrow 4_{11}$  at 3.0, 6.5, 0.5, and 9.1 GHz, respectively, are expected to show up in anomalous absorption

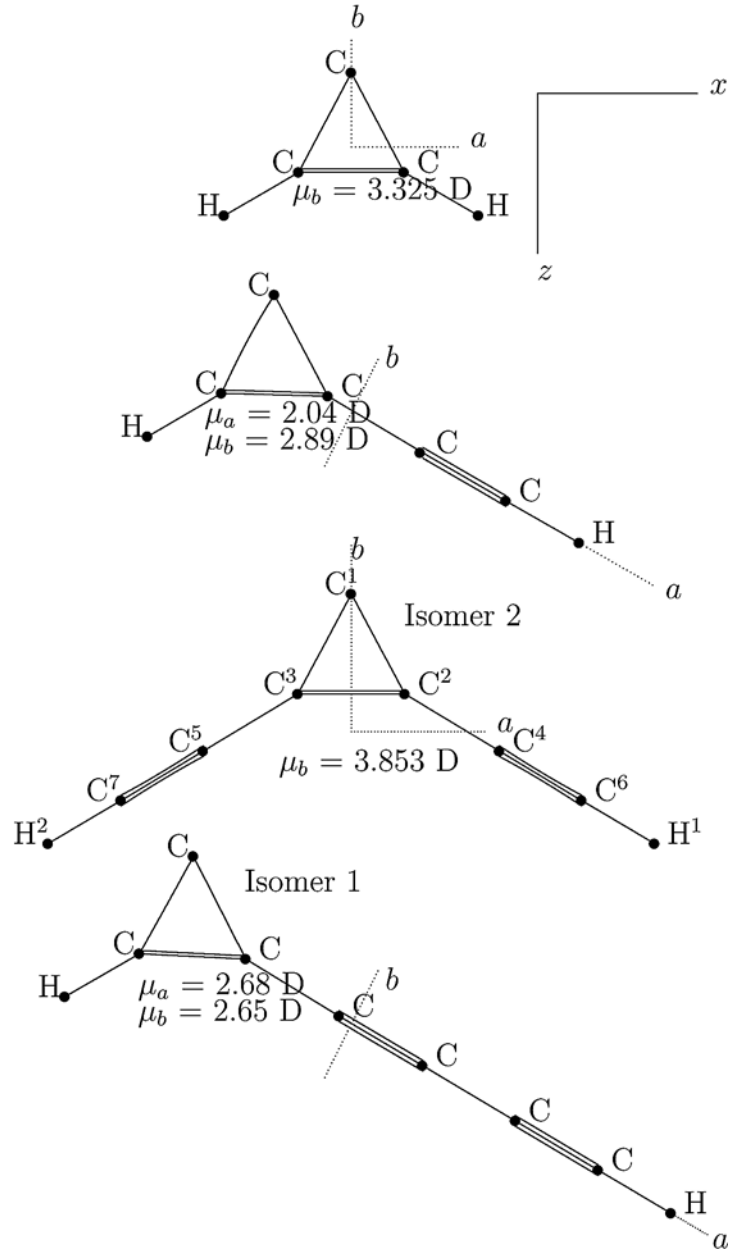


Fig. 1 – Structures of cyclic  $c\text{-C}_n\text{H}_2$  ( $n = 3, 5, 7$ ) molecules along with their electric dipole moment. The two isomers (isomer 1 –  $C_s$ , isomer 2 –  $C_{2v}$ ) of  $c\text{-C}_7\text{H}_2$  possess almost equal energy.

against the CMB and might be useful for the identification of  $c\text{-C}_7\text{H}_2$  ( $C_{2v}$ ) in cool cosmic objects.

## 2. MOLECULAR DATA

### 2.1. STRUCTURE OF THE MOLECULE AND ROTATIONAL CONSTANTS

Our electronic structure calculations for the two isomers of  $c\text{-C}_7\text{H}_2$  were based on a density functional theoretical approach employing the gradient corrected exchange-correlation functional B3LYP [10, 11] in conjunction with the extended correlation consistent cc-pVTZ basis set [12, 13]. The accuracy of this level of theory has been tested on numerous molecules [14]. Thereupon the geometry of the molecule was fully optimised. A subsequent frequency analysis within the harmonic oscillator approximation showed that the eigenvalues of the Hessian matrix are all positive indicating that this structure represents a true local minimum on the ground state potential energy surface. The coordinates of this optimised geometric configuration of the molecule (isomer 2- $C_{2v}$ ) are given in Table 1. In order to distinguish between various identical atoms, a superscript has been attached. Considering this structure as rigid, we calculated the

Table 1

Coordinates of atoms of  $c\text{-C}_7\text{H}_2$  (isomer 2 –  $C_{2v}$ )

	$x$ [Å]	$y$ [Å]	$z$ [Å]
C <sup>1</sup>	0.000000	0.000000	-1.727175
C <sup>2</sup>	0.671246	0.000000	-0.474661
C <sup>3</sup>	-0.671246	0.000000	-0.474661
C <sup>4</sup>	1.858215	0.000000	0.241012
C <sup>5</sup>	-1.858215	0.000000	0.241012
C <sup>6</sup>	2.890678	0.000000	0.858719
C <sup>7</sup>	-2.890678	0.000000	0.858719
H <sup>1</sup>	3.805201	0.000000	1.398367
H <sup>2</sup>	-3.805201	0.000000	1.398367

Table 2

Molecular constants of both  $c\text{-C}_7\text{H}_2$  isomers

	Isomer 2	Isomer 1	
	B3LYP cc-pVTZ	B3LYP cc-pVTZ	Laboratory
A [MHz]	7852.8326	35385.3517	34722.136
B [MHz]	1565.0617	1052.1565	1045.20523
C [MHz]	1304.9804	1021.7748	1014.25700
$\Delta_J$			$17.2 \times 10^{-6}$
$\Delta_{JK}$			$7.06 \times 10^{-3}$

rotational constants given in Table 2. In order to estimate the errors introduced by the rigid rotator approximation, we performed similar calculations for isomer 1 of  $c\text{-C}_7\text{H}_2$ , for which laboratory data are available [8]. Calculated and measured molecular constants are also listed in Table 2. For these two sets of data of isomer 1, we find that most of the frequencies differ less than 2%. Due to its higher symmetry, isomer 2 should be more rigid than isomer 1 and, consequently, the uncertainties should be smaller.

## 2.2. ROTATIONAL ENERGY LEVELS AND EINSTEIN A-COEFFICIENTS

In absence of information about the distortional constants, we calculated the rotational energy levels in the rigid rotor approximation up to  $15\text{ cm}^{-1}$  and the rotational quantum number  $J = 11$ . There are 60 levels for each of the ortho and para species of isomer 2. The rotational energy levels are given in Table 2.

Since in case of isomer 2, the electric dipole moment lies along the axis of intermediate moment of inertia, it is a  $b$ -type asymmetric top molecule. The Einstein  $A$ -coefficients for radiatively allowed transitions were calculated following the method outlined by Chandra *et al.* [9, 15]. (The numerical results are available from the authors upon request.)

Table 3

Rotational energy levels of isomer 2 of  $c\text{-C}_7\text{H}_2$  (rigid)

Orthospecies				Paraspecies			
Level	E[ $\text{cm}^{-1}$ ]	Level	E[ $\text{cm}^{-1}$ ]	Level	E[ $\text{cm}^{-1}$ ]	Level	E[ $\text{cm}^{-1}$ ]
1 <sub>01</sub>	0.096	8 <sub>36</sub>	5.380	0 <sub>00</sub>	0.000	8 <sub>35</sub>	5.383
1 <sub>10</sub>	0.314	6 <sub>43</sub>	5.437	2 <sub>02</sub>	0.287	6 <sub>42</sub>	5.437
2 <sub>12</sub>	0.488	10 <sub>29</sub>	6.103	1 <sub>11</sub>	0.305	10 <sub>19</sub>	5.683
3 <sub>03</sub>	0.573	7 <sub>43</sub>	6.109	2 <sub>11</sub>	0.514	7 <sub>44</sub>	6.109
3 <sub>12</sub>	0.814	11 <sub>0,11</sub>	6.157	3 <sub>13</sub>	0.762	11 <sub>1,11</sub>	6.208
4 <sub>14</sub>	1.127	9 <sub>36</sub>	6.250	4 <sub>04</sub>	0.953	10 <sub>28</sub>	6.219
2 <sub>21</sub>	1.144	11 <sub>1,10</sub>	6.766	2 <sub>20</sub>	1.144	9 <sub>37</sub>	6.245
5 <sub>05</sub>	1.427	5 <sub>50</sub>	6.788	4 <sub>13</sub>	1.214	5 <sub>51</sub>	6.788
3 <sub>21</sub>	1.432	8 <sub>45</sub>	6.876	3 <sub>22</sub>	1.431	8 <sub>44</sub>	6.877
5 <sub>14</sub>	1.713	10 <sub>38</sub>	7.207	5 <sub>15</sub>	1.583	11 <sub>2,10</sub>	7.147
4 <sub>23</sub>	1.813	11 <sub>29</sub>	7.309	4 <sub>22</sub>	1.817	10 <sub>37</sub>	7.215
6 <sub>16</sub>	2.130	6 <sub>52</sub>	7.363	6 <sub>06</sub>	1.992	6 <sub>51</sub>	7.363
5 <sub>23</sub>	2.301	9 <sub>45</sub>	7.741	5 <sub>24</sub>	2.292	9 <sub>46</sub>	7.741
3 <sub>30</sub>	2.501	7 <sub>52</sub>	8.034	6 <sub>15</sub>	2.311	7 <sub>53</sub>	8.034
7 <sub>07</sub>	2.648	11 <sub>38</sub>	8.279	3 <sub>31</sub>	2.501	11 <sub>39</sub>	8.265
6 <sub>25</sub>	2.865	10 <sub>47</sub>	8.701	7 <sub>17</sub>	2.766	10 <sub>46</sub>	8.701
4 <sub>32</sub>	2.885	8 <sub>54</sub>	8.801	6 <sub>24</sub>	2.883	8 <sub>53</sub>	8.801

Table 3 (continued)

Orthospecies				Paraspecies			
Level	E[cm <sup>-1</sup> ]	Level	E[cm <sup>-1</sup> ]	Level	E[cm <sup>-1</sup> ]	Level	E[cm <sup>-1</sup> ]
7 <sub>16</sub>	3.008	9 <sub>54</sub>	9.665	4 <sub>31</sub>	2.885	9 <sub>55</sub>	9.665
5 <sub>32</sub>	3.364	6 <sub>61</sub>	9.717	5 <sub>33</sub>	3.364	6 <sub>60</sub>	9.717
8 <sub>18</sub>	3.493	11 <sub>47</sub>	9.759	8 <sub>08</sub>	3.394	11 <sub>48</sub>	9.759
7 <sub>25</sub>	3.565	7 <sub>61</sub>	10.388	7 <sub>26</sub>	3.533	7 <sub>62</sub>	10.388
6 <sub>34</sub>	3.940	10 <sub>56</sub>	10.624	8 <sub>17</sub>	3.803	10 <sub>55</sub>	10.624
9 <sub>09</sub>	4.228	8 <sub>63</sub>	11.155	6 <sub>33</sub>	3.940	8 <sub>62</sub>	11.155
8 <sub>27</sub>	4.296	11 <sub>56</sub>	11.680	9 <sub>19</sub>	4.309	11 <sub>57</sub>	11.680
4 <sub>41</sub>	4.383	9 <sub>63</sub>	12.018	8 <sub>26</sub>	4.348	9 <sub>64</sub>	12.018
7 <sub>34</sub>	4.613	10 <sub>65</sub>	12.977	4 <sub>40</sub>	4.383	10 <sub>64</sub>	12.977
9 <sub>18</sub>	4.695	7 <sub>70</sub>	13.171	7 <sub>35</sub>	4.612	7 <sub>71</sub>	13.171
5 <sub>41</sub>	4.862	8 <sub>72</sub>	13.937	5 <sub>42</sub>	4.862	8 <sub>71</sub>	13.937
10 <sub>1,10</sub>	5.214	11 <sub>65</sub>	14.032	10 <sub>0,10</sub>	5.149	11 <sub>66</sub>	14.032
9 <sub>27</sub>	5.233	9 <sub>72</sub>	14.800	9 <sub>28</sub>	5.152	9 <sub>73</sub>	14.800

### 2.3. COLLISIONAL RATE COEFFICIENTS

Unfortunately, also the rate coefficients due to collisions with H<sub>2</sub> molecules, the most abundant molecular species in interstellar environments, are not available in the literature. Therefore, the rate coefficients for downward transitions  $J'k'_ak'_c \rightarrow Jk_ak_c$  at a kinetic temperature  $T$  are taken as [16]

$$C(J'k'_ak'_c \rightarrow Jk_ak_c) = \frac{1 \times 10^{-11}}{(2J' + 1)} \sqrt{\frac{T}{30}}$$

Since downward and upward collisional rate coefficients are related through detailed equilibrium [17], the upward collisional rate coefficients can be obtained from the corresponding downward rate coefficients by applying this concept of detailed balance.

### 3. NLTE RADIATIVE TRANSFER

In order to get an idea about the relative rotational line strengths, we performed NLTE radiative transfer calculations, *i.e.*, we solved the coupled set of rate equations and radiative transfer equations. We treated the radiative transfer rather crudely using a large velocity gradient (LVG) code [18]. The external radiation field, impinging on the cloud under investigation was assumed to be the CMB only.

#### 4. RESULTS

Observation of a spectral line in absorption against the CMB is an unusual phenomenon [19]. The transition  $1_{10} \rightarrow 1_{11}$  of  $\text{H}_2\text{CO}$  and  $2_{20} \rightarrow 2_{11}$  of  $c\text{-C}_3\text{H}_2$  are good examples of anomalous absorption. The basic requirement for anomalous absorption is that the brightness temperature  $T_B$ , excitation temperature  $T_{ex}$  of the line must satisfy the condition:  $0 < T_{ex} < T_B < T_{bg}$ , where  $T_{bg}$  is the cosmic microwave background temperature 2.73 K [6].

Like for the other members of  $c\text{-C}_n\text{H}_2$  series, our calculations indicate that a number of transitions of the symmetric isomer 2 of  $c\text{-C}_7\text{H}_2$  should show up in absorption against the CMB. A significant effect is shown by the  $4_{23} \rightarrow 5_{14}$ ,  $3_{22} \rightarrow 4_{13}$ ,  $1_{11} \rightarrow 2_{20}$ , and  $3_{21} \rightarrow 4_{14}$  transitions at 3.0, 6.5, 0.5, and 9.1 GHz,

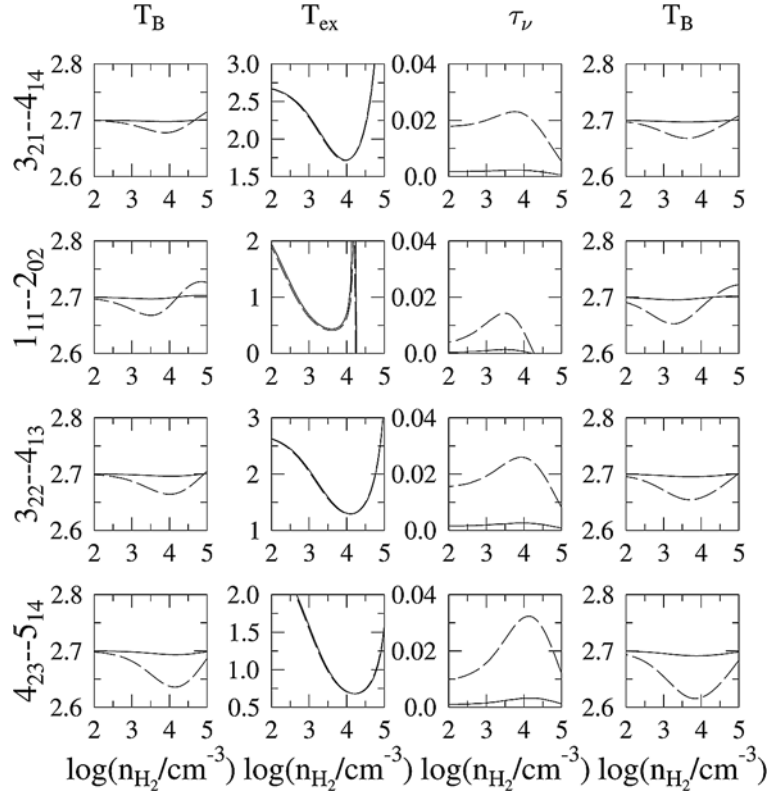


Fig. 2 – Variation of brightness temperature  $T_B$  [K] (column 1), excitation temperature  $T_{ex}$  [K] (column 2), optical depth  $\tau$  (column 3) versus hydrogen density  $n_{\text{H}_2}$  for kinetic temperature 10 K for the transitions written on the left side. Solid line is for  $\gamma = 10^{-6} \text{ cm}^{-3} (\text{km/s})^{-1} \text{ pc}$  and the dotted line for  $\gamma = 10^{-5} \text{ cm}^{-3} (\text{km/s})^{-1} \text{ pc}$ . For the brightness temperature  $T_B$  [K] in column 4, the collisional rates for the transitions with  $\Delta k_a = 0$  are increased by a factor of 10.

respectively. For the molecular hydrogen density  $n_{H_2} = 10^2 \text{ cm}^{-3}$ – $10^5 \text{ cm}^{-3}$ , kinetic temperature  $T = 10 \text{ K}$  and  $\gamma = 10^{-6} \text{ cm}^{-3} (\text{km/s})^{-1} \text{ pc}$  and  $10^{-5} \text{ cm}^{-3} (\text{km/s})^{-1} \text{ pc}$ , the variations of the brightness temperature  $T_B$  (column 1), excitation temperature  $T_{ex}$  (column 2) and optical depth  $\tau$  (column 3) are depicted in Fig. 2. Other lines  $3_{31} \rightarrow 4_{22}$ ,  $4_{32} \rightarrow 5_{23}$ ,  $3_{30} \rightarrow 4_{23}$ , and  $2_{21} \rightarrow 3_{12}$  also show weak anomalous absorption.

In order to investigate the sensitivity of our results to the roughly determined collisional rates, we enhanced the collisional rates for the transitions with  $\Delta k_a = 0$  by a factor of 10, which may be taken as an extreme case. The results with these enhanced rates are also given in column 4 of Fig. 2. Comparison of column 1 with column 4 shows that the finding of anomalous absorption does not seem to be sensitive to the collisional rates. However, owing to the use of the scaled values for collisional rates, the present investigation for anomalous absorption may be considered as qualitative in nature.

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