

# Is C<sub>3</sub>H<sup>+</sup> Present in the Horsehead Nebula?

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## Information

Rotational spectroscopy is the most conclusive way in which molecules can be detected in the interstellar medium, circumstellar envelopes, and, even, the atmospheres of various extrasolar planets. The reason for this comes from the clear progressions of transitions resulting from the

$$\Delta J = \pm 1 \quad (1)$$

selection rules. Additionally, the pure rotational spectra of most molecules are fairly straightforward to understand. From the second-order fitting of the rotational energy level function,

$$E_J = 2B(J + 1) \quad (2)$$

given in Pety and coworkers<sup>2</sup>, the primary rotational constant,  $B$ , for a linear molecule can be straightforwardly derived with only one energy level. Remember that the rotational constant is a geometric parameter inversely proportional to the moment of inertia,  $I$ . This value is simply defined as:

$$I = \sum m_i x_i^2, \quad (3)$$

However, the value of  $E_J$  derived as such from Eq. 2 is not as accurate as it could be. Since the molecule is spinning, the energy is affected by centrifugal distortions. To account for this, a quadratic term can be derived to give an equation a more correct form given as:

$$E_J = 2B(J + 1) - 4D(J + 1)^3. \quad (4)$$

again from Pety and coworkers.<sup>2</sup> Additional terms can be added continually for sextic, octic, etc. corrections. However, most molecules are well-described with Eq. 4.

The opposite side of the algebra can also be employed, which is actually the most common case. The energy levels are observed and fit to the model equation like Eq. 4. Two energy levels are necessary to solve for  $B$  and  $D$  in Eq. 4 since there are two unknowns (remember algebra?). By plugging in the energy levels and rearranging the two equations, one may solve for the unique rotational constants of a given molecule. Often this is done with linear regression software, but this simple algorithm is robust enough to make the point.

In looking at the paper from Pety and coworkers<sup>2</sup>, the bottom portion of Figure 1 reports rotational lines observed in Horsehead nebula photodissociation region/photon-dominated region (PDR). A fitting from Eq. 4 and another sextic formula give the derived rotational constants and are given in Table 1. You can tell that  $B$  and  $D$  do not vary greatly between the quartic and sextic distortion levels. From some computational reference data, these observed interstellar lines are attributed to the linear C<sub>3</sub>H<sup>+</sup> cation.

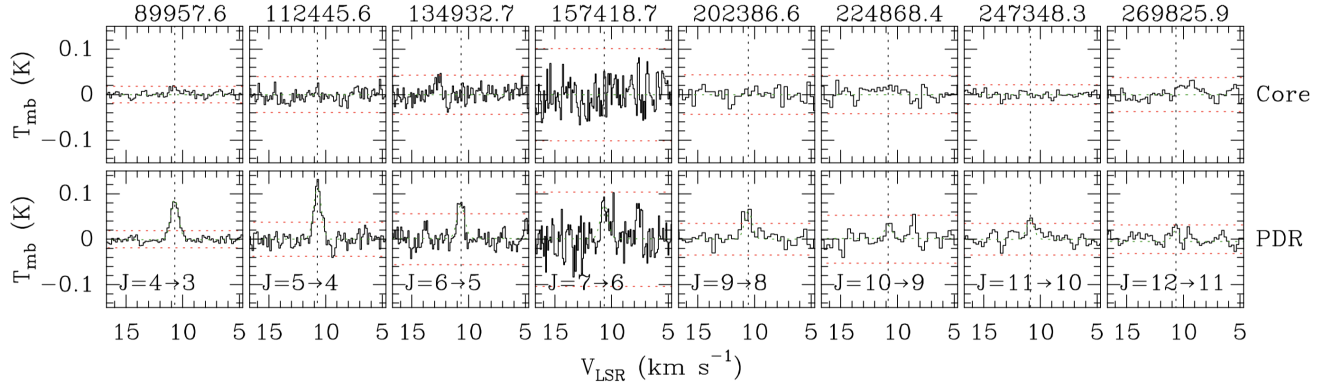


Figure 1: Millimeter lines attributed to the  $1\text{-C}_3\text{H}^+$  cation in the PDR (lower panels) and the dense core (upper panels) positions. The numbers above each panel are the line rest frequencies in MHz. The spectra and the Gaussian fits are shown as black histograms and green curves, respectively. The inferred rest frequencies are displayed as vertical dotted black lines for  $\nu_{\text{lsr}} = 10.7 \text{ km s}^{-1}$  and  $\pm 3\sigma$  noise levels as horizontal dotted red lines.

Order	$\ln(\mathcal{L})^a$	Parameter	Value	Unit
Second	2797.9	B	$11244.9474 \pm 0.0007$	MHz
		D	$7.652 \pm 0.011$	kHz
Third	2802.5	B	$11244.9512 \pm 0.0015$	MHz
		D	$7.766 \pm 0.040$	kHz
		H	$0.56 \pm 0.19$	Hz

Table 1: Results for the simultaneous fit of the  $1\text{-C}_3\text{H}^+$  line parameters and the associated spectroscopic modeling

However, the mathematical model in Eq. 4 assumes the molecule to be linear. Can this equation be used to fit nonlinear molecules? Of course, but  $B$  and  $D$  (and even  $H$ ) will not be exact. These create what are called *effective* rotational constants:  $B_{\text{eff}}$  &  $D_{\text{eff}}$ . These are a “map” of the actual rotational constants onto the linear framework. This will be discussed more in Procedure Part 3 and the relationship of  $B$  and  $C$  to  $B_{\text{eff}}$  is left as an exercise.

Computational chemistry can help to resolve rotational spectra fairly easily. All one really needs is the geometry, and computation produces this routinely and accurately as long as you use a decent basis set and level of theory. Hence, you will employ computational tools to explore the rotational spectra of molecules flying around and between stars. Remember to use complete and correct sentences when answering any free-response question.

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<sup>2</sup>J., Gratier, P., Guzman, V., et al. 2012, A&A, 548, A68

## Part 1 $\text{C}_3\text{H}^+$ B-type Rotational Constants

1. Login to WebMO.
2. Create perfectly linear  $\text{C}_3\text{H}^+$  in the WebMO editor remembering to adjust the bond angles by hand to create perfect  $180.0^\circ$  angles.
3. Using PSI4 as your computational program, perform a geometry optimization with Hartree-Fock (HF) and STO-3G that has the proper charge and spin multiplicity for a restricted wavefunction. Name this job "(yourinitials) C3H+ HF/STO-3G".
4. Once the job is completed, click on the magnifying glass or the blue name line to take you to the job output.
5. Click the "Raw Output" link on the left-hand side of the molecule image. Search for "Rotational constants (MHz):" in this file and record the values for the LAST entry of these values (*i.e.* the ones closest to the bottom).
6. Record these values. Close the raw output.
7. Select "New job using this geometry" at the bottom of the molecule viewing window. Do the same geometry optimization procedure as above but with HF/6-31G(d) named in a similar convention as before.
8. Select "New job using this geometry." Do the same as above but with HF/cc-pVTZ.
9. Those showed the difference in basis sets. We now move on to levels of theory. Select "New job using this geometry." Do the same as above but with HF/cc-pVDZ.
10. Select "New job using this geometry." Do the same as above but with B3LYP/cc-pVDZ. Here you must choose "DFT" as the method and "B3LYP" as the functional.
11. Select "New job using this geometry." Do the same as above but with MP2/cc-pVDZ which is just the "MP2" method, no need for functionals here.
12. Select "New job using this geometry." Do the same as above but with CCSD/cc-pVDZ.

## Part 2 *B*-type rotational constants of other linear molecules

Is  $\text{C}_3\text{H}^+$  the carrier of these rotational lines? Is another molecule a better carrier? Now, you will examine the *B*-type rotational constants of some other closed-shell linear molecules.

13. Create a new linear molecule: HCN.
14. Perform a geometry optimization with B3LYP/cc-pVDZ. What is this molecule's charge and spin multiplicity? Can this molecule be the carrier of these lines?
15. Optimize the B3LYP/cc-pVDZ geometries of the following linear molecules:
  - a) HCCF
  - b)  $\text{HC}_3\text{N}$
  - c)  $\text{C}_4\text{H}^-$
  - d)  $\text{C}_2\text{O}$

## Part 3 Rotational constants for non-linear molecules

Now, you will compute the rotational constants of a few non-linear molecules and fit their rotational constants to the linear model in Eq. 2.  $\text{HCCO}^-$  will be the example.

16. Create non-linear  $\text{HCCO}^-$  in the molecule creation editor.
17. Perform a geometry optimization with B3LYP/cc-pVDZ.
18. Now, you will need to compute the first few energy levels for  $\text{HCCO}^-$  from the *A*-, *B*-, and *C*-type constants from this computation. The equilibrium (non-distortion constant including) pseudo-linear form of Eq. 2 is simply:

$$E_J = (B + C)(J + 1) \quad (5)$$

The *A*-type constant is necessary for describing the distortion factor, but this model in Eq. 5 does not include it for the  $E_J$  computation due to the pseudo-linear nature of the applicable molecules.

19. Find  $B_{\text{eff}}$  for  $\text{HCCO}^-$ . (Hint: There are two equivalent algebraic approaches involving Eqs. 2 & 5 where one  $B$  can be thought of as  $B_{\text{eff}}$ .)

20. Repeat this process for similar non-linear molecules, with all bond angles less than  $180^\circ$ :

a)  $\text{NNOH}^+$

b)  $\text{HOCO}^+$

c)  $\text{C}_3\text{H}^-$

d)  $\text{HCCN}$

e)  $\text{HOCN}$

## Is $\text{C}_3\text{H}^+$ Present in the Horsehead Nebula?

Name \_\_\_\_\_ Date \_\_\_\_\_

Lab Partner \_\_\_\_\_

### Part 1 $\text{C}_3\text{H}^+$ B-type Rotational Constants

$\text{C}_3\text{H}^+$  B-type rotational constants (in GHz)

HF/STO-3G	
HF/6-31G(d)	
HF/cc-pVTZ	
HF/cc-pVDZ	
B3LYP/cc-pVDZ	
MP2/cc-pVDZ	
CCSD/cc-pVDZ	

1. How does the change in basis set affect the primary rotational constant for this molecule?
2. How does the change in method affect the primary rotational constant for this molecule?
3. What is the most accurate method; what is the most accurate basis set; what would be the most accurate method/basis set combination?

4. Would you expect this combination to give the most accurate result? Why or why not?

## Part 2 *B*-type rotational constants for linear molecules

B3LYP/cc-pVDZ *B*-type rotational constants (in GHz)

HCCN	
HCCF	
$\text{HC}_3\text{N}$	
$\text{C}_4\text{H}^-$	
$\text{C}_2\text{O}$	

## Part 3 Rotational constants for non-linear molecules

B3LYP/cc-pVDZ non-linear rotational constants (in GHz)

	$\text{HCCO}^-$	$\text{NNOH}^+$	$\text{HOCO}^+$	$\text{C}_3\text{H}^-$	HCCN	HOCN
A						
B						
C						
$B_{\text{eff}}$						

5. You may have noticed that all of the molecules chosen, whether they are cations, anions, or neutrals, are all closed-shell. The reason comes from the very close fine-splitting observed in rotational lines of open-shell molecules. The lines observed did not have this splitting present. This is one way to eliminate carriers of lines. Another is simply by the size of the molecules. How does this let you eliminate some of the above molecules as carriers, and what molecules did you easily eliminate?

6. Compare all of the B3LYP/cc-pVDZ  $B$  and  $B_{\text{eff}}$  values. Which three have the closest  $B$ -type constant to that from the lines originally observed in Horsehead nebula PDR?

7. What molecule do you believe is the carrier of these astronomical rotational lines? Why, and what may you not be considering (Hint: Don't forget  $A$ )?