Identifying small molecules present in the Horsehead nebula

# Aim

In this hands-on workshop you will use WebMO and Psi4 to compute the rotational constants of small molecules and compare them to the rotational lines observed in a region of the Horsehead nebula. The aim is to use quantum chemical methods to identify which molecule(s) may be present. You will also examine how changing the method and basis set affects both the results and the time taken to carry out the calculation.

# Rotational spectroscopy

Rotational spectroscopy can provide a wealth of information about a gas phase molecule’s geometry and dipole moment. Quantum chemistry calculations can also be used to resolve/assign rotational spectra as rotational constants can be easily computed from optimised structures. The combination of rotational spectroscopy and quantum chemical calculations is commonly used in astrochemistry.

Briefly, the rotational selection rule for linear rotating molecules is , where is the angular momentum quantum number. A pure rotational absorption spectrum of a linear molecule hence has a clear progression of transitions. The energy of one of these rotational transitions in a linear molecule () can be given as:

,

where is the primary rotational constant. This rotational constant is inversely proportional to the moment of inertia, , which can be determined from a molecule’s geometry.

As the molecule is spinning, the energy of the transition is also affected by centrifugal forces that distort the molecular geometry, which is taken into account in the expression:

,

where is the centrifugal distortion constant.

# The Horsehead nebula

The Horsehead nebula (see Figure 1) is an interstellar cloud in the constellation Orion. A study by Pety et al.[[1]](#footnote-1) reports rotational lines observed in a region of the Horsehead nebula with, after spectroscopic modelling, the parameters:

.

From some computational reference data, these interstellar lines are attributed in the study to the linear C3H+ cation. The small value of here suggests that to simplify our investigation we can make the approximation that:

.



# Calculation of *B* for C3H+

Using WebMO, create a perfectly linear C3H molecule. Use “Adjust mode” to ensure all angles are 180.0°. This should result in a point group symmetry of *C*∞v.

Use the “Configure PSI4 Job Options” interface to perform a geometry optimisation with the HF method and the STO-3G basis set. Remember to set the “Charge” to be 1. Then click the “Advanced” tab. In the “Additional Keywords” box, add the following text (without the quotes) “opt\_coordinates=cartesian”, then run the calculation.

Once the job has completed, click on the magnifying glass to load the results. Click on the “Raw output” link on the left-hand side of the molecule. This displays the text output file produced by Psi4.

Search (using Ctrl-F) for “Rotational constants” in the file and record the last value of (in MHz) that appears in the file. Ensure this is the value of that is the closest to the bottom of the file – this is the value that corresponds to the optimised geometry. Ask a demonstrator if you are unsure. You can then close the raw output file.

Once you have this information it is time to repeat the calculation using other combinations of method/basis set. It is advantageous to start this by selecting the “New Job Using This Geometry” button when viewing your results. You should work your way through the table below.

Table 1. Computed rotational constants for C3H+ at various levels of theory.

| Method | Basis | (MHz) |
| --- | --- | --- |
| HF | STO-3G |  |
| HF | 6-31G(d) |  |
| HF | cc-pVDZ |  |
| HF | cc-pVTZ |  |
| B3LYP | cc-pVDZ |  |
| MP2 | cc-pVDZ |  |
| CCSD | cc-pVDZ |  |

This type of “benchmarking” exercise is useful in determining the method/basis combination to be used in a theoretical investigation. Using your results, consider how the change in basis set affects the value of the rotational constant. Similarly, how does changing the method affect the rotational constant?

Use your results and knowledge of the underlying theory to choose a method/basis combination to use in the rest of this workshop. You should consult a demonstrator if you are unsure.

# Calculation of B for other linear molecules

You can now consider if some other linear molecule or ion may be responsible for the rotational lines detected in the Horsehead nebula.

Using the method/basis combination you have selected, optimise the geometry and record the value of the rotational constant for the following linear chemical species:

* HCN
* HCCF
* HC3N
* C4H–
* C2O

By comparing your calculated data with the experimentally derived value of Pety et al. given above, which molecules/ions can you safely eliminate from consideration as being the species detected?

# Rotational constants for non-linear molecules

The model used thus far has assumed the molecule to be linear, but by making some further approximations we can fit non-linear molecules too. By using what are known as effective rotational constants, , which “map” the actual rotational constants onto a linear framework, we can obtain rotational constants that can be compared to the experimental value. Assuming “pseudo-linear” molecules are chosen and not including the distortion constant:

,

where is a rotational constant around a second axis.

By comparing this equation with the analogous energy equation for a linear species, it is possible to determine a value of for non-linear molecules.

Start by creating the non-linear anion HCCO– in the molecule building interface, then optimise the geometry at your chosen level of theory. Obtain the rotational constants from the raw output file – note that you will need both and for non-linear species. Calculate a value of for HCCO–.

Repeat the process for the following non-linear chemical species:

* NNOH+
* HOCO+
* C3H–
* HCCN
* HOCN

# Reflection

Compare all the and values to lines observed in the Horsehead nebula. Which of the chemical species considered do you believe is the species detected (and why)? How could this investigation be improved? Hint: Don’t just consider the method/basis chosen.

Consider the relationship between the size of the chemical species and the rotational constants. What does this imply about any chemical species that may be responsible for the rotational lines observed but have not been considered in this workshop?

**The essay:**

In one paragraph, try to explain why you're doing this investigation, the main question you're trying to answer, the main things you found, and what they mean. It should be able to make sense on its own, even if the reader hasn't read the rest of the report.

# Computational procedure

State the method and basis set you have chosen to use, along with a justification. You should cite the original papers describing the method and basis set. The Gaussian website is a good source for this. If you’ve attempted something “out of the ordinary” you should state what you’ve done here, in enough detail for someone to reproduce your work.

# Results

You’ve probably noticed there’s no introduction, it’s not required in this assessment as the word limit is 1000 words (not including title, author details and references) plus or minus 10%. You should focus on accurately and concisely reporting what you’ve done. You should also interpret the results to answer the main question(s) of the workshop.

# Discussion

Place your work into the wider context of theoretical chemistry and the area it is being applied to. The “reflection” points from the workshop sheet should be used to help guide your thinking. Insightful analysis and critical thinking are what differentiates between good and excellent marks.

You should also discuss how this theoretical chemistry investigation could be improved. What resources would your proposal require?

# References:

Harvard

1. J. Pety, P. Gratier, V. Guzmán et al. *Astronomy & Astrophysics*, **548** (2012) A68. [↑](#footnote-ref-1)