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SPECTROSCOPY

Aromatic astrochemistry


Rachael Tremlett/Macmillan Publishers Limited

We know that polycyclic aromatic hydrocarbons (PAH) are out in space, but we do not know their exact structures or origins. A big step towards structure elucidation comes with the first detection of rotational features of an aromatic compound bearing a six-membered ring in the interstellar medium. Indeed, a group led by Brett McGuire have reported in *Science* an assignment of spectroscopic data to signatures of benzonitrile (C_6H_5CN) — a possible precursor of the PAHs.

Vibrational and rotational spectroscopies are common techniques used in most labs to study molecular structure and dynamics. The same techniques are used to study the properties of molecules present in the interstellar medium, although the complexity of these spectra makes their a priori interpretation difficult. Most of the emission bands in the mid-infrared region arise from molecular vibrations, but many have yet to be attributed to specific molecules. However, emissions have been observed at energies comparable to the vibrational transitions of aromatic C–C and C–H bonds — an indication that some of these unassigned infraredbands might belong to the family of PAHs. Yet, the structures of these PAHs and how they came to be in space remain open questions to astrochemists. Searching for an answer, McGuire and co-workers explored an alternative approach by looking for possible precursors of large hydrocabons in the Taurus Molecular Cloud 1 (TMC-1), a dense area in space in which stars will eventually form. TMC-1 is of particular interest because it is known to contain unsaturated hydrocarbons such as cyanopolyynes.

The characterization of the interstellar medium is not a new scientific endeavour and both rotational and vibrational spectra of hundreds of potential interstellar molecules, either measured or predicted, have been collated. "Sergei Kalenskii — a co-author of the present study — started analysing archival data from TMC-1 using a clever trick to see if there was signal from large, undetected molecules hiding under the noise signal," explains McGuire. "He chose to look for aromatic molecules because they have long fascinated astronomers and astrochemists, but have eluded nearly all our attempts at detection so far". The group selected 12 small aromatic molecules — including cyclopentadiene, furan, pyrrole, phenol, fluorene and C_6H_5CN — and in each case added all the spectra that contained positive intensities corresponding to known signals of that particular molecule. The signal-to-noise ratio should increase if a particular spike corresponds to a specific vibrational or rotational transition. Among the 12 molecules analysed, only C_6H_5CN exhibited an enhancement of the signal-to-noise ratio in the summed spectra. After seeing the signal-to-noise enhancement in the archival data, the group of scientists obtained a completely new and vastly superior set of high resolution measurements of specific rotational transitions of C_6H_5CN. Eight of the nine rotational transitions observed were in agreement with predictions, thus confirming the presence of C_6H_5CN in the interstellar medium.

The obvious next question is: how does C_6H_5CN form in space? The group led by McGuire modelled the temporal evolution of the column density — the amount of material per unit area in a cloud in space — for C_6H_5CN and other organics such as benzene and cyanopolyynes. This model takes into account most of the known possible formation pathways for these molecules. For C_6H_5CN in particular, the neutral-neutral reaction between CN and C_6H_6 was included as a possible path. These models appear to be in good agreement with experimental data. Also, certain unassigned infrared bands are attributable to C_6H_5CN and as a result the group hypothesize that it is a plausible precursor to PAHs in the interstellar medium.

"We have detected C_6H_5CN, the largest molecule ever seen by radioastronomy in terms of number of atoms, and the first ever seen with a six-membered aromatic ring. Detection of this molecule in a molecular cloud representing one of the earliest stages of star and planet formation means that we can now investigate aromatic chemistry at the furthest point back in its evolutionary history," points out McGuire. "This detection, in combination with theoretical work and modelling, indicates that we can use C_6H_5CN as a reliable tag for C_6H_6, which is invisible to radioastronomy," he concludes. This capability opens up opportunities to investigate the historical evolution of aromatic molecules.

Gabriella Graziano

> "Detection of benzonitrile in a molecular cloud means that we can now investigate aromatic chemistry at the furthest point back in its evolutionary history"

ORIGINAL ARTICLE McGuire, B. A. *et al.* Detection of the aromatic molecule benzonitrile (c-C_6H_5CN) in the interstellar medium. *Science* **359**, 202–205 (2018)