Disclosing Identities in Diffuse Interstellar Bands

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Just as detectives use fingerprints to pin down criminals, astronomers use spectral information to identify molecules in interstellar space. Astronomical spectroscopy, especially spectroscopy of molecular ions, is developing rapidly. Numerous interstellar negative ions, such as H₂O⁺, H₃⁺, and CH⁺, have all been discovered during the last few years (1). In contrast to these rapid developments in the discovery of new molecular spectra, the sharp features can be thought of as clean fingerprints, and there exists a group of several hundred intriguing broad optical spectra (see the figure, panel A) called the diffuse interstellar bands (DIBs). These blurry fingerprints have defied attempts by many astronomers, physicists, and chemists to understand them for many decades. Maier et al. (2) now have a suspect in custody as the molecule responsible for DIBs—the linear carbene molecule, l-C₂H₃—but more evidence will be needed to get a conviction.

The strongest DIB, at the wavelength of 4430 Å, was initially observed by Annie Jump Cannon, the first astronomer to classify stars systematically by spectroscopy, sometime between 1911 and 1919 (3–5). The carriers of DIBs are molecules, not atoms or solid grains, and they are not in the stars but are in huge diffuse clouds between the stars and us. More than that is not known with certainty. It is difficult to hunt criminals by using blurry fingerprints. In comparison, radio detections of molecules are clear-cut because their fingerprints (rotational spectra) are extremely sharp. Milestone discoveries of molecules, like H₂O, H₂CO, CO, HCO⁺, and HC₅N, were initially claimed by detecting one spectral line, and there have not been any mistakes.

Numerous hypotheses, many from eminent spectroscopists and astronomers, have been proposed to explain DIBs, and most of these hypotheses look far-fetched in hindsight. The chemist Bill Klemperer once said that “there is no better way to lose a scientific reputation than to speculate on the carriers for the diffuse bands” (6). During the past 10 years, candidates have included C⁺, C₂H⁺, C₂H₃⁺, and HC₅H⁺, proposed on the bases of their laboratory spectra. However, they have not been accepted because their fingerprints were not a good enough match to DIBs. There have been many more proposals not based on laboratory spectra, but these are more speculative, and akin to naming a suspect based on circumstantial evidence.

Maier et al.’s proposal that two DIBs at 4881 Å and 5450 Å are caused by l-C₂H₃ has stirred
great interest within the astrophysical community. Maier is a leader in the field of laboratory spectroscopic astrophysics, and, using a variety of newly developed techniques, has been amazingly productive in discovering new visible and ultraviolet spectra of carbon-containing unstable molecules, which are likely carriers of DIBs (only the almost collision-free environment of interstellar space allows such molecules to exist in abundance there; in the lab, they are difficult to prepare). This particular candidate molecule had already been observed by radio emission in dense interstellar clouds (~100 times denser than diffuse clouds where DIBs are observed) nearly 20 years ago (7). Cyclic C₂H₂ has been observed in diffuse clouds (8), so the presence of I-C₃H₂ may not be surprising. Related molecules such as C₃, C₂H, and C₁ have also been seen in diffuse clouds, and such a simple molecule is more appealing than very complicated molecules whose spectra are difficult to obtain in the laboratory.

Maier’s group had previously recorded sharp fingerprints of I-C₃H₂ in the laboratory in the 6150 to 6330 Å region, which correspond to this molecule’s lowest-energy electronic transition (9, 10). The major breakthrough in the present work was the proof that two much broader bands at 4881 and 5450 Å are also caused by a higher electronic transition of I-C₃H₂. The broad spectral lines of a simple molecule like I-C₃H₂ appear to be the result of the extremely short lifetime (~3 × 10⁻¹³ s) of the second electronic excited state. This interpretation follows from the uncertainty principle—a shorter transition time corresponds to higher uncertainty in energy and hence a broader spectral line.

The match of the two broad bands to DIBs seems reasonable, but with such “blurry fingerprints,” it does not constitute proof beyond a reasonable doubt. In panel B of the figure, the interstellar spectra (solid curves) and simulations from laboratory data (dashed curves) are shown, with the 4881 Å DIB at left and the 5450 Å DIB at center. Maier et al. also searched for the sharp transitions of I-C₃H₂ in the 6150 to 6330 Å region; the match with their spectra of interstellar clouds is promising, but not entirely convincing (panel B of the figure, lower right). Unfortunately, different stars were used in the searches for the broad and sharp bands, so it remains to be seen whether all of the supposed I-C₃H₂ transitions appear in a single diffuse cloud, and whether the intensities of all these transitions have a constant ratio in all clouds (as they should if they are caused by the same molecule).

Another aspect of the work by Maier et al. is difficult to accept is the apparently high abundance of I-C₃H₂ toward the star HD 183143 (center of panel B of the figure). This line of sight, which has been famous in the DIB community since the pioneering work of Herbig (11), is remarkable in that it contains very few carbon–chain molecules, such as C₁₂ (12) or C₁₃ (13). In this respect, HD 183143 is an extreme case; its polar opposite is the star HD 204827, which has by far the highest C₁ and C₁₂ column densities of all sightlines so far studied and led to the discovery by our co-workers and ourselves of a group of DIBs called “C₁ DIBs” whose intensities correlate well with the C₁ column densities (12). These two sightlines have also served as contrasting prototypes for detailed compilations of the DIBs (14, 15). If Maier’s claim about I-C₃H₂ is correct, this molecule must be more than two orders of magnitude more abundant than C₁ and C₁₂ in HD 183143. Although the chemical mechanism for producing hydrocarbon molecules in diffuse clouds is not well understood, it is hard to imagine such a tremendous discrepancy in the abundance of C₁₂ and I-C₃H₂.

At present, we conclude that there is insufficient evidence to “convict” I-C₃H₂ as a carrier of the DIBs. Searches for both the sharp and broad I-C₃H₂ bands in a number of diffuse clouds could establish whether the sharp bands are a perfect match, and whether the broad bands have a constant intensity ratio in different clouds. It may also be possible to search for I-C₃H₂ in diffuse clouds through its pure-rotational transitions (16); however, a direct comparison of absorption in the optical and the radio spectrum would require a background source that is bright at both wavelengths.

Microbiology

Another Microbial Pathway for Acetate Assimilation

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In a salt-loving Archaean, a patchwork of enzymes creates a variation of the glyoxylate cycle.

Countless students in introductory biochemistry classes have heard the adage “fats burn in the flame of carbohydrates.” It refers to the inability of vertebrates to convert acetyl coenzyme A (acytetyl-CoA), an important metabolic molecule, into intermediate compounds that replenish carbon in the citric acid cycle and enable the synthesis of glucose. In contrast, plants and certain bacteria, fungi, and invertebrates have solved this barrier to “anabolism from acetate” by using a variation of the citric acid cycle. This variation is called the glyoxylate cycle, and it allows acetyl-CoA to be used as a replenishing source for carbon in the synthesis of glucose and other important reactions (J). However, a number of acetate-using microorganisms lack one of the signature enzymes involved in the glyoxylate cycle, isocitrate lyase, demonstrating that other pathway(s) for acetate assimilation must exist (2–4). In 2007, fully 50 years after the discovery of the glyoxylate cycle, investigators revealed the first complete details of one of these alternate pathways (5). Now, on page 334 of this issue, Khomyakov et al. (6) describe yet another acetate-assimilation pathway. It is in a salt-loving (halophilic) microorganism belonging to the Archaea, and incorporates

1. Those developments were hotly debated at a recent symposium, “Spectroscopy of molecular ions in the laboratory and in (extraterrestrial) space,” held in Kos, Greece, 3 to 6 October 2010; http://fermi.uchicago.edu/~smiles/.
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