HEAVY-MOLECULE ASTROCHEMISTRY: PRECURSORS TO LIFE?

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1. HEAVY MOLECULES

Most known interstellar molecules are small and have their lowest transitions in the millimeter wavelength range. Heavier molecules have their lowest transitions in the microwave range and are especially prominent at the low temperatures that characterize many dense molecular clouds. Moreover, low frequencies are crucial for identifying heavy molecules. Any individual heavy molecule has low abundance, and in the plethora of lighter molecular lines at mm wavelengths they fall below the confusion level. But the lighter molecules don't have low frequency lines, so the low frequencies are free of confusion and heavy molecules stand out clearly and unambiguously.

While any individual heavy molecule has low abundance, there are *many* possibilities for forming diverse kinds of heavy molecules. Therefore, the *total mass* residing in heavy molecules might well be high—in dense molecular clouds, heavy molecules and dust grains might well soak up more heavy elements than the more commonly observed light molecules.

2. GALACTIC AND EXTRAGALACTIC ASTROCHEMISTRY: PRECURSORS TO LIFE?

The past few years have seen fascinating results from spectral scans and targeted molecular searches at microwave frequencies. In the Milky Way, Kalenskii et al. (2004) scanned the cyanopolyyne peak in TMC-1 from 4-6 and 8-10 GHz and observed about a dozen heavy molecules, about half of which were new discoveries. Heavy anions have also been discovered here; these discoveries have kicked off the explosively emerging field of heavy anionic chemistry in dense molecular clouds, discussed below.

Astronomical molecular spectroscopy isn't confined to the Milky Way. They should be visible in external galaxies, too, particular under the exotic conditions and rampant star formation characteristic of ULIRGS. Salter et al. (2007) and Ghosh et al. (2007) used Arecibo to begin a spectral scan in the ULIRG Arp 220 from 1.1-10 GHz and discovered several new molecules, including the pre-biotic CH_2NH (methanimine) and possibly HCOOH (formic acid). Methanamine is a pre-biotic molecule which can play a part in forming glycine, the simplest amino acid, either indirectly through combining with hydrogen cyanide (HCN) and then reacting with water molecules, or directly through combining with formic acid (HCOOH). The methanamine in Arp 220 appears to be a kilomaser or a megamaser, similar to the OH megamasers in many ULIRGS.

We see ourselves at the beginning of a new field: *extragalatic astrochemistry.* Heavy molecular spectroscopy is a developing subject, with new results from the terrestrial laboratory leading the way to astronomical discovery, which in turn feeds back to point the direction for future lab work. This interchange represents the best scientific tradition: an intimate, rich interchange between the sky and the lab. It underscores the need for sensitive spectroscopic surveys in the GHz range because only they can provide definitive and unambiguous molecular identifications, free from the confusion of the forest of lines from light molecules at mm wavelengths.

With all these new detections of large molecules, we see once again the principal finding of molecular astrophysics: dense clouds in space contain an astonishingly rich collection of both familiar and exotic molecules in various states of ionization and excitation. It means that there are many more ways to build large organic molecules in these environments than have been previously explored. These add to the number of paths available for making the complex organic molecules and other large molecular species that may be the precursors to life.

3. POLYCYCLIC AROMATIC HYDROCARBONS—PAHs

Laboratory molecular spectroscopy is now exploring PAHs (Thorwirth et al. 2007); see Figure 1. PAHs are known to be common in the ISM because their vibrational and bending modes produce easily detectable IR lines. As a result, PAHs have long been recognized as highly important for ISM heating, not just in dense but also in diffuse regions, where their heating dominates all other mechanisms. They might also play important roles in astrochemistry, particularly for heavy molecules. They might also produce the unidentified 3-20 μm IR bands, the diffuse unidentified visible absorption lines, and even the 2400 Angstrom UV absorption bump.

However, these IR lines change very little from one PAH to another, so it has been impossible to take an inventory of interstellar PAHs. Microwave spectroscopy offers the possibility to take this detailed inventory. Currently, laboratory spectroscopy data exist for ancenaphthene ($C_{12}H_{10}$; Figure 1), ancenaphthylene ($C_{12}H_8$), and fluorene ($C_{13}H_{10}$). The lowest rotational transitions are in the GHz range and are now accessible with large radio telescopes. Reliable transition frequencies can be calculated from the centimeter- into the millimeter-wave regime to probe both the cold and warm molecular objects, but identifications are always more reliable at lower frequencies because of the molecular line confusion problem at mm wavelengths.

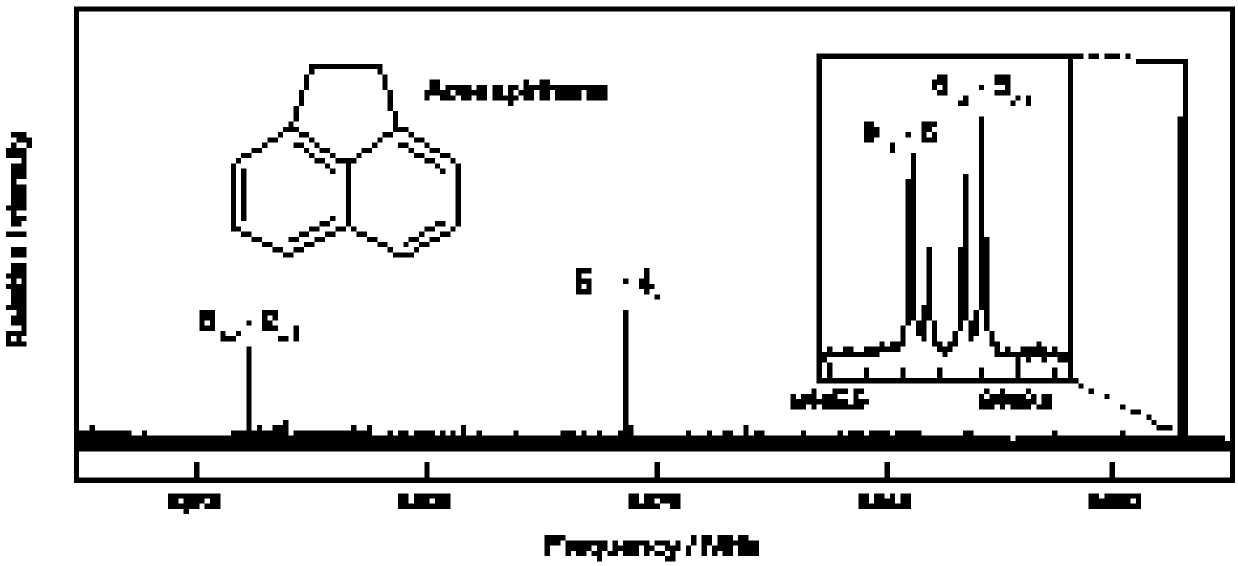

Fig. 1.— Laboratory rotational spectrum of the PAH acenaphthene at 8.4 GHz.

4. HEAVY MOLECULAR ANIONS: MODERATORS OF THE MAGNETIC FIELD IN STAR FORMATION?

The past year has seen a remarkable development in molecular cloud chemistry: the insurgence of heavy anions such as C_6H^- (McCarthy et al. 2006) and C_8H^- (Brünken et al. 2007; Remijan et al. 2007) as important interstellar constituents. Until recently, all the astrochemical reaction networks have ignored anions. This can no longer be the case.

The impact of these anions on star formation may offer a radical new insight into the the magnetic field's role in star formation. The anions have soaked up otherwise free electrons, which reduces the conductivity, decreases the degree of magnetic flux freezing, and increases the rate of ambipolar diffusion—all of which make star formation easier and faster within dense molecular clouds, a trend that vitally influences the star formation process.

These anions are discovered in two widely differing environments. One is the nearest and most prolific molecular gold mine, the "cyanopolyyne peak" in Taurus Molecular Cloud-1. This nearby reservoir of cold, dense gas offers terrestrial astronomers the richest source of molecular detections that are not influenced by massive stars. At the opposite extreme is the stellar envelope of IRC+10216, an unshielded warm stellar envelope subject to intense IR flux. The presence of these anions in widely differing environmental conditions indicate that anions are not only surprisingly abundant in particular environments, but reside in almost all dense environments with temperatures and radiation fields that range from shielded cold clouds to unshielded warm gas. The ramifications for the magnetic field's influence might be surprisingly widespread.

It might seem paradoxical that the first molecular anion in space is larger than nearly all the neutral molecules that have been found and larger than all the cations. But size confers stability, and the cross section for electron radiative attachment increases with size to favor the formation of large ions (Lepp & Dalgarno 1988a, 1988b). Another crucial factor favoring C_nH is the unusual stability for large even n (odd n molecules are not so stable). The anions possess an exceptionally high electron binding energy, which strongly favors electron attachment. The isoelectronic nitrogen analogs, C_nN^-, may also be plentiful.

These recent discoveries are the result of a program of laboratory measurements and a realization of the importance of a new formation mechanism for heavy molecules and their anionic counterparts (Wright et al. 2006). In forming the anions, the first step is to form their uncharged molecular counterparts. This is initiated by the combination of C_2H_2 with C_2 to form C_4H; and thenceforth, the repetitive successive combination of C_nH with C_2. The next step is the electron attachment to form the anion, $C_6H + e^- \rightarrow C_6H^- + h\nu$. With these heavy molecules, there is a high density of vibrational states which are available to dissipate the excess energy of formation by photon emission. Spectroscopic and quantum considerations, together with the large dipole moment of the anions, make their lines strong and easy to detect.

5. INSTRUMENTAL NEEDS

5.1. The Need for Complete 0.5-10 GHz Spectral Scans

The feedback between observers of the sky and experimenters in the lab traditionally goes two ways: astronomers provide unidentified lines and frequencies; experimenters provide identified lines and frequencies. Performing a spectral scan over the 0.5-10 GHz range with existing equipment is a prohibitively time-expensive proposition because at most telescopes the widest band is $\lesssim 100$ MHz; there are ninety-five 100 MHz chunks in the 0.5-10 GHz range! Much better is to cover the range in one 9 GHz or two smaller chunks, saving observing time by two orders of magnitude. In cold regions, line are narrow, particularly for heavy molecules; a frequency resolution ~ 1 kHz is appropriate at the lower end; somewhat wider is acceptable at the higher end. For the full 0.5-10 GHz range, this amounts to $\gtrsim 10^7$ frequency channels.

We envision a number of these scans: one in TMC-1, one in IRC+10216, one in Arp 220, and few more in selected Galactic regions and active galaxies. Sensitivity is paramount: with such coverage one could spend a few tens of hours on each region, producing exquisite sensitivity that should allow exploration of anions, PAHs, and numerous other heavy molecules, both known and unknown.

5.2. Telescopes and Wideband Spectral Coverage

We envision these observations occurring at either, or both, the Allen Telescope Array and Arecibo. Only Arecibo has the point-source sensitivy needed for external galaxies, and only the ATA has the combination of angular resolution and field of view required to observe, simultaneously over wide bandwidths with high spectral resolution, Galactic molecular clouds where the positional concentrations of heavy molecules are unknown.

Covering the 0.5-10 GHz spectral range in one or two chunks requires either a 20:1 or two 4:1 bandwidth low-noise receivers. The 20:1 bandwidth is part of the current design of the Allen Telescope Array. Arecibo envisions the possibility of 4:1 bandwidth receivers as a future development.

5.3. A Wideband, High-Resolution, Interference-Resistant Spectrometer

Covering the 1-10 GHz spectral range in one or two chunks requires a capable spectrometer. It seems impractical to pursue a single spectrometer that covers the full range: not only does this push modern digital electronics, but it also makes the spectrum susceptible to strong interference occurring anywhere in the band. A number of smaller-bandwidth spectrometers with the abovementioned spectral resolution is appropriate.

6. REFERENCES

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