Author: Bacalla, X.
Title: Electronic spectroscopy of molecules of astrophysical interest
Issue Date: 2019-07-02

Summary

This year, 2019, marks the centenary of the discovery of the diffuse interstellar bands or DIBs. The origin of these circa 500 absorption features which appear in the spectra of starlight crossing interstellar clouds of dust and gas have since eluded the understanding of many astronomers. Through the years, various proposals for the absorbers or ‘carriers’ that cause the DIBs have been put forth, from microscopic dust particles to molecules both large and small. The strongest contenders among these candidates include families of long carbon chains and rings, polycyclic aromatic hydrocarbons (PAHs), and fullerenes. This consensus has resulted from the collective effort of astronomers, experimentalists, theorists, and modelers. In 2015, two (to five) DIBs were attributed to the buckminsterfullerene cation C_{60}^+, which was confirmed recently in space-based observations. This development breathes new life into DIB research and leads us closer to the next piece to the puzzle.

In this thesis, the electronic spectra of carbon chains are measured and analyzed in the laboratory, and the abundance of molecules in the diffuse interstellar regions of our Galaxy is quantified to provide some insight on the nature of the DIB carriers and of the environments where they are found.

Chapter 2 describes the experimental techniques that were employed in recording spectra specific to the study of carbon-chain radicals. These are namely Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy (IBBCEAS) and Cavity Ring-Down Spectroscopy (CRDS). The two methods are used in a complementary fashion; combining the advantage of the fast data acquisition and wide wavelength coverage of IBBCEAS together with the high resolution of CRDS ensures an efficient search and identification of [new] spectral features that may be directly compared with astronomical DIB spectra. Details on the synthesis of molecules through hydrocarbon plasma expansions are also provided.

Chapters 3 and 4 focus on the hexatriynyl radical, C_6H and its heavier isotopologue, $^{13}C_6H$. The C_6H carbon chain was first found in space before its spectra was even recorded in the laboratory using millimeter-wave spectroscopy. Despite failing the criteria for a DIB carrier, the electronic spectrum of this molecule is rich with information unraveled using high-resolution CRDS which can nevertheless provide

insight on how, for instance, band profiles can change with subtle intramolecular interactions. In these chapters, the electronic origin band of $^{13}C_6H$ is reported, and an extensive energy level scheme for C_6H is formulated on the basis of rovibronic assignments and literature data (mm-wave, matrix isolation, and hollow-cathode spectra, ab-initio calculations, and isotopic substitution). Additionally, a Renner-Teller analysis is invoked to explain and assign the different electronic transitions.

Finally, in Chapter 5, electronic transitions of the hydroxyl cation OH^+ are searched for in astronomical spectra from the ESO Diffuse Interstellar Bands Large Exploration Survey (EDIBLES). The interstellar abundance of OH^+ is quantified and from this the rate of cosmic ray ionization (CRI) in diffuse-translucent clouds is inferred. This quantity is especially important for modeling the chemical evolution of various interstellar species in these environments which may well include the molecular DIB carriers. It is found that the rates are higher than what was previously derived through submillimeter, infrared, and UV observations. This is due to a revised formulation of the OH^+ abundance – CRI rate relation using updated oscillator strength values for the OH^+ transitions. It is possible, however, that these sightlines have inherently high concentrations of OH^+, and thus, lead to a high rate of CRI derived. Nevertheless, the results serve as a complementary check to other methods of deriving the CRI rate, using ground-based observations of multiple OH^+ transitions in the UV.

All in all, the identification of the DIB carriers is as important as ever, now that ${C_{60}}^+$ has, thus far, withstood scrutiny as a candidate. Pinning down the identity of the DIB carriers may shed light on our Galactic carbon budget as several of the accumulated DIB studies point to carbon-based species. Thus, having a fast and sensitive spectrometer to survey various carbon-based gas mixtures will definitely aid in screening potential candidates. High-resolution spectra will also be useful for learning more about the molecule, and spectroscopic constants derived from it can be used for simulating absorption features under interstellar conditions. Lastly, other known molecules can be used as probes for the physi-chemical properties of DIB carrier environments.

As we try to unravel the nature of DIBs, we try to unravel the properties of the interstellar medium of our Galaxy.