

Diffuse interstellar bands: A comprehensive laboratory study

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Abstract

As a result of the search for the identity of the chromophores responsible for producing the diffuse interstellar bands, a comprehensive exposition of experimental data is presented, which implicates the following molecules: (1) The extremely stable organic molecules, magnesium tetrabenzoporphyrin (MgTBP) and H₂TBP. (2) A paraffin matrix (referred to as “grains”) containing TBPs. (3) A low concentration of pyridine (also within the grains), whose transmission window at 2175 Å, accounts for the ubiquitous UV bump. The blue emission spectra associated with the central star, HD44179, of the Red Rectangle displays the fluorescence excitation spectra of *bare* MgTBP. This unique spectrum matches the low temperature lab data of MgTBP in the vapor phase. An effective grain temperature of 2.728 K (± 0.008) was deduced, based on MgTBP’s lowest measured vibrational state of 341 GHz.

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1. Introduction

Since 1921, diffuse interstellar bands (DIBs) have presented an extreme challenge to both astronomers and spectroscopists. These bands are seen primarily in the spectroscopic data of distant, bright background stars, whose light has undergone multiple scattering associated with grains within intervening, interstellar clouds. The interstellar origin of DIBs was established by Merrill [1]. At first, only a handful of these features were discovered, with one particular feature, the 4428 Å DIB, being the most prominent. Several hundred DIBs are now being reported, a large number as yet unverified and unpublished. The quest for a solution to the DIB enigma has recently gained increased attention; its solution is regarded as potentially far-reaching in its implied cosmological significance.

Herbig [2] reviewed the historical background relating to the discovery of the DIBs, and discussed numerous proposals for their identification. The earliest summary of experimental work on the DIB enigma was presented in 1965 [3], concluding with the suggestion of complex hydrocarbon molecules as the carrier of the DIBs. Snow’s review article [4], emphasized the experimental search for gas-phase molecules, overlooking crit-

ical solid-state literature, which includes high-quality Shpolskii spectral data [5–29].

The Shpolskii technique [8] is unique in that it facilitates the expression of well-resolved vibronic spectra of complex molecules such as porphyrins and phthalocyanines in frozen paraffin matrices. Moreover, Shpolskii spectral bandwidths are comparable to those of narrow DIBs, whose bandwidths are characterized as “diffuse” (in contrast to the sharp atomic spectral lines).

2. Proposed solution

The proposed solution to the DIB enigma utilizes the extensive and meticulously accumulated observations of Herbig [2,30–36], survey data [37], and the Red Rectangle fluorescence emissions [38,39], plus 36 years of accumulated lab data of magnesium-tetrabenzoporphyrin (MgTBP) (Fig. 1) and the free-base variety, H₂TBP [40–42]. These highly stable, abiotic molecules belong to a sub-class of a larger category of molecules known as, “porphyrins and metalloporphyrins” [43–45]. Porphyrins are extensively studied for their importance in biochemistry and biology. They have also held center stage in a large variety of photochemical studies where they serve as photosensitizers [46–51]. In fact, MgTBP has been used by Goedheer [52,53] as a chlorophyll analogue.

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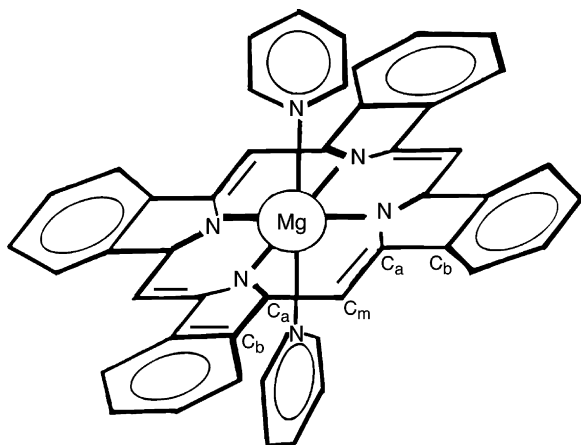


Fig. 1. Dipyridyl magnesium tetrabenzoporphyrin ($\text{MgC}_{46}\text{H}_{30}\text{N}_6$).

Preliminary results have been given previously [5,6,41,42,54–63] (this paper supersedes, and amends all previous work on this subject). The two postulated DIB chromophores are within two special classes of organic compounds (grains) composed of the solvent pyridine and mixtures of paraffins. The primary assumption is that the main chromophores, MgTBP and H_2TBP , are situated within a set of grain types where the “A-type” produces the quasilines (via Shpolskii matrices) and the “B-type” produces the inhomogeneously broadened features. Overlapping vibronic transitions account for wider DIB line widths as well as for some of their enigmatic substructure line shapes. Factors such as, different experimental conditions and techniques, various equipment and technologies, and scientific contributions from others contributed to the 40-year quest for a unique solution.

3. Experimental techniques

A systematic spectroscopic survey of a large number of organic compounds [57] was performed on a Beckman DK9 spectrophotometer. Low-temperature absorption and fluorescence data collection utilized a 3/4 m Jarrell Ash spectrometer (dispersion of 20 Å/mm) and was recorded on 5" × 7" photographic plates. Light sources included a high intensity tungsten lamp, HeNe, argon ion and/or HeCd (4416 Å) lasers.

MgTBP samples were prepared according to Linstead [64], Koehorst et al. [65] by various chemists over a 10-year period. One sample was a gift from Dr. Frank Träger. The Shpolskii matrix isolation method [8] was attempted throughout, with the tetrabenzoporphyrin samples first dissolved in pyridine and then diluted with either *n*-octane, *n*-nonane or *n*-decane.

Sample thickness was varied from about 1–5 mm. Absorption data required exposures of the order of minutes, whereas, fluorescence data would vary from 15 min to 5 h. A typical run would be seven separate exposures recorded on a single photographic plate. About two-dozen CSUF physics undergraduates collaborated in the data collection. Preliminary Shpolskii data reported previously [41,42] plus over 120 spectral plates were meticulously re-measured by Perry Rose. Some of the plates were recently rescanned by David Weinkle, using modern tech-

nology, in order to facilitate an improved spectral representation of the data.

Room temperature FTIR spectra were taken of MgTBP using both reflection and transmission set-ups. Raman spectra of MgTBP was obtained via Dr. Markwort.

The Q-band $S_1 \leftarrow S_0$ region of “bare” MgTBP was measured by Dr. Brumbaugh at the University of Chicago. The laser induced fluorescence (LIF) spectra covered the optical region from 5650 to 6165 Å. MgTBP was first heated to 425 °C to produce a vapor, which was subsequently cooled by means of a supersonic jet of helium.

Preliminary measurements of the $S_2 \leftarrow S_0$ transitions of “bare” MgTBP were taken by Dr. U. Even at Tel Aviv University. The experimental arrangement incorporates the following innovations:

- (a) Pulsed supersonic gas expansion and simultaneous molecular ion mass determination.
- (b) Molecular photo ionization is achieved by means of two synchronously pulsed laser beams, where one has a fixed and the other a variable frequency. Their combined energy was in slight excess of 7.3 eV.

4. Results

The search originated with an earlier, unsuccessful experimental study at Columbia University involving F-centers in alkali hydrides [66].

Subsequent research involved absorption measurements of hundreds of diverse types of compounds, including a large variety of neutral polycyclic aromatic hydrocarbons (PAHs). The resulting spectra were inconsistent with the known DIB spectra [57]. In addition, an extensive library search provided the important clues, which led to the TBPs.

MgTBP is designated as the primary molecule. At room temperature [40] with MgTBP in a pyridine solution, the dominant spectral features are the Soret band at 4422 Å, the Q band at 6344 Å, the weaker Q (0, 1) broad structure at 5900 Å and a vibronic structure at 4161 Å. These features are far better resolved at temperatures of 77 K and below, with slight temperature related spectral shifts. The peak of the 4422 Å Soret shifts to 4428 Å (and is weakly dependent on the pyridine/paraffin ratio); the 4161 Å becomes 4175 Å. The latter value is consistent with astronomical data by Herbig and co-workers [2,67]. The Q (0, 1) and the Q bands show well-resolved structures, both in the lab and DIB data.

4.1. Lab quasiline Shpolskii spectra at 77 K

The successful production of quasilines depends primarily on the paraffin solvents, on sample cooling rates and on the resulting microcrystalline structural environment in the vicinity of the MgTBP hosts. In addition, critical parameters include sample preparation, sample thickness, and the proper experimental techniques for producing and recording the spectra.

Mixtures were generally of arbitrary concentrations and, hence, resulted in a good diversity of absorption and fluores-

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