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PORPHYRINS IN THE INTERSTELLAR MEDIUM (IN GRAINS)

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Preliminary results of this work were presented previously (Johnson, 1972, 1991, and 1993).

To satisfy the variable DIB Band Width requirements: I postulate two types of grain matrices:
A. Shpolskii type,
B. in homogeneously broadened bands in random matrices.

Next separate out bands belonging to H_2TBP in A & B type grains, 6597, 6175, 6592Å and predict 4385 Å Soret Band. At 77°K the Soret Band of MgTBP in a frozen paraffin/pyridine mixture is at 4428Å (+/- 1Å) is also the major DIB.

Unless one grows single crystals with MgTBP interspersed, it is exceedingly difficult to achieve type A grains alone, without admixtures of type B. In fact, only one in three or four attempts will yield any type of Shpolskii (type A) matrices. Thus, out of over 120 attempts only 40 plates showed good Shpolskii matrices and the desired quasilines. Each plate consisted of about 6-8 absorption and fluorescent spectra. Representative spectra are shown in Figure 1.

Now comes the toughest challenge: to solve the complete energy level scheme:
(1) Find the electronic origins for the S_1 and S_2 states as a function of sites.
(2) Determine the complete set of vibrations.

Confidence in the validity of the MgTBP vibrations is increased by comparisons with other measurement techniques: (FTIR, Raman, bare molecule), related tetrabenzoporphyrins such as H_2TBP, CdTBP, ZnTBP, and porphyrin MgP as well as work by other experimenters.

One can now confront the totality of experimental data with the available DIB data as well as the fluorescent ERE data from the Red Rectangle emission region. The preprint was kindly provided by Dr. P. J. Sarre (Scarott, Watkins, Miles, & Sarre,1992).

Individual wavelengths from the Red Rectangle emission plot were measured directly from an enlarged version. Within experimental errors, there are 35 lab and RR emission coincidences out of 57 Red Rectangle bands, far in excess of RR coincidences with Herbig's DIB absorption data. The possible vibronic transitions required to produce this spectrum are consistent with the measured MgTBP vibrations.

Five "sites" of the S_1, electronic state were determined from the lab data. In the S_2 electronic state, only one site, split by 35 cm^{-1} has so far been found.
All the five S_1 sites are split by 36 cm^{-1}, which is characteristic of the pyridine environment in which MgTBP is situated. In a pure single crystal of n-octane P & C obtained a crystal field splitting for the S_1 state of 30 cm^{-1}.

The "Family" scheme according to Johnson is based on the following: the primary molecule is MgTBP in a paraffin/pyridine mixture. Two subspecies are derived from MgTBP, viz. a nondescript molecule (unidentified so far) called Ø, whose sole spectroscopic signature is the broad 4882Å band (Johnson's lab data at 4890Å). The other molecule is the free base H_2TBP characterized by bands 6597Å, 6175Å, 6591Å, and 4385Å (predicted).

Proposed solution to DIB and UIR Bands

The Family of DIBs (according to Johnson) consists of the following:

Band 4882Å → Ø ← MgTBP → H_2TBP

H_2TBP	
Sharp Qx band 6597Å	Qy narrow band is not resolved
Broad Qx band 6591Å	Qy broad band 6175Å
(See Fig. 1)	

All chromophores are in either Type A (Shpolskii)
Type B (inhomogeneously broadened)

MgTBP
Shpolskii Matrices

Overlapping vibronic bands (usually show structure) width range from 5 to 75 cm^{-1}	Single site vibronic transitions FWHM 3 to 4 cm^{-1}

S_2 state one site (so far) split by 35 cm^{-1}
Origins at 22444 and 22479 cm^{-1}.
Lab Soret at 4428Å Absorption only.
S_1 State consists of 5 + 1 sites
5 of which are split by 36 cm^{-1} (Johnson)
1 site split by 30 cm^{-1} (MgTBP single crystal of n-octane 4K, LIF spectra by Platenkamp & Canters 1981)

Composition of grains clearly affects spectra. In random mixtures, Type B grains will result. In well defined environments only (Shpolskii matrices) does one achieve relatively sharp line (diffuse) vibronic transitions.
For each of the electronic states, there is superimposed a manifold of vibrational states. Thus, subject to the Quantum mechanics selection rules, the following possible transitions are examined in the Lab and in the DIB data:

1	S_0 (0) -->S_1(v)	Absorption	6 sites
2	S_0 (0) -->S_2(v)	Absorption	1 site
3	S_1 (0) -->S_0(v)	Fluorescence	5 sites
4	S_0 (v) -->S_1(0)	Absorption	5 sites
5	S_0 (v) -->S_2(0)	Absorption	1 site

Tables of each set of data were assembled and correlated. The following examples illustrate the procedure using just three of the over 200 vibrations of MgTBP.

238 cm^{-1}	6231.3Å	S_0 --> S_1 (238)	Site 5 x
(Snow, 1992)	6194.6Å	S_0 --> S_1 (238)	Site 4 y
1320	5780.2Å	S_0 --> S_1 (1320)	Site 3 y
(Snow & Seab, 1991)	5790Å	S_0 --> S_1 (1320)	Site 1 y
	5792Å	S_0 --> S_1 (1320)	Site 3 x
DIB + Lab + Red Rectangle	5813Å	S_0 --> S_1 (1321)	Site 2 x

	4408.7Å	S_0 --> S_2 (238)	x
(Knoechel & Moffat 1982)	4402Å	S_0 --> S_2 (238)	y
& (Herbig, 1966).	4394.6Å	S_0 --> S_2 (311)	x
	4387.9Å	S_0 --> S_2 (311)	y

Spectroscopic Summary: LAB, DIBs, RR fluorescence & UIR

Abbreviated Name		Optical coincidences are +/- 1Å Vibrations +/- 1 cm^{-1}				
Free-base	H_2TBP	3 bands	6597Å	6592Å	6175Å	4385Å predicted
ϕ	? ϕ	1 Band	4890Å			
Chi (χ)	MgTBP	92 bands Total	4428Å +17 DIBs (red region)	+ 26 new DIBs (blue region)	+ 35 RR fluorescence bands*	+13 possible (abs. bds in yellow region)

Over 200 individually measured vibrations in MgTBP are seen in the DIB spectra to +/- 1 cm^{-1}.

Line widths: All Shpolskii lines correspond to DIB narrow bands.
Soret [4428Å] Lab width is 28Å, DIB measures 20Å (Herbig, 1966).
Overlapping vibronic bands are exactly accounted for.

Intensity: Integrated intensity ratio of Soret to sum of Q bands is consistent with lab data of MgTBP.

Interstellar abundance: H_2TBP and MgTBP are of comparable abundance, in line of sight for HD 183143: 5×10^{14} & 2×10^{14} respectively.

UIR: Vibrations from MgTBP match detailed UIR spectra.
IR vibrations can be correlated with DIB observed transitions and correspond to ALLOWED IR transitions in MgTBP.

Internal self consistency: Repetition of the same vibrations in different transitions.

e.g. (a) same vibrational frequencies in S_0 connect with S_1 and S_2 states and multiple sites.

(b) great number of identical vibrations are involved in S_0, S_1, and S_2 states because of MgTBP's relatively rigid molecular structure.

All known DIBs are presently accounted for, plus many predicted, and hundreds more found.

UIR Bands

MgTBP is optically pumped in the **visible** region (4400Å --> 6200Å). Accidental overlap of allowed vibronic transitions with allowed IR transitions is one of the necessary conditions for observing IR emission bands. The relatively narrow UIR bands arise from Shpolskii type A grains. Grains B yield the broad UIR bands.

A good quality UIR spectrum* showing some of the more detailed structure is superimposed with the allowed IR vibrations (see Figure 2). The UIR spectrum for NGC 7027 and the Orion bar is adapted from Roche, Aitken, and Smith, 1991.

DIB Vibrations: a list was compiled of all the observed DIB vibrations using the lab established sites. There are more than 200 DIB vibrations which coincide to +/- 1 cm-1 with the measured lab vibrations. This data alone would more than suffice as a unique chemical identification.

Implications

The spectral sensitivity of the chromophores to their immediate chemical environment establishes some of the chemical constituents of the grains in which they reside. These are

(A) PARAFFINS such as octane, nonane, decane, and others... (needed for Shpolskii matrices and producing quasilines)

(B) PYRIDINE.

The presence of pyridine is required not only to produce the spectral DIB matching, but also to produce the 36 cm^{-1} crystal field splitting of the S_1 electronic state. The presence of pyridine in the grains can be confirmed spectroscopically. Pyridine produces a transmission window at 2175Å, matching exactly the well know UV "hump" (see figure 3). On grain reflection, some of the incoming UV radiation is absorbed into the grain's outer layers. "Spikes" in the lab and in the astronomical data are due to vibronic transitions in pyridine.

The lab spectroscopy reported here clearly establishes the presence of MgTBP, H_2TPB, and pyridine in the interstellar grains. The high fluorescence efficiency of MgTBP (being optically pumped in the visible) apparently accounts for all the observed UIR emissions. The presence of three related porphyrins has obvious important implications as to their chemical origins (Johnson, Bailey, and Wegner, 1973), their relationship to each other, and other broader cosmological questions (Johnson, 1976).

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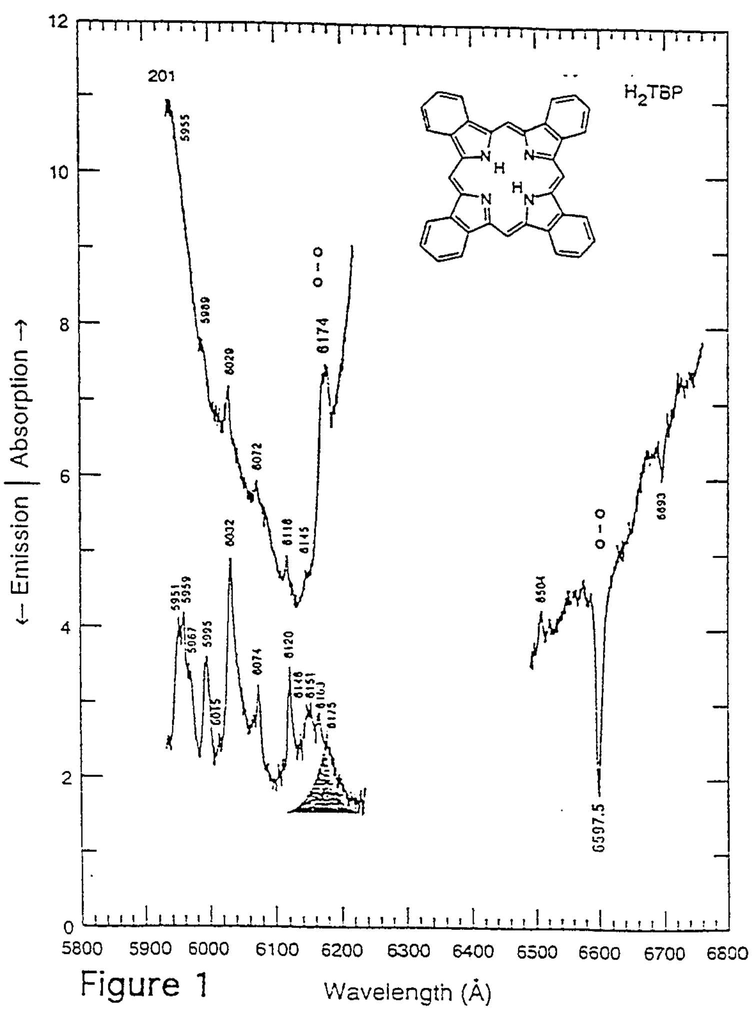


Figure 1

Table 1

<		Mg TBP				>	Cd TBP	< Zn TBP	>	MgP	H TBP
Johnson		Platenkamp & Canters		Johnson			P & C				Johnson
		Matrix		Matrix					Matrix	Matrix	Matrix
Bare Molecule		n-octane 4K		Quatiline 77K		FTIR	4K	Bare		4K	77K
8_1	8_2	8_1	8_2	8_0	8_1	8_0	<8>	<8>	<8>		<8>
1	2	3	4	5	6	7	8	9	10	11	12
238	238	239	vs 238	238			238	238		236	
312		311	311	311		311	309				
1320			1321		1321	1322				1319	

Only the three examples discussed in the text were selected from the extended table containing over 200 vibrational entries.

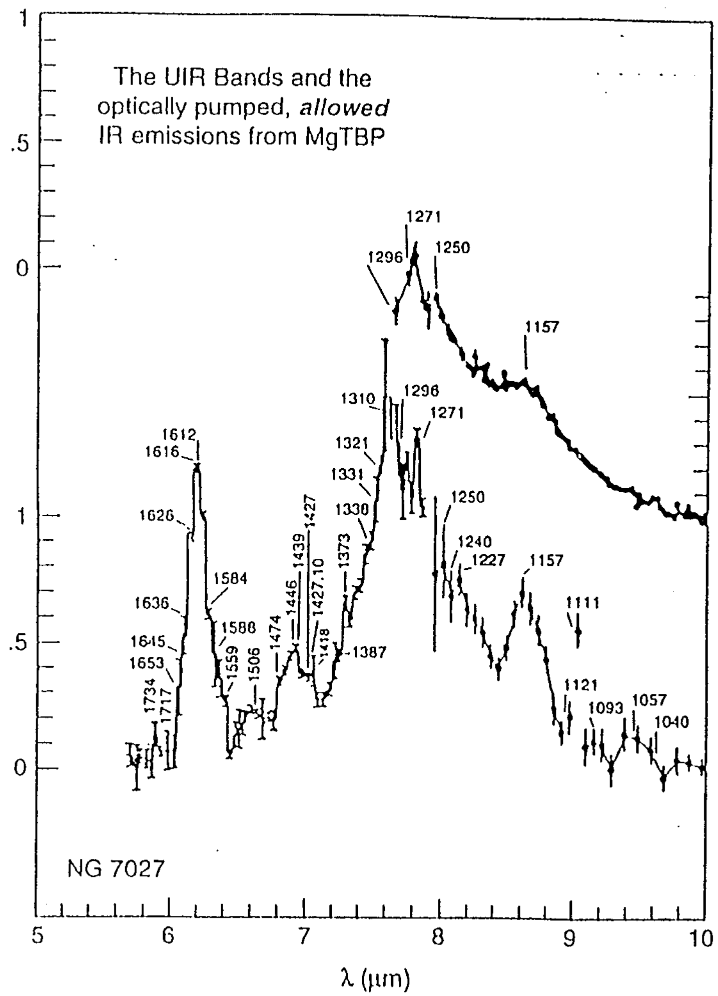
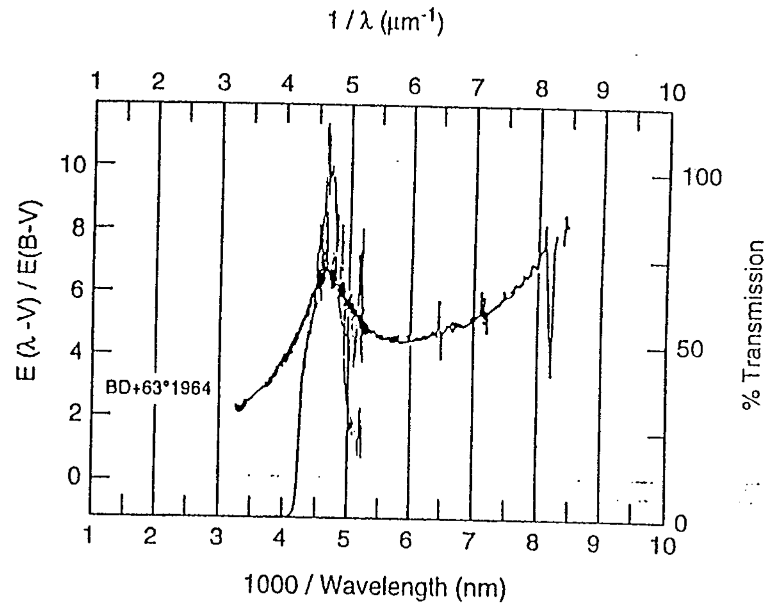


Figure 2



The Spectrum of PYRIDINE superimposed on a typical UV "Hump".

Figure 3