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Chemical Processes in the Interstellar Medium: On the Nature of the Carrier of the Diffuse Interstellar Bands [and Discussion]

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Chemical processes in the interstellar medium: on the nature of the carrier of the diffuse interstellar bands

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The great progress of the past decade in molecular astronomy, primarily by millimetre radio observations, has focused attention upon the synthesis of observed gas-phase species. We briefly discuss chemical modelling of the gas phase. The major portion of this article is devoted to the discussion of the nature of the carrier of the diffuse interstellar bands. The detailed observational study by G. H. Herbig (*Astrophys. J.* **196**, 129 (1975)) provides a quantitative basis against which suggestions for the nature of the carrier of the diffuse bands may be tested. The present paper suggests that the carrier is transition metal ions interacting with the polysulphide ions S_2^- and S_3^- in oxidic lattices.

The nature of chemical processes in the interstellar medium is a topic with considerable history. Since species observed by sharp line spectra are most positively identified, the most discussed chemistries involve mechanisms for the formation of these gas-phase species. The past decade of millimetre radio astronomy has emphasized this point. In discussing chemistries appropriate to the interstellar medium it is perhaps worthwhile asking what is wanted. The list of interstellar species observed is striking in its preponderance of organic molecules (Thaddeus, this symposium). In its own right this is important since it clearly establishes that selective molecular order is the rule under non-biotic conditions. It is of course the goal of the analyst to show that this order is simply the result of natural laws.

The simplest chemistries are, in our opinion, essentially gas-phase processes of a low density, cold (i.e. 20 K) medium with an elemental composition similar to cosmic abundance (for reviews see Watson (1978) and Dalgarno & Black (1976)). The observation of ionic species in dense molecular clouds shows clearly that equilibrium thermodynamical arguments are poor tools upon which to base chemistries. Likewise, even for neutral species, the reaction

$$CO + 3H_2 = CH_4 + H_2O$$

has at 20 K an equilibrium constant

$$\frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3} = 10^{460}(\mathrm{cm^3/molecule})^2,$$

in effect ruling out the existence of carbon monoxide under equilibrium conditions. We are therefore impressed with the need for kinetic models for virtually all gas-phase chemical processes.

The abundance of the elements is such that by number 99.9% of the cosmic material is hydrogen and helium. Depletion of elements from the interstellar gas will only increase this number. It is clear then that the chemistries will depend upon these two elements in particular. The condition of hydrogen is ionized H^+, atomic H or molecular H_2. The nature of the high-energy flux and its coupling to the hydrogen species required to maintain disequilibrium is such that sharp boundaries are expected between any two of these regions. In a homogeneous gas-phase chemistry, we would expect that any species that reacts rapidly with hydrogen will not be observed. Expanding this statement with a particular example, consider H_2^+ and CO^+ These are the positive ions of the most abundant molecules. We can discuss their stability in the three aforementioned regions. In a molecular region, i.e. H_2, the reactions

$$H_2^+ + H_2 = H_3^+ + H$$

and

$$CO^+ + H_2 = HCO^+ + H$$

proceed at the Langevin rate, i.e. with a rate constant equal to 2×10^{-9} s^{-1}, the orbiting collision frequency. In order that, say, $[CO^+]/[CO] = 10^{-6}$, the production of CO^+ from the ionization of CO would require an ionization rate near 10^{-10} s^{-1}, which is probably seven orders of magnitude higher than reality. A similar argument can be made for H_2^+. In a region of atomic hydrogen, H_2^+ is unstable with respect to charge exchange since the reaction

$$H_2^+ + H = H^+ + H_2$$

is exothermic. Similarly, CO^+ is likely to be unstable since the analogous reaction

$$CO^+ + H = CO + H^+$$

is also exothermic. Unless these charge exchange reactions are severely kinetically inhibited we would not expect them to permit the existence of H_2^+ or CO^+, even without concerning ourselves about the formation of H_2^+ and CO^+ in atomic regions.

It may be possible that in H II regions complex stellar injection mechanisms permit sufficient CO^+ and H_2^+ to be formed and that the normally rapid dissociative electron attachment processes of low electron temperatures are slow at the elevated temperatures of these regions, to permit existence of these ions in observable density. Clearly H II regions are not normally considered in discussions of interstellar chemistry. Whether molecular species can exist in these regions at sufficient density to permit observation is, of course, interesting although it would appear to us to be currently of a relatively exotic interest.

The review of gas phase processes in atomic and molecular hydrogen regions is not the intent of this paper. A considerable body of work devoted to modelling molecular process in the interstellar medium with a view to understanding molecular abundances now exists. (A recent interesting specialized review with further references to more general reviews is given by Green (1981).) The breadth of observational data in the area of molecular astronomy that now exists, together with the ever-increasing spectral range of high-resolution observations, indicate that continual progress in the detailed chemistry of the gas component of the interstellar medium will persist.

It is with this progress in mind that we turn to a very different problem. The diffuse interstellar bands have been known for 50 years and continue to stimulate both observation and interpretation. The challenge to arrive at understanding these features arises both from their antiquity and from their ubiquitous occurrence in the spectrum of reddened stars. There are few molecular astronomers who have not been concerned, at least privately, about the carrier of the diffuse bands. The casual interpreter is fortunate to have available the detailed report of Herbig (1975). This most remarkable work provides an abundance of quantitative data of the spectral characteristics of the diffuse interstellar bands. This paper deals with 39 features in the wavelength region 440–685 nm; however, a number of diffuse interstellar bands exist to the red of 685 nm. A recent paper by Sanner *et al.* (1978), for example, establishes interstellar features between 650 and 890 nm. Throughout this report we shall refer to the article of Herbig and detailed sections therein. The unique importance of that paper in virtually its entirety makes reproduction of sections of it in this report pointless.

There are a number of reasons why the diffuse interstellar bands are perplexing. Foremost is the spectral region in which they are observed. In general, most stable molecules do not have transitions in the visible region. Herbig establishes that the bands terminate at a short wavelength limit of 442.8 nm. The entire system is in the visible and near infrared. This is a very far from typical situation for most substances and has even led to speculations that the carrier is a complex organic dye. Secondly, the frequency distribution of features appears erratic with no simple progressions. The intensity distribution of the features is also erratic, with a range of absorption strengths of approximately 200-fold. No elementary progressions among strong features are evident. The strongest feature is that at 442.8 nm, which apparently terminates the systems. Finally the half-intensity widths of the features show wide and erratic variation over a range of 1–100 cm^{-1}. There is no evident correlation between the observed widths and either their frequency or intensity. (It must be noted that the existence of further weak broad features cannot be easily ruled out due to the nature of the observations.) A most convenient representation of this information is by Herbig in his Figure 8.

The diffuse interstellar bands are observed in the spectrum of reddened stars. Since their absorption features lie in the visible region they can only be observed in regions of not too high extinction. In the stars listed by Herbig the most reddened star has a colour excess of 2.0 (E(B – V)), corresponding to 6 magnitudes of extinction. Thus the diffuse interstellar bands are observed in diffuse clouds.

Herbig shows two essential correlations. First, the relative equivalent widths of the individual features of the diffuse interstellar bands in a given stellar spectrum are fixed. Secondly, the equivalent width of any feature varies linearly with colour excess. Since the latter quantity is determined by the column density of material observed in the stellar spectrum, the abundance of the carrier is linearly proportional to the quantity of interstellar material.

The variation of the *shape* of individual features with interstellar region has been examined by Savage (1976) (see also Welter & Savage 1977). There does not appear to be a dramatic variation in shape, say characterized by half-intensity width.

These arguments suggest that any system proposed for the carrier of the diffuse bands must be consistent with conditions existing in diffuse clouds. In particular it is necessary that the relative abundance of the carrier is not a function of gas density. It would appear to us that the linear correlation of carrier abundance with reddening in regions of low extinction is essential in assessing the identity of the carrier.

The absorption intensity of the diffuse interstellar bands is appreciable. The linear correlation of equivalent width of features with colour excess under the assumption of a linear curve of growth leads to the relation between column absorbance and gas column density

$$n_{\mathrm{c}} f_{\mathrm{c}} = 10^{-9} n_{\mathrm{H}}.$$

Here n_{c} is the column density of carrier, f_{c} the oscillator strength of the transition, and n_{H} the column density of hydrogen (see Dulay 1979). Some appreciation of the constraints that this places upon the nature of the carrier is evident by comparison with the ubiquitous diatomic species CH^{+}.

The abundance of CH^+ in diffuse clouds is typically

$$n_{CH^+} = 10^{-8} n_H.$$

It is clear then that the carrier of the diffuse interstellar bands must be similar in abundance to CH^+.

The continual discovery of rotational emission spectra of increasingly complex polyatomic molecules in molecular clouds has stimulated suggestions that the carrier of the diffuse bands is a polyatomic molecule or a group of related polyatomic molecules. This would appear to be useful for explaining the spectral region and complexity of the diffuse bands. There appear to be a number of arguments that can be brought to argue against the possibility that the carrier of the diffuse interstellar bands is a gas-phase species. First, the linear correlation of carrier density with colour excess extends to regions with less than one magnitude of extinction. In no diffuse clouds have polyatomic molecules been observed. (See, however, Bell *et al.* (1981), who have observed the cyanopolyacetylenes in the direction of several diffuse clouds.) Furthermore, as stated, typically in diffuse clouds the column density of the ubiquitous diatomic species CH^+ is $n_{CH^+} = 10^{-8} n_H$. It is difficult to understand how currently unknown polyatomic gas-phase species could be formed in diffuse clouds in the high abundance required. Clearly a gas-phase diatomic species can be virtually ruled out by the irregular frequency distribution of the diffuse features.

There are further arguments against a gas phase carrier. The widths of many of the diffuse features cannot be due to unresolved rotational fine structure if the carrier has an electric dipole moment, since it is well established, in diffuse clouds, that there is a 3 K rotational temperature. Assignment of the width of the features to a predissociation process has the difficulty of reforming the carrier at a rate sufficient to maintain its high concentration.

There has been an effort to understand the diffuse interstellar bands in terms of the spectra of hydrocarbons. Douglas (1977) has suggested that the breadth of spectral features may be the result of internal conversion rather than predissociation, thus avoiding the difficulty of rapid species formation. Closely related to this suggestion is a second vexing problem with hydrocarbon species, namely that of ionization. It is well known that carbon exists primarily in diffuse clouds as C^+. Since the ionization potentials of hydrocarbons are in general somewhat lower in energy than that of carbon, it would be expected that any hydrocarbon would be ionized at least as rapidly as atomic carbon. The electron attachment rate to atomic ions is slow compared with that expected for molecular ions, where in general this attachment is dissociative. These processes of efficient photoionization and dissociative attachment would effectively remove hydrocarbons from the diffuse clouds. P. Thaddeus (personal communication 1981) has argued that for a sufficiently large system, electron attachment will not be dissociative owing to efficient interval conversion mechanisms similar in character to those suggested by Douglas for electronic transitions.

The most attractive type of carrier is the impurity absorber in the solid component of the diffuse matter, as discussed by Herbig (1975). This general remark has been suggested by many. The requirement of visible transitions at first sight makes transition metal ions in oxidic lattices attractive candidates. The general octahedral symmetry of the oxide ions surrounding the transition metal ion does not sufficiently induce appreciable intensity in the spin- and parity-forbidden transitions of these ions. The average oscillator strength near $f = 10^{-6}$, together with cosmic abundances in the range 3×10^{-6} to $3 \times 10^{-5} n_H$, is at least two orders of magnitude below that required by the constraint

$$n_c f_c = 10^{-9} n_H.$$

Terrestrial minerals containing large amounts of iron often show relatively sharp absorptions near 443 nm. All of these minerals – especially those that show the strongest ligand field bands – have a very intense absorption beginning just to the blue of 440 nm. This oxygen–iron charge transfer transition is allowed, with an oscillator strength of approximately 10^{-2}. It is difficult to see how the 443 nm band could be a small shoulder on a much larger absorption.

Dulay has reviewed the arguments for transition metal ions as the carrier of the diffuse bands. He suggests that lattice defects could enhance activity, through breaking parity selecting rules, by the required several orders of magnitude. We shall return to this point shortly.

A very different system, the polysulphide ions S_2^- and S_3^-, have been the subject of recent study. Surprisingly it is only in the last decade that much analysis of their colours and the colours of ionic lattices (including glasses) doped with these species have been understood.

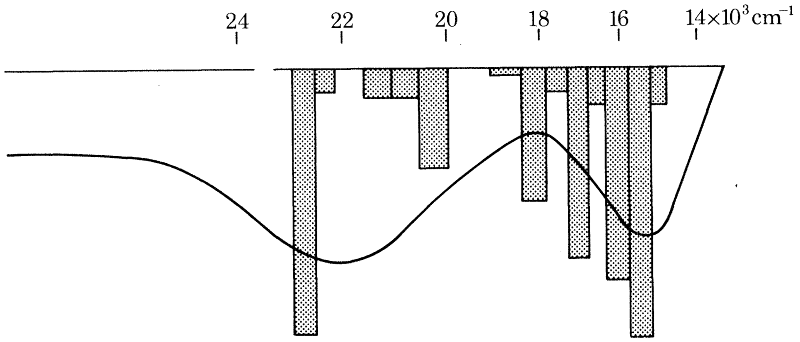

FIGURE 1. Frequency distribution of the equivalent widths of the diffuse spectra. (Data taken from Herbig (1975), Table 1.) The solid curve is the spectrum of commercial borosilicate glass, showing the absorption S_2^- near 450 nm and S_3^- near 620 nm.

Figure 1 presents a low-resolution histogram of the equivalent width frequency distribution in 500 cm^{-1} intervals of the diffuse bands. The data are in HD 183143 of Herbig (1975). In view of the linear correlation discussed earlier, the histogram should be universal. Shown also in figure 1 is a laboratory spectrum of the species S_2^- and S_3^- in a borosilicate glass. The broad transition centred at 16000 cm^{-1} is that of S_3^- while the transition at 22000 cm^{-1} is that of S_2^-. It is clear that the polysulphide negative ions have an excellent spectral match with the diffuse interstellar bands. Furthermore, it is noteworthy that there are no further resonances of S_2^- or S_3^- in the near ultraviolet. Sulphur has a relatively high cosmic abundance, namely 2×10^{-5} that of hydrogen. The oscillator strength of the S_2^- band system at 450 nm is 0.05. Thus the abundance intensity product requirement

$$n_c f_c = 10^{-9} n_H$$

is readily met. The formation of S_2^- and S_3^- in oxidic glasses is extremely insensitive to the method of glass formation. A wide variety of sulphur-containing forms when added to oxide glasses give S_2^- and S_3^-. The absorptions in the visible have been known for a long time; their assignment to S_2^- and S_3^- is relatively recent. A recent discussion of spectra, together with electron structure calculations, is given by Cotton *et al.* (1976).

There are several, seemingly intrinsic, difficulties in suggesting that the carrier of the diffuse bands is the polysulphide ions. The spectra of the species S_2^- and S_3^- would be expected to show vibrational progressions. The vibration frequency of S_2^- has been assigned as 365 cm^{-1} (Huber & Herzberg 1979). There is little evidence of these in the diffuse interstellar bands. The narrow widths shown by the diffuse interstellar bands do not appear to match well the observed spectra of the polysulphides. We have examined the spectra of some materials containing both S_2^- and S_3^- at 4 K, with the obvious hope that structure resembling intervals observed in the diffuse interstellar bands would appear. Our present results are indifferent. The two broad features observed in a borate glass show no change upon cooling from room temperature to 4 K. We have also examined the absorption spectrum of thin (300 μm) sections of the mineral sodalite cut from gem-quality lapis lazuli. The beautiful blue of this mineral is due to S_3^-. While a considerable change in the spectrum is observed upon cooling from 298 to 4 K, the features that develop are broad at 4 K compared with the diffuse interstellar bands. Our attempts to diffuse sulphur into crystalline $MgSiO_3$ were unsuccessful.

Although the polysulphide ions are attractive as the carrier of the diffuse interstellar bands from the excellent match of electronic energy interval and high intensity, it appears unlikely that their spectra in essentially inert oxidic lattices can match the detailed features of the diffuse interstellar bands.

We thus return to the suggestion of Dulay that the diffuse interstellar bands are transitions of transition metal ions in oxidic lattices perturbed by lattice defects. We suggest that the specific defects responsible for the intensity are the polysulphide ions S_2^- and S_3^-. The optical strength of the transition metal is obtained from resonantly matched transitions in either of the polysulphide ions. It is clear from the observed spectra of these ions that they match appropriate transitions of the transition metal ions. We note further that both S_2^- and S_3^- are spin doublets; thus any coupling with the transition metal systems can break down the spin selection rule in addition to parity selection rules. In particular the Fe^{3+} system has ground state (d^5) $^6S \rightarrow {}^6A_1$ in an octahedral field. The upper states of Fe^{3+} in transitions observed in the visible region are all quartet derived primarily from ^4G and ^4D (Hush & Hobbs 1962).

Since iron is by far the most abundant transition metal, there is a considerable utility in a mechanism in which the visible transitions of Fe^{3+} can obtain appreciable intensity. As discussed by Dulay, the collection of transition metal ions in oxidic lattices is expected to produce an erratic distribution of transition frequencies.

The present proposal for the carrier of the diffuse interstellar bands is virtually devoid of chemical processes. It is likely that the oxidic lattices doped with transition metal ions and the polysulphide ions are formed in stellar envelopes under high-temperature conditions, rather than by accretion in cold interstellar regions. The indication that the diffuse bands are not observed in circumstellar shells (Smith *et al.* 1977) is interpreted to mean that the features of the spectra show sufficient broadening as a function of temperature to become obscured at the higher temperatures of circumstellar material.

The present suggestion for the carrier of diffuse interstellar bands satisfies the correlations shown by Herbig. First, it is essentially an elemental explanation. Thus within the constancy of cosmic abundance in the transition metals, the features are expected to show covariant equivalent widths. Secondly, if the scattering material, i.e. the origin of colour excess is uniform, at least statistically, than there will be a covariance of equivalent width with colour excess.

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Discussion

L. J. ALLAMANDOLA (*Laboratory of Astrophysics, Leiden University, The Netherlands*). At Leiden University we have been carrying out experimental research designed to further our understanding of the role that interstellar grain mantles play in the spectroscopy and chemistry of the interstellar medium by investigating the photophysical and photochemical properties of 10 K mixtures whose composition (CO, H_2O, NH_3, CH_4) is chosen to mimic that which would be expected to make up the accretion mantle of an interstellar grain (Hagen *et al.* 1979, 1980). This laboratory work is based on the premise that, apart from H_2 and perhaps a fraction of the CO, most collisions between the interstellar gas (50–100 K) and dust (10–15 K) in molecular clouds will result in the molecules' accreting onto the grains and being photolysed by the diffuse interstellar radiation that penetrates the cloud (Greenberg *et al.* 1972).

To study the kinds of photo-induced chemical processes that can take place in the grain mantle, Mr C. van de Bult has been studying the infrared spectra of 'ices' that have been subjected to ultraviolet radiation. New but weak absorptions appear in the infrared, showing that new molecules such as NH_2HCO, H_2CO, C_3O_2, CO_2 and O_3, and radicals such as HCO and NH_2 are produced and stabilized. Alterations also occur in the visible region of the spectrum. Dr F. Baas has been studying these changes and has found that, apart from three weak absorptions (O.D. $\approx 10^{-4}$) that grow in at the same wavelength and with the same width as three of the strongest interstellar bands, those at 443.0, 577.8 and 579.7 nm, no other absorptions occur. A comparison is shown in figure d1. Figures d1*a* and d1*b* show the 443.0 nm (Wampler 1966) and 577.8 nm (Herbig 1975) interstellar features respectively, while figures d2*c* and d2*d* show the corresponding laboratory features. It is significant that the strongest interstellar bands are those corresponding to the features that Dr Baas has measured, and because the laboratory features are weak, although possessing an *f* number estimated to be between 10^{-2} and 1.0, it is reasonable to assume that as experimental sensitivity is improved, more absorptions may come to light.

Finally, in view of the fact that all of the complex interstellar molecules seen in the gas phase should be accreted onto the grains in a time much shorter than molecular cloud lifetimes, there must be a means of getting them off the grains even though the nominal grain temperature is of the order of 10 K, a temperature at which normal evaporation mechanisms cannot play a role. Mr L. d'Hendecourt has found that when an ice that was at 10–15 K during irradiation is slowly warmed, significant quantities of molecules are ejected between 25 and 30 K. This subthermal molecule ejection is driven by the thermally promoted release of the reactive species that were formed during photolysis and have been 'frozen' into the lattice, occupying non-reactive sites. At approximately 25 K some of these species are released from their sites and free to diffuse through the lattice until they react. The heat generated by these reactions results in an explosion-like ejection of material. Since a small fraction (10^{-5}) of the energy of reaction is released as chemiluminescence, the correlation of bursts of light with pulses in pressure would confirm this reaction-induced subthermal molecule ejection scheme. Such evidence is shown in figure d2. Nearly all of the material in the ice is ejected in the very intense pressure burst that occurred at 27 K. A viable triggering mechanism is required for this process to occur in the interstellar medium; at present grain–grain and cosmic ray–grain collisions are being considered.

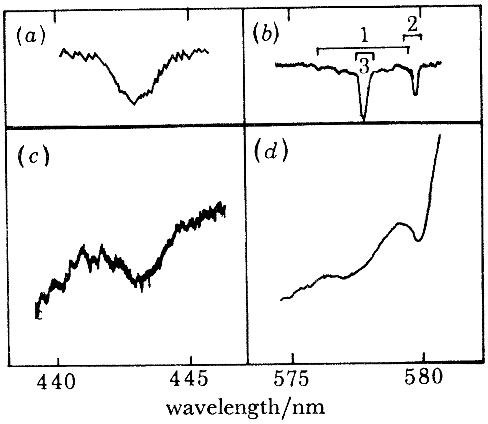

FIGURE d1. Comparison of (*a*, *b*) the 443.0, 577.8 and 579.7 nm diffuse interstellar bands with (*c*, *d*) the absorptions that appear upon photolysis of a mixture of CO, CH_4, NH_3 and H_2O at 10 K.

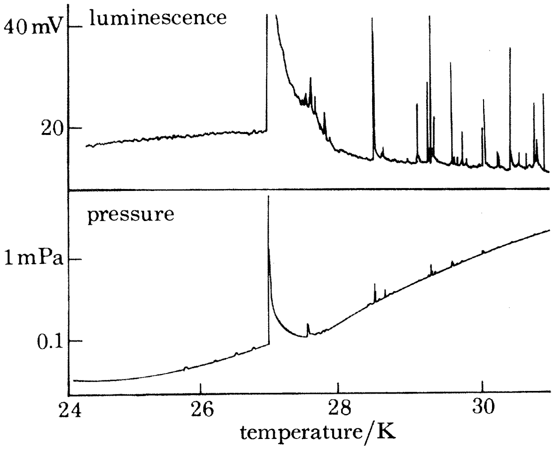

FIGURE d2. Correlation of chemiluminescence spikes with pressure bursts from the mixture $CO:H_2O:NH_3:CH_4$ (10:1:1:4); after three cycles of deposition for 10 min and photolysis for 2 h were carried out at 10 K.

Summarizing, we believe that accretion mantles occur in the interstellar medium as evidenced by the infrared spectra of certain interstellar infrared sources. Laboratory photolysis of

10 K ices produce absorptions in the visible that resemble, both in frequency and band profile, some of the more intense diffuse interstellar bands, including the well known 443.0 nm feature. Furthermore, this irradiation also produces reactive species within the ice itself, providing the means by which many of the molecules that make up grain mantles can be released back into the gas phase.

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