Organic Molecules in Translucent Interstellar Clouds

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Abstract  Absorption spectra of translucent interstellar clouds contain many known molecular bands of CN, CH+, CH, OH, OH+, NH, C₂ and C₃. Moreover, one can observe more than 400 unidentified absorption features, known as diffuse interstellar bands (DIBs), commonly believed to be carried by complex, carbon-bearing molecules. DIBs have been observed in extragalactic sources as well. High S/N spectra allow to determine precisely the corresponding column densities of the identified molecules, rotational temperatures which differ significantly from object to object in cases of centrosymmetric molecular species, and even the $^{12}$C/$^{13}$C abundance ratio. Despite many laboratory based studies of possible DIB carriers, it has not been possible to unambiguously link these bands to specific species. An identification of DIBs would substantially contribute to our understanding of chemical processes in the diffuse interstellar medium. The presence of substructures inside DIB profiles supports the idea that DIBs are very likely features of gas phase molecules. So far only three out of more than 400 DIBs have been linked to specific molecules but none of these links was confirmed beyond doubt. A DIB identification clearly requires a close cooperation between observers and experimentalists. The review presents the state-of-the-art of the investigations of the chemistry of interstellar translucent clouds i.e. how far our observations are sufficient to allow some hints concerning the chemistry of, the most common in the Galaxy, translucent interstellar clouds, likely situated quite far from the sources of radiation (stars).

Keywords  Galaxy · Interstellar matter · Cloud chemistry · Biochemistry · Biophysics

Introduction

Absorption spectra of translucent interstellar clouds consist of:

– continuous interstellar extinction which is a direct sum of two phenomena: absorption and scattering, caused by small dust particles of diameters smaller than the light wavelength (Krełowski & Papaj, 1993). The Extinction curve (i.e. the difference between flux distributions of reddened star and unreddened standard of the same Sp/L) depends on
size, shape, chemical composition and crystalline structure of grains which also (if non-spherical and aligned) cause polarization of starlight.

- spectral lines of interstellar atomic gas. The $H$ and $K$ doublet of CaII was discovered by Hartmann (1904). The vast majority of atomic interstellar lines (resonance ones) are accessible only to space-borne instruments; the low frequency of inter-atomic collisions makes populations of excited states negligible. The heavy elements in the interstellar medium (ISM) are strongly depleted in comparison to their abundances in stellar atmospheres likely because of dust formation from heavy elements and chemical reactions leading to the formation of different (possibly complex) molecules,

- molecular bands of simple polar radicals ($CH$, $CN$, $CH^+$) have been discovered and identified long ago (McKellar 1940). For a long period they were believed to be the only possible interstellar molecules. In 1970s also homonuclear molecules ($H_2$, $C_2$) have been found. At the same time rotational emission features revealed the presence in the interstellar matter of many complex molecules with an electric dipole; the full list of these polar species (mostly carbon-bearing) contains currently more than 200 entries according to Wikipedia (http://en.wikipedia.org/wiki/List_of_interstellar_and_circumstellar_molecules) and demonstrates clearly a very rich carbon chemistry in interstellar clouds,

- diffuse interstellar bands (DIBs): the longest standing unsolved problem of the spectroscopy in general. The first two such features were discovered in 1921 by M.L. Heger (1922). The application of solid state detectors to DIB observations led to discoveries of new features. Currently, the list of known DIBs contains more than 400 entries (Hobbs et al. 2008, 2009); a majority of them - very shallow. Even more importantly, the fine structure (reminiscent of the rotational contours of bands of polyatomic molecules) has recently been detected in some DIBs (Kerr et al. 1998). Nearly all conceivable forms of matter - from the hydrogen anion to dust grains - have been proposed as DIB carriers, so far with no generally accepted success.

During the last few years interest in interstellar molecules has increased substantially and resulted in the birth of a new discipline – astrochemistry, marked with the 280 IAU Symposium “The molecular Universe” held in Toledo (Spain) in May 2010. According to existing models, chains of chemical reactions which very likely occur in interstellar clouds, in most of cases involve carbon atoms. Out of over 200 identified interstellar molecules (including 15 cations and 5 anions), organic ones, in particular those built up on carbon chains (of up to 11 C atoms), make the vast majority. Such species are mostly observed in vicinities of stars (in the circumstellar medium). The general ISM is of too low density and thus dark clouds (prestellar?) are the sites where many molecules of astrobiological importance can be formed whereas carriers of DIBs survive in low density, translucent clouds. Interactions between dust and molecular species can play an extremely important (but so far unknown) role in physico-chemical processes in the ISM. The role of dust is particularly important in the evolution of interstellar gas in the direction of an extended chemical complexity. Dust particles do not simply guarantee the survival of the molecular component of the gas in an environment that is otherwise hostile, but are themselves sites of molecule formation, depending on their composition and surface structure, playing an important catalytic role.

The still unknown nature of DIB carriers is one of the most challenging problems that astrochemists are facing. Many hypotheses have been formulated on this subject, ranging from dust grains to several gas-phase free molecules to even the hydrogen negative ion. The spectral region, where DIBs occur (from visible to near infrared), is characteristic for electronic transitions of complex chemical species. The nearly constant positions and nearly unchanged
profiles of DIBs, irrespective of the line of sight, point to free gas-phase molecules as the carriers of these bands. Among the proposed carriers the most likely ones are: (hydro) carbon chains, Polycyclic Aromatic Hydrocarbons (PAHs) and fullerenes. High resolution, high S/N profiles of DIBs may play a decisive role in the identification of their carriers by means of comparison with laboratory gas-phase spectra. It is of fundamental importance to understand the limitations of both laboratory and astrophysical spectra.

Molecules can be formed in the gas phase and on grains; it is important to divide them into such groups of species – this has not been done yet. It is evident that grains, present in different interstellar clouds, differ in optical (physical) parameters. The recent, precise survey of interstellar extinction curves (Fitzpatrick & Massa, 2007), shows many “peculiar” extinction curves. It seems natural that these differences may be related to different levels of heavy element depletions; however, it is not clear how different chemical composition may influence surface parameters of dust particles and thus – their possibilities to facilitate some chemical reactions. One of the interesting questions is whether different shapes of extinction curves are related in a way to abundances of simple interstellar radicals and carriers of diffuse interstellar bands.

It is commonly accepted that main components of observable interstellar molecules are hydrogen, carbon, oxygen and nitrogen. This follows abundances considerations. Other abundant elements are noble gases which most likely do not participate in chemical reactions. The recent publication by Barlow et al. (2013) reports, however, the first detection of the $^{36}$ArH$^+$ molecule in the Crab Nebula. The same abundant and reactive elements are likely main components of dust particles. The optical properties of the latter may, however, depend not only on their chemical composition; they likely depend on the structure of the bulk material but also on details of the surfaces. The latter not only absorb or scatter the light but also may play important catalytic role in formation of some molecular species.

Physical parameters of translucent interstellar clouds may significantly differ from object to object. One of the simplest evidences of the above thesis is a comparison of the intensity ratio of neighbouring spectral features: the A-X (0,0) transition of the CH$^+$ molecule (near 4,232.5 Å) and the CaI 4,226.7 Å line. Figure 1 compares these two features in spectra of HD207198 and HD24912. The strength ratio is dramatically different and proves clearly that the parameters of the intervening clouds are very different. The extinction curves, derived from the spectra of these targets, are also evidently different (Wegner 2002). That of HD24912 resembles closely the so called σ type curve while that of HD207198 – is rather of ζ type (see Fig. 1).

![Fig. 1](image_url) Two neighbour interstellar features seen in two high resolution spectra. Note the evident difference in physical conditions in both (or more) intervening clouds.
later). One can also see that radial velocities of \( \text{CH}^{+} \) and \( \text{CaI} \) are not necessarily identical. Likely more than one cloud is being intersected by the chosen sightlines. This is a very common situation. In such cases one can try to divide the spectral lines into individual Doppler components of single clouds; this is, however, impossible in the case of extinction which naturally involves all, likely different, contributions from all intervening clouds with unknown proportions, producing thus an ill-defined average, which is hard to interpret in terms of physical processes.

Another interesting question is whether all interstellar spectral features, observed along the same sightline, originate in the same gas. The answer is seemingly negative (Fig. 2). As we see the radial velocities of \( \text{CH} \) and \( \text{CH}^{+} \) lines may differ by more than 7 km/s. They are likely formed in different clouds as one cloud cannot have two very different radial velocities. In any case the diffuse band spectrum and, even more likely, the extinction curves, are formed in more than one cloud along a sightline and what we observe is an ill-defined average of contributions added by all clouds intersected by the line of sight. This fact makes physical considerations very complicated because the spectral features (especially DIBs), originate in different clouds, and are practically never fully resolved because their widths are much larger than those of atomic lines or the molecular features depicted in Figs. 1 and 2.

It is important to mention that simple, carbon-bearing radicals are observed not only inside the Milky Way but also in extragalactic objects. The strongest \( \text{CH} \) feature at 4,300 Å was observed e.g. in the Andromeda galaxy (Cordiner et al. 2011). Such observations prove clearly that the physical conditions inside our Galaxy do not differ seriously from those in other galaxies, even reasonably distant. Practically all absorption interstellar features, observable in Galactic objects, can be found in other galaxies as well. Diffuse bands have already been observed with very reasonable red-shifts (up to 1,200 km/s - Sollerman, J., 2005). However, since the vast majority of interstellar features are very shallow, it is very difficult to detect them in spectra of extragalactic objects, being naturally faint, which deteriorates the S/N ratio and/or resolution of their spectra.

Specific Properties of Interstellar Molecules

The above mentioned molecules are polar species and thus their rotational temperatures should be very close to that of the cosmic background radiation (CMBR) as such species must easily cool by means of rotational transitions. In fact there is only one object in which we observe
until now \(CH\) and \(CH^+\) transitions from rotationally excited levels – Herschel36 (Oka et al. 2013). In this particular case the rotational temperature of the \(CH\) and \(CH^+\) radicals are about 14 K (Fig. 3) which the value is very high as for the interstellar medium because the expected one is that of CMBR i.e. 2.725 K.

Initially it was expected that excitations are entirely absent in interstellar space. However, soon after the \(CN\) radical was discovered, its violet band near 3,875 Å demonstrated two transitions from the first rotationally excited level (McKellar 1940). The source of this phenomenon was found only a quarter of century later when the cosmic background radiation was discovered. Although all (then) known interstellar molecules are polar species and should be excited by the same CMBR, transitions from excited levels are commonly observed only in the case of \(CN\). This is because the wavelengths of exciting photons are very far from the CMBR Planck maximum in the cases of \(CH\) and \(CH^+\). In the case of \(CN\) one can trace in very high S/N spectra not only transitions from the first but also from the second excited level. The population of the first one is about 40 % of the ground one while that of the second – only about 2 %. This is why it was observed until now only in a few objects (Fig. 4).

The intensity ratio of the R(0) to R(1) lines should be 3.72 if the published oscillator strengths are accurate. The recent analysis of the very high S/N spectra from Kueyen/UVES and 3.6 m/HARPS spectrographs (Krełowski et al. 2012) proved that the observed ratio is quite ridiculous: it is equal to \(\pi\) (Fig. 5)! This may be due to either an additional pumping mechanism, leading to the \(CN\) rotational temperature 2.966 K, or to errors in the published oscillator strengths.

Diffuse bands are believed to be carried by some complex, carbon-bearing molecules. It is very interesting to check how they behave in evidently different physical conditions. Let’s select the two objects, well known as \(\sigma\) and \(\zeta\) types. They have been found by Krełowski & Westerlund (1988) as the two objects in which the strength ratio of 5780 and 5797 major DIBs was different. Their extinction curves are also very different – see Fig. 4.20 and 4.21 of Fitzpatrick & Massa (2007). In the case of \(\sigma\)Sco (HD147165) we observe a very strong and “slim” 2,200 Å bump and rather low far-UV extinction. The ratio of total to selective extinction seems to be higher than the “canonical” value of 3.1. On the other hand \(\zeta\)Oph (HD149757) demonstrates a weak and broad extinction bump, rapid far-UV growth of extinction and a ratio of total to selective extinction lower than 3.1. Figure 6 below demonstrates the molecular bands (\(CN\) and \(CH\)) in these two targets as well as the major 5780 and 5797 DIBs. It is evident that, despite very similar colour excesses, the molecular bands are much stronger in

![Fig. 3](image)

Fig. 3 The transitions from the first rotationally excited levels of the \(CH^+\) molecule observed in the spectrum of Herschel36; \(T_{rot}\) is close to 14 K. The upper spectrum is that of the “Red Rectangle” and contains emission lines
ζ Oph; this is especially striking in the case of CN. On the other hand the major 5780 DIB is much stronger in the case of σ Sco. The narrow 5797 DIB seems to be of similar intensity in both objects but in σ Sco one can see the neighbour 5795 feature which may be a separate DIB or the 5797 wing – a result of e.g. higher rotational temperature of the carrier. It is emphasized that polar species may reach high temperatures only in exceptional conditions in contrast to centrosymmetric species which may be of quite high rotational temperatures (Ádámkovics et al. 2003).

It is thus interesting whether the σ and ζ cases differ also if centrosymmetric molecules are considered. The most easily available ones are C_2 and C_3. The former is available in near infrared while the latter – in the violet. The bands of centrosymmetric species contain typically many lines because many rotationally excited levels can be populated in such species since their cooling goes through forbidden transitions. Figure 7 presents the most easily available

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**Fig. 4** Very high S/N UVES spectrum containing the CN B^2Σ^+ - X^2Σ^+ (0,0) band; below – the scheme of the excitation levels

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![Diagram](image)

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**Fig. 5** Unforseen ratio of the R(0) and R(1) equivalent widths of the CN B^2Σ^+ - X^2Σ^+ (0,0) band lines. Only unsaturated lines are included. Note three objects where the rotational temperature is evidently higher than the average. Lack of opposite cases proves that this is not a scatter

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Phillips A$^1\Pi_u - X^1\Sigma^+_g$ (2,0) band in the objects depicted also in Fig. 6. It is evident that the $C_2$ molecule is much more abundant in $\zeta$Oph, i.e. resembles the behaviour of CN. It is impossible to estimate rotational temperature in $\sigma$Sco; that, seen in $\zeta$Oph is quite high because the high rotational levels are populated sufficiently to cause detectable lines.

Figure 8 depicts the $C_3$ $\Pi_u - \Sigma + g$ (000,000) molecular band (the only one observed until now) in both targets. The spectrum of $\sigma$Sco is the average of 17 exposures done using the ESO HARPS spectrograph (resolution $R=115,000$). It is compared with the ESO UVES spectrum of $\zeta$Oph being the average of 150 exposures (resolution $R=80,000$). The band is below the level of detection in the former object as well as that of $C_2$. In $\zeta$Oph the band is evident and

![Figure 6](image1.png)

**Fig. 6** The archetypes of $\sigma$ (HD147165) and $\zeta$ (HD149757) type clouds. The former carries very strong broad DIBs (like 5780), the latter – very strong molecular bands, especially of CN. It is not clear whether the 5795 DIB is a separate feature or it is a wing of 5797, caused by e.g. higher rotational temperature of the carrier.

![Figure 7](image2.png)

**Fig. 7** The $C_2$ Phillips $A^1\Pi_u - X^1\Sigma^+_g$ (2,0) absorption band seen in $\sigma$Sco and $\zeta$Oph. The band falls below the detection limit in the former case. In the latter highly excited levels are populated which indicates relatively high rotational temperature.
also demonstrates a relatively high rotational temperature (the presence of the bandhead towards the blue). Unfortunately we cannot compare the rotational temperatures of the centrosymmetric species in these two objects. Anyway one can conclude that the abundances of the di- and tricarbon molecules are high in $\zeta$ type objects as well as that of $CN$. The currently available data do not allow to be sure whether the rotational temperature of simple centrosymmetric species influences DIB profiles or not.

Conclusions

Generally it is very difficult to find reddened stars in which interstellar features are free of Doppler splitting. In the vast majority of cases one can observe only ill-defined averages when a sightline intersects several clouds. This makes possible detections of certain species but a determination of their relative abundances is very difficult. Also the rotational temperatures and their relations to e.g. diffuse band profiles remain uncertain. We have demonstrated above that physical parameters of individual clouds may be drastically different. It is thus necessary to concentrate on very rare single cloud cases as only there can one expect specified physical conditions. Our examples seem to be such cases. What do they suggest?

Three different spectral features apparently vary in unison; they are: continuous extinction, abundances of simple (identified) radicals and carriers of diffuse bands. A change of shape of extinction curve is followed by different relative abundances of all other species. It is, unfortunately, impossible to interpret at the moment this complex phenomenon. Dust grains, responsible for the extinction, may play more than one role. They can protect molecular species against UV stellar radiation but they can also play a catalytic role in the formation of certain molecules ($H_2$ is believed to be formed on surfaces of grains). However, simple molecules can also be abundant because they are possible products of disruption of more complex species. Both processes (fusion and disruption) can be responsible for high $CN$, $C_2$ and $C_3$ abundances in $\zeta$ type clouds. The different extinction curves reveal different grains (of different optical properties); this is however, accompanied with different abundances of DIB carriers which, as we believe, are complex, carbon-bearing molecules. The currently available data do not allow to decide which of the processes takes place in the interstellar clouds.

Fig. 8 The $C_3$ $\Pi_u - \Sigma^+ (000,000)$ band observed in $\sigma$Sco and $\zeta$Oph. The species is of high rotational temperature in $\zeta$Oph (note the bandhead near 4,050 Å); in $\sigma$Sco it falls below the level of detection.
There are several single cloud reddened stars which may be used to investigate physical properties of the interstellar matter. They are: HD27778 (ζ type object), HD62542 (ζ type object) and HD154445 (σ type object). All these examples show the same properties. It seems to be of basic importance to select a larger sample of targets with “peculiar” extinction curves and to determine the behaviour of molecular features and diffuse bands in such spectra.

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