

# The diffuse interstellar bands: a dipole–bound state hypothesis

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## ABSTRACT

It is proposed that some, possibly many, of the unidentified diffuse interstellar absorption bands arise from rovibronic transitions between the ground states of negatively charged molecules and/or small grains, and shallow dipole–bound electronic states which lie close to the electron detachment threshold. Under this hypothesis the attributes for the neutral ‘molecular’ frameworks are electron affinities between 1 and 3 eV and permanent electric dipole moments of  $\sim 2$  debye or greater. Bound–bound spectra involving the lowest rotational levels have not been detected in the laboratory, but these proposed carriers appear to be capable of satisfying the main observational astronomical constraints: transitions that lie in the range from the near-ultraviolet to the near-infrared; a wide range of widths; band wavelengths that are invariant; and a large number of related but distinct carriers. The wavelengths of the lowest rotational lines of the  $0_0^0$  band of the transition between the ground and a dipole–bound electronic state of the  $\text{CH}_2\text{CN}^-$  molecule appear to be consistent with a diffuse band near 8037 Å.

**Key words:** molecular processes – stars: individual: HD 183143 – dust, extinction – ISM: molecules.

## 1 INTRODUCTION

The problem of identification of the carriers of the diffuse interstellar bands is a major challenge (Herbig 1975, 1995). The bands are unusual in that they fall only in the range 4000–13 000 Å ( $\sim 1$ –3 eV) and have widths that range between  $\sim 1$  and 30 Å. They now number over 200 (Jenniskens & Désert 1994), which suggests that there is a large collection of carriers. Searches for regular spacings in the spectrum have proved fruitless with one exception (Herbig 1988). The spectrum has characteristics reminiscent of both solid-state carriers and free gas-phase molecules, and many proposals for the absorbers have been made. These range from atomic anions to porphyrins, and include impurities in or on grains (Herbig 1995). Possible carriers recently discussed include  $\text{H}_2$  (Sorokin & Glowina 1996),  $\text{C}_{60}^+$  (Foing & Ehrenfreund 1997), and pure carbon chain anions (Tulej et al. 1998) for which matches between laboratory and the astrophysical data have been found.

The hypothesis presented here is based on the assumption that there exists a set of negatively charged molecules and/or small dust grains in diffuse interstellar space for which the neutral ‘core’ has an electron affinity between 1 and 3 eV and a permanent electric dipole moment of at least 1.625 debye. The latter attribute is responsible for the existence of electronic dipole–bound state(s), which form the upper electronic states of the transitions.

## 2 THE NATURE OF DIPOLE–BOUND STATES

The problem of an electron in a dipole field has been studied theoretically for many years (Fermi & Teller 1947; also see references in Turner 1977; Clary 1988; Bates 1991). Although the moment of inertia and dipole length influence the critical value of the dipole moment needed to sustain a bound state for the electron (Garrett 1970), binding energies of up to at least  $100\text{ cm}^{-1}$  are predicted. The origin of the bound state(s) is the long-range  $-1/r^2$  attractive potential for an electron in the dipole field. This electron is only loosely attached and is located in an orbital with a mean distance up to many tens of Ångström units from the positive end of the dipole. The molecular rotational constants of the dipole–bound state are therefore virtually the same as those of the free neutral molecule.

The existence of dipole–bound states has been demonstrated in electron photodetachment experiments on substituted acetophenone enolate anions (Zimmerman & Brauman 1977; Jackson, Zimmerman & Brauman 1979), acetaldehyde enolate,  $\text{CH}_2\text{CHO}^-$  (Jackson, Hiberty & Brauman 1981; Mead et al. 1984),  $\text{CH}_2\text{CN}^-$  (Marks et al. 1986; Lykke et al. 1987),  $\text{CH}_2\text{CC}^-$  (Yokoyama et al. 1996a,b) and other molecular systems (Bates 1991). In these studies the presence of the state is revealed through photoexcitation to autoionizing levels of the dipole–bound state and detection of the electron or the neutral molecular fragment. From spectroscopic analysis and also through observation of excitation to bound levels which are subsequently rendered unstable by electric field-induced detachment (Mead et al. 1984), the reality of

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dipole-bound states of molecular anions that lie below the ionization threshold has been unambiguously confirmed. It is notable that the long-range nature of the dipole-bound state implies that the same physical principles apply whether the neutral core is described as a ‘molecule’ or as a cluster of atoms in the form of a small grain.

### 3 DIPOLE-BOUND STATES AND THE DIFFUSE BAND SPECTRUM

Dipolar molecules and grains in diffuse cloud environments should relax radiatively to close to the 3K background temperature. Hence an absorption spectrum will arise by excitation from the lowest levels of the electronic ground state to *bound* levels of the dipole-bound state just below the ionization threshold. The  $0_0^0$  band necessarily occurs at a wavelength determined principally by the electron affinity of the corresponding neutral molecule, and the electronically excited system may be pictured as an internally cold neutral polar entity loosely associated with a distant electron. Transitions may also occur to autodetaching vibronic levels, giving a wide range of absorption widths depending on the strength of the coupling between the optically pumped states and the ionization continua. This problem has been explored experimentally (see e.g. Marks et al. 1986; Lykke et al. 1987; Yokoyama et al. 1996a,b) and theoretically (Clary 1988), and this aspect of the hypothesis is closely related to the atomic pre-ionization and molecular pre-dissociation suggestions of Herzberg (1955). Internal conversion following excitation to bound levels could also lead to broadening of the bands, perhaps particularly for larger ‘molecular’ systems. Excitation of anions to both fully bound and quasi-bound levels of dipole-bound states is therefore expected within this hypothesis, yielding a superposition of both types of spectra as well as a contribution to the extinction continuum arising from bound-free photodetachment. The possible contribution of transitions to dipole-bound states to the diffuse band spectrum does not preclude transitions to excited valence states of some anions, as, for example, occurs in  $C_7^-$  where the first excited electronic state lies below the detachment threshold (Tulej et al. 1998).

The ions may be formed in diffuse clouds through radiative association (and possibly dissociative electron attachment) reactions with characteristics established for ion-molecule reactions involving *dipolar* neutral targets, including a high cross-section and a negative temperature dependence for the reaction rate (Clary 1985; Adams, Smith & Clary 1985; Clary, Smith & Adams 1985). For the case of polycyclic aromatic hydrocarbon (PAH) structures, which are likely good examples of the molecules/small grains considered here, model calculations have shown that a large fraction of PAHs in diffuse clouds would be negatively charged, notwithstanding efficient destruction through collisions with positive ions (Lepp et al. 1988). The collision rate for a ground-state PAH<sup>-</sup> molecule with positive ions in a diffuse cloud is of the order of  $5 \times 10^{-14} \text{ s}^{-1}$  (Omont 1986), and, although the transitory dipole-bound state has a larger spatial extent, its decay rate of  $\sim 10^3\text{--}10^6 \text{ s}^{-1}$  or faster is extremely high compared with this collision rate.

A very high-resolution ion beam photodetachment study of  $\text{CH}_2\text{CN}^-$  (Lykke et al. 1987) allowed assignment of 1298 rotational lines of the  $0_0^0$  band, and yielded molecular parameters for both ground and dipole-supported states. Transitions involving the lowest rotational levels of this band were not observed because the optically accessible excited-state levels lie below the

detachment threshold. However, the wavelengths of these potentially astronomically significant lines can be calculated. Using the tabulated data from Lykke et al. (1987), an estimate of the wavelengths of the first few lines of the  $K = 1 \leftarrow 0$  sub-band has been made, taking the values of  $A$ ,  $B$  and  $C$  for the two states. The  ${}^1R_0(0)$ ,  ${}^1Q_0(1)$  and  ${}^1P_0(2)$  lines fall at 8037.3, 8037.8 and 8038.6 Å. These are consistent with a diffuse band recorded towards HD 183143 which is reported at 8037.7 Å as part of a broader structure with a second component near 8040 Å (Herbig & Leka 1991), and with the wavelengths of two components of an asymmetric diffuse band quoted at 8037.24 and 8038.48 Å (Jenniskens & Désert 1994). Comparison between astrophysical data and computed spectra, convolved to the observational resolution, will be presented elsewhere. Higher signal-to-noise ratio astrophysical spectra and calculations of the lines using the full Hamiltonian are needed to be able to make a definitive statement as to whether  $\text{CH}_2\text{CN}^-$  is the carrier of this band.

### 4 COMMENT AND CONCLUSION

As far as I am aware, the possible role of specifically dipole-bound states in the context of the diffuse band problem has not been mentioned previously, although the likely enhancement of the formation of molecular anions through the electron-dipole interaction and some general considerations for negative molecular ions have been aired previously (Sarre 1980, 1998). It is of interest that dipolar grains (large molecules) have recently been invoked in connection with the detection of cosmic microwave radiation in the 14–50 GHz range, which is possibly attributable to emission from ‘spinning’ dipolar dust grains (Draine & Lazarian 1998).

It may be possible to apply the experimental technique of two (sequential) photon photodetachment to the exploration of this hypothesis. It was first used in a study of transitions of the  $C_2^-$  ion by Lineberger & Patterson (1972), and has more recently been applied to longer carbon anions (Tulej et al. 1998). Experiments and calculations directed towards a more detailed understanding of dipole-bound states of both large ‘molecular’ anions and negatively charged grains would seem worth pursuing.

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