FULLERENES AND THE λ4430 DIFFUSE INTERSTELLAR BAND

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ABSTRACT

The photoabsorption spectra of single-shell icosahedral fullerenes is investigated in the region of the strongest diffuse interstellar band at 4430 Å. According to Hückel and Pariser-Parr-Pople models several fullerenes (C_{80}, C_{240}, C_{320} and C_{540}) present transitions in the vicinity of this band. The same semiempirical models also predict a high density of transitions in the UV that may explain the 2175 Å bump in the extinction curve of the interstellar medium (Iglesias-Groth 2004). It appears that fullerenes could be responsible of these two major features of interstellar absorption. Using the theoretical cross sections and available empirical data on the 4430 Å band we estimate for these fullerenes abundances of $\sim$0.05 molecules per million hydrogen atoms in regions of the interstellar medium with excess color index of E(B-V)=0.1.

Subject headings: ISM:molecules—ISM:lines and bands—ISM:abundances

1. Introduction

Since the discovery of diffuse interstellar bands (DIBs) by Heger (1921) more than 300 interstellar features have been identified in this category (Jenniskens and Désert 1994; Herbig 1995; Galazutdinov et al. 2000 and references therein). The origin of the DIBs is still a mistery. The list of potential carriers goes from negative hydrogen and linear carbon chains to polycyclic aromatic hydrocarbons (PAHs), fullerenes and dust grains. In most DIBs some substructure can be seen (see e.g. Ehrenfreund and Foing 1996) suggesting that gas-phase molecules are likely carriers, but so far no satisfying explanation for the origin of these intriguing interstellar bands could be given.

Among optical DIBs, the 4430 Å band is the strongest. This band is remarkably broad with a width (FWHM) of order a few tens of Å. Krelowski and Walker (1987) assign the two broad DIBs $\lambda\lambda$ 4430 and 6177 Å to the same family and Krelowski (1989) and McIntosh and Webster (1993) note that the carrier of this family appears to prefer denser interstellar gas than other carriers. There is also evidence of a positive correlation beween the 4430 Å band and the strongest feature in the interstellar extinction curve, the UV bump at 2175 Å (Webster 1993, Nandy and Thompson 1975). It is therefore plausible that these two bands are produced by the same type of molecule.

Bands of the C_{60}^{+} have been tentatively identified with DIBs in the near infrared (Foing and Ehrenfreund 1994). It has been argued that fullerenes could be the carriers of the UV bump in the extinction curve and may also contribute to other processes in the interstellar medium (Iglesias-Groth 2004, 2005). If fullerenes were a major contributor to the UV bump absorption, they would be ubiquitous in the various phases of the interstellar medium, locking a significant amount ($\geq$ 10%) of interstellar carbon, and could also contribute to the interstellar absorption at 4430 Å. While the existence of fullerenes in the interstellar space has not been proved yet (see e.g., Herbig 2000), detection of C_{60-400} in meteorites (Becker et al. 1993, Becker et al. 1994, Becker and Bunch 1997; Pizzarello et al. 2001) provides a strong argument in favor. In this paper we investigate the photoabsorption of fullerenes in the spectral region of the DIB at 4430 Å using the same type of semiempirical models previously employed to study the role of fullerenes in the UV bump.

2. MOLECULES AND MODELS.

The electronic structure of the fullerene C_{60} and carbon nanotubes has been successfully studied using semi-empirical models as Hückel ($tight-binding$) and Pariser-Parr-Pople (e.g. Cioslowski 1995). These models are an alternative to $ab-initio$ computations for molecules with very large number of atoms and are known to reproduce well the one-electron level structure of fullerenes. We use here both Hückel and PPP models to investigate the electronic photoabsorption spectra of single-shell icosahedral fullerenes with a number of carbon atoms $N = 60$, 80, 180, 240, 320, 500, 540, 720, 960 and 1500 in the region of the 4430 Å band. The molecules under consideration belong either to the family N=60n^2 of Goldberg polyhedra or to the family N=20 (n+1)^2 (where n=1,2,3...).

The theoretical approach essentially consists of an effective one-electron model to represent the system Hamiltonian and its interaction with the radiation field. Screening effects, very relevant in these highly correlated electron systems, are taken into account by means of the semiclassical random phase approximation (Ruiz et al. 2001). Iglesias-Groth et al. (2002) computed spectra for the first five stable fullerenes of the icosahedral family using a Hückel model for the σ-like electrons and a PPP model for the π-like electrons and discuss the reliability of these computations. This type of models are able to reproduce well the C_{60} experimental photoabsorption cross-sections and its static polarizability. They also verify tests based on two spectral sum rules; namely the S(0) and S(-2) rules. The former rule provides the system number of electrons from the integrated photoabsorption cross-sections, and the latter relates the system static polarizability with these cross-sections. Both consistency criteria support the adequacy and reliability of the theoretical description of the electron motion.

We fix first the model parameters and those of the molecule radiation interaction by fitting the experimental photoabsorption cross sections of C_{60} in the energy range 1-30 eV (Leach et al. 1992, Berkowitz 1999, Jaensch and Kamke 2000, Herbig 2000). Then, parameters for the larger fullerenes are adjusted conveniently (see Table 1 in Iglesias-Groth et al. 2002 for details). Photoabsorption spectra for each icosahedral single-shell fullerene with less than 1500 atoms are computed using the appropriate parameters. In addition, we also obtained photoabsorption spectra for each fullerene assuming a Hückel model for both π and σ-electrons with a constant hopping parameter (t^{π}=-2.57 eV) between neighbor C atoms. In the optical, the differences between both models of π-electrons are small and essentially translate in slightly different energies and intensities for the transitions which gives and indication of the level of uncertainty for our predictions. The differences between models progressively vanish as the size of the fullerene size increases. The Hückel models were able to reproduce well the experimental data on C_{60} at energies close to that of the 4430 Å interstellar band. In particular, the C_{60} band at 3.77 eV (3284 Å) is better reproduced by these models. Unless otherwise stated in the text, the results presented in the following sections were obtained using Hückel models for both types of electrons (hereafter referred as the Hückel model).

In Figure 1 we plot the resulting transitions in the wavelength range from 1800 to 6800 Å for icosahedral fullerenes with total number of carbon atoms N<1500. In each subpanel we present the theoretical cross-sections for the bands convolved with a Lorentzian function of width Γ_{ω} (the parameter in Eq. 12 of Iglesias-Groth et al. 2002). Results are plotted for two values of the Γ_{ω} parameter: 0.01 eV (set of narrow transitions) and 0.3 eV (broad features).

The transitions resulting for C_{60} coincide with the well known laboratory bands of this molecule (Leach et al. 1992, Herbig 2000). Using a time-dependent density functional theory (TDDFT), Bauernschmitt et al. (1998) calculated photoelectron spectra for fullerenes C_{60} to C_{80} in gas phase which reproduce well the laboratory bands of these molecules when matrix shifts are taking into account. Since our model parameters are adopted to reproduce the experimental data on C_{60}, our predictions consistently agree for this molecule. At energies below 2.5 eV, we can also compare results for C_{80}. Their strongest transitions for this molecule are found at 1.22, 2.13 and 2.24 eV while we find reasonably close transitions at

1.19 and 2.09 eV. At higher energies, where no TDDFT calculations are available, we obtain a much stronger transition at 2.80 eV, remarkably close to the strongest feature in the experimental data for C_{80} (D_2) plotted in Fig. 8 of Bauernschmitt et al., and to the energy of the DIB at 4430 Å. Accurate laboratory measurements are also available for the C_{82} and C_{84} fullerenes (Hino et al. 1993). These two molecules do not belong to the families under consideration, but we note the close proximity of the energy of their bands (2.2, 3.3, 4.6, 5.3, 6.5 and 7.8 eV) to those resulting in our computations for the C_{80} molecule. Overall, this suggests that in spite of their limitations, our models may provide useful guidance on the transitions of larger fullerenes.

It is quite apparent in Fig. 1 that all the fullerenes display a rich spectrum of transitions which becomes denser as the total number of atoms in the molecule increases. This rise in the density of transitions is much higher in the high energy region where the UV bump is located. At low resolution this causes the remarkable broad band in the range 5-6 eV which coincides approximately with the UV bump in the interstellar extinction curve (Fitzpatrick 1999) as previously discussed by Iglesias-Groth (2004).

3. FULLERENES AND THE INTERSTELLAR BAND AT 4430 Å

To compare the relative strength of the transitions relevant to the analysis of the 4430 Å band we expand in Figure 2 the region between approx. 2 and 3 eV (the location of the band is indicated by a vertical dashed line) and directly plot the theoretical cross-section values versus wavelength. For the fullerenes under consideration, the largest cross section predicted at energies below 4 eV corresponds to the C_{320} fullerene and it is located at approx. 4430 Å. Interestingly, rather strong transitions at a similar wavelength are also predicted for the C_{80}, C_{240} and C_{540} molecules. It appears that this band is a rather common spectral feature of icosahedral fullerenes with a moderate number of atoms. We checked that both H*ü*ckel and PPP models predict this band with similar strengths for each molecule and that differences in the predicted wavelengths are less than 10 Å. However, this band is not predicted by the models for C_{60}, which is neither found in laboratory measurements of this archetypical fullerene. Accurate laboratory measurements of this band for the larger fullerenes would be extremely valuable.

We have also investigated whether multishell fullerenes (buckyonions) may also display the 4430 Å band. Following the approach described in Iglesias-Groth (2003) we carried out computations for the most stable buckyonions with an external shell of N= 240 and 540 carbon atoms, i.e the C_{60}@C_{240} and C_{60}@C_{240}@C_{540}. The right panels of Fig. 2 show the results. Essentially the addition of internal shells do not change significantly the number, strength and wavelength of the bands predicted for the external fullerene. We interpret this result as further indication of the robustness of the predictions for the 4430 Å band.

As shown in Fig. 2 other transitions are also predicted for fullerenes at optical wavelengths. The next larger cross-section is found for the C_{240} molecule at a wavelength remarkably close to the second strongest optical DIB at 6177 Å (position marked with a vertical dotted line in Fig. 2). The measurements available for this DIB (see e.g. Table A1 of Herbig 1995) give an equivalent width approximately 60% of the 4430 Å band and FWHM of order 20 Å. A similar relative strength is found in our computations. The two broad DIBs $\lambda\lambda$ 4430 and 6177 may belong to the same family according to Krelowski and Walker (1987). A straightforward explanation would be provided by our models which suggest transitions of several fullerenes may contribute to both bands.

The third strongest DIB in the optical is found at 6284 Å very close to one of the transitions predicted for the fullerene C_{540} for which we also predict a transition close to the location of another two well known strong DIBs at 5778 and 5780 Å . Given the resolution of our computations these two bands would be unresolved in our spectra. Predictions for these and other weaker bands in the optical are however, more uncertain and deserve a careful analysis which will be presented elsewhere. Here we emphasize that the relatively simple models employed to study the photoabsorption of fullerenes in the optical predict their strongest optical transitions in the vicinity of the 4430 Å band. Fullerenes of various sizes up to R$\sim$ 10.5 Å may therefore play a role as carriers of this and several other strong DIBs. The same molecules were also postulated as carriers of the UV bump, and therefore provide a natural explanation to the empirical correlations found among the UV bump and some of the strongest DIBs. It is important to verify that such assumptions lead to a consistent estimate for the abundance of fullerenes in the interstellar medium.

3.1. Fullerene abundance.

Assuming that fullerenes are responsible of the λ4430 interstellar band, we derive now the abundance of these molecules in the interstellar medium using the theoretical values of the cross sections given by our models. The central depth of the λ4430 feature ranges between 0.05 and 0.2 (see e.g Figure 4 in Herbig 2000) with a dependence on the color excess index E(B-V). In order to estimate the abundance we will assume a central depth A_c=0.1 for the band in a line of sight with E(B-V)=1. The extinction at the central wavelength of the band A(λ) can be related to the number of fullerenes in the line of sight per unit area, $\rho(C_N)$, and to the cross section of the intervening particles $\sigma(\lambda)$ as follows:

$$A(\lambda) = -2.5log(I(\lambda)/I_0) \sim log(e)\rho(C_N)\sigma(\lambda). \quad (1)$$

In this approximation we consider that the extinction is caused by absorption of the intervening particles, disregarding scattering processes, and adopt as cross section for extinction the result of our computations. Since the models indicate that the major contribution at λ4430 is provided by the band of the fullerene C_{320}, let us assume for the moment that this molecule is the major carrier of the band and adopt the predicted cross section of $\sim 10^4$ Mbarn. We infer a density of N(C_{320})= 5.76 10^{14} cm^{-2}. For an excess colour index E(B-V)=1 the hydrogen column density is, according to Bohlin et al. (1978), N(H)=5.9 x 10^{21} cm^{-2}. Thus, the relative number of C_{320} to that of hydrogen atoms in such a medium would be 0.09 ppm. Given that other fullerenes may also contribute to the 4430Å band, this is an overestimate of the real abundance of this molecule. Interestingly, this value is close to the abundance of fullerenes in the interstellar medium obtained by Iglesias-Groth (2004) under the assumption that these molecules are the carrier of the UV bump at 2175 Å.

The position, width and intensity of the UV bump was explained by Iglesias-Groth (2004) as the result of absorption by a mixture of fullerenes in the interstellar medium with a size distribution law of the form n(R)= $(R/R_0)^{-m}$ where m ranged between 2.5 and 4.5 and R_0 is a constant. For fullerenes smaller than the C_{180} the abundance was assumed independent on the radius of the fullerene, while the abundance of larger fullerenes decreased according to the previous size distribution law. The best fit to the UV bump led to values of 0.1-0.2 ppm for the smallest fullerenes considered (C_{60} and C_{180}). Adopting the same approach we compute the equivalent cross section of the 4430 Å band for a mixture of single shell fullerenes with N$<$ 1000 atoms following the same size distribution law. In Fig. 3 we show the predicted cross sections for three values of the power-law index (m=1.5, 2.5 and 3.5, respectively). The line-width parameter in Fig. 3 was arbitrarily set at 0.01 eV in order to compare with the observational data. This parameter slightly overestimates the true observed width of the interstellar feature (FWHM$\sim$20 Å). The strength of the cross sections for these fullerene mixtures changes significantly with the index of the power-law since not all the fullerenes contribute in the same way to this band.

The value m=3.5 was found by Iglesias-Groth (2004) as adequated to explain the UV bump in the extinction curve of the diffuse interstellar medium characterized by the dimensionless optical parameter R_V=3.1. If we adopt the cross section predictions for m=3.5 to interpret the observed central depth of A_c= 0.1 of the 4430 Å band we obtain for the fullerenes with transitions contributing to the band an abundance of $\sim$ 0.05 molecules per million hydrogen atoms. If we adopt R_0=6.1 Å (the radius of the C_{180}), in the description of the size distribution of fullerenes the larger radii of the C_{320} and C_{540} (approx. 8.2

Å and 10.6 Å, respectively) would lead to abundances of order 0.1-0.2 ppm for the smallest fullerenes C_{60-180} in clouds of the interstellar medium with E(B-V)=0.1. The same interstellar abundance of fullerenes is obtained from observations of the UV bump and the 4430 Å band. The value is also similar to that found in meteorites. The consistency of these results reinforces the view that fullerenes could be ubiquitous in the interstellar medium and lock a significant fraction of interstellar carbon (10-20 %).

4. CONCLUSIONS

The strongest diffuse interstellar band λ4430 is discussed in the light of theoretical cross-sections computed for icosahedral fullerenes with less than 1500 atoms. In the optical (4000-7000 Å), the strongest transition predicted by any of our fullerene photoabsorption models lies very close in wavelength to this interstellar feature. Transitions potentially associated to the 4430 Å band are found with the highest intensity in the theoretical spectrum of C_{320} and also with significant strength in our predictions for the C_{80}, C_{240} and C_{540} fullerenes. Consistently with laboratory data our models do not predict this band for the archetypical fullerene C_{60}. Theoretical spectra of multishell fullerenes with 240 and 540 atoms in the external layer also display the 4430 Å band which seems to be a rather robust feature of our models independent on whether a Hückel or a PPP description is adopted for the π-like electrons.

The next most intense optical bands found in the theoretical spectra of fullerenes also appear very close in wavelength to the strongest known DIBs. The $\lambda\lambda$ 6177 and 6284 DIBs could be associated with fullerenes. The models predict a rise in the number of weaker transitions as the size of the fullerene increase, but also the uncertainties in the predictions of the models increase, so any detailed account of weaker DIBs will require more refined models.

In order to compare with the observed strength of the 4430 Å interstellar band we compute the average cross section for a mixture of fullerenes following a power-law size distribution in interstellar space. The same range of power-law indexes that gives a plausible explanation of the UV bump in the interstellar extinction curve appears valid to explain the intensity of the 4430 Å band for a total interstellar abundance of fullerenes of order 0.1-0.2 ppm. These estimates rely on the goodness of the modelling of photoabsorption cross-sections by semiempirical models, precise laboratory spectroscopy of fullerenes in the optical would be extremely valuable to confirm these predictions and it will be crucial to conclusively establish the role of these molecules as DIB carriers.

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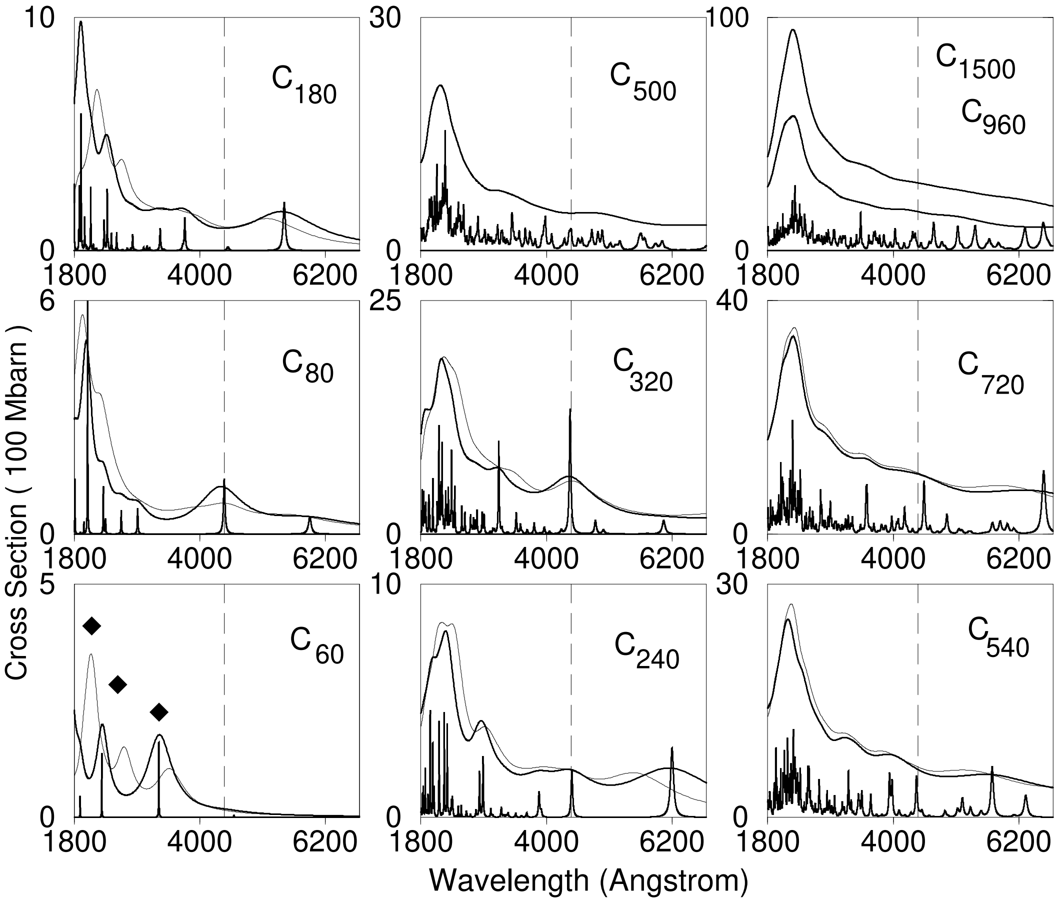

Fig. 1.— Photoabsorption cross sections for single fullerenes as a function of wavelength. The narrow transitions are the model predictions convolved with a a Lorentzian function of width Γ=0.01 eV. The thick and thin line envelope curves (Hückel and PPP models, respectively) represent a convolution of the spectrum with Γ= 0.3 eV. A broad feature is observed in all these molecules in the the region of the UV bump at 2175 Å. A vertical dashed line indicates the position of the $\lambda 4430$ interstellar band. The narrow transitions have been scaled down by arbitrary factors for clarity in the figure.The diamonds indicate the position of experimental bands for C_{60} as measured by Leach et al. (1992).

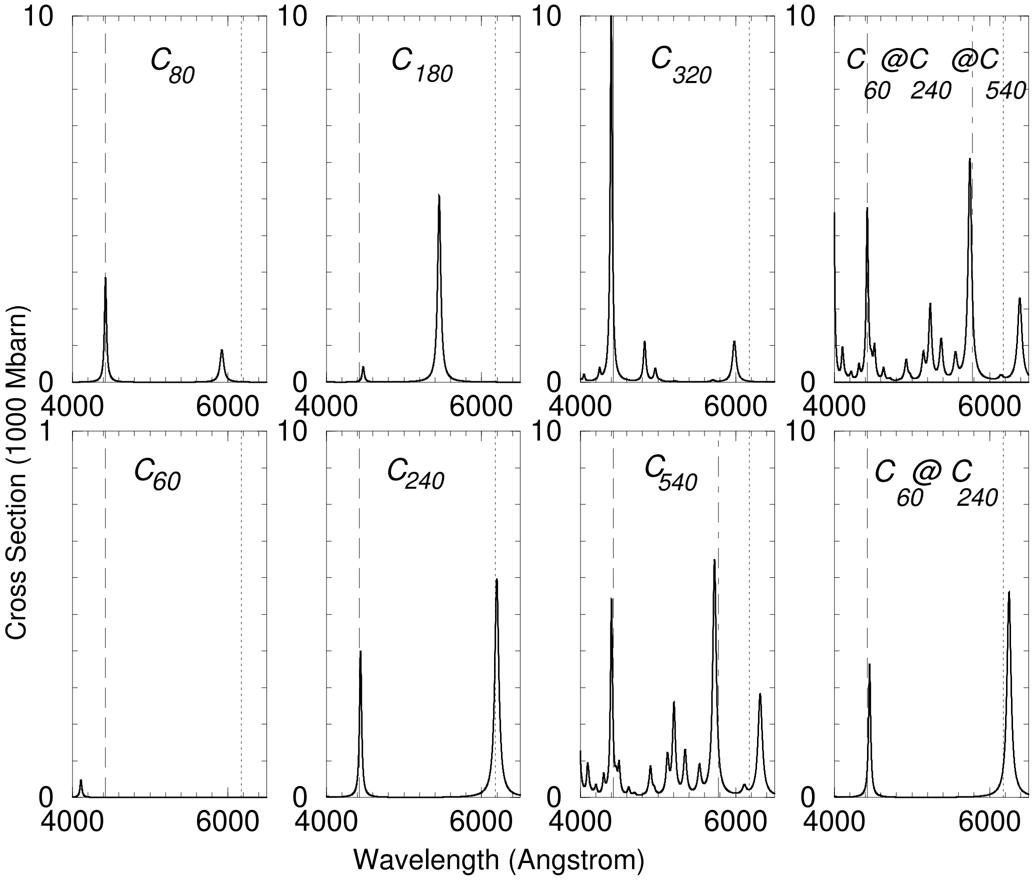

Fig. 2.— Photoabsorption cross sections for fullerenes as a function of wavelength. The thin dashed vertical lines indicate the position of the λ4430 interstellar banda. The dotted line marks the position of the λ 6177 interstellar band. The dot-dashed line marks the position of the λ5780 band.

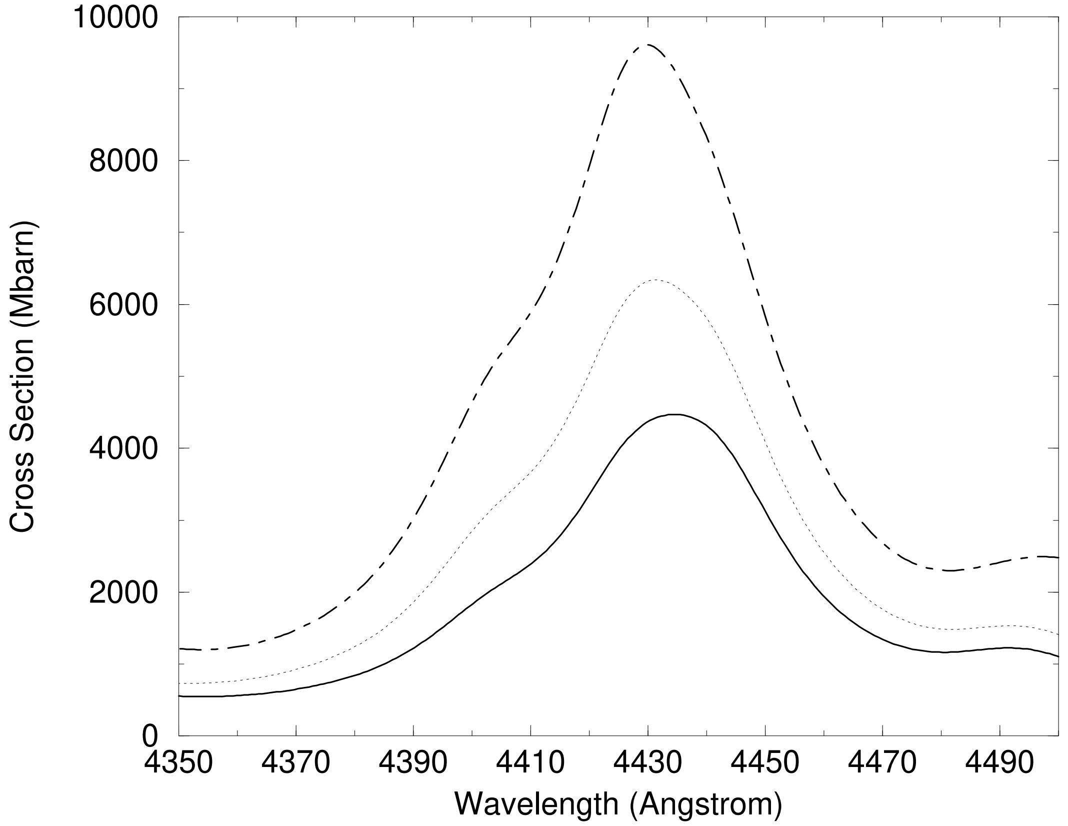

Fig. 3.— Photoabsorption cross sections as a function of wavelength for a mixture of single-shell fullerenes in the spectral region of the DIB at 4430 Å. Curves are plotted for various indexes of the size distribution power-law: m=3.5 (solid line), m=2.5 (dotted line) and m=1.5 (dot-dashed line). The spectra have been convolved with a Lorentzian function of line-width parameter $\Gamma = 0.01$ eV.