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# THE C<sub>4</sub>H RADICAL AND THE DIFFUSE INTERSTELLAR BANDS. AN AB INITIO STUDY

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## INTRODUCTION

Linear carbon chains have been proposed as carriers of the diffuse interstellar bands (DIB) as long as 20 years ago (Douglas 1977). Recent experimental results by Fulara et. al. (1993) give new arguments for this interpretation of the origin of the DIBs. These authors show that several DIBs can be attributed to the species containing carbon and hydrogen atoms only. In particular, they suggest that the absorption features observed at 6077 Å and 7728 Å correspond to the diffuse interstellar bands centered at 6089.7 and 7721.7 Å and attribute them to the  $^2\Pi$ - $^2\Pi$  transitions in C<sub>6</sub>H and C<sub>8</sub>H, respectively.

Recently Watson (1994) investigated the possibility that the linear carbon-containing chains may be the carriers of DIBs. Watson used a particle-in-the-box model to investigate the electronic transitions in homologous series of carbon-chain molecules.

In the C<sub>2n</sub>H chains, C<sub>2</sub>H and C<sub>4</sub>H have  $^2\Sigma^+$  ground states, with electron configurations  $\dots(n-1)\pi^4n\pi^4(4n+1)\sigma$ . Two low lying excited states of  $^2\Pi$  symmetry are described by  $\dots(n-1)\pi^4n\pi^3(4n+1)\sigma^2$  and  $\dots(n-1)\pi^3n\pi^4(4n+1)\sigma^2$  configurations. Longer chains have the  $^2\Pi$  ground state, with the configuration  $\dots(n-1)\pi^4n\pi^3(4n+1)\sigma^2$  (Pauzat & Ellinger 1989; Pauzat et. al. 1991), so the (strong and parallel)  $^2\Pi$ - $^2\Pi$  transition leads to the  $\dots(n-1)\pi^3n\pi^4(4n+1)\sigma^2$  configuration. We report here the results of an *ab initio* study of the electronic spectrum of C<sub>4</sub>H and relate it with the DIBs problem.

## METHODS

The basis set used here is of valence triple-zeta (Dunning 1971), double polarization (Dunning 1989) quality and consists of 110 contracted gaussian type orbitals. All geometry optimizations were performed at the complete active space SCF (CASSCF) level, correlating one  $\sigma$  and eight  $\pi$  electrons on nine orbitals, using program GAMESS (Schmidt et. al. 1990). The geometry optimizations were restricted to the linear geometries. All four inter-atomic distances were optimized.

The multireference configuration interaction (MR-CI) calculations were performed for several linear geometries of the molecule using MRD-CI method (Buenker & Peyerimhoff 1974; Buenker 1980; Buenker 1982). In those calculations 17 valence electrons were correlated within 86 molecular orbitals. The standard selection/extrapolation procedure with Davidson correction (Langhoff & Davidson 1974) was used. The resulting energies are denoted MR-CI(+Q). It has been shown (Knowles et. al. 1990) that this treatment

State	Method/basis	$C_1-C_2$ Å	$C_2-C_3$ Å	$C_3-C_4$ Å	$C_4-H$ Å	B MHz	ref.
$X^2\Sigma^+$	Experiment					4758.6567	<sup>a</sup>
$X^2\Sigma^+$	CASSCF/TZP2P	1.2095	1.3854	1.1820	1.0546	4785.0	<sup>b</sup>
$A^2\Pi$	CASSCF/TZP2P	1.2613	1.3505	1.2139	1.0538	4706.3	<sup>b</sup>
$B^2\Pi$	CASSCF/TZP2P	1.2544	1.3534	1.2716	1.0526		<sup>b</sup>

<sup>a</sup> (Guelin et.al. 1982)

<sup>b</sup> this work

	$X^2\Sigma^+$ eq.	$A^2\Pi$ eq.	$B^2\Pi$ eq.	
State	MR-CI(+Q) (eV)	MR-CI(+Q) (eV)	MR-CI(+Q) <sup>a</sup> (eV)	$\mu^b$ Debye
$X^2\Sigma^+$	0.00 <sup>b</sup>	—	—	0.93
$A^2\Pi$	0.35	0.01	—	5.41
$B^2\Pi$	3.70	3.34	<b>3.24</b>	8.83
$\tilde{C}^2\Sigma^+$	4.99	4.61	—	1.09

<sup>a</sup> all MR-CI(+Q) energies relative to -152.3367709  $E_H$

<sup>b</sup> Dipole moment

results in less than 1 kcal/mole ( 0.06 eV) errors in the estimation of the full-CI limit. Use of a basis set of triple zeta - double polarization quality should lead to similar errors. Thus, the relative energies here are accurate to better than 0.1 eV, which translates to 130 Å at 4000 Å.

#### AB INITIO RESULTS

We have optimized bond distances in the three lowest-lying electronic states of  $C_4H$ :  $X^2\Sigma^+$ ,  $A^2\Pi$ ,  $B^2\Pi$ . Table 1 shows the bond distances obtained in this study.

The optimized geometries were then used in the multireference CI calculations of the vertical and adiabatic excitation energies for four lowest lying states of  $C_4H$ . The results are shown in Table 2. The boldface in the table indicates the adiabatic excitation energies. In addition we have calculated restricted bending potentials for the terminal C and H atoms, to confirm the linearity of the molecules in the ground and excited electronic states. The bending potentials in three lowest electronic states have minima at linear conformations of the molecule.

The ground state of  $C_4H$  is  $X^2\Sigma^+$ , but the  $A^2\Pi$  state is very low-lying, at only 0.01 eV at MR-CI(+Q) level. The vertical excitation energy is 0.35 eV. The calculated energy difference of 0.01 eV does not give a conclusive assignment of the ground state. Kiefer et. al. (1992) do not obtain clear-cut assignment of the ground state of  $C_4H$  and similar problems are discussed by Pauzat and Ellinger (1989). The rotational spectrum of  $C_4H$

Table 3. Theoretical band origins of  $C_4H$ 

Transition	$\lambda_{00}$ (Å)	transition moment (Debye)
$A^2\Pi-X^2\Sigma^+$	infrared	0.56
$B^2\Pi-X^2\Sigma^+$	3884	0.13
$C^2\Sigma^+-X^2\Sigma^+$	2484	0.11
$B^2\Pi-A^2\Pi$	3869	2.57

has been observed in the  $^2\Sigma^+$  state, but this does not preclude non-zero population of the radiatively long lived  $^2\Pi$  state. On the other hand one may expect significant vibronic coupling between the  $\Sigma$  ( $A'$  in bent configurations) and  $\Pi$  ( $A'$  and  $A''$ ) states (Yamamoto et. al. 1987). This effect may contribute to the fact that our calculated B values for the  $^2\Sigma^+$  and  $^2\Pi$  states bracket the results of astronomical observations.

The vertical and adiabatic excitation energies between the B-X and B-A states differ by 0.46 eV ( 3.70 vs. 3.24 eV) and 0.09 eV ( 3.34 vs. 3.24 eV), consistent with the changes in the equilibrium geometries (see Table 1).

Prediction of the band origins from *ab initio* requires estimation of the zero point energies of the involved states. Using harmonic vibration frequencies for the X and A states, reported by Kiefer et. al. (1992), the corresponding zero point energies are 5639 and 5456  $cm^{-1}$ , respectively. In particular, the  $\nu_3$  frequency (one of the triple C-C bond stretches) decreases from 2116 to 1864  $cm^{-1}$ , reflecting the weakening of this bond. Based on the increase in the  $C_3-C_4$  bond length, one may expect a similar effect on the  $\nu_2$  frequency (other triple C-C bond stretch) in the B state, reducing its zero point energy. We will assume that the zero point energy of the B state will be reduced to 5250  $cm^{-1}$ .

The above information, together with the term values reported in Table 2. and the values of the dipole transition moment, allows for a prediction of the general features of the electronic spectrum of  $C_4H$ . We will consider the following four electronic transitions: A-X, B-X, C-X, and B-A. The red end of the absorption spectrum will occur at the 0-0 transition energy and the maximum intensity should occur at the vertical excitation energy, corrected for the zero point energy of the lower state (provided it is larger than 0-0 transition energy). The blue end of the spectrum is difficult to predict in the absence of detailed vibrational analysis, but one should expect relatively short progressions, as the changes in the bond lengths are not very large. The main parameters of the four electronic transitions are given in Table 3.

Both B-X and B-A bands have a very similar origin  $\lambda_{00}$ . A vibrational progression in the B-X system may occur because of the difference in the  $C_1-C_2$  bond lengths of 0.06 Å between the lower and upper states. In the B-A system, the  $C_1-C_2$  bond lengths are very similar, but the  $C_3-C_4$  distances differ by 0.06 Å. Consequently, a very similar vibrational progression may occur. However, the oscillator strengths differ by two to three orders of magnitude, parallel transition B-A being stronger. Thus, depending on the conditions and possible pathways to populate the very low lying  $A^2\Pi$  state, it may be possible to observe absorption from both states. Both bands should begin at around 3900 Å and should overlap considerably. It is important to point out that the B-A band corresponds to the transition in the particle-in-the-box discussed by Watson. The C-X band, originating at 2500 Å may also be observable.

#### PARTICLE-IN-THE-BOX

Chains longer than  $C_4H$  have  $^2\Pi$  ground state (Pauzat & Ellinger 1989) and should

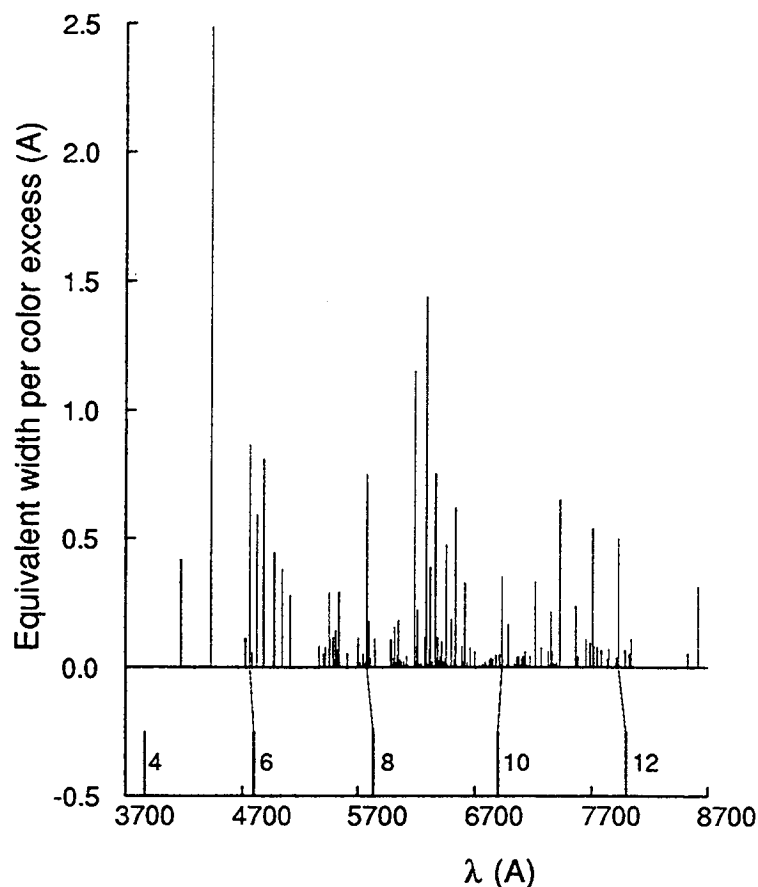


Figure 1. Parallel bands in  $C_{2n}H$  series and the DIBs

have strong absorption spectra at low temperatures, between the  $\dots\pi^4\pi^3$  and  $\dots\pi^3\pi^4$  configurations. In a  $C_{2n}H$  chain the  $(n-1)\pi$  and  $n\pi$  molecular orbital have a nodal structure of the  $(n-1)^{th}$  and  $n^{th}$  eigenfunctions of the particle-in-the-box model. The electronic transition between those levels has been discussed recently by Watson (1994). In the case of a  $C_{2n}H$  chain, the equivalent box length and the wavelength of the transition between two lowest  $\Pi$  states are given by the following relations:

$$\lambda(\text{\AA}) = 329.72 \times l^2(\text{\AA}) / (2n - 1)$$

$$l(\text{\AA}) = ((2n - 1) \times \lambda(\text{\AA}) / 329.72)^{1/2}$$

where  $\lambda$  is the transition wavelength and  $l$  is the effective length of the box. The wavelength of the parallel absorption band is changes linearly with the box length and consequently number of C atoms in a chain.

#### $C_4H$ AND THE DIBs

It has been proposed (Bell et. al. 1983), that the 4428 Å diffuse interstellar band is carried by  $C_4H$ . This assignment is consistent with a recent proposition of Fulara et.al.: Application of the simple model described above to extrapolate the proposed  $C_8H$  and  $C_6H$  lines to  $C_4H$  gives the wavelength of around 4430 Å. However, it is rather unlikely that  $C_4H$  is responsible for the 4428 Å DIB, as  $C_4H$  is predicted here not to absorb above 4000 Å. Consequently, the 6077 and 7728 Å lines seem to be too far into the red to

Table 4. Wavelengths of parallel transitions of  $C_{2n}H$  species, with  $n=2,3,4,5$ , and 6.

Species	box length (Å)	wavelength (Å)
$C_4H$	5.93	3869 <sup>a</sup>
$C_6H$	8.53	4798
$C_8H$	11.13	5834
$C_{10}H$	13.73	6906
$C_{12}H$	16.33	7993

<sup>a</sup> from MRD-CI calculations

arise from (relatively) short  $C_6H$  and  $C_8H$  molecules and to be too far apart to arise from molecules differing by only two carbon atoms.

However, it is interesting to predict the wavelengths of the transitions in  $C_{2n}H$  series by using the particle-in-the-box model. Our best estimate of the energy of the  $B^2\Pi-A^2\Pi$  transition in  $C_4H$  corresponds to the wavelength of 3869 Å. The equivalent box length is 5.93 Å. We will now assume that the effective box length for the  $C_{2n}H$  molecules is equal to the length of the box of the previous member of the series, augmented by 2.6 Å. 2.6 Å is a reasonable estimate of the sum of the lengths of two adjacent C-C bonds in a  $^2\Pi$  state of the molecule ( see Table 1).

Table 4. shows the predicted transition energies for  $C_4H - C_{12}H$ , using the box lengths described above. Figure 1. shows a plot of the diffuse interstellar bands observed against HD183143, with the data taken from (Jenniskens 1992). In the figure, the height of the bar is proportional to the equivalent width per color excess and the values from Table 4. are shown with thick lines, with an arbitrary intensity.

The following coincidences can be observed between the predicted frequencies for  $C_{2n}H$  species and strong diffuse interstellar lines: (4798; 4761.67), (5834; 5779.48), (6906; 6939.00), and (7993; 7927.80). Obviously, the *ab initio* calculations can not achieve spectroscopic accuracy. Thus, the assignments shown above are quite tentative and serve more as an illustration than the genuine assignment of the lines, particularly considering the simplicity of the model used.

Nevertheless, the RMS deviation of the assignment given above is only 50 Å and is smaller than errors in *ab initio* calculations and comparable with the matrix shifts in absorption spectra. The coincidence of the calculated transition wavelengths with four of the intense diffuse interstellar bands is generally consistent with the idea that DIBs originate not from one, but from a small group of molecules (Watson 1994). Also, this interpretation of the origin of the DIBs is consistent with the lack of observation of DIBs in ultraviolet.

A very similar reasoning should also apply to the  $C_{2n-1}N$  series, as the CH group is isoelectronic with the N atom. An *ab initio* study of  $C_3N$  (Sadlej & Roos 1991) predicts the wavelength of the  $^2\Pi-^2\Pi$  transition at around 3600 Å, consistent with a shorter length for the terminal C-N bond in  $C_3N$ , compared to the C-C bond in  $C_4H$ .

## CONCLUSIONS

We have presented an *ab initio* study of the low-lying electronic states of  $C_4H$ . This species has a  $X^2\Sigma^+$  ground state and two low lying  $\Pi$  states. Based on the vertical and adiabatic excitation energies between those states we suggest that the 4428 Å diffuse

interstellar band *is not carried by*  $C_4H$ . The application of the particle in a box model shows strong coincidences between the strong DIBs and predicted wavelengths of  $\Pi$ - $\Pi$  transitions in  $C_{2n}H$  series. Based on those coincidences, we suggest the  $C_{2n}H$  species as good candidates for carriers of diffuse interstellar bands.

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