SPECTROSCOPIC CONSTANTS OF THE CH RADICAL. THE $^4\Sigma^-$ STATE.

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Abstract : We report preliminar results of ab initio calculations on the low lying $\tilde{a}^4\Sigma^-$ state of CH radical , which has been recently detected . Spectroscopic constants are presented to support the experimental assignments.

1. Introduction.

It is known that CH radical participates in a wide variety of chemical reactions in the interstellar medium. From the four states that arise from the first excited eletronic configuration, the $\tilde{a}^4\Sigma^-$ state is supposed to be involved in the chemistry of CH, since it is low lying and long lived. However, there was no direct observation of it until 1988 [1].

We performed *ab initio* calculations on the $X^2\Pi$ and $\tilde{a}^4\Sigma^-$ states of CH, in order to provide sufficient (and accurate enough) data to support the recent experimental assignments.

2. Computational Details.

The calculations were carried out using the Dunning [2] valence double zeta (DZ) contraction of the Huzinaga [3] Gaussian basis set, augmented with two sets of d polarization functions (α=0.75 and α=0.3), one set of diffuse s and p functions (α=0.05), all of them in the carbon atom, plus a set of p polarization functions (α=1.0) on the hydrogen.

The considered states have been solved self-consistently at the MCSCF level. For the $X^2\Pi$ state we correlated the bond pair and also the hybrid pair (see figure 1). For the $\tilde{a}^4\Sigma^-$ state only the bond pair was correlated at this level of calculation (see figure 2).

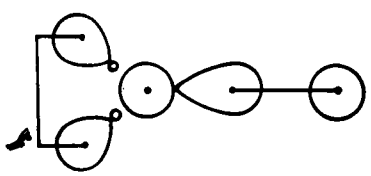


Fig. 1. VB description of CH radical, $X^2\Pi$ state

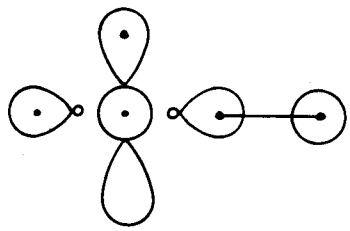


Fig. 2. VB description of CH radical, $\tilde{a}^4\Sigma^-$ state

The self consistent molecular orbitals obtained at the MCSCF level were used to perform the CI calculations. Two sets of CI calculations have been considered. In the first set of calculations the CI space was formed by all the occupied orbitals plus a set of virtual orbitals ($2\sigma + 2\pi$). In the second one, the virtual space consisted of four orbitals of each one of the σ, π and δ symmetries. The CI calculations were performed allowing up to quadruple excitations in the full CI spaces (10 and 20 orbitals respectively).

The calculations have been performed at twenty different internuclear distances. The potential curves obtained were fitted with cubic splines and the motion of the nuclei determined by numerical integration of the radial Schrödinger equation. The term values for the anharmonic oscillator are given by

$$G(\upsilon) = \omega_e\left(\upsilon + \tfrac{1}{2}\right) - \omega_e x_e\left(\upsilon + \tfrac{1}{2}\right) + \cdots$$

where υ is the vibrational quantum number and $\omega_e x_e \ll \omega_e$. The dissociation energy is given by

$$D_e = \frac{\omega_e^2}{4\,\omega_e x_e}$$

If we do not neglect the interaction of vibration and rotation, then the value of the rotational constant is

$$B_e = h / 8\pi^2 c\mu\, r_e^2 = h / 8\pi^2 c\, I_e$$

From the shape of the potential curve we can obtain the mean value of the rotational constant and therefore one can evaluate the ro-vibrational coupling constant. If the Morse function is used as first approximation to the real potential then this value is, according to Pekeris[4],

$$\alpha_e = \frac{\sqrt{\omega_e x_e\, B_e^3}}{\omega_e} - \frac{6\, B_e^2}{\omega_e}$$

and the rotational constant β_e can be expressed in a truncated power series. From the Birge-Dunham equation we find

$$\beta_e = D_e \left(\frac{8\,\omega_e x_e}{\omega_e} - \frac{5\,\alpha_e}{B_e} - \frac{\alpha_e^2\,\omega_e}{24\,B_e^3} \right)$$

In this work Dunham [5] expressions were used to take into account the effect of fine ro-vibrational interaction on the values of the spectroscopic constants, in order to obtain highly accurate values for the available experimental parameters.

3. Results and Discussion.

Figure 3 shows the potential curves obtained at the higher level of CI calculation. The basis set superposition error is less than 0.17 eV. Tables 1 and 2 present the results of calculated spectroscopic constants compared to the available experimental data[1,6] and also to the theoretical results of Hinze [7]. Herzberg notation is used throughout the table.

The general good agreement between the two calculations shows that with a much simpler description we are able to reproduce the results of extensive calculations [8]. The very good agreement with the experimental data reflects the quality of our description of the $\tilde{a}^4\Sigma^-$ state and gives strong support to the experimental assignment [1].

Table 1. Calculated Spectroscopic Constants for CH, $\tilde{a}^4\Sigma^-$ State.

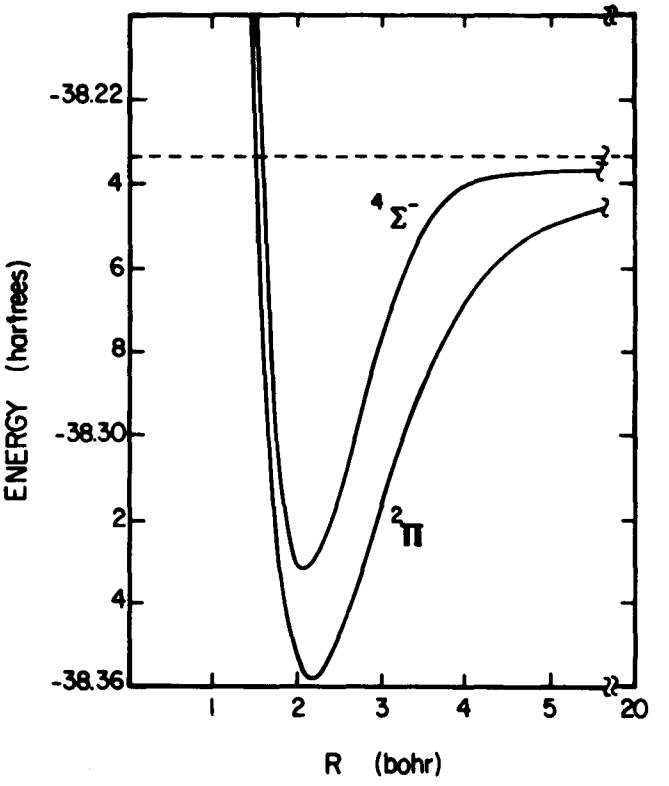
Constant	Hinze's Value [7]	This Work	Experimental Value [1,6]
R_e(bohr)	2.053	2.056	...
T_o(eV)	0.669 *	0.713	0.742
E_o	1555.4	1548.4	...
D_e(eV)	2.84	2.667	...
ω_e	3145.7	3125.8	...
$\omega_e x_e$	71.80	67.701	...
B_e	15.364	15.249	...
α_e	0.553	0.329	...
B_o(GHz)	452.26	452.247	451.138
D_o(MHz)	42.87	44.863	44.53

All values in cm^{-1} except when explicit.
* Goddard & Harding have reported a value of 0.70 eV. See reference [8].

Table 2. Calculated Spectroscopic Constants for CH, $X^2\Pi$ State.

Constant	Hinze's Value [7]	This Work	Experimental Value [1,6]
R_e(bohr)	2.113	2.116	2.116
E_o	1424.4	1548.4	1415.5
D_e(eV)	3.51	3.428	3.63
ω_e	2886.1	2712.9	2858.5
$\omega_e x_e$	82.00	68.952	63.00
B_e	14.498	13.716	14.457
α_e	0.589	0.5611	0.530

All values in cm^{-1} except when explicit.



4. Acknowledgement.

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5. References.

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