# LETTERS TO THE EDITOR

## COMMUNICATIONS

# The spectroscopic observation of the CH radical in its $a\ ^4\Sigma^-$ state[a]

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Four electronic states arise from the first excited configuration of the CH radical ($1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2$). Three of them, $A\ ^2\Delta$, $B\ ^2\Sigma^-$, and $C\ ^2\Sigma^+$, have been identified through electronic transitions from the ground $^2\Pi$ state and are reasonably well characterized.[1] However, there is no direct spectroscopic information on the fourth, the $a\ ^4\Sigma^-$ state. Ab initio CI calculations[2] suggest that it is low lying, only $0.63 \pm 0.12$ eV above the $X\ ^2\Pi$ state. This is consistent with a value of $0.742 \pm 0.008$ eV determined from the photoelectron spectrum of $CH^-$.[3] No electronic transitions have yet been observed between the quartet states of CH although the $a\ ^4\Sigma^-$ state must be metastable. The CH radical in its doublet states is known to participate in a wide variety of chemical reactions, e.g., in flames and combustion processes[4] and in the interstellar medium.[5] Since the $a\ ^4\Sigma^-$ state is both low lying and long lived, it is very likely to be involved in the chemistry of CH also.

We report the first spectroscopic observation of CH in the $a\ ^4\Sigma^-$ state, in which spin components of the first two rotational transitions have been detected in the far infrared by laser magnetic resonance.[6] The molecule was generated in a discharge-flow system in the reaction between fluorine atoms and methane (with a trace of oxygen added) or be-

tween oxygen atoms and acetylene at a total pressure of about 1 Torr. Experiments with $^{18}O_2$ showed that the carrier of the spectrum did not contain oxygen. Several resonances associated with the $N = 1 \leftarrow 0$ transition of $^4\Sigma^-$ CH were observed at three separate laser wavelengths (333.3, 332.1,[7] and $331.3\,\mu m$[8]) while those for the $N = 2 \leftarrow 1$ transition were observed at two wavelengths (166.7 and $166.6\,\mu m$). Each observed Zeeman component consists of a well split doublet arising from proton hyperfine structure. This doubling can be seen in Fig. 1 which shows a portion of the spectrum recorded with the $331.3\,\mu m$ laser line. The analysis was complicated by the presence of other radicals in both the reaction mixtures used. Many of these other species also caused signals with a doublet structure and it was far from clear beforehand which lines were to be associated with CH.

Preliminary measurements of 67 lines in the CH spectrum have been fitted with an effective Hamiltonian for a molecule in a $^4\Sigma$ state.[9] The standard deviation of the fit is 5.5 MHz; the values of the molecular parameters obtained are given in Table I. The assignment of our observations to CH in its $a\ ^4\Sigma^-$ state is based on

(i) the chemical methods used for the production of the spectrum,

(ii) our ability to fit all aspects of the Zeeman and hyperfine structure to a model Hamiltonian for a $^4\Sigma$ state, and

(iii) the reasonable accord between the parameter values obtained in the fit and those expected for CH in the $a\ ^4\Sigma^-$ state. For example, Lie et al.[2] have calculated values for $B_0$ and $D_0$ to be 452.4 GHz and 43.2 MHz, respectively, which agree well with the values in Table I. It is also possible to estimate the proton Fermi contact parameter $b_F$ from the
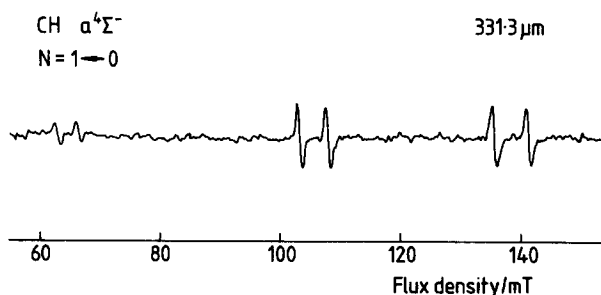


CH $a^4\Sigma^-$
N = 1 ← 0
331.3 μm

FIG. 1. A portion of the laser magnetic resonance spectrum of the CH radical in the $a\ ^4\Sigma^-$ state, recorded in perpendicular polarization ($\sigma$) with the $331.3\,\mu m$ line of $N_2H_4$ (Ref. 8). The partial pressures used for recording this spectrum were $p(\mathrm{He}) = 110$ Pa, $p(\mathrm{F}_2) = 6$ Pa, $p(\mathrm{CH}_4) = 2$ Pa with a small trace of $O_2$ ($\sim 1$ Pa) added to the $F_2$ discharge. The rotational transition involved is $N = 1 \leftarrow 0$, $J = \frac{3}{2} \leftarrow \frac{1}{2}$. The spectrum consists of three separate $M_J$ components, each split into a doublet by the proton hyperfine structure.

TABLE I. Preliminary values (in MHz) for the molecular parameters of CH in $v = 0$ level of the $a\ ^4\Sigma^-$ state, from the analysis of its LMR spectrum.

| | | | |
|---|---|---|---|
| $B$ | 451 138.78(70)[a] | $D$ | 44.53(10) |
| $\lambda$ | 2 783.99(80) | $\gamma$ | −21.8(62) |
| $b_F$ | 106.6(18) | $c$ | 62.3(69) |

[a] The figures in parentheses represent $1\sigma$ of the least-squares fit, in units of the last quoted decimal place.

value measured for CH in the $A\,^2\Delta$ state[10] (which arises from the same configuration). The value obtained of 180 MHz is comparable with that determined from the spectrum.

It is of course an assumption that our spectrum refers to CH in the $v = 0$ level of the $a\,^4\Sigma^-$ state. However, past experience with discharge-flow reactions suggests that this is quite probable.

It is necessary to make more careful measurements of the identified resonances and to extend the observations to other laser lines. A complete analysis of all the data will then yield an optimum set of molecular parameters for CH in the $a\,^4\Sigma^-$ state. The observation of this spectrum is yet another tribute to the remarkable sensitivity of the laser magnetic resonance technique.

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[5] W. W. Duley and D. A. Williams, *Insterstellar Chemistry* (Academic, London, 1984).
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[7] The frequency of the 332. 1 $\mu$m line of $CH_3OD$, pumped by the $9R(4)$ line of a $CO_2$ laser, was measured for this work in the NBS laser frequency synthesis laboratory in Boulder, Colorado as 902 630. 2 $\pm$ 0. 2 MHz.
[8] The 331. 3 $\mu$m line of $N_2H_4$ oscillates with the same $9P(12)$ pump line as the 331. 7 $\mu$m line of $N_2H_4$ but at a slightly different offset frequency. It is therefore a new lasing line and its frequency was measured as 904 889.5 $\pm$ 0. 2 MHz. The 331. 7 $\mu$m line is about twice as strong as the 331. 3 $\mu$m line.
[9] J. T. Hougen, Can. J. Phys. **40**, 598 (1962).
[10] C. R. Brazier and J. M. Brown, Can. J. Phys. **62**, 1563 (1984).

# NOTES

# Note on the finite number of interacting neighbors and the finite number of *k*-point effects on the total electronic energy of a metallic polymer

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Let us consider a SCF LCAO method with the ZDO approximation. The Hartree–Fock exchange enters the total energy of the metallic state of an infinite linear polymer bearing one orbital per unit cell through a term porportional to the integral[1]:

$$I = \sum_{n=1}^{\infty} \int_{-\pi/2}^{\pi/2} \int_{-\pi/2}^{\pi/2} n^{-1} \cos[n(k - k')]\,dk\,dk'$$
$$= (7/2)\zeta(3), \qquad (1)$$

where $\zeta(3) \approx 1.202\,056\,903\,159\,594\,285\,40$ is Rieman's zeta function of 3. In practical calculations the above integral is not calculated in the exact way. Inclusion of only a finite number of neighbors, $N$, corresponds to a truncation of the infinite sum in Eq. (1) at the $N$ th term; whereas a finite number of the points in $k$ space, $M$, corresponds to approximation of the integrals through a $M$-point trapezoidal quadrature.

In real systems, the situation is much more complicated, since each unit cell possesses many orbitals and the real Coulombic interaction does not die off exactly like $1/R$, the magnitude of the electron–electron interaction cannot be evaluated analytically like in our simplified model. However, the goal of the present communication is to demonstrate how

the truncation of the number of interacting neighbors and the finite mesh in $k$ space contribute to the error in the calculated electronic energy of a polymer.

The approximate integral that bears both the effects of the sum truncation and the finite quadrature assuming the trapezoidal rule reads

$$I \approx \sum_{n=1}^{N} 2n^{-3}[1 - (-1)^n](u \cot u)^2, \qquad (2)$$

where

$$u = n\pi/(2M - 2). \qquad (3)$$

The analytical form of the approximate integral (2) allows us to study the errors in both a numerical and analytical way. First we present the results of numerical calculations.

One of the immediate conclusions from the inspection of Table I is that the error diminishes quite slowly with increasing $N$ and $M$. The $M^{-2}$ type of asymptotics in error can be expected from the general theory of the trapezoidal quadrature as applied to polymer electronic theory,[2] while the $N^{-2}$ type of asymptotics is characteristic to metallic polymers.[3] For insulators the error dies off exponentially with increasing $N$.[3(a)] There is one interesting observation concerning