

LASER PHOTOELECTRON SPECTROMETRY OF CH^- *

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Fixed-frequency laser photoelectron spectrometry has been utilized to study photodetachment of CH^- ions by 4880 Å laser radiation. Transitions involving low-lying excited states of $^1\Delta$ and $^4\Sigma^-$ symmetry have been observed for CH^- and CH , respectively. The electron affinity of CH was determined to be (1.238 ± 0.008) eV. The $a^4\Sigma^- \text{CH}$ term energy was found to be (0.742 ± 0.008) eV and other spectroscopic constants for $X^3\Sigma^- \text{CH}^-$, a $^1\Delta \text{CH}^-$, and a $^4\Sigma^- \text{CH}$ have been determined.

1. Introduction

Laser photoelectron spectrometry of negative ions is a high resolution technique for the determination of atomic and molecular electron affinities (EA) [1-5]. Most recently, the method has been used to study the spectra of Si^- , SiH^- , and SiH_2^- and to observe multiple bound excited states in Si^- and SiH^- [6]. In this paper, we report the use of laser photoelectron spectrometry to study CH^- in order to obtain the electron affinity of CH and to determine whether or not CH^- and CH possess low-lying bound excited states.

The only previous photodetachment study of CH^- was performed by Feldmann [7] who measured the CH^- photodetachment cross section in the photon

energy range (0.5-2.0) eV. Feldmann observed two sharp thresholds in this energy range, one at (0.74 ± 0.05) eV and a second at approximately 1.95 eV. He attributed the lower threshold to the $X^2\Pi \text{CH} \leftarrow X^3\Sigma^- \text{CH}^-$ threshold, from which he obtained an electron affinity of 0.74 eV. The higher energy threshold was attributed to the opening of the channel $a^4\Sigma^- \text{CH} \leftarrow X^3\Sigma^- \text{CH}^-$.

The CH^- ion and the CH radical have been the subject of numerous theoretical studies. Among the more recent are the calculation of the electron affinity of CH by Cade [8], and the calculations of the location of a $^4\Sigma^-$ state of CH by Lie et al. [9] and Liu and Verhaegen [10]. The $a^4\Sigma^- - X^2\Pi$ intercombination transition in CH has not been observed spectroscopically.

2. Technique

The experimental apparatus used in this work has been described previously [1]. A beam of CH^- , produced in a low pressure methane discharge, is accelerated to 680 eV and mass analyzed by a Wien

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filter. Upon entering the interaction region, the ions are crossed with the intra-cavity beam of a cw argon-ion laser operating at 4880 Å (2.540 eV). Photodetached electrons entering the acceptance angle of a hemispherical electrostatic monochromator are energy analyzed (resolution ≈ 50 meV fwhm) and then detected by a particle multiplier. The complete (0–2.54 eV) energy spectrum of the photodetached electrons is digitally accumulated.

The spectra, corresponding to dipole-allowed detachment transitions between electronic states of CH^- and CH, are fitted to asymmetric gaussian line shapes [1]. The peak centers are determined to 1 meV and observed line widths are ≈ 70 meV. Because a time-varying contact potential E_{cp} may exist between the interaction region and the monochromator, all energy measurements must be calibrated against a reference atom produced simultaneously in the ion source. The reference atom used in this experiment is O^- because the oxygen affinity, (1.462 ± 0.003) eV, is well known [3,11]. The CH^- detachment energies E are defined by the following expression:

$$E(\text{CH}^-) = EA'(\text{O}) + 1.016(\Omega_{\text{O}^-} - \Omega_{\text{CH}^-}) + mW(1/M_{\text{O}^-} - 1/M_{\text{CH}}), \quad (1)$$

where Ω_{O^-} , Ω_{CH^-} are the laboratory energies of the O^- and CH^- photodetached electrons at the peak centers, W is the kinetic energy of the ions, m is the electron mass, M_{O^-} , M_{CH} are the O and CH masses, respectively, and $EA'(\text{O}) = 1.465$ eV is the effective oxygen affinity when spin-orbit splittings in O^- and O are not resolved. The factor of 1.016 multiplying the electron energy difference compensates for a well-studied compression effect due to our electron analyzer [4–6]. The third term is a kinematic correction [1]. Detachment energies calibrated in the above manner are obtained to $\pm(2-5)$ meV.

3. Data and analysis

Fig. 1 depicts the photoelectron spectrum of CH^- . The four observed sharp peaks can only be due to dipole-allowed transitions involving the two lowest states of CH^- ($\sigma^2\pi^2\ ^3\Sigma^-$, $^1\Delta$) and the two lowest states of CH ($\sigma^2\pi\ X^2\Pi$, $\sigma\pi^2\ a^4\Sigma^-$). The low intensity diffuse feature at ≈ 1.5 eV electron energy is due

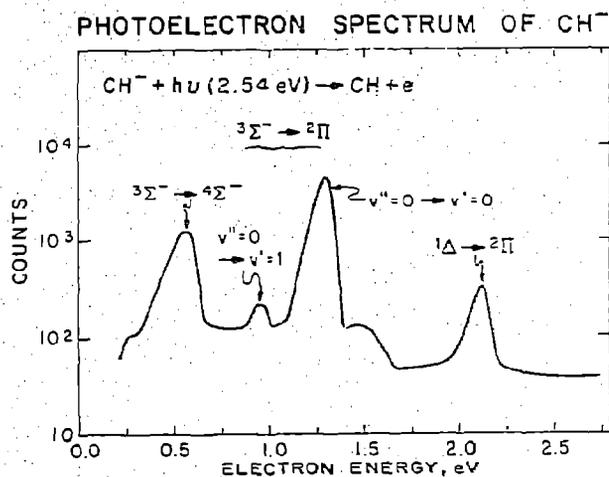
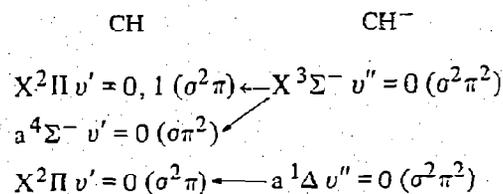


Fig. 1. Photoelectron spectrum of CH^- . The number of electrons striking the detector is plotted logarithmically against electron energy. The sharp drop in counts at electron energies below ≈ 0.3 eV is due to the transmission cut-off of the analyzer.

probably to CH_2^- . The energy ordering of the $\sigma^2\pi^2$ CH^- states is initially assumed to be that of NH ($X^3\Sigma^- < a^1\Delta$) [12–14]. The energy ordering of the two lowest CH states is well understood [9,10,15]. The four well-defined peaks are tentatively assigned to the following transitions:



These assignments are supported by several arguments. A change in source conditions does not alter the relative intensities of the peaks assigned to the $X^2\Pi$, $a^4\Sigma^-$ $\text{CH} \leftarrow X^3\Sigma^-$ CH^- transitions, proving that these transitions originate from the same state. The photoelectron spectrometry selection rule of $\Delta S = \pm 1/2$ shows that these transitions must originate from the $^3\Sigma^-$ rather than the $^1\Delta$ state of CH^- . (This selection rule is derived from the necessity of conserving total electronic spin in the detachment process.) The intensity of the peak assigned to the $X^2\Pi$ $\text{CH} \leftarrow a^1\Delta$ CH^- transition is changed relative to the other

peaks when source conditions are changed. Consequently, our assignment is the only possible one. The initial assumption that the $X^3\Sigma^-$ state of CH^- is the ground state is proved to be correct. The $a^1\Delta$ state is sufficiently metastable to survive the 20 μs flight time from ion source to interaction region.

Our resolution (50 meV) is insufficient to resolve vibrational sequences. Since the vibrational temperature of our ion source $T_{\text{vib}} \leq 1000$ K, the sequences are labelled by the lowest possible quantum numbers even though some of the intensity of the peaks is due to higher vibrational levels. As in the analogous case of SiH^- [6], nearly diagonal Franck-Condon factors are observed.

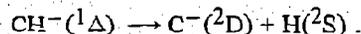
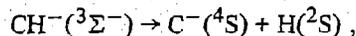
A weak $v' = 1 \leftarrow v'' = 0$ satellite is seen alongside the larger $v' = 0 \leftarrow v'' = 0$ peak in the dominant $X^2\Pi\text{CH} \leftarrow X^3\Sigma^- \text{CH}^-$ transition. From the intensity ratio of these two peaks, we can, via a harmonic Franck-Condon analysis, determine the magnitude of the difference in equilibrium internuclear distance (r_e) between $^2\Pi\text{CH}$ and $^3\Sigma^- \text{CH}^-$. In addition, if we assume that $r_e''(^3\Sigma^- \text{CH}^-) < r_e'(^2\Pi\text{CH})$ because the internuclear distance in $^3\Sigma^- \text{NH}$ (isoelectronic with CH^-) is 0.08 Å less than that in $^2\Pi\text{CH}$ [16], we can determine r_e'' in $^3\Sigma^- \text{CH}^-$. The vibrational frequency ω_e'' of $^3\Sigma^- \text{CH}^-$ is not determined in our experiment because no distinct hot bands are observed. However, the Franck-Condon analysis is insensitive to the assumed value of ω_e'' [6].

Using the value $r_e' = 1.120$ Å for CH [15], we obtain $r_e'' = (1.089 \pm 0.010 / -0.005)$ Å. An approximate value of ω_e'' can then be obtained from Badger's rule [17]: $\omega_e'' = 3025 \text{ cm}^{-1}$. From the measured separation between the $v' = 0, 1 \ ^2\Pi\text{CH} \leftarrow v'' = 0 \ ^3\Sigma^- \text{CH}^-$ transitions, we determine $\omega_e' - 2\omega_e'x_e'$ to be $(2740 \pm 50) \text{ cm}^{-1}$. This value agrees with the spectroscopic value of 2732.5 cm^{-1} [15].

Our measured detachment energies are differences between centers of gravity of large numbers of unresolved transitions. These transitions connect rotational (and often spin-orbit split) levels of electronic states in the ion and the neutral species. To obtain values for the electron affinity of CH (defined as the energy separation between the lowest vibration-rotation level in $X^3\Sigma^- \text{CH}^-$ and the lowest such level in $X^2\Pi\text{CH}$) and the term energies T_0 of excited states in CH^- and CH , we must estimate the differences between our measured "vertical" detachment energies

and the energies separating the lowest vibration-rotation levels of the electronic states in the ion and the neutral species. A procedure for doing this has been outlined in a previous paper [6]. Briefly, we assume that the centroid of a measured detachment peak corresponds to the ensemble coverage of the energies of $\Delta N = 0$ ($N =$ rotational quantum number) transitions. If the rotational temperature of our ion source is assumed to be $500 \text{ K} \leq T_r \leq 1500 \text{ K}$ [18], we obtain corrections to our measured detachment energies of $\leq 50 \text{ cm}^{-1}$. Uncertainties in these corrections caused by our lack of knowledge of T_r , approximations made in determining the correction formulae, and uncertainties in the internuclear distances, are on the order of $\pm 50 - \pm 100 \text{ cm}^{-1}$. We note that in the correction to the measured energy for the $^2\Pi\text{CH} \leftarrow ^3\Sigma^- \text{CH}^-$ peak we have assumed that $r_e''(^3\Sigma^- \text{CH}^-) < r_e'(X^2\Pi\text{CH})$.

Table 1 lists the spectroscopic information obtained in this experiment for the $^3\Sigma^-$ and $^1\Delta$ states of CH^- and the $^4\Sigma^-$ state of CH . Reported dissociation energies are based on a value for $D_0(X^2\Pi\text{CH})$ of 3.45 eV [15]. The chosen dissociation limits for the CH^- states are the lowest atomic states of the correct symmetry:



The term energy of $\text{C}^-(^2\text{D})$ is taken from Bennett [19] and Π' in [20]. The internuclear distance for $^1\Delta \text{CH}^-$ is an approximate value, based on our lack of observation of any non-diagonal vibrational peaks in the $X^2\Pi\text{CH} \leftarrow a^1\Delta \text{CH}^-$ transition. Once $r_e(a^1\Delta)$ is known roughly, the vibrational frequency of this state is determined from an empirical rule [16].

4. Discussion

The electron affinity of CH determined in this experiment, $(1.238 \pm 0.008) \text{ eV}$, compares reasonably well with Cade's calculated value of $(1.61 \pm 0.30) \text{ eV}$ [8]. It is somewhat difficult to make a direct comparison with the data of Feldmann. Our data indicate that in the photodetachment measurements of the type performed by Feldmann, one should see thresholds at photon energies of approximately 0.39, 1.24

Table 1
 Constants determined for CH^- , CH

	CH^-		CH	
	$X^3\Sigma^-$	$a^1\Delta$	$X^2\Pi$	$a^4\Sigma^-$
EA (eV)	1.238 ± 0.008	0.393 ± 0.015		
T_0 (eV)	—	0.845 ± 0.012	—	0.742 ± 0.008
r_e (Å)	$1.089^{+0.010}_{-0.005}$	$1.10^{+0.02}_{-0.05}$	1.120 a)	1.083 b)
ω_e (cm^{-1})	3025 c)	≈ 3000 c)	2858 a)	3160 b)
D_0 (eV)	3.44 ± 0.02	3.83 ± 0.03	3.47 d)	2.73 ± 0.01 (2.68 b)

a) Ref. [15]; b) ref. [9]; c) determined by empirical rule, see text; d) ref. [16].

and 1.98 eV. Feldmann definitely observes a threshold corresponding to our predicted location of 1.98 eV, and, since the 0.4 eV threshold corresponds to detachment from an excited state of CH^- , this onset might be rather weak in the photodetachment experiments of Feldmann. In any case his data are not inconsistent with such a threshold. On the other hand, Feldmann observes a strong threshold at 0.74 eV photon energy which we do not see. Feldmann does not observe what should be a very strong threshold at 1.24 eV. The strong peak we observe at a detachment energy of 1.24 eV, assigned to the transition $X^2\Pi \text{CH} \leftarrow X^3\Sigma^- \text{CH}^-$, cannot be due to C^- (EA(C) = (1.27 ± 0.010) eV [21]) because the C^- peak is observed at slightly higher detachment energy when our mass filter is tuned to pass C^- . The arguments which we have advanced concerning the CH^- and CH state identifications seem to us to be completely convincing and we can offer no explanation for the results of Feldmann. When several electronic states are observed, fixed frequency laser photoelectron spectrometry is generally a preferable technique to photodetachment cross section measurements because the former method produces differential spectra whereas the latter method produces only a total cross section as a function of photon energy, which can be very difficult to unfold.

It is interesting to note that the measured electron affinity of CH is within 0.05 eV of the carbon affinity [21]. Thus, the CH^- $2p\pi$ electron being detached is essentially in a non-bonding carbon $2p$ orbital.

Assuming that $r_e''(X^3\Sigma^- \text{CH}^-) < r_e'(X^2\Pi \text{CH})$, we have determined r_e'' to be $(1.089^{+0.010}_{-0.005})$ Å. For the series $X^3\Sigma^- \text{CH}^-$, $X^2\Pi \text{CH}$, and $X^1\Sigma^+ \text{CH}^+$, the

equilibrium internuclear distances are 1.089 Å, 1.120 Å, and 1.131 Å [15, 22].

The intercombination difference ($X^3\Sigma^- - a^1\Delta$) measured here for CH^- (0.845 ± 0.012) eV, is much smaller than the analogous quantity in isoelectronic NH, where experimental and theoretical studies indicate an energy difference of 1.5–1.6 eV [12–14]. The term energy T_0 of (0.742 ± 0.008) eV that we have determined for a $^4\Sigma^- \text{CH}$ is within the calculated limits of 0.52–0.75 eV obtained by Lie et al. [9]. Liu and Verhaegen have calculated a term energy of 0.93 eV for the $a^4\Sigma^-$ state [10]. (The $a^4\Sigma^-$ state was observed by Feldmann [7] to be (1.94 ± 0.05) eV above the ground state of CH^- , a result in reasonable agreement with our own. Feldmann's value of $T_0(a^4\Sigma^-) = 1.2$ eV differs from ours, however, because his value of the CH affinity differs from ours.) Now that the position of the $a^4\Sigma^- \text{CH}$ state is known approximately, it might be possible to observe the weak $a^4\Sigma^- - X^2\Pi \text{CH}$ intercombination bands. Photoelectron spectrometry of negative ions is in general quite valuable in the determination of intercombination splittings in neutrals since transitions from the ground state of the negative ion to both the ground state and first excited metastable state of the neutral species are often dipole-allowed.

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