

TABLE I. Energy values for $J = 1$ of observed $A\ ^1\Sigma_u^+$ levels (cm^{-1}), using ground state term values from Ref. 5.

| | |
|-----------|-----------|
| ν | 15 179.00 |
| $\nu + 1$ | 15 301.37 |
| $\nu + 2$ | 15 420.07 |
| $\nu + 3$ | 15 534.68 |
| $\nu + 4$ | 15 648.42 |
| $\nu + 5$ | 15 761.98 |
| $\nu + 6$ | 15 878.51 |
| $\nu + 7$ | 15 991.75 |
| $\nu + 8$ | 16 105.67 |
| $\nu + 9$ | 16 220.29 |

underway and will be presented elsewhere.¹³ The term energies for the ten observed vibrational levels of the A state appear in Table I. Since ^{40}Ca has zero spin, the lowest rotational states are $J = 1$ in the A state. Approximate constants for the A state are given in Table II; they are referenced to the lowest observed level, which is not necessarily $\nu' = 0$.

Analysis of the spectrum shows unequivocally that the red and green systems share the same lower $X\ ^1\Sigma_g^+ (^1S + ^1S)$ ground state. The upper states of the red and green systems are thus $A\ ^1\Sigma_u^+ (^1S + ^1D)$ and $B\ ^1\Sigma_u^+ (^1S + ^1P)$, where the labels give each state's dissociation limit. Both states will also be important in describing the higher alkaline earth dimers, such as Sr_2 .

TABLE II. Approximate constants of the $A\ ^1\Sigma_u^+$ state (cm^{-1}) with respect to lowest observed level, uncertainty in parentheses.

| | |
|----------------|-------------------------|
| T_{∞} | 15143.4(5) |
| ω_v | 121.0(1) |
| ω_{x_v} | 0.4(1) |
| B_v | 0.0615(5) |
| D_v | $3.0(4) \times 10^{-8}$ |
| α_v | $3.0(4) \times 10^{-4}$ |
| R_v | 3.72 Å |

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Laser photoelectron spectroscopy of vibrationally relaxed CH_2^- : A reinvestigation of the singlet-triplet splitting in methylene^{a)}

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In view of the many questions concerning the photoelectron spectrum of CH_2^- ,^{1,2} we have reinvestigated this system using a new experimental apparatus which incorporates a flowing afterglow ion source, providing vibrational and rotational cooling of the sample ions. Results presented here enable several previously observed spectral features to be positively identified as vibrational hot bands, leading to a revised determination of the singlet-triplet splitting in methylene.

The determination of the relative energies of the ground 3B_1 state and the first excited 1A_1 state of methylene has been a subject of lively interest during the past decade.³ As one of the simplest organic species CH_2 has served as a benchmark system in the development of theoretical models, and numerous *ab initio* calculations of its singlet-triplet splitting have been reported.³⁻¹³ Recent theoretical investigations indicate energy gaps of 9-11 kcal/mol,⁴⁻¹³ consistent with several indirect experimental determinations based on photochemical studies,¹⁴⁻¹⁷ scattering results,¹⁸ and measurements of the heats of formation of singlet^{19,20} and triplet²¹ methylene. Substantial methylene concentrations are difficult to prepare and thus few direct spectroscopic measurements of the singlet-triplet splitting are available.

One such direct determination has been obtained from the photoelectron spectrum of CH_2^- , in which transitions to both the 3B_1 and the 1A_1 states of CH_2 are concurrently observed.^{1,2} This experiment yielded a singlet-triplet splitting of at least 19.5 kcal/mol,^{1,2} in disagreement with the results of a number of indirect determinations,¹⁴⁻²⁰ as well as with the recent 9.05 ± 0.06 kcal/mol measurement obtained from singlet/triplet perturbations in the far-IR laser magnetic resonance spectrum of CH_2 .²² The photoelectron results also provided a constraint on the sum of the electron affinity and the singlet-triplet splitting of methylene, leading to renewed theoretical efforts to determine the electron affinity.¹² The central problem in extracting the methylene singlet-triplet splitting from the CH_2^- photoelectron spectrum was to determine the extent of hot band activity in order to correctly identify the origin of the triplet band system.^{1,2,6,7,23} The possible presence of hot bands was tested through the use of diverse ion source conditions known to produce a wide range of vibrational temperatures in other ionic samples. From the observed invariance of the $\text{CH}_2^- (^2B_1) \rightarrow \text{CH}_2 (^3B_1) + e^-$ vibronic band intensity distribution to these different conditions, it was concluded that vibrationally excited CH_2^- ions did not make significant

contributions to the observed vibrational progressions.² However, subsequent experiments²⁴ reporting an unexpectedly low value of 963 cm^{-1} for the bending frequency of triplet methylene cast significant doubt over the original interpretation of the photoelectron results.

To obtain additional information concerning the contribution of hot bands to the CH_2^- photoelectron spectrum, a new photoelectron spectrometer with a 1000-fold increase in sensitivity has been constructed,^{25,26} permitting the replacement of the conventional gas discharge ion source with a flowing afterglow ion source.²⁷⁻³⁰ CH_2^- ions prepared in the new apparatus reside in a relatively high pressure (~ 0.3 Torr) field-free flow tube for several milliseconds prior to their gentle extraction into the collisionless regions of the spectrometer. During this time, collisions with the room temperature helium buffer gas seeded with ethylene provide vibrational as well as rotational cooling of the sample ions.

Figure 1 contrasts the photoelectron spectrum reported previously^{1,2} with that of cooled CH_2^- prepared in the flowing afterglow source. The prominent peak labeled "G" in both spectra represents the $\text{CH}_2^- (^2B_1) \rightarrow \text{CH}_2 (^1A_1) + e^-$

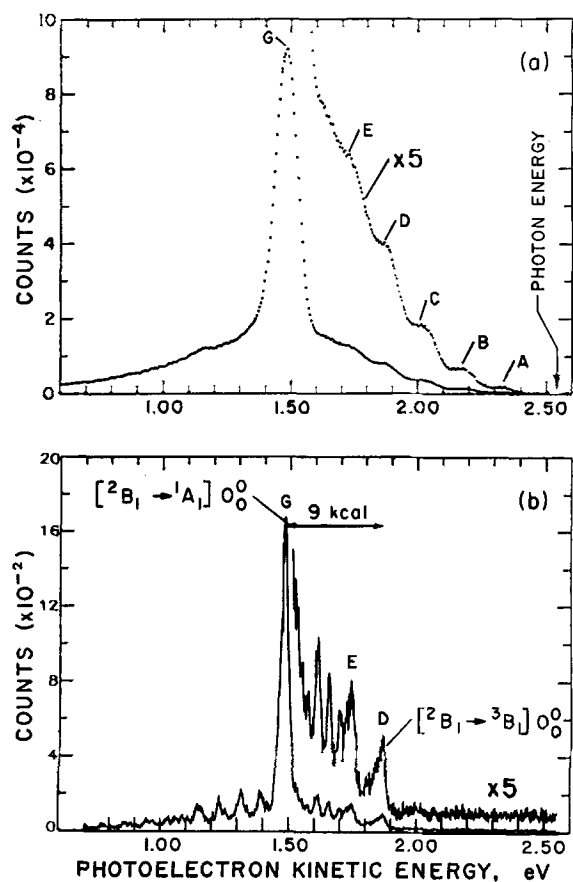


FIG. 1. CH_2^- photoelectron spectra following 2.54 eV (488 nm) excitation. (a) Previously reported spectrum (Refs. 1 and 2) obtained with a gas discharge ion source. (b) Spectrum of vibrationally and rotationally cooled CH_2^- prepared in a flowing afterglow ion source. The instrumental resolution is 60 meV in (a) and 10 meV in (b). The absence of peaks A, B, and C in (b) establishes their hot band nature and gives a singlet-triplet splitting of 9 kcal/mol .

transition, whose "vertical" appearance is consistent with the similar geometries of the ionic^{6,7} and the neutral singlet^{31,32} species. The weaker features observed on either side of the singlet peak are associated with the $\text{CH}_2^- (^2B_1) \rightarrow \text{CH}_2 (^3B_1) + e^-$ excitation. This transition is accompanied by a considerable increase in the equilibrium HCH angle, from $\sim 103^\circ$ ^{6,7} to $\sim 134^\circ$,³³ and thus gives rise to an extended bending (ν_2) progression in the photoelectron spectrum.

In our previous reports,^{1,2} the band labeled "A" in Fig. 1(a) was assigned as the origin of the transition to triplet methylene, and peaks A-E were attributed to a 3B_1 progression in ν_2 . According to this assignment, the observed spacing between peaks A and G implies a singlet-triplet splitting of 0.845 eV , or 19.5 kcal/mol .^{1,2} However, the relative decrease in the intensities of peaks A-C in the spectrum of the cooled ion [Fig. 1(b)] demonstrates that these features are actually due to transitions from vibrationally excited CH_2^- ions. The $980 \pm 20\text{ cm}^{-1}$ interval observed in the new spectrum between peaks D and E, which display similar rotational contours, is consistent with the known 3B_1 bending frequency of 963 cm^{-1} .²⁴ In view of the Franck-Condon intensity profile predicted for the ν_2 progression,^{2,6,7} the low signal level in the region of peak C relative to D ($\leq 1:15$) rules out the possibility that this progression extends beyond peak D. Therefore, peak D is the true origin of the $\text{CH}_2^- (^2B_1) \rightarrow \text{CH}_2 (^3B_1) + e^-$ system. This result implies a $\text{CH}_2 (^3B_1)$ electron affinity near 0.67 eV , and a singlet-triplet splitting of $\sim 9\text{ kcal/mol}$, with the consequence that all recent experimental and theoretical determinations⁴⁻²³ are essentially in agreement. At present, we have no explanation as to why all previous attempts to modify the CH_2^- vibrational state distribution were unsuccessful.

The cooling obtained in the flowing afterglow ion source, combined with the sixfold improvement in instrumental resolution achieved in our new photoelectron spectrometer,^{25,26} enables the observation of rovibronic structure up to $10\,000\text{ cm}^{-1}$ above the origin of the $^2B_1 \rightarrow ^3B_1$ transition. Since vibrational intervals above $\nu_2 = 1$ have not been directly observed by other spectroscopic methods, the photoelectron spectrum of cooled CH_2^- promises to provide an important test of theoretical models of the methylene potential surface at energies near and above the barrier to linearity in the 3B_1 ground state. A detailed discussion of these results is in preparation.

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NOTES

Fe⁺ production from electron impact on Fe(CO)₅Brian C. Hale^{a)} and John S. Winn^{b)}*Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720*

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It is well known¹ that the electron impact positive ion mass spectrum of Fe(CO)₅ is dominated by Fe⁺ and FeCO⁺ for electron energies ≥ 25 eV. For photoionization of Fe(CO)₅ by 21.2 eV photons, similar fragment ion yields are obtained.² The neutral dissociation pathways for Fe(CO)₅ energized by vacuum-ultraviolet photolysis³ and metastable atom impact⁴ at ≥ 11 eV have been studied by atomic iron fluorescence analysis. Nonfluorescent atomic iron production is presumed to occur at lower excitation energies; the threshold³ for production of Fe from Fe(CO)₅ is 6.10 eV.

In this Note we report the atomic iron fluorescence accompanying electron impact on Fe(CO)₅ in a crossed beam experiment. The apparatus was a modified version of that used by Horák and Winn.³ Briefly, a strong effusive beam of Fe(CO)₅ (mass flow of 0.14 g/s) was directed into a stainless steel chamber equipped with extensive liquid nitrogen cooled surfaces. An electron beam crossed this flow at a right angle. The electron beam was produced⁵ by a modified Pierce gun and was monitored by a Faraday cup located on the opposite side of the chamber. The electron energy could be varied from ~ 60 to 180 eV without significant change in electron beam current, but, due to the baffles and electron lens system used to reduce the filament emission light and shield the 2% Th/W filament from Fe(CO)₅ poisoning, the electron current was limited to $\sim 10^{-7}$ A. During the course

of an experiment, the emission current was observed to decline slowly due to poisoning, or to fail abruptly. Data could be accumulated for ~ 30 min before a combination of electron flux decrease or Fe(CO)₅ reservoir depletion terminated an experiment. Fluorescence along the third axis was collected by quartz optics and monitored by a photomultiplier tube. Data acquisition and control of the Fe(CO)₅ flow were handled by a microcomputer in a manner similar to that of Ref. 3.

Two types of experiments were performed. In one, the total fluorescence in the 200-600 nm range was recorded at various electron energies. In the second, the electron energy was set at 100 eV and the fluorescence was dispersed with a scanning 0.25 m monochromator and collected in a multi-channel mode with 2 nm wavelength resolution. In all experiments, the Fe(CO)₅ was purified of N₂ and CO by freeze-pump-thaw cycles.

From a Beer's law analysis of the electron beam attenuation, based on a calculated effusive Fe(CO)₅ flux distribution, a total scattering cross section of $4.7 \pm 0.4 \text{ \AA}^2$ was measured at 100 eV. This represents the production of *all* final states—ions, neutral fragments, etc. From the total fluorescence experiments, a fluorescence quantum yield could be calculated, given the measured signals, the quantum efficiency of the photomultiplier, geometric factors, and the re-