more complete account after we have investigated the variation of critical pulse width as a function of the potentials at which the electrode is pulsed and biased and as a function of the time since the last trigger wave. Because a trigger wave propagates at a rate influenced by the time since passage of the preceding wave, the spacings of pulses received at the platinum electrode should differ in predictable ways from the spacings between the initiating pulses.

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Supplementary Material Available: Detailed experimental procedures for those wishing to reproduce our observations (1 page). Ordering information is given on any current masthead page.

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Laser Photoelectron Spectrometry of CH_2^-. Singlet-Triplet Splitting and Electron Affinity of CH_2[1]

Sir:

Laser photoelectron spectrometry of CH_2^- has been utilized to determine the electron affinity (EA) and the intercombination ($^1A_1 \leftarrow {}^3B_1$) energy difference in methylene. These experimental results, coupled with ab initio calculation, and a Franck-Condon factor analysis have enabled construction of accurate potential surfaces for $CH_2^-(^2B_1)$ and $CH_2(^3B_1)$ and ($^1A_1$). The $^3B_1$ ground state of methylene is found to be bent with ∠HCH of 138 ± 4°, and the intercombination separation is 0.845 ± 0.03 eV (19.5 ± 0.7 kcal/mol).

The experimental method employed consists of crossing a mass-analyzed CH_2^- ion beam with an argon ion laser operating at 488 nm (2.540 eV). The CH_2^- ions are extracted from discharges in both CH_4 and CH_2N_2 gas at ~1 Torr. Those photodetached electrons that enter the acceptance aperture of a hemispherical electrostatic monochromator are energy analyzed and counted. The electron binding energies are obtained to a first approximation[2] by subtracting the measured electron kinetic energy from the laser photon energy. The absolute electron energy scale is determined by simultaneous photodetachment of CH_2^- and O^-, the latter EA being well known.[3]

The CH_2^- photoelectron spectrum results from one-electron, dipole allowed transitions between the ground electronic state of CH_2^- and the several low lying states of CH_2. The CH_2^- ion possesses the same symmetry and molecular orbital configuration as the isoelectronic species NH_2: $(1b_2)^2(3a_1)^2(1b_1)^2\tilde{X}(^2B_1)$. From this state, the following low energy transitions are possible.

$$\begin{tikzcd} CH_2^- & CH_2 \\ & (1b_2)^2(3a_1)^1(1b_1)^1\tilde{X}(^3B_1), \text{ or } \tilde{b}(^1B_1) \\ (1b_2)^2(3a_1)^2(1b_1)^1\tilde{X}(^2B_1) \arrow[ur] \arrow[dr] & \\ & (1b_2)^2(3a_1)^2\tilde{a}(^1A_1) \end{tikzcd}$$

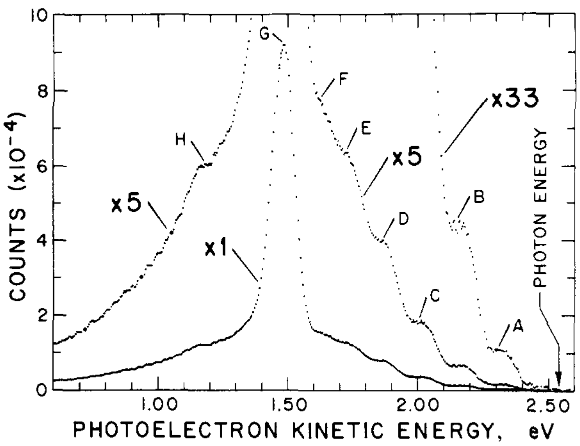

Figure 1. Experimental photoelectron spectrum of CH_2^-.

Past work[4] on OH^-, CH^-, SiH^-, and SiH_2^- indicates that the ground state geometries of hydride negative ions are very similar to those of their neutral isoelectronic neighbors. Comparing with NH_2, we thus expect the structure of $CH_2^-(^2B_1)$ to be $r_e \approx 1.1$ Å, and $\theta_e \approx 100°$. This conclusion has been verified with a double zeta configuration interaction calculation of the CH_2^- geometry. The spectroscopically obtained[5] structure of $\tilde{a}\ ^1A_1$ CH_2 is $r_e \sim 1.11$ Å, $\theta_e = 102.4°$. Thus the ejection of the CH_2^- nonbonding $1b_1$ electron results in production of $CH_2(^1A_1)$ with a virtually identical geometry. Franck-Condon factors allow essentially only diagonal ($\Delta v = 0$) transitions and a single intense peak is expected in the photoelectron spectrum of this state. In contrast, transitions to the $^3B_1$ and $^1B_1$ states involve ejection of an electron from a $3a_1$ orbital with more bonding character and a large geometry change, such that an extended bending vibrational progression is expected for these states.

The observed photoelectron spectrum of CH_2^- (Figure 1) is in accord with these expectations. The prominent peak, G, is assigned as the transition to $v = 0$, $CH_2(^1A_1)$; the much weaker peaks A → F spaced at approximately 1200 cm^{-1} are assigned as a bending progression. The apparent regularity of this progression coupled with a constant photoelectron angular distribution over the peaks A → F (differing markedly from that for peak G) and the theoretical Franck-Condon analysis discussed below allows unambiguous assignments of peaks A → F as the $^3B_1$ CH_2 bending progression. The possibility of CH_2^- hot bands is ruled out by the identical photoelectron spectra produced from parent CH_4 or CH_2N_2.

A similar spectrum results from photodetachment of CD_2^- ions; the spacing of the 1200-cm^{-1} progression drops to about 900 cm^{-1} and the single peak "G" essentially does not move. The isotope shift can be used to obtain the vibrational level numbering in the long progression. Based upon these shifts, the only possible identification for the transition "A" is $v = 0$ of $CH_2(^3B_1)$. After small corrections for energy scale nonlinearities and rotational effects, the following direct experimental results are obtained:

$$EA(CH_2) = (0.210 \pm 0.03)\ \text{eV}$$

$$\Delta E(^1A_1 \leftarrow {}^3B_1) = (0.845 \pm 0.03)\ \text{eV}$$

The present value for the intercombination splitting (19.5 ± 0.7 kcal/mol) is significantly higher than most photochemical estimates. These studies place the $^1A_1$ state above the $^3B_1$ state by about 1-8 kcal/mol.[6] Theoretical computations of this singlet-triplet splitting were initially reported to be 24 kcal/mol but over the past 15 years increasingly sophisticated computational efforts[7] have yielded an extrapolated value of 10-12 kcal/mol.

To confirm the above interpretations, ab initio calculations

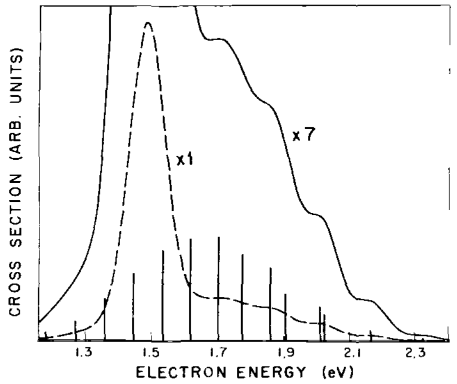

Figure 2. Model photodetachment spectrum of $CH_2^-(^2B_1) \rightarrow CH_2(^3B_1$ and $^1A_1)$. The vertical bars represent Franck-Condon factors for the various vibrational levels of the $^3B_1$ state only. The curves were obtained by folding the Franck-Condon factors obtained from the potentials of Figure 3 with an assumed Gaussian experimental line shape and an experimental ratio of the $^2B_1 \rightarrow {}^3B_1$ and $^2B_1 \rightarrow {}^1A_1$ electronic transition moments.

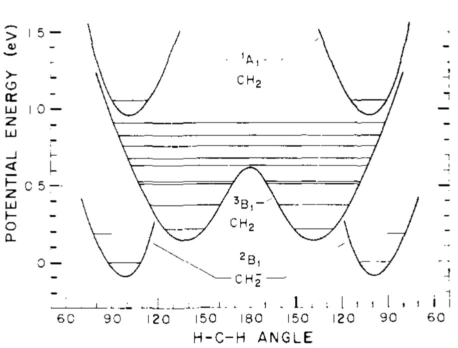

Figure 3. Calculated bending potential curves and pertinent vibrational levels for CH_2 and CH_2^-. This model considers vibrational energy levels only and ignores rotational coupling. The two lowest levels of $^3B_1$ and the lowest indicated levels of $^2B_1$ and $^1A_1$ are nearly degenerate pairs and are unresolved in the figure. The (0-0) splittings are fixed by experiment.

were carried out for a range of HCH angles, with the C-H distances held near their equilibrium positions. Double zeta configuration-interaction calculations were performed for $CH_2^-(^2B_1)$ to supplement similar earlier $CH_2(^1A_1)$ results.[8] Extended basis[9] SCF calculations were carried out for the $CH_2(^3B_1)$ ground state to obtain what is believed to be a reliable[10] barrier height of 3900 cm^{-1}. Bending Franck-Condon factors between $v = 0$ of the $CH_2^-(^2B_1)$ and $CH_2(^1A_1$ and $^3B_1)$ were calculated variationally in a B-spline basis. Combining these with the experimentally determined $^1A_1 \leftarrow {}^3B_1$ splitting, and folding with the experimental line shape, yielded a simulated photoelectron spectrum consisting of a single sharp peak and a long, partially resolved progression in the $^3B_1$ state. Simple parameterized forms of the $^2B_1$ and $^3B_1$ curves were then adjusted to give the simulated spectrum shown in Figure 2, the resulting equilibrium bond angles being $(99 \pm 3°)$ $CH_2^-(^2B_1)$ and $(138 \pm 4°)$ $CH_2(^3B_1)$.

The allowable adjustments of the $^2B_1$ bond angle are severely restricted, since the $^1A_1$ bond angle is accurately known,[5] and the absence of a distinct bending progression in the $^1A_1$ state constrains the change in the HCH angle such that $|\angle{}^2B_1 - \angle{}^1A_1| \lesssim 3°$. The triplet photoelectron spectrum shown in Figure 2 is very sensitive to the *difference* in bond angle between $CH_2^-(^2B_1)$ and $CH_2(^3B_1)$, and the *qualitative* fit indicated deteriorates markedly as this bond angle difference is varied by $\pm 2°$. The indicated error bars were determined by this bond angle-difference sensitivity, and absolute angles are relative to the optically determined $^1A_1$ bond angle. The $^3B_1$ geometry is in good agreement with that obtained in matrix ESR studies.[11,12] These optimized potential curves are shown in Figure 3. Using these potentials, a simulated CD_2^- spectrum gives excellent agreement with the experimental CD_2^- spectrum.

These calculations confirm the assignment of the observed peaks (A → F of Figure 1) to a partially resolved bending progression in the $^3B_1$ state, and provide a refined potential surface for ground state methylene. Detailed discussion[13] of these studies in in preparation.

Acknowledgments. The assistance of Dr. A. Kasdan in an early phase of this work is gratefully acknowledged. We would like to dedicate this paper to Professor George J. Schulz, whose untimely death has deprived the scientific community of an invaluable colleague, and an irreplaceable friend.

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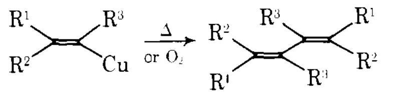
Oxidative Coupling of Optically Active Vinylcopper Reagents. Stereospecific Generation of a Novel Dissymmetric Conjugated Diene

Sir:

Alkenylcopper(I) reagents couple thermally[1] or oxidatively[2] to give 1,3-dienes with retention of configuration at the double bond (eq 1). As part of a general study of the formation and stereochemical stability of optically active organocopper reagents[3] we have investigated the oxidative coupling and al-



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