

izing background  $1 - \rho \int c^0(r) dr$  is just the (dimensionless) inverse isothermal compressibility  $\beta \partial P / \partial \rho$ ; thus the second moment condition for such systems is rigorously assured when they are compressible. Moreover, for them we can express  $\xi^{-2}$  as  $\kappa^2 A^{1/2}$  and  $A^{1/2}$  as  $\partial \rho / \partial \beta P$ ; thus the asymptotic forms of  $G(r)$  and  $\tilde{G}(k)$  can be expressed wholly in terms of thermodynamic quantities.<sup>6</sup>

For the case of the one-component plasma, Vieillefosse and Hansen<sup>7</sup> (VH) have recently derived the asymptotic  $\tilde{G}(k)$  results on the basis of fluctuation arguments much like those used by SL in obtaining (3). The strict asymptotic result for  $G(r)$ , however, is a stronger one (see footnote 6) and is in fact inconsistent with the result  $G(r) \sim O(r^{-8})$  shown by Stillinger and White<sup>8</sup> to follow from (3) on the basis of plausible assumptions on  $\epsilon(k)$ . This interesting inconsistency between the results of these two different approaches is one we hope to pursue in collaboration with Groeneveld.

For a symmetric solute of charged spheres in a solvent of dipolar spheres, we can extend our  $G(r)$  result to the solute-solute, solute-solvent, and solvent-solvent distribution functions  $G_{UU}(r)$ ,  $G_{UV}(r)$ , and  $G_{VV}(r)$ . In terms of the corresponding pair potentials,  $\phi_{UU}(r)$ ,  $\phi_{UV}(r)$ , and  $\phi_{VV}(r)$ , we have  $G_{UU}/\phi_{UU} \sim -\beta e^{-\lambda r}/\epsilon$ ,  $G_{UV}/\phi_{UV} \sim -\beta(\epsilon - 1)(1 + \lambda r)e^{-\lambda r}/3y\epsilon$ , and  $G_{VV}/\phi_{VV} \sim -\beta(\epsilon - 1)^2(1 + \lambda r + \frac{1}{2}\lambda^2 r^2)e^{-\lambda r}/(3y)^2\epsilon$  as  $r \rightarrow \infty$ , for either  $q \rightarrow 0$  or solvent  $\rho \rightarrow 0$ , where  $\epsilon$  is solvent dielectric constant and  $\lambda$  is  $\epsilon^{-1/2}\kappa$ .

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<sup>6</sup>One has  $\tilde{S}(k) = 1 + \rho \tilde{G}(k) = [1 - \rho \tilde{C}(k)]^{-1}$  with  $\tilde{C}(k) = \tilde{c}^0(k) - 4\pi\beta q^2 k^{-2}$ . Therefore  $\tilde{S}(k) \rightarrow A^{1/2} k^2 [\kappa^2 A^{1/2} + k^2]^{-1}$  as  $k \rightarrow 0$  as long as  $\tilde{c}^0(k) = \tilde{c}^0(0) + O(k^\sigma)$ ,  $\sigma > 0$ , with  $A^{-1/2} = 1 - \rho \tilde{c}^0(k)$ . We note that this immediately implies a fourth-moment condition  $\tilde{S}(k)^{-1} \sim \kappa^2 k^{-2} \rightarrow A^{-1/2}$  as  $k \rightarrow 0$  for  $\sigma > 0$ , but only for a one-component system will  $A^{-1/2} = \beta \partial P / \partial \rho$ . The  $r \rightarrow \infty$  result requires additional assumptions; it hinges on a cluster-expansion analysis of the sort discussed in the Appendix of the contribution by G. Stell in *Statistical Mechanics-Part A: Equilibrium Techniques*, Modern Theoretical Chemistry, Vol. 5, edited by Bruce Berne (Plenum, New York, 1977). From that analysis one concludes that  $c^0(r)$  decays faster than any inverse power of  $r$  as  $r \rightarrow \infty$ , from which our  $G(r)$  result follows [The  $\tilde{G}(k)$  result requires only that  $c^0(r)$  decay like  $O(r^{-3\sigma})$ ,  $\sigma > 0$ .] The observation that in a one-component system the reference  $(\beta \partial P / \partial \rho)^0 = A^{-1/2}$  is the full  $\beta \partial P / \partial \rho$  follows immediately from the degenerate nature of the neutralizing background as usually defined, which contributes to the stability of the system but not the thermodynamic  $\beta \partial P / \partial \rho$  (see Ref. 7 for a good discussion of this).

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## Ab initio studies on the singlet-triplet splitting of methylene (CH<sub>2</sub>)<sup>a</sup>

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In recent years there has been a great deal of interest<sup>1-12</sup> in the relative energies of the three lowest states of methylene (CH<sub>2</sub>): <sup>3</sup>B<sub>1</sub>(σπ), <sup>1</sup>A<sub>1</sub>(σ<sup>2</sup>), and <sup>1</sup>B<sub>1</sub>(σπ), where the A<sub>1</sub> state has both nonbonding electrons in the σ orbital while the B<sub>1</sub> states have one electron each in the σ and π orbitals. It is universally agreed that the ground state is <sup>3</sup>B<sub>1</sub>(σπ). Theoretical studies led to <sup>1</sup>A<sub>1</sub>-<sup>3</sup>B<sub>1</sub> separations that decreased from 1.39 eV (1969)<sup>7</sup> to 0.52 eV (1972)<sup>9</sup> as electron correlation effects and better basis sets were included. Early photochemical studies (1970)<sup>2</sup> led to a <sup>1</sup>A<sub>1</sub>-<sup>3</sup>B<sub>1</sub> separation of 0.06 ± 0.02 eV, while later such studies have pushed this value up to 0.39 eV,<sup>3,4</sup> in reasonable agreement with the best theoretical number, 0.52 eV.<sup>9</sup> Recently the first direct measure of the <sup>1</sup>A<sub>1</sub>-<sup>3</sup>B<sub>2</sub> separation was made by

Lineberger *et al.*,<sup>5</sup> who obtained a value of 0.84 eV, quite at variance with both theory and the (indirect) photochemical studies. This is a serious discrepancy since methylene is a prototype for a number of important reaction intermediates and since an error of 0.3 to 0.5 eV can in some cases lead to a significant effect on the expected chemistry.

An additional problem is associated with the separation of the two singlet states of CH<sub>2</sub>. Herzberg and Johns<sup>6</sup> estimated the  $v=0$  to  $v=0$  separation for <sup>1</sup>B<sub>1</sub>-<sup>1</sup>A<sub>1</sub> to be 0.88 eV; however, the lowest observed transition was at 1.34 eV.<sup>6</sup> Hay *et al.*<sup>9</sup> calculated a <sup>1</sup>B<sub>1</sub>-<sup>1</sup>A<sub>1</sub> separation of 1.36 eV and suggested that the first observed transition at 1.34 eV is in fact the 0-0 transition (the

TABLE I. Adiabatic (0-0) excitation energies for CH and CH<sub>2</sub>.<sup>a</sup>

	HF		GVB-POL-CI			Experimental
	This work <sup>b</sup>	Previous Work	HF-CI	GVB-CI	This work <sup>c</sup>	
CH $^4\Sigma^- - ^2\Pi$	-0.22	-0.26 <sup>d</sup>	0.69 <sup>d</sup>	0.38 <sup>e</sup>	0.70	0.74 <sup>f</sup>
CH <sub>2</sub> $^1A_1 - ^3B_1$	1.08	1.10 <sup>g</sup>	0.63 <sup>b</sup>	0.52 <sup>h</sup>	0.48	0.39, <sup>i</sup> 0.84 <sup>k</sup>
CH <sub>2</sub> $^1B_1 - ^3B_1$	1.72	1.71 <sup>g</sup>		1.88 <sup>h</sup>	1.56	...
CH <sub>2</sub> $^1B_1 - ^1A_1$	0.64	0.61 <sup>g</sup>		1.36 <sup>h</sup>	1.08	0.88 <sup>l</sup> - 1.34 <sup>l</sup>

<sup>a</sup>Zero-point corrections of +0.02, +0.02, -0.02, and -0.04 eV have been added onto the calculated excitation energies in rows 1-4, respectively, in order to compare directly with the experimental 0-0 excitation energies.

<sup>b</sup>The total energies of CH( $^2\Pi$ ) and CH<sub>2</sub>( $^3B_1$ ) are -38.27396 and -38.92774 h, respectively.

<sup>c</sup>The total energies of CH( $^2\Pi$ ) and CH<sub>2</sub>( $^3B_1$ ) are -38.38409 and -39.04215, respectively.

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<sup>i</sup>The lowest observed transition from Ref. 6, assigned as 0-0 by Ref. 9.

<sup>j</sup>Reference 4.

<sup>k</sup>Reference 5.

<sup>l</sup>Reference 6.

vibrational assignment had been based on extrapolation of isotope shifts in the observed spectrum).

In order to settle these questions, we carried out far more extensive theoretical studies as reported herein.<sup>13</sup> In addition to CH<sub>2</sub> we also studied the corresponding states of CH (the Lineberger group<sup>14</sup> has also determined the excitation energies in this system) in order to provide a more extensive base for assessing the accuracy of the calculations.

To provide a flexible basis set, the basis for these studies included (i) two sets of *d* functions ( $\alpha = 0.7$  and  $0.3$ ) on the carbon, (ii) a set of *p* functions ( $\alpha = 1.0$ ) on each hydrogen, (iii) a set of diffuse *s* and *p* functions ( $\alpha = 0.05$ ) on the carbon, and (iv) all added to a Dunning-Huzinaga valence double zeta contraction of Gaussian basis functions.<sup>15,16</sup> For lower levels of electron correlation in CH and CH<sub>2</sub>, we also explored the effect of *f* functions and found a negligible effect (0.01 eV) upon the excitation energies of interest; consequently *f* functions are excluded from all calculations reported here. Thus the final basis for CH<sub>2</sub> consisted of 35 contracted basis functions. The geometries used for CH<sub>2</sub><sup>17-19</sup> are  $R_{CH} = 1.11 \text{ \AA}$ ,  $\angle HCH = 105^\circ$  for  $^1A_1$ ;  $R_{CH} = 1.08 \text{ \AA}$ ,  $\angle HCH = 135^\circ$  for  $^3B_1$  and  $^1B_1$ ; and  $R_{CH} = 1.12 \text{ \AA}$  for CH.

Because the  $^1A_1$  and  $^3B_1$  states have different electronic configurations, the electron-correlation effects will be different and it is necessary to ensure a consistent treatment of electron correlation. A common approach is to start with the Hartree-Fock wavefunction and to include all single and double excitations within the complete basis set. However, we have found that ignoring the higher order excitations can lead to

errors of  $\sim 0.2$  eV in excitation energies, and hence we have developed a scheme in which the important higher order configurations are also included. To keep the calculations manageable, we solve self-consistently for four or five correlating orbitals<sup>20,21</sup> for each pair of electrons of each state, determining thereby a set of "valence orbitals" (14 for the states of CH<sub>2</sub>)<sup>22</sup> that are appropriate for describing the major electron correlation effects. The remaining orbitals (19 for CH<sub>2</sub>) are referred to as virtual orbitals and are used for lower order excitations. The CI calculations contain the following configurations: (i) within the set of 14 valence orbitals, we allow all quadruple excitations from the dominant configuration; (ii) using the full set of 33 orbitals, we allow all double excitations in which at most one electron is excited to a virtual orbital; and (iii) in addition, for the electrons in nonbonding orbitals (two for CH<sub>2</sub> and three for CH) we have allowed all excitations to the full basis. Restrictions on the above CI were that (i) no excitations were allowed out of the  $1s$  orbital and (ii) for CH<sub>2</sub> the ten natural orbitals describing the CH bonds were restricted to contain between three and six electrons. The resulting wavefunction is referred to as GVB-POL-CI.

The GVB-POL-CI calculations involved 2875, 1528, 4088, 5548, and 3656 spin eigenfunctions (4610, 1717, 12084, 7916, and 11572 determinants) for the CH  $^2\Pi$ , CH  $^4\Sigma^-$ , CH<sub>2</sub>  $^1A_1$ , CH<sub>2</sub>  $^3B_1$ , and CH<sub>2</sub>  $^1B_1$  states, respectively. Because of the use of self-consistent correlating orbitals for each state, these calculations are the equivalent of very high order HF-CI calculations.

The results are given in Table I. For CH we calculate the  $^4\Sigma^- - ^2\Pi$  excitation energy as 0.70 eV, in excellent agreement with the experimental value of 0.74 eV. For CH<sub>2</sub> we calculate the  $^1A_1 - ^3B_1$  separation as 0.48 eV, which is 0.36 eV below the direct photoionization experiments. Considering the level of CI performed here, we estimate that the maximum error consistent with the theoretical results is 0.1 eV. If we assume that the CH<sub>2</sub> beams produced in these experiments contain vibrationally excited CH<sub>2</sub> molecules (as is observed for SiH<sub>2</sub>),<sup>23</sup> the theoretical and experimental results can be rationalized by assuming that the lowest two or three observed peaks are hot bands with the third or fourth band being the 0-0 process.

From our calculated  $^1B_1 - ^1A_1$  separation of 1.08 eV (estimated to be accurate to  $\pm 0.1$  eV), we conclude that the lowest observed transition<sup>6</sup> at 1.34 eV is either 4-0 or 2-0 (it was originally assigned<sup>6</sup> as 6-0). These assignments and the observed vibrational spacings lead to a predicted  $^1B_1 - ^1A_1$  0-0 separation of 1.00 or 1.17 eV. Combining this with the theoretical  $^1B_1 - ^3B_1$  separation of 1.56 eV (estimated to be accurate to  $\pm 0.02$  eV) leads to a predicted  $^1A_1 - ^3B_1$  separation of 0.56 or 0.39 eV, respectively. Indeed, assigning the third or fourth bands in the photoionization spectrum of CH<sub>2</sub> as corresponding to  $^3B_1(v=0)$  leads to  $^1A_1 - ^3B_1$  separations of 0.54 or 0.38 eV, respectively. Either of these values is consistent with our calculated  $^1A_1 - ^3B_1$  separation of  $0.48 \pm 0.1$  eV, and at least the lower values would be consistent with the photochemical experiments. Thus there appears to be a consistent rationalization of both

the experimental and theoretical results. An excellent test of these results would be to determine experimentally the 0-0 transition for  ${}^1B_1-{}^1A_1$ .

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## Electron attachment to carbon dioxide clusters in a supersonic beam<sup>a</sup>

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Carbon dioxide is a linear molecule. Its negative ion,  $\text{CO}_2^-$ , has a potential energy minimum at  $\sim 135^\circ$ , lying approximately 0.4 eV above the ground state of the neutral.<sup>1-3</sup> Ground state  $\text{CO}_2^-$  is thus metastable with respect to autodetachment. The ion has been made by charge-transfer from negative ions<sup>4</sup> and from fast cesium<sup>5,6</sup> or potassium atoms<sup>6</sup> to carbon dioxide, and via dissociative electron capture by molecules containing bent and extended  $\text{CO}_2$  substructures.<sup>7</sup> The lifetime of  $\text{CO}_2^-$  against autodetachment is  $\sim 60\text{--}90 \mu\text{sec}$ .<sup>6,7</sup>

While studying electron attachment to clusters of carbon dioxide formed in the rapid expansion from a sonic nozzle, we have observed negative ions, in a time-of-flight mass spectrometer, with charge-to-mass ratios corresponding to the formula  $(\text{CO}_2)_n^-$ , with  $2 \leq n \leq 6$ . No effort was made to observe larger homologs.  $\text{CO}_2^-$  was conspicuously absent.

No metastable decay of the ions, either via autodetachment or dissociation, could be detected. We estimate that any such decay would have been observed if the ions had been metastable with lifetimes less than 2

msec. Thus the adiabatic electron affinity of the carbon dioxide dimer may be positive.

From a study of the observed signals as a function of stagnation pressure up to 2.5 atm (stagnation temperature 245 °K, nozzle diameter 25  $\mu\text{m}$ ) we conclude that  $(\text{CO}_2)_2^-$  arises largely from electron attachment to clusters larger than the trimer, although a small component arising from the latter cannot be excluded.

Because of low beam intensity, we have not been able to obtain an accurate measure of formation cross-sections as a function of electron energy.  $(\text{CO}_2)_2^-$  sets in close to 0 eV collision energy and rises to a maximum near 3 eV. We have also observed with considerably greater intensity ions with the general formula  $\text{O}^-(\text{CO}_2)_n$ , with  $0 \leq n \leq 6$ . A study of  $\text{CO}_3^-$  as a function of stagnation pressure indicates that it arises largely from the trimer. Its intensity as a function of electron energy is shown in Fig. 1, as measured using a retarding potential difference (RPD) technique with 0.1 eV resolution. We also show the  $\text{O}^-$  signal, measured simultaneously, with the energy scale set by locating the  $\text{O}^-$  peak at 4.4 eV.<sup>8</sup>