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Is the $\tilde{c}$ state of CH_2 linear or bent?

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Abstract. The $\tilde{c}$ state of CH_2 is found to be bent at the highest levels of theory used in this work, but the energy difference between the linear and bent geometries is only about 10 cm^{-1}. Improving the basis set or correlation treatment favors the linear geometry over the bent, thus it is impossible to definitively determine if the $\tilde{c}$ state has a barrier in its bending potential. If there is a barrier, it is clear that it will be so small that the $\tilde{c}$ state will be quasilinear.

Key words: Structure or geometry – Excited state – Electron correction

1 Introduction

Yamaguchi et al. [1] recently reported the results of calculations on the four lowest states of CH_2. One interesting result was the geometry of the $\tilde{c}\ ^1A_1$ state, which they found to be slightly bent with an angle of 171.6°. They noted that improving the treatment from a two configuration multiconfiguration self-consistent-field (MCSCF) calculation to a multireference configuration interaction (MRCI) calculation or improving basis set tended to decrease the angle. They also noted that the $\tilde{c}$ state was the second root of $^1A_1$ symmetry and therefore more difficult to describe than the lowest state of a given symmetry.

In several recent studies, it has been found [2–4] that improvements in the basis set or in the treatment of the electron correlation stabilized the linear geometries with respect to the bent geometries. Unlike the $\tilde{c}$ state studied by Yamaguchi et al., all of these studies were performed for the ground state. As we show below, the energy difference between the linear and bent geometries of the $\tilde{c}$ state of CH_2 is so small that the first vibrational level would lie above any barrier, and therefore it might be difficult to establish the shape of the potential from the experiment. However, it is still of interest to investigate the basis set requirements for the linear and bent geometries of the $\tilde{c}$ state of CH_2.

2 Methods

The augmented correlation consistent polarized valence (aug-cc-pV) triple zeta (TZ), quadruple zeta (QZ) and quintuple zeta (5Z) basis sets of Dunning and coworkers [5–7] were used. The effect of C 1*s* correlation was tested using the core valence (CV) basis set from Ref. 8. This basis set was derived from the cc-pVQZ set by more flexibly contracting the *s* and *p* spaces and augmenting with compact *d* and *f* functions. Only the pure spherical harmonic components of the basis functions were used.

All calculations were performed using C_{2v} symmetry and thus the $\tilde{c}$ state was obtained as the second root of $^1A_1$ symmetry for both linear and bent geometries. The orbitals were optimized as the second root in a complete-active-space self-consistent-field (CASSCF) calculation. That is, there is no problem with variational collapse of the second root, and hence no need to use state averaging. More extensive correlation was added using the MRCI approach. MRCI calculations with no additional constraints as well as those with internal contraction [9,10] (IC) were performed. The importance of higher excitations was estimated using the multireference analog of the Davidson correction. The carbon 1*s*-like electrons were not correlated in the MRCI calculations, except for the calculations designed to compute the 1*s* effect. All configurations in the CASSCF calculations were used as references in the MRCI calculations. Two active spaces were used; the small active space had the carbon 2*s* and 2*p* and hydrogen 1*s* orbitals as active, which was denoted (3210) to indicate that there were three active a_1 orbitals, two active b_2 orbitals, one active b_1 orbital, and no active a_2 orbitals. The larger active space, kept the carbon 1*s* orbital inactive and expanded the active space to (6331). This active space was selected using the natural orbital occupation numbers from the MRCI calculations. For this big active space, the reference accounts for 98.6% of the MRCI wave function. The MRCI calculations were performed using MOLECULE-SWEDEN [11] while the ICMRCI calculations were performed using MOLPRO96 [12].

3 Results and discussion

We first consider the energy difference between linear and bent as a function of basis set and choice of active space. The geometries used in these test calculations are r(C—H) = 1.070 Å and ∠(HCH) = 180.0 or 170.0°. The results of these calibration calculations are summarized in Table 1. We find the bent structure to be more stable than the linear at all levels considered. Using internal contraction and the small active space, the energy difference decreases slightly as the basis set is improved from aug-cc-pVTZ to aug-cc-pV5Z (compare the first three entries in Table 1). For this choice of active space the complete basis set (CBS) limit separation is about 18.4 and 17.6 cm^{-1} at the ICMRCI and ICMRCI + Q levels of theory. That is, the aug-cc-pVTZ value is about 4 cm^{-1} too large.

Expanding the active space using the aug-cc-pVTZ basis set, but retaining internal contraction reduces the energy separation between linear and bent by 8 cm^{-1}. It is interesting to note that using the small active space, but not using internal contraction yields an energy difference that is very similar to that obtained using internal contraction and the larger active space. Expanding the active space, but without using internal contraction, hardly affects the MRCI separation. Expanding the active space slightly increases the MRCI + Q value bringing it into better agreement with the MRCI and big active space ICMRCI + Q values.

If one assumes that the correlation and basis set effects are additive, the best estimate for the separation can be obtained by subtracting 4 cm^{-1} from the MRCI or big active space ICMRCI separations; this yields a value of about 10 cm^{-1}, with the bent being lower than the linear. However, if the basis set requirements for the linear and bent geometries were sufficiently different, the extrapolation to the CBS limit might not work as well as in other cases. Therefore one additional MRCI calculation was performed where the linear and bent calculations used the exact same basis set, namely the hydrogen basis functions at both the linear and bent geometries were used in the same calculation. It is perhaps not too surprising to find that this basis set is linearly dependent, and it was necessary to delete the six functions (three a_1 and three b_2) with the smallest eigenvalues of S^2. Using this merged basis set and the small active space, the MRCI separation is only 6 cm^{-1}.

In the final series of calculations the geometry of the linear and bent structures were fully optimized and the results are summarized in Table 2, along with the energy differences. Optimizing the geometries increase the energy differences relative to those in Table 1 by about 2 cm^{-1}. The CASSCF calculations have smaller angle and larger energy difference than do the ICMRCI results, showing that adding more extensive correlation favors the linear. Expanding the active space results in a smaller angle and larger energy separation at the CASSCF level, however, when more extensive correlation is added using the ICMRCI approach, the big active space ICMRCI calculations yield a larger angle and smaller separation than the small active space ICMRCI calculations, suggesting that higher levels of theory favor the linear geometry. The changes between the CASSCF and ICMRCI calculations also support the view that improving the correlation treatment favors the linear. Improving the basis set also increases the angle and decreases the energy difference between linear and bent. Finally we note adding carbon 1s correlation, using the CV basis set at the ICMRCI/aug-cc-pVQZ geometries, lowers the linear relative to the bent by 0.36 and 0.42 cm^{-1} at the ICMRCI and ICMRCI + Q levels, respectively.

The trends that we have observed in the present work are consistent with other systems that have been studied recently [2–4], namely that it is harder to achieve convergence of the one- and n-particle basis sets for the linear structures than for the bent structures. It is disappointing, however, that improving the basis set in a small active space favors the bent structure [1] while it favors the linear structure for the larger active spaces used in the present work.

Table 1. Energy diferences (in cm^{-1}) between linear and bent (170°) structures with r(C—H) = 1.07 Å

IC	Active	Basis	MRCI	MRCI + Q
Yes	Small	aug-cc-pVTZ	22.1	21.5
Yes	Small	aug-cc-pVQZ	19.4	18.6
Yes	Small	aug-cc-pV5Z	18.7	17.9
Yes	Big	aug-cc-pVTZ	14.1	13.2
No	Small	aug-cc-pVTZ	13.7	11.4
No	Big	aug-cc-pVTZ	13.6	12.7
No	Small	merged aug-cc-pVTZ	5.6	2.9

Table 2. Summary of computed results

Basis	Calculation	Bent		Linear	ΔE
		r	angle	r	
aug-cc-pVTZ	CASSCF	1.076	170.6	1.074	36.4
aug-cc-pVTZ	ICMRCI	1.070	171.6	1.069	24.4
aug-cc-pVTZ	ICMRCI + Q	1.070	171.6	1.070	24.5
aug-cc-pVQZ	ICMRCI	1.068	171.9	1.069	21.7
aug-cc-pVQZ	ICMRCI + Q	1.069	171.9	1.069	21.6
aug-cc-pV5Z	ICMRCI	1.068	171.9	1.067	20.6
aug-cc-pV5Z	ICMRCI + Q	1.068	172.0	1.068	20.8
aug-cc-pVTZ	big-CASSCF	1.073	169.2	1.071	42.8
aug-cc-pVTZ	big-ICMRCI	1.070	172.4	1.067	16.6
aug-cc-pVTZ	big-ICMRCI + Q	1.070	172.4	1.068	16.2

4 Conclusions

At the ICMRCI level of theory, we find that improving the basis set or expanding the active space lowers the linear geometry relative to the bent. At our best level of theory the bent structure is slightly lower than the linear, however the energy difference is so small that we cannot definitively determine if the $\tilde{c}$ state of CH_2 is linear or bent. The lowering of the linear with respect to the bent is similar to other systems that have been studied recently.

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