# Transition state barrier height for the reaction $H_2CO \rightarrow H_2 + CO$ studied by multireference Møller–Plesset perturbation theory

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The second-order multireference Møller–Plesset perturbation method (MRMP) was applied to the accurate estimation of the transition state barrier height of $H_2CO \rightarrow H_2 + CO$ reaction. The best estimate for the classical barrier height is 84.5 kcal/mol at the highest level of MRMP theory with the quadruple zeta plus triple polarization basis set and with the active space of 12 electrons in 11 active orbitals. The inclusion of zero-point vibrational energy correction reduces the activation energy to 79.1 kcal/mol, which is in excellent agreement with the experimental value of 79.2±0.8 kcal/mol [Polik, Guyer, and Moore, J. Chem. Phys. **92**, 3453 (1990)]. Analysis of the second-order energies in terms of internal, semi-internal, and external contributions shows that the present MRMP provides a well balanced treatment for the estimation of the energy difference between the equilibrium and transition state structures.
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## I. INTRODUCTION

The potential energy surface of the reaction $H_2CO \rightarrow H_2 + CO$ has been extensively studied both experimentally and theoretically to clarify the mechanism of the photodissociation process:

$$\begin{aligned} &H_2CO(S_0) \xrightarrow{h\nu} H_2CO(S_1) \\ &\qquad\qquad\qquad \downarrow \\ &\qquad\qquad\qquad H_2CO(S_0) \rightarrow H_2 + CO. \end{aligned}$$

In particular, a precise estimation of the $S_0$ barrier height of the unimolecular dissociation precisely is still significant. The recent experimental study by Polik, Guyer, and Moore[1] has confirmed the activation energy of this reaction to be 79.2±0.8 kcal/mol. They obtained the value by varying the barrier height so as to obtain the best fit of the RRKM (Rice–Ramsperger–Kassel–Marcus) rate constant to experimentally observed $S_0$ decay rates.

*Ab initio* calculations for the reaction were first carried out by Jaffe, Heys, and Morokuma[2] in the mid-70s. Using the SCF+CI method with a 4-31G basis set, they obtained 99.2 kcal/mol for the classical barrier height. Then Jaffe and Morokuma[3] implemented an 18 configuration MCSCF geometry optimization with 4-31G basis to estimate the barrier. The MCSCF yielded 104.9 kcal/mol (4-31G basis) and 120.4 kcal/mol (6-31G* basis) for the classical barrier height, respectively. They also performed CI with the valence shell double excitations using 4-31G basis at the MCSCF geometry and estimated the barrier height to be 104.2 kcal/mol.

In the beginning of the 1980s, Goddard, Yamaguchi, and Schaefer[4] performed analytical CI calculations to locate the stationary point and the transition state with the double zeta plus polarization (DZp) basis set. The CISD with DZp basis yields a barrier height of 94.2 kcal/mol (including Davidson's correction). They also estimated a zero-point vibrational energy (ZPVE) of 5.3 kcal/mol, leading to the final prediction that the barrier height is 88.9 kcal/mol. They estimated from careful analysis of the results that the barrier height is in the range of 82–87 kcal/mol.

At about the same time, Frisch, Krishnan, and Pople[5] obtained the classical barrier height of 85.8 kcal/mol using MP4 with the triple zeta plus polarization (TZp) basis. The equilibrium and transition state geometries were optimized at the MP2 level with DZp basis set. Their best value including ZPVE is 79.6 kcal/mol.

Scuseria and Schaefer[6] implemented coupled cluster (CC) calculations with connected triple excitations. Using as large as TZ plus double polarization (TZ2p) basis, they predicted the classical barrier height to be 86.8 kcal/mol. The activation energy is predicted to be 81.4 kcal/mol with correction for zero-point vibrational energies.

It is apparent from the previous calculations that the computation of the contribution of dynamic correlation to the barrier heights corresponding to transition structures is a problem that requires special attention. The methods using a single reference function for the computation of electron correlation are poorly converged (in the case of MPn) or require the inclusion of more than double excitation in the case of CI and CC based on an SCF reference. For example, MP4(SDQ) yields 83.3 kcal/mol for ZPVE corrected barrier height while MP4(SDTQ) gives 79.6 kcal/mol.[5] Similarly, CCSD gives 85.0 kcal/mol, while the introduction of triple excitations in the form of CCSD-T lowers the barrier height to 81.4 kcal/mol.[6] These changes turned out to be the need of multireference approaches.

Dupuis *et al.*[7] performed a multireference CI starting with a CASSCF reference wave function with (6,6), where six electrons are distributed among six orbitals. They estimated the effects of electron correlation, the basis set, and the transition state structure from their convergence patterns, and obtained 80.9±3.0 kcal/mol as the best estimation.

Although the recent theoretical prediction is approaching the experiment, it is still a little higher compared to the experiment. In this paper, we present the results of the second-order multireference perturbation theory. We have developed multireference perturbation theories based on CASSCF reference wave functions: the multireference Møller–Plesset (MRMP) method[8] for a single-state problem and MCSCF reference quasidegenerate perturbation theory (MC-QDPT)[9] for a multi-state problem. These techniques have been applied in molecular structure calculations in a routine manner.[10] These theories use the CASSCF wave functions as a zeroth-order function and dynamical electron correlation is taken into account by second-order perturbation energies.

One important advantage of multireference based perturbation theory against other multireference based methods such as MRCI (configuration interaction) and MRCC (coupled cluster) is that it can be used with relatively large basis sets and reference spaces. In fact, there is no essential limitation on the size of basis set besides an integral transformation step. The program[11,9] is based on the diagrammatic perturbation theory: the energy (or effective Hamiltonian) is expressed by just a sum of products of molecular integrals, transition density matrix between the target state, and reference CSF, the inverse of an energy denominator. Thus, it is not necessary to form the first-order interacting space (one and two electron excited CSF space) which rapidly becomes very large as the number of references increases, which often makes MRCI and MRCC intractable.

## II. CALCULATED RESULTS AND DISCUSSIONS

We performed the second-order multireference Møller–Plesset (MRMP) calculations at the equilibrium structure and the transition state of the reaction. We used the geometries determined by CCSD with TZ2p by Scuseria *et al.*[6] The reaction is Woodward–Hoffmann forbidden and the highly asymmetric transition structure, as shown in Fig. 2 of Ref. 6. Their optimized equilibrium geometry is in good agreement with experiment.[12] The basis sets used in the present calculations are Dunning's correlation-consistent basis set: cc-pVDZ, cc-pVTZ, and cc-pVQZ.[13] For the polarization functions of cc-pVQZ, $g$ functions on C and O and $f$ functions on H were not included.

We used a fixed value of 5.4 kcal/mol as the correction for zero-point vibrational energy (ZPVE), which is the same value employed by Polik *et al.*[1] They used the experimental frequencies determined by Reisner *et al.*[14] for the equilibrium structure (16.8 kcal/mol, 11 772.1 $\text{cm}^{-1}$), and the scaled theoretical frequencies for the transition state structure (11.4 kcal/mol, 7999.9 $\text{cm}^{-1}$). Recent accurate theoretical estimate is very close to this value: CASSCF with (10,10) gives 5.1 kcal/mol[7] and CCSD yields 5.4 kcal/mol[6] for ZPVE.

Qualitative chemical considerations based on a correlation diagram connecting $H_2CO$ to dissociating products have been given by Dupuis *et al.*[7] Diabatically $H_2CO(^1A_1)$ dissociates to $H_2(^1\Sigma_g^+)+CO(^1\Pi)$ while $H_2(^1\Sigma_g^+)$ and $CO(^1\Sigma^+)$ interact repulsively and correlate with an excited state of $H_2CO$. An avoided crossing of these two diabatic potential surfaces gives rise to a barrier for dissociation on the adiabatic ground state potential surface. Thus, accurate description of the potential surface near the avoided crossing region requires a balanced treatment of both diabatic states.

A qualitative correct description of the dissociation process requires at least four active electron in the two CH bonds of $H_2CO$. During the dissociation process, two electrons, one from each CH bond, pair up to form the HH bond, while the other two form a lone pair on C in CO. A CASSCF wave function including all configurations generated by distributing these four electrons in four active orbitals, two CH bonding and antibonding pairs, describes the dominant nondynamical correlation of the reaction. This active space is denoted by (4,4). The abbreviation $(n,m)$ is used to define the active electrons and active orbitals of CASSCF. The $n$ is the number of active electrons and $m$ is the number of active orbitals. The most important dynamical correlation originates from the doubly excited $\pi^2 \rightarrow \pi^{*2}$ configuration, which must be significant at all stages of the reaction including the equilibrium and transition state structures. The oxygen lone pair orbital delocalizes toward C near the transition state leading to a strong mixing with the CH bonds. At the final stage of the reaction, it becomes the third component of the triple bond of CO. Thus, the correlation effect associating with this orbital should change significantly during dissociation. The CO bond length decreases by 0.041 Å in proceeding from the equilibrium geometry to the transition structure geometry since it strengthens the triple bond character. A proper description of this bond shortening requires excitations from the CO $\sigma$ bonding orbital to the antibonding orbital.

The above consideration can easily be confirmed by simple CISD wave functions. The CISD wave functions with cc-pVDZ basis based on the Hartree–Fock (HF) reference function for the equilibrium and transition state structures are represented by

$$\Psi_{\text{Eq}} = 0.9559(\text{HF}) - 0.1131(\pi^2 \rightarrow \pi^{*2}) + \cdots,$$

$$\begin{aligned}\Psi_{\text{Tran}} = {} & 0.9479(\text{HF}) - 0.1320((lp+\sigma)^{*2} \rightarrow (lp+\sigma)^{*2}) \\ & - 0.0965(\pi^2 \rightarrow \pi^{*2}) + \cdots .\end{aligned}$$

Here $\pi$ stands for the CO($\pi$) orbital and $(lp+\sigma)$ for the orbital with a mixed character of O($lp$) and CH($\sigma$) orbitals. The most important contribution arises from the doubly excited $\pi^2 \rightarrow \pi^{*2}$ configuration. This expresses the transferable dynamical correlation. For the transition state structure, the doubly excited configuration of $(lp+\sigma)^2 \rightarrow (lp+\sigma)^{*2}$ is found to be important while it has a minor effect on the equilibrium structure. This arises from rearrangement of electrons and spin couplings during the dissociation process. The electron correlation described by this configuration is called the nondynamical correlation. It is very state specific and becomes more significant as the reaction proceeds.

TABLE I. Total energies (hartree) of $H_2CO$ of the equilibrium and transition state geometries computed with CASSCF and MRMP.

| Method basis set/ active space | Equilibrium geometry |  | Transition state geometry |  |
|---|---|---|---|---|
|  | CASSCF | MRMP | CASSCF | MRMP |
| cc-pVDZ |  |  |  |  |
| (4,4) | −113.910 870 | −114.193 467 | −113.766 641 | −114.061 062 |
| (6,6)/$lp$ | −113.922 157 | −114.194 812 | −113.784 703 | −114.059 456 |
| (10,10) | −114.028 199 | −114.195 420 | −113.890 652 | −114.061 147 |
| cc-pVTZ |  |  |  |  |
| (4,4) | −113.947 496 | −114.306 569 | −113.802 634 | −114.172 976 |
| (6,6)/$lp$ | −113.959 579 | −114.309 284 | −113.821 036 | −114.169 932 |
| (10,10) | −114.065 685 | −114.306 138 | −113.927 132 | −114.170 981 |
| cc-pVQZ |  |  |  |  |
| (0,0)[a] | −113.920 656 | −114.333 995 | −113.759 807 | −114.190 670 |
| (4,4) | −113.956 495 | −114.333 182 | −113.811 708 | −114.199 852 |
| (6,6)/$lp$ | −113.968 892 | −114.335 538 | −113.830 233 | −114.196 280 |
| (6,6)/$\pi$ | −113.995 048 | −114.334 473 | −113.846 186 | −114.199 197 |
| (12,10) | −114.054 170 | −114.335 072 | −113.922 998 | −114.197 638 |
| (10,10) | −114.075 035 | −114.332 086 | −113.936 478 | −114.197 328 |
| (12,11) | −114.080 449 | −114.331 833 | −113.951 659 | −114.197 134 |

[a] MP2 results based on a single reference HF function.

In view of the preceding discussion, it seems likely that the CASSCF wave functions with (10,10) where ten electrons are distributed among ten active orbitals, {two CH($\sigma$,$\sigma$*), O($lp$,$lp$*), CO($\sigma$,$\sigma$*), and CO($\pi$,$\pi$*)} becomes-the preferred zeroth-order wave function for the accurate de-scription of the dissociation process. The antibonding oxygen lone pair orbital is required as an active orbital to represent the so-called in–out correlation. The rest of the remaining dynamical correlation is mainly composed of the short-range pair correlation and it can be estimated to a good approximation by second-order perturbation theory based on the CASSCF reference function.

In order to examine a convergent sequence of results, we employed various choices of CASSCF reference functions. The systematic expansion of CASSCF reference functions adopted in this study is the following:

$$\text{CASSCF with } (4,4);\{\text{two CH}(\sigma,\sigma^*)\},$$

$$\text{CASSCF with } (6,6)/\pi;\ \{\text{two CH}(\sigma,\sigma^*),\ \text{CO}(\pi,\pi^*)\},$$

$$\text{CASSCF with } (6,6)/lp;\ \{\text{two CH}(\sigma,\sigma^*),\ \text{O}(lp,lp^*)\},$$

$$\text{CASSCF with } (10,10);\ \{\text{two CH}(\sigma,\sigma^*),\ \text{O}(lp,lp^*),\ \text{CO}(\sigma,\sigma^*),\ \text{CO}(\pi,\pi^*)\},$$

$$\text{CASSCF with } (12,11);\ \{\text{two CH}(\sigma,\sigma^*),\ \text{O}(lp,lp^*),\ \text{CO}(\sigma,\sigma,^*),\ \text{CO}(\pi,\pi^*),\ \text{O}(2s)\}.$$

The (12,11) is the largest size of the active space treated here. In addition, we used the active space of (12,10) where all valence electrons are distributed among ten valence active orbitals. In this choice, the antibonding oxygen lone pair orbital ($lp$*) is excluded from the active space. We also carried out the CASSCF calculations with (8,8) active space defined by {two CH($\sigma$,$\sigma$*), O($lp$,$lp$*), CO($\pi$,$\pi$*)}. But we found the convergence problem in the calculations for the transition state. This active space cannot describe the strong mixing between the CH and CO $\sigma$ bonds which becomes important at the transition state region. This physically unbalanced choice of active space leads to a worse description of the transition structure and may lead to the convergence problem.

We summarized total energies in Table I. In each basis set, results are arranged in an order of decreasing energy of the variational CASSCF method. The CASSCF energies are sensitive to the choice of the active space. For instance, CASSCF with (10,10) yields by more than 0.1 hartree (62.8 kcal/mol) lower energy than CASSCF with (4,4). It is seen from the cc-pVQZ results that CASSCF with (6,6)/$\pi$ gives much lower energy than the corresponding CASSCF with

TABLE II. CASSCF and MRMP classical barrier height (kcal/mol) for the reaction $H_2CO \rightarrow H_2+CO$. Values in parentheses include the zero-point energy correction.

| Method basis set/ active space | Barrier height | |
|---|---|---|
| | CASSCF | MRMP |
| cc-pVDZ | | |
| (4,4) | 90.5(85.1) | 83.1(77.7) |
| (6,6)/*lp* | 86.3(80.9) | 84.9(79.5) |
| (10,10) | 86.3(80.9) | 84.3(78.9) |
| cc-pVTZ | | |
| (4,4) | 90.9(85.5) | 83.8(78.4) |
| (6,6)/*lp* | 86.9(81.5) | 87.4(82.0) |
| (10,10) | 86.9(81.5) | 84.8(79.4) |
| cc-pVQZ | | |
| (0,0)[a] | 100.9(95.5) | 89.9(84.5) |
| (4,4) | 90.9(85.5) | 83.7(78.3) |
| (6,6)/*lp* | 87.0(81.6) | 87.4(82.0) |
| (6,6)/$\pi$ | 93.4(88.0) | 84.9(79.5) |
| (12,10) | 82.3(76.9) | 86.2(80.8) |
| (10,10) | 86.9(81.5) | 84.6(79.2) |
| (12,11) | 80.8(75.4) | 84.5(79.1) |
| Expt.[b] | 79.2±0.8 | |

[a] MP2 results based on a single reference HF function.

[b] W. F. Polik, D. R. Guyer, and C. B. Moore, J. Chem. Phys. **92**, 3453 (1990).

(6,6)/*lp*. However, the difference between CASSCF energies with (6,6)/$\pi$ and (6,6)/*lp* decreases in proceeding from the equilibrium geometry to the transition state geometry. This is consistent with the discussions described above. That is, the $\pi$ orbitals are involved in the dynamical correlation while the lone pair orbitals are involved in the nondynamical correlation, which becomes more significant at the transition state geometry.

On the other hand, MRMP energies are less sensitive to the reference CASSCF wave functions. The overall accuracy of MRMP is surprisingly high. In spite of starting with the different CASSCF reference functions, calculated MRMP energies in a given basis set agree within an accuracy of 0.003 hartree. This is true for the transition state geometry. This implies that MRMP constitutes a good extrapolation to the full CI in a given basis set space.

MRMP with (4,4) and (6,6)/$\pi$ has a lower energy than that constructed with larger active spaces at the transition state geometry. This suspects that second-order perturbation theory overestimates the dynamical correlation. On the other hand, the MRMP calculations at equilibrium geometry show good convergence. These suggests that the MRMP barrier heights calculated with (4,4) and (6,6)/$\pi$ might be underestimated to some extent.

The (0,0) in Table I indicates MP2 results based on the HF single reference function. HF gives an acceptable zeroth-order wave function for the equilibrium $H_2CO$ electronic structure and the MP2 energy is very close to the more accurate MRMP results. However, since the H–H bond distance is stretched to almost double its value in the $H_2$ molecule at the transition state, the diabatic surface is not well represented at the HF level with respect the H–H stretch, leading to a poor description at the transition state.

The calculated barrier heights are given in Table II. Values in parentheses include the ZPVE correction, which can be directly compared with the experimental estimate of 79.2 ±0.8 kcal/mol. We begin by observing that the basis set has little effect on the barrier height of this system. At each level of theory the barrier height does not change significantly with extending the basis set from cc-pVDZ to cc-pVQZ. The difference between cc-pVTZ and cc-pVQZ is less than 0.2 kcal/mol. Thus, the one electron function is completely converged for the describing the dissociation process at the level of the cc-pVQZ basis set.

On the other hand, the active space is found to have a rather significant effect on the activation energy. The HF results are poor, as shown in the previous literature. The classical barrier (ZPVE corrected value in parentheses) calculated with cc-pVQZ is 100.9 (95.5) kcal/mol, which is about 15 kcal/mol larger than the experiment.

CASSCF represents a great improvement over the HF approximation. CASSCF with the smaller active space such as (4,4), (6,6)/*lp*, and (6,6)/$\pi$ reduces the HF barrier height by about 10 kcal/mol, although it is still larger compared to the experiment. The computed barrier height decreases with increasing the size of the active space. However, CASSCF with (12,10) and (12,11) underestimates the barrier height considerably. The accurate barrier height is determined by the proper balance of the correlation energy difference between two structures involved. Proper treatment of the dynamical and nondynamical correlations is also required. CASSCF takes most of the nondynamical correlation into account but inclusion of the dynamical correlation is not sufficient enough. The most notable deficiency due to the unbalanced treatment is a systematic overestimation and underestimation of the barrier height. Namely, CASSCF leads to the overestimation of the barrier height when the active space is small and the underestimation when the active space is large.

Now let us compare the CASSCF (cc-pVQZ) results with (6,6)/$\pi$ and (6,6)/*lp*. The former gives 93.4 (88.0) kcal/mol while the latter gives 87.0 (81.6) kcal/mol. As described above the former includes the important dynamical $\pi^2 \rightarrow \pi^{*2}$ excitation, while the latter includes the nondynamical $lp^2 \rightarrow lp^{*2}$ instead of $\pi^2 \rightarrow \pi^{*2}$. At the CASSCF level of theory, the latter gives a closer result to the experimental value, but in proceeding from CASSCF to MRMP the situation reverses. This point will be discussed later.

The MRMP theory corrects the deficiency and represents a great improvement over CASSCF. When the active space is small, CASSCF overestimates the barrier height. On the other hand, when the active space is chosen to be large enough, CASSCF underestimates the barrier height. This defect is corrected by introduction of the dynamical correlation through the second-order perturbation. All barrier heights calculated at the MRMP level are in the range of 83.1 (77.7)–87.4 (82.0) kcal/mol. Even MRMP with relatively small (4,4) and (6,6)/$\pi$ active spaces gives a good agreement with the experiment. This agreement could be fortuitous due

TABLE III. The second-order energy (hartree) partitioning into internal, semi-internal and external contribution (% in parentheses) calculated with cc-pVQZ.

| Active space | Internal | Semi-Internal | External | Total |
|---|---|---|---|---|
| Equilibrium geometry | | | | |
| (0,0)[a] | 0.0 | 0.0 | −0.413 339 (100.0) | −0.413 339 |
| (4,4) | −0.000 474 (0.1) | −0.029 747 (7.9) | −0.346 466 (92.0) | −0.376 687 |
| (6,6)/*lp* | −0.000 670 (0.2) | −0.075 475 (20.6) | −0.290 502 (79.2) | −0.366 647 |
| (6,6)/$\pi$ | −0.003 957 (1.2) | −0.082 115 (24.2) | −0.253 353 (74.6) | −0.339 425 |
| (12,10) | 0.0 | −0.095 887 (34.1) | −0.185 014 (65.9) | −0.280 902 |
| (10,10) | −0.002 232 (0.9) | −0.085 633 (33.3) | −0.169 269 (65.8) | −0.257 135 |
| (12,11) | 0.0 | −0.078 001 (31.0) | −0.173 384 (69.0) | −0.251 384 |
| Transition state geometry | | | | |
| (0,0)[a] | 0.0 | 0.0 | −0.430 862 (100.0) | −0.430 862 |
| (4,4) | −0.002 701 (0.7) | −0.059 051 (15.2) | −0.326 137 (84.0) | −0.388 143 |
| (6,6)/*lp* | −0.008 244 (2.3) | −0.099 161 (27.1) | −0.258 643 (70.7) | −0.366 048 |
| (6,6)/$\pi$ | −0.013 198 (3.7) | −0.101 025 (28.6) | −0.238 788 (67.6) | −0.353 011 |
| (12,10) | 0.0 | −0.093 008 (33.9) | −0.181 632 (66.1) | −0.274 640 |
| (10,10) | −0.002 512 (1.0) | −0.093 575 (35.9) | −0.164 762 (63.2) | −0.260 850 |
| (12,11) | 0.0 | −0.077 996 (31.8) | −0.167 480 (68.2) | −0.245 476 |
| Differences (transition state energy-equilibrium energy) | | | | |
| (0,0)[a] | 0.0 | 0.0 | −0.017 523 | −0.017 523 |
| (4,4) | −0.002 227 | −0.029 304 | 0.020 329 | −0.011 456 |
| (6,6)/*lp* | −0.007 574 | −0.023 686 | 0.031 859 | 0.000 599 |
| (6,6)/$\pi$ | −0.009 241 | −0.018 910 | 0.014 565 | −0.013 586 |
| (12,10) | 0.0 | 0.002 879 | 0.003 382 | 0.006 262 |
| (10,10) | −0.000 280 | −0.007 942 | 0.004 507 | −0.003 715 |
| (12,11) | 0.0 | 0.000 005 | 0.005 904 | 0.005 908 |

[a] MP2 results based on a single reference HF function.

to the overestimation of the dynamical correlation as we have discussed previously. However, MRMP starting with an adequate zeroth-order CASSCF reference function of (10,10) and (12,11) with cc-pVQZ gives almost the same results, i.e., 84.6 (79.2) and 84.5 (79.1) kcal/mol. These results are most likely not artifacts. Thus, it is safe to say that the many-electron wave function is almost converged at this level of theory. The agreement of the results with experimental data of 79.2±0.8 kcal/mol is also complete. On the basis of these convergence patterns of the one electron function and the many-electron wave function, we concluded that MRMP with the use of cc-pVQZ basis set and the sufficiently large active space such as (12,11) and (10,10) has reached a quantitative correct description for the barrier height of the reaction.

In Table III we summarized second-order correlation energies partitioned into external, semi-internal, and internal contributions. In terms of the Fermi sea determined by the reference CASSCF function, the first-order corrections to the wave function may be classified in terms of the number (0, 1, or 2) of external orbitals introduced as internal, semi-internal, and external. The differential correlation contributions with respect to the equilibrium structure are also listed in the table.

On the whole, the second-order energies decreases with increasing the size of the active space of the reference CASSCF wave function. The external contribution also decreases with the size of the active space since the external term resembles the dynamical pair correlation of the closed-shell theory. The external contribution in the transition state is smaller compared to that in the equilibrium. On the other hand, the semi-internal contribution does not show such a simple feature. The semi-internal term includes significant single excitations which arise from the failure of the reference function to satisfy the Brillouin theorem. Physically, the semi-internal contribution represents the dynamical polarization effects. Thus, the magnitude of the semi-internal term depends significantly on the choice of the active space. We can see that the total correlation energy difference between two geometries is mainly determined by the difference of the semi-internal contributions. The internal contribution was found to be negligibly small as expected. It must be noted that the MRMP results with (12,10), (10,10), and (12,11) active spaces indicate that the contributions from internal, semi-internal, and external terms are well balanced between the equilibrium and transition state structures. This is a sharp contrast to the results with smaller active spaces of (4,4), (6,6)/$\pi$, and (6,6)/*lp*.

As we have discussed, in transition structure calculations we should aim to use a zeroth-order wave function that is expected to be of a similar accuracy that in the region of the equilibrium geometry. The quality of the wave function calculated at different geometries can be checked more straightforwardly by the comparison of the weight of the CASSCF reference function in the first-order wave function,

$$W = \frac{\langle \Psi_{\mathrm{ref}} | \Psi_{\mathrm{ref}} \rangle}{\langle \Psi_{\mathrm{ref}} + \Psi^{(1)} | \Psi_{\mathrm{ref}} + \Psi^{(1)} \rangle} = \frac{1}{1 + \langle \Psi^{(1)} | \Psi^{(1)} \rangle}.$$

TABLE IV. The weights of the reference function in percent in the first-order wave functions of MRMP calculated with cc-pVQZ.

| Active space | Reference | Internal | Semi-Internal | External |
|---|---|---|---|---|
| Equilibrium geometry | | | | |
| (0,0)[a] | 89.9 | 0.0 | 0.0 | 10.1 |
| (4,4) | 91.0 | 0.0 | 0.9 | 8.1 |
| (6,6)/$lp$ | 91.2 | 0.0 | 2.1 | 6.7 |
| (6,6)/$\pi$ | 92.5 | 0.2 | 2.6 | 4.7 |
| (12,10) | 94.2 | 0.0 | 2.5 | 3.3 |
| (10,10) | 94.9 | 0.1 | 2.1 | 2.9 |
| (12,11) | 94.8 | 0.0 | 1.9 | 3.3 |
| Transition state geometry | | | | |
| (0,0)[a] | 88.2 | 0.0 | 0.0 | 12.8 |
| (4,4) | 90.2 | 0.1 | 2.3 | 7.4 |
| (6,6)/$lp$ | 90.8 | 0.3 | 3.1 | 5.8 |
| (6,6)/$\pi$ | 91.5 | 0.7 | 3.3 | 4.4 |
| (12,10) | 93.9 | 0.0 | 2.6 | 3.5 |
| (10,10) | 94.4 | 0.1 | 2.6 | 2.1 |
| (12,11) | 94.6 | 0.0 | 2.1 | 3.3 |

[a] MP2 results based on a single reference HF function.

This weight is a measure for estimating the quality of the perturbed wave function. The relative weight calculated in different geometries gives a measure of how balanced the calculation is. The weights are summarized in Table IV. In addition to the weight of the CASSCF reference, we also listed the weight of the first-order wave function in terms of internal, semi-internal, and external contributions. It can be seen that the reference wave function has a very good quality. Even for the single reference MP2 case, the weight is about 90%, both at the equilibrium and transition state structures. In the case of CASSCF with (12,10), (10,10), and (12,11), the weight is almost 95%, which implies that the second-order perturbation treatment is a good approximation to take account the rest of the correlation energy. It is noted that not only the weight of the reference function but also the weight of internal, semi-internal, and external terms are, on the whole, close to each other for the equilibrium and transition state structures. In particular, in the case of (12,11), the weight of each contribution is almost the same for the equilibrium and transition state structures. This indicates that the calculation is well balanced with respect to the treatment of electron correlation. This also supports our theoretical estimation of the barrier height.

## III. SUMMARY

In this paper, we have presented the classical barrier height of the $H_2CO \rightarrow H_2 + CO$ dissociation reaction calculated by MRMP. We obtained 84.5 (79.1) kcal/mol as the best estimate for the classical barrier height. The agreement between the experimental and theoretical estimates is complete. This agreement could be fortuitous but the same level of theory (MRMP with the QZ3p basis and large active space) also yields very accurate transition energies in different electronic states.[15] To check the balance of the calculation for the equilibrium and transition state structures, we analyzed the second-order energies by partitioning them into internal, semi-internal, and external contributions and also examined the reference weight in the first-order wave function. These data also support that the present method gives a proper description of the electronic structure at the transition state geometry as well as at the equilibrium geometry. The present approach can account for the proper balance of the correlation energy difference between two structures involved. This leads to the success of the calculations of the activation energies. Thus, we believe that the close agreement of the result computed at the highest level of theory with experiment is most likely not artifacts.

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