Accurate Theoretical Prediction of Relative Energy: Barriers to Linearity, Inversion, and Internal Rotation in Polyatomic Molecules

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An *ab initio* investigation of high-level accuracy on the magnitude of barriers to linearity, inversion, and internal rotation in the potential energy surfaces of water, ammonia, and ethane has been carried out using various bases and correlation treatments. It is shown that the increase of basis set size generally reduces the calculated barrier heights with correlation methods, and the proper account of one-particle basis set is necessary for the observation of systematic change of the calculated barrier heights according to electron correlation. A careful examination of core correlation effect on the calculated barrier height shows that freezing the core orbitals in correlated calculations would yield a slightly higher value than the actual barrier height, and it is important to include appropriate core-correlating functions in the basis for accurate prediction of relative energies such as internal barriers of polyatomic molecules. From this study, we predict that the barrier height to internal rotation in ethane would not exceed 960 cm^{-1}, which appears to be quite lower than previous theoretical results reported so far. The barrier height to linearity in water was found to be least convergent with basis set, probably due to the presence of the most lone pair electrons in the molecule.

I. Introduction

An accurate theoretical prediction of relative energies, such as activation energy, isomerization energy, or barrier height to linearity, inversion, and internal rotation (torsion), in polyatomic molecules is of central importance in chemistry, which requires a careful investigation of total energies at respective geometries. In principle, it can be achieved by employing high level correlation methods such as full configuration interaction (FCI) with a large enough basis set to reduce the error in respective geometries of molecules. In practice, however, the accuracy of a quantum chemical calculation is severely limited by the computational resources and one usually has to resort to approximate correlation method with a basis set of manageable size. Although there have been remarkable progresses both in theory and computational algorithm for calculating the correlation energy of a molecule, the results within the chemical accuracy (less than 1 kcal/mol) are still limited to relatively small molecular systems and it becomes rapidly difficult to obtain them as the number of atoms and corresponding number of basis functions increase. The errors in predicting an atomic and molecular property of a given theoretical model can come from both approximate treatment of electron correlation and the incompleteness of one-particle basis set employed. In the case of internal barrier height of a molecule, which corresponds to the energy difference between the equilibrium and saddle point (transition structure) geometries, the accuracy of calculated barrier height depend not only on the closeness of obtained total electronic energy to the exact energy at a given geometry but also on variation of the errors of various approximations at both geometries. Therefore, it is strongly desirable in this case to choose a theoretical model which can cancel out the errors at each geometry of a molecule. In this respect, size consistency should be the necessary feature of the theoretical method employed for accurate prediction of the relative energy of a molecular system. This would be even more true when the effect of core correlation on relative energies is explored for the prediction of the molecular property with high-level accuracy.[1,2]

One of the most frequently used approximations in calculating the relative energy or potential energy surface of a molecule with electron correlation treatment is the frozen-core approximation (FCA), which neglects the effect of electron correlation by core electrons. In estimating the effect of core correlation on absolute or relative energies, it is important to employ a basis set properly representing the motion of inner shell electrons as well as valence electrons. Although it is generally known that the shape of potential energy surface is little affected by the frozen-core approximation in the correlated calculations,[34] the change in the relative energy made by the liberation of core electrons could be nonnegligible in some cases and must be explored in quantum calculations of high-level accuracy. Furthermore, it still needs to be clarified how much core correlation (activating core orbitals) is affected by the choice of the basis set and correlation level in the calculation of relative energy such as internal barrier height of a molecule.

In this paper we examine the effect of electron correlation and basis set on internal barrier height of water, ammonia, and ethane, which could be considered as the prototype of having a potential barrier to linearity, inversion, and internal rotation, respectively. Although there have been a lot of theoretical and experimental studies on these molecular systems on an individual basis,[5−21] there appear to be few systematic studies at this time which could provide an insight on the results of more general quantum chemical calculations. In this process we examine the effectiveness of various approximations, such as FCA and neglect of triply substituted configurations in correlated methods, which can substantially reduce the computation time in practical calculations. In section II we explain the theoretical methods and basis sets along with computational details employed in this study. The results are presented and analyzed in section III. The conclusions are in section IV.

II. Computational Details and Calculations

We have calculated the barrier heights to linearity for water, inversion for ammonia, and internal rotation for ethane in the ground electronic states using three different theoretical methods: Hartree−Fock (HF), Moller-Plesset perturbation theory at

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TABLE 1: Effect of Basis Set and Electron Correlation on Barrier Height to Linearity[a] for H_2O

method	barrier height	basis set						exptl
		6-31+G(d)	6-311++G(d, p)	6-311++G(3df, 3pd)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ[b]	
HF	E_s[c]	75.962 866 0	76.002 919 6	76.007 783 3	75.988 886 1	76.008 956 8	76.014 994 6	
	E_e[c]	76.017 743 2	76.053 423 4	76.059 350 7	76.041 843 4	76.060 260 3	76.066 676 2	
	V_b[d]	12 044	11 084	11 318	11 623	11 260	11 343	10967[e]
MP2	E_s	76.156 890 1	76.223 542 0	76.274 189 4	76.208 628 5	76.278 257 7	76.301 852 3	
	E_e	76.209 776 6	76.274 920 4	76.324 286 5	76.260 909 7	76.328 992 1	76.351 910 0	
	V_b	11 607	11 276	10 995	11 474	11 135	10 986	
MP3	E_s	76.159 807 1	76.225 049 9	76.276 078 8	76.212 478 2	76.280 118 4	76.301 873 0	
	E_e	76.213 795 7	76.277 549 8	76.326 960 4	76.265 525 3	76.331 601 9	76.352 607 0	
	V_b	11 849	11 522	11 167	11 642	11 299	11 135	
MP4DQ	E_s	76.162 100 2	76.227 111 0	76.276 592 9	76.213 817 8	76.280 501 9	76.301 758 7	
	E_e	76.216 313 5	76.279 559 6	76.327 705 6	76.267 064 9	76.332 241 6	76.352 756 9	
	V_b	11 898	11 511	11 218	11 686	11 356	11 193	
MP4SDQ	E_s	76.163 527 5	76.228 894 0	76.278 276 2	76.215 515 5	76.282 208 2	76.303 362 7	
	E_e	76.217 656 9	76.281 418 0	76.329 582 7	76.268 829 3	76.334 142 3	76.354 604 1	
	V_b	11 880	11 528	11 260	11 701	11 398	11 246	
MP4SDTQ	E_s	76.166 260 0	76.234 450 5	76.287 460 0	76.221 222 3	76.291 841 0	76.313 966 4	
	E_e	76.220 384 9	76.287 251 4	76.338 698 9	76.274 509 8	76.343 672 6	76.365 083 0	
	V_b	11 879	11 588	11 246	11 695	11 376	11 219	
QCISD	E_s	76.163 996 5	76.229 202 8	76.278 296 5	76.215 826 3	76.282 184 8	76.303 343 9	
	E_e	76.218 265 2	76.281 750 8	76.329 637 1	76.269 215 2	76.334 160 0	76.354 620 3	
	V_b	11 911	11 533	11 268	11 718	11 407	11 254	
QCISD(T)	E_s	76.166 064 9	76.233 949 8	76.286 377 7	76.220 623 6	76.290 643 2	76.312 594 7	
	E_e	76.220 552 9	76.286 841 6	76.337 682 8	76.274 130 0	76.342 560 2	76.363 782 4	
	V_b	11 959	11 608	11 260	11 743	11 394	11 234	

[a] Energies beyond MP2 level were calculated at MP2-optimized geometry. [b] Energies beyond MP2 level were calculated using MP2/aug-cc-pVTZ-optimized geometry. [c] E_s and E_e are total electronic energies at optimized linear and bent geometries in units of hartree. Negative sign has been omitted for total electronic energies in all tables. [d] V_b is the difference between E_s and E_e, in units of cm^{-1}. [e] From ref 8.

second-, third- and fourth-order correction (MP2, MP3, and MP4)[22] and quadratic configuration interaction method including single and double substitutions (QCISD) and QCISD(T) method,[23] in which a noniterative triple correction term is added to QCISD energy. All theoretical methods are size consistent. The quadratic configuration interaction method has been developed to restore the size consistency for limited configuration interaction method and can be considered as a simplified approximate form of coupled cluster method.[24] In a previous study,[23] QCISD(T) energies were found to be highly successful in describing the correlation energy for NH_2, CH_2, and H_2O at geometries close to equilibrium, comparing well with the FCI energies. The calculation of relative energies between equilibrium and saddle point geometry has been carried out by optimizing the geometries at the given theoretical level and calculating energies at respective geometry. For example, in the case of ethane, the energies at the equilibrium and saddle point were obtained by optimizing C−H, C−C bond lengths and the H−C−H bond angle simultaneously in the staggered and eclipsed conformation, respectively. The optimization to locate the minimum for equilibrium and saddle point geometries has been obtained using the method developed by Peng et al.[25] For the correlation methods higher than second-order Møller-Plesset perturbation theory (MP2), the energy has been calculated using the geometry optimized at MP2 level because the change in geometry with further correlation effects was negligible in most cases. The relative energy obtained in this way was found to be very close to the relative energies when fully optimized geometry for the given theoretical level was used instead. (The typical error for this approximation was less than 2 cm^{-1} in most cases.)

The basis sets employed in this study can be classified into two types: segmented contracted 6-31G and 6-311G type basis set augmented by multiple polarization functions[26,27] and correlation-consistent polarized valence basis set, cc-pVXZ (X = D, T, and Q).[28] The correlation-consistent basis sets have been shown to be very effective in describing the molecular correlation effects, comparing well with the results of corresponding atomic natural orbital basis sets of Almlöf and Taylor with more primitive functions.[29] In the case of water and ammonia, additional diffuse functions were included to describe the lone-pair electrons (++ and aug). In addition to this conventional valence basis sets, correlation-consistent polarized core-valence basis set cc-pCVTZ, which includes extra core-correlating functions to cc-pVTZ, has also been employed to investigate the effect of freezing and activating the core orbitals in correlated calculations. Following the suggestions of previous studies,[34] frozen-core approximation was adopted initially for all correlated calculations. All calculations were performed using the Gaussian 94 program package.[31]

III. Results and Discussion

In Tables 1−3 we present the change of the relative energies according to basis set and correlation level between the equilibrium and transition state configurations of water, ammonia, and ethane, respectively. First of all, it appears that the barrier heights in general tend to go lower as the basis set becomes larger at correlated levels. This is especially true for the changes between the same type of basis set, for example, 6-311++G(d,p) and 6-311++G(3df,3pd) or aug-cc-pVDZ and aug-cc-pVTZ (or aug-cc-pVQZ). This suggests that it is important to employ the basis set of the same contraction scheme in increasing the size of the basis set for systematic convergence of relative energies. Meanwhile, the results at HF levels or results with smaller basis set such as 6-31G for ethane do not follow this behavior as the calculated energies strongly suffer from the lack of electron correlation and basis functions. This confirms the inadequacy of HF method and necessity of employing a significantly large basis set in predicting the accurate relative energies between two molecular configurations. This kind of behavior was also shown in a recent study[32] of torsional barriers of various polyatomic molecules including C_2H_6 and CH_3NH_2 at MP2 level. The fact that the relative energies tend to decrease with the size of the basis set is rather surprising considering most basis functions are optimized in the

TABLE 2: Effect of Basis Set and Electron Correlation on Barrier Height to Inversion[a] for NH_3

method	barrier height	basis set						exptl
		6-31+G(d)	6-311++G(d, p)	6-311++G(3df, 3pd)	aug-cc-pVDZ	aug-cc-pVTZ[b]	aug-cc-pVQZ[b]	
HF	E_s[c]	56.180 777 0	56.207 373 4	56.211 190 0	56.197 422 4	56.213 114 6	56.216 879 4	
	E_e[c]	56.189 499 4	56.214 754 4	56.218 834 5	56.205 590 4	56.220 806 6	56.224 503 8	
	V_b[d]	1 914	1 620	1 678	1 793	1 688	1 673	1839 ± 46[e]
MP2	E_s	56.355 189 9	56.407 490 7	56.448 876 4	56.396 459 6	56.452 484 4	56.469 986 4	
	E_e	56.363 197 0	56.415 523 6	56.456 824 4	56.404 889 9	56.460 540 9	56.477 766 3	
	V_b	1 757	1 763	1 744	1 850	1 768	1 707	
MP3	E_s	56.365 452 7	56.417 860 8	56.458 890 2	56.408 729 6	56.462 648 0	56.477 858 7	
	E_e	56.373 999 3	56.426 416 7	56.467 188 2	56.417 493 4	56.471 000 0	56.485 893 1	
	V_b	1 876	1 878	1 821	1 923	1 833	1 763	
MP4DQ	E_s	56.367 568 9	56.419 292 3	56.458 981 3	56.409 801 4	56.462 572 1	56.477 364 9	
	E_e	56.376 321 0	56.427 910 3	56.467 413 8	56.418 693 0	56.471 054 5	56.485 530 4	
	V_b	1 921	1 891	1 851	1 951	1 862	1 792	
MP4SDQ	E_s	56.368 496 8	56.420 459 8	56.460 177 4	56.410 753 7	56.463 732 7	56.478 591 5	
	E_e	56.377 330 8	56.429 158 3	56.468 770 5	56.419 770 6	56.472 385 8	56.486 944 4	
	V_b	1 939	1 909	1 886	1 979	1 899	1 833	
MP4SDTQ	E_s	56.371 161 5	56.425 650 1	56.468 281 4	56.415 932 2	56.472 098 5	56.487 743 2	
	E_e	56.380 147 0	56.434 562 8	56.477 036 2	56.425 150 2	56.480 931 0	56.496 276 2	
	V_b	1 972	1 956	1 921	2 023	1 939	1 873	
QCISD	E_s	56.369 261 2	56.420 901 1	56.460 309 1	56.411 206 4	56.463 849 1	56.478 722 3	
	E_e	56.378 154 0	56.429 616 0	56.468 933 5	56.420 258 4	56.472 533 3	56.487 103 3	
	V_b	1 952	1 913	1 893	1 987	1 906	1 839	
QCISD(T)	E_s	56.371 892 5	56.425 916 7	56.468 054 1	56.416 368 4	56.471 849 6	56.487 326 8	
	E_e	56.380 950 2	56.434 852 1	56.476 811 5	56.425 624 9	56.480 678 3	56.495 850 3	
	V_b	1 988	1 961	1 922	2 032	1 938	1 871	

[a] Energies beyond MP2 level were calculated at MP2-optimized geometry. [b] MP2/6-311++G(3df,3pd)-optimized geometry used beyond HF level. [c] E_s and E_e represents the energies at optimized planar (saddle point) and pyramidal (equilibrium) geometries, respectively, in units of hartree. [d] V_b is the difference between E_s and E_e, in units of cm^{-1}. [e] From ref 15.

TABLE 3: Effect of Basis Set and Electron Correlation on Barrier Height[a] to Internal Rotation for Ethane

method	barrier height	basis set						exptl
		6-31G	6-31G(d)	6-311G(3df, 3pd)	cc-pVDZ	cc-pVTZ[b]	cc-pVQZ[c]	
HF	E_s[d]	79.193 177 3	79.223 994 1	79.253 553 6	79.229 697 6	79.255 204 3	79.260 379 5	
	E_e[d]	79.197 572 3	79.228 754 8	79.258 404 8	79.234 944 6	79.260 034 8	79.265 230 2	
	V_b[e]	965	1 045	1 065	1 152	1 060	1 065	1009[f]
MP2	E_s	79.380 710 0	79.489 730 7	79.625 696 0	79.532 303 5	79.625 278 1	79.652 939 9	
	E_e	79.385 604 2	79.494 740 2	79.630 389 0	79.537 475 8	79.629 908 3	79.657 455 5	
	V_b	1 074	1 099 (1 068)[g]	1 030	1 135	1 016	991	
MP3	E_s	79.403 587 6	79.516 035 2	79.654 043 0	79.564 859 0	79.654 222 1		
	E_e	79.408 366 5	79.520 894 2	79.658 577 1	79.569 864 5	79.658 711 9		
	V_b	1 049	1 066	995	1 099	985		
MP4DQ	E_s	79.409 534 5	79.519 777 5	79.654 522 0	79.567 959 0	79.654 620 0		
	E_e	79.414 239 5	79.524 587 8	79.659 050 8	79.572 943 6	79.659 110 1		
	V_b	1 033	1 056	994	1 094	985		
MP4SDQ	E_s	79.409 984 8	79.521 643 5	79.656 514 6	79.569 120 3	79.656 557 1		
	E_e	79.414 684 2	79.526 446 4	79.661 046 2	79.574 111 7	79.661 052 4		
	V_b	1 031	1 054	995	1 095	987		
MP4SDTQ	E_s	79.413 383 1	79.527 941 1	79.669 505 3	79.576 567 9	79.669 378 7		
	E_e	79.418 124 3	79.532 789 4	79.674 018 1	79.581 592 8	79.673 860 7		
	V_b	1 041	1 064	990	1 103	984		
QCISD	E_s	79.417 262 7	79.523 200 3	79.656 912 3	79.569 992 9	79.656 937 1		
	E_e	79.412 631 9	79.527 965 1	79.661 442 3	79.574 966 2	79.661 431 6		
	V_b	1 016	1 046	994	1 092	986		
QCISD(T)	E_s	79.416 483 8	79.529 760 5	79.670 189 7	79.578 208 2	79.670 087 6		
	E_e	79.421 151 8	79.534 562 6	79.674 687 2	79.583 200 6	79.674 554 9		
	V_b	1 025	1 054	987	1 096	980		

[a] Energies beyond MP2 level were calculated at MP2-optimized geometry. [b] MP2/6-311G(3df, 3pd)-optimized geometry used beyond HF level. [c] Geometries optimized with 6-311G(3df, 3pd) at respective level were used. [d] E_s and E_e represent the energies at optimized eclipsed (saddle point) and staggered (equilibrium) configurations, respectively, in units of hartree. [e] V_b is the difference between E_s and E_e, in units of cm^{-1}. [f] From ref 20. [g] The value in parentheses is the barrier height with 6-31+G(d) basis set.

atomic calculations rather than in molecular environment at equilibrium. The convergence of the calculated relative energies according to basis set appears to be quite slow, especially for ammonia and water, implying that larger basis set than 6-311++G(3df,3pd) or aug-cc-pVTZ basis sets appears to be necessary to accurately predict the barrier height for these molecules. This would be probably related to the difficulty in the description of lone-pair electrons in these molecules which can be spread over the wider region than bonding electrons.

The effects of electron correlation on calculated barrier height are more difficult to analyze as the energies vary differently according to basis set and type of molecular motion. While it is shown that the increase of electron correlation level generally increases the barrier height in ammonia and water, the reverse appears to be true for ethane, although there are some exceptions for HF to MP2 results with smaller basis sets. For example, while the barrier heights in water and ammonia at HF level are lower than the barrier heights at MP2 level for most basis sets,

TABLE 4: Effect of Frozen-Core Approximation (FCA) on Barrier Height to Linearity[a] for H_2O

		basis set					
		6-311++G(3df,3pd)		aug-cc-pVTZ		aug-cc-pCVTZ[b]	
method	barrier height	FCA	full	FCA	full	FCA	full
MP2	E_s	76.274 189 4	76.298 223 9	76.278 257 7	76.293 846 0	76.281 672 4	76.334 692 7
	E_e	76.324 286 5	76.347 699 0	76.328 992 1	76.344 148 2	76.332 397 6	76.384 992 8
	V_b	10 995	10 856	11 135	11 040	11 133	11 040
MP3	E_s	76.276 078 8	76.300 579 2	76.280 118 4	76.295 727 5	76.283 062 0	76.337 419 0
	E_e	76.326 960 4	76.350 848 3	76.331 601 9	76.346 801 3	76.334 553 6	76.388 518 6
	V_b	11 167	11 033	11 299	11 209	11 301	11 215
MP4SDTQ	E_s	76.287 460 0	76.312 035 0	76.291 841 0	76.307 472 6	76.295 068 2	76.349 646 6
	E_e	76.338 698 9	76.362 673 6	76.343 672 6	76.358 897 8	76.346 920 1	76.401 137 4
	V_b	11 246	11 114	11 376	11 287	11 380	11 301
QCISD	E_s	76.278 296 5	76.302 664 7	76.282 184 8	76.297 676 8	76.285 126 0	76.339 304 1
	E_e	76.329 637 1	76.353 399 8	76.334 160 0	76.349 241 6	76.337 117 1	76.390 921 3
	V_b	11 268	11 135	11 407	11 317	11 411	11 329
QCISD(T)	E_s	76.286 377 7	76.310 926 0	76.290 643 2	76.306 256 7	76.293 813 6	76.348 331 2
	E_e	76.337 682 8	76.361 624 3	76.342 560 2	76.357 761 9	76.345 739 9	76.399 878 0
	V_b	11 260	11 127	11 394	11 304	11 397	11 313

[a] Energies beyond MP2 level were calculated at MP2-optimized geometry. [b] Energies calculated at MP2/aug-cc-pVTZ-optimized geometries at each level (FCA and full).

HF results are higher than MP2 results for 6-31+G(d) basis set. This again shows the importance of using converged basis set in investigating the effect of electron correlation on the relative energy. Since the early SCF calculation by Pitzer and Lipscomb,[16] the torsional barrier in ethane has long been regarded as the prototype of exhibiting insensitive barrier height according to electron correlation and basis set changes. Although the barrier heights in ethane show less significant changes with basis set and electron correlation compared to other cases, the effect of electron correlation coupled with basis set changes appears to have a nonnegligible effect on barrier height, especially from double-ζ to triple-ζ quality basis set. The large deviation of the barrier heights at 6-31G and cc-pVDZ basis set from the other results at HF level could be attributed to the lack of polarization functions (6-31G) and inadequacy of the basis set at HF level (cc-pVDZ), respectively. Our estimate of the torsional barrier in ethane at QCISD(T)/cc-pVQZ level would be about 960 cm^{-1}, which was deduced by considering the change from MP2 to QCISD(T) level with cc-pVTZ basis set. Since this change in correlation level with cc-pVTZ basis set reduces the barrier height by 36 cm^{-1} and this effect appears to diminish as the basis set becomes larger, the torsional barrier height in ethane would be close to 960 cm^{-1}. This value then could be further lowered by the addition of diffuse functions in the basis set as demonstrated in the results with 6-31G(d) and 6-31+G(d) basis set. In the case of water, the barrier height to linearity varies in a nonmonotonous manner with electron correlation as the results at MP2 and MP4 level differ from HF result in opposite direction for most basis sets except 6-311++G-(d,p) set. This kind of behavior is often observed in the correlated calculation of relative energies such as activation or isomerization energies. It has been known for isomerization energy change of HCN and H_2CO that MP2/6-31G results overcorrects the HF results and further corrections at third and fourth order (MP3 and MP4) correct the MP2 results in reverse direction.[33] It also appears clear that, while barrier height at the HF limit is lower than the exact barrier height for inversion of ammonia, the reverse is true for internal rotation of ethane. This implies that, unlike ethane, which exhibits stronger correlation effect in the eclipsed conformation rather than in the staggered conformation (possibly due to the stronger electron localization in the eclipsed form), the effect of electron correlation for ammonia is more important at equilibrium pyramidal geometry than at saddle point planar geometry.

The effect on the barrier heights of including triply substituted configurations in correlated calculations appears to be most significant in NH_3, which is considered to bring up significant geometrical changes from equilibrium pyramidal to planar configuration. However, even in this case, it has only minor effect (40 cm^{-1} at most) on the calculated barrier height. It is interesting to note that, while barrier heights at MP4SDQ and MP4SDTQ level are clearly closer each other than the barrier heights at MP4DQ and MP4SDQ for water, it does not hold true for ammonia and ethane. This could be related to the larger geometrical changes in ammonia and ethane compared to water between equilibrium and saddle point geometries and subsequent significance of triply substituted configurations in such geometrical changes. This is in accord with the previous result which showed the importance of triply substituted configurations in the description of highly stretched molecular state.[34]

It has been noticed in recent studies[13,15] that freezing the core orbitals in correlated calculations (FCA) increased the relative energies slightly compared to the case of activating all orbitals including core. To test the generality of this premise, we calculated the barrier heights with all orbitals active in correlated calculations. In Tables 4−6 we present the results with frozen core and full activation of orbitals including core in correlated calculations. For NH_3 and H_2O, the barrier height is reduced by the activation of the core orbitals regardless of basis set employed. On the other hand, for ethane, the trend is reversed: the barrier height is increased by the activation of core orbitals. It has to be noted, however, that, even in the case of ethane, the barrier height with FCA and aug-cc-pVTZ basis set is still higher than the barrier height with full actuation of orbitals and aug-cc-pCVTZ, which has extra core-correlating functions in addition to the aug-cc-pVTZ basis set. Such extra core-correlating functions should be present to properly account for the core-valence correlation effect on the magnitude of relative energies in high-level *ab initio* calculations.[36] The core correlation effect on absolute energy is obviously most significant when the basis set includes the core-correlating functions in addition to the conventional valence-optimized basis set. Not only the total energy is substantially lowered by the presence of the core-correlating functions but the change in calculated barrier height is nonnegligible, especially in the case of ammonia and ethane. While the core correlation effect is clearly dependent on the basis set used, its variation according to level of electron correlation appears to be consistent throughout once

TABLE 5: Effect of Frozen-Core Approximation (FCA) on Barrier Height[a] to Inversion for NH_3

		basis set					
		6-311++G(3df,3pd)		aug-cc-pVTZ		aug-cc-pCVTZ	
method	barrier height	FCA	full	FCA	full	FCA	full
MP2	E_s	56.448 876 4	56.472 370 4	56.452 484 4	56.469 950 1	56.454 457 1	56.504 890 7
	E_e	56.456 824 4	56.480 024 1	56.460 540 9	56.477 487 1	56.462 481 7	56.512 677 9
	V_b	1 744	1 680	1 768	1 654	1 761	1 709
MP3	E_s	56.458 890 2	56.483 058 9	56.492 629 2	56.480 470 1	56.464 299 6	56.516 339 1
	E_e	56.467 188 2	56.491 065 2	56.501 084 1	56.488 276 2	56.472 623 3	56.524 436 5
	V_b	1 821	1 757	1 833	1 713	1 827	1 777
MP4SDTQ	E_s	56.468 281 4	56.492 629 2	56.472 098 5	56.490 037 4	56.473 954 8	56.526 365 2
	E_e	56.477 036 2	56.501 084 1	56.480 931 0	56.498 312 5	56.482 760 2	56.534 942 6
	V_b	1 921	1 856	1 939	1 816	1 933	1 883
QCISD	E_s	56.460 309 1	56.484 407 5	56.463 849 1	56.481 598 0	56.465 521 5	56.517 497 6
	E_e	56.468 933 5	56.492 737 3	56.472 533 3	56.489 729 2	56.474 179 5	56.525 932 2
	V_b	1 893	1 828	1 906	1 785	1 900	1 851
QCISD(T)	E_s	56.468 054 1	56.492 343 3	56.471 849 6	56.489 747 9	56.473 649 8	56.525 941 9
	E_e	56.476 811 5	56.500 798 7	56.480 678 3	56.498 016 8	56.482 450 3	56.534 509 9
	V_b	1 922	1 856	1 938	1 815	1 931	1 880

[a] All energies calculated at MP2/6-311++G(3df,3pd)-optimized geometries at each level (FCA and full).

TABLE 6: Effect of Frozen-Core Approximation (FCA) on Barrier Height[a] to Internal Rotation for Ethane

		basis set					
		6-311G(3df,3pd)		cc-pVTZ		cc-pCVTZ[b]	
method	barrier height	FCA	full	FCA	full	FCA	full
MP2	E_s	79.625 696 0	79.669 933 4	79.625 278 1	79.657 250 0	79.627 589 4	79.722 762 1
	E_e	79.630 389 0	79.674 702 7	79.629 908 3	79.662 133 7	79.632 195 1	79.727 379 1
	V_b	1 030	1 047	1 016	1 072	1 011	1 013
MP3	E_s	79.654 043 0	79.700 144 7	79.654 222 1	79.687 250 4	79.656 168 4	79.755 199 3
	E_e	79.658 577 1	79.704 758 0	79.658 711 9	79.692 013 3	79.660 632 3	79.759 671 3
	V_b	995	1 013	985	1 045	980	981
MP4SDTQ	E_s	79.669 505 3	79.716 102 9	79.669 378 7	79.702 656 1	79.671 543 7	79.771 274 2
	E_e	79.674 018 1	79.720 708 4	79.673 860 7	79.707 410 1	79.675 997 6	79.775 732 3
	V_b	990	1 011	984	1 043	978	978
QCISD	E_s	79.656 912 3	79.703 021 7	79.656 937 1	79.689 870 8	79.658 907 3	79.757 936 5
	E_e	79.661 442 3	79.707 641 3	79.661 431 6	79.694 640 7	79.663 377 8	79.762 416 6
	V_b	994	1 014	986	1 047	981	983
QCISD(T)	E_s	79.670 189 7	79.716 703 1	79.670 087 6	79.703 303 5	79.672 203 7	79.771 770 4
	E_e	79.674 687 2	79.721 294 9	79.674 554 9	79.708 043 5	79.676 643 6	79.776 215 6
	V_b	987	1 008	980	1 040	974	976

[a] Energies beyond MP2 level were calculated at MP2-optimized geometry. [b] Energies calculated at MP2/cc-pVTZ-optimized geometries at each level (FCA and full).

the basis set is chosen. It is important to note that, in the case of valence-optimized basis sets, such as 6-311++G(3df,3pd) and aug-cc-pVTZ, the barrier heights with FCA rather than with full activation of all orbitals are closer to barrier heights with aug-cc-pCVTZ basis set and full activation of orbitals for ethane and ammonia. This suggests that in the case of valence-optimized basis sets full activation of orbitals does not always guarantee the better results than the results with FCA and clearly shows the importance of including appropriate core-correlating functions to investigate the correlation effect by inner shell electrons in such calculations.[36]

IV. Conclusions

We have performed a systematic investigation on the effect of basis set and electron correlation on the barrier heights in water, ammonia, and ethane. The conclusions of this work can be summarized as follows: (1) The barrier height and its variation according to electron correlation clearly depend on specific molecular motion of interest and the basis set employed. This is especially true when the basis set is unconverged. As the basis set becomes larger, the effect of electron correlation on barrier height becomes more systematic and converging. It is important to employ a large enough basis set to systematically examine the effect of electron correlation on relative energies for internal molecular motions.

(2) In correlated calculations, the increase of the basis set size with FCA generally reduces the barrier height. This is especially true for the basis sets of the same type obtained by the same contraction scheme. The proper description of lone-pair electrons would necessiate the use of larger basis set than bonding electrons. Therefore, in our examples, ethane needs a basis set of the smaller size than ammonia to get converged relative energy. Water appears to need the basis set of the largest size as it has the most lone pair electrons among them.

(3) The core correlation effect on calculated barrier height made by the activation of core orbitals in correlated calculations is clearly dependent upon basis set employed. However, once the basis set is chosen, its variation according to the level of electron correlation appears to be almost constant. The calculated barrier height with valence-optimized basis sets and FCA has always been found slightly higher than the barrier height obtained with the addition of core-correlating functions to the original basis set and full activation of all orbitals in correlated calculations. The activation of core orbitals with valence-optimized basis sets could lead to the barrier height, which is more erroneous than the barrier height with FCA. Therefore, it is necessary to employ a basis set which can properly account for core correlation effect when core orbitals are activated.

(4) The barrier height at full MP4 (MP4SDTQ) level could be approximated as the barrier height at MP4SDQ or even MP4DQ level in some cases, which can substantially reduce the computational time in practical calculations. In the worst case of ammonia examined in this work, the error of MP4SDQ and MP4DQ from MP4SDTQ level did not exceed about 40 and 80 cm^{-1}, respectively. On the other hand, this also implies that triple contribution to relative energy could be nonnegligible in some cases where large geometrical changes are accompanied. In the similar manner, the barrier height at QCISD would be a good approximation to the barrier height at QCISD(T) for water and ethane. The barrier height at MP4SDTQ is very close to the barrier height at QCISD(T).

(5) On the basis of our calculations, we estimate the barrier height to internal rotation in ethane at QCISD(T)/cc-pCVQZ with full activation of orbitals would be close to 956 cm^{-1} as the increase of correlation level and addition of core-correlating functions in the basis set could lower the barrier height by about 31 and 4 cm^{-1}, respectively, from barrier height at MP2/cc-pVQZ level. Moreover, there is a possibility that this value could be further lowered by the addition of more diffuse functions in the basis set. Therefore, it seems reasonable to conclude that the classical barrier height to internal rotation in ethane would not exceed 960 cm^{-1}. This value is much lower than previous theoretical results and close to the experimental results reported so far.[19−21] In the case of barrier to linearity for water and inversion barrier for ammonia, it is difficult to put an upper bound as the increase of electron correlation and basis set could affect the relative energy in an opposite direction. From our results of the core correlation effects in water and ammonia, we estimate the barrier height to linearity for water and inversion for ammonia at QCISD(T)/aug-cc-pCVQZ level with all orbitals active would be close to 11153 and 1813 cm^{-1} as the change from QCISD(T)/aug-cc-pVTZ with FCA to QCISD(T)/aug-cc-pCVTZ with full activation of orbitals lowers the barrier height by 81 and 58 cm^{-1}, respectively, in each case. While it is expected that the barrier height to linearity in water would be lowered further by the employment of larger basis set than aug-cc-pVQZ and approach the experimental value very recently derived,[8] the calculated barrier height to inversion in ammonia is relatively in good agreement with experimental value considering the approximations inherent in the fitting procedures of limited rovibrational transition data in this case.[15]

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