

Calculated Infrared Frequencies and Intensities of the HO₂ Radical

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A systematic study of basis set and correlation effects on the harmonic frequencies and infrared intensities of the HO₂ radical has been conducted. Correlation consistent basis sets were employed at the SCF, MBPT(2) through MBPT(4), and CCSD levels of theory. The basis set effects yield the anticipated trends for the geometries and harmonic frequencies. The MBPT(*n*) calculations significantly overestimate the infrared intensities for HO₂. Even at the CCSD level with the largest basis set used (aug-cc-pVTZ), the intensities are 36.2 (*I*₁), 41.9 (*I*₂), and 32.2 km/mol (*I*₃), overestimating the experimental values by factors of 8.0, 3.2, and 4.1, respectively. Comparison with previous work on HO₂ and a discussion of the predictive ability for these methods are made.

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I. Introduction

The radical species HO₂ is an important reaction intermediate in both combustion and atmospheric chemical reactions. For many of these reactions it is important to monitor *in situ* the concentration of HO₂ in order to understand complicated reaction sequences. One way to accomplish this is to examine one of the HO₂ IR absorption lines. Recent experimental work has provided the absolute IR absorption intensities for the ν_1 and ν_2 bands^{1,2} (a follow-up on the determination of the intensity of the ν_3 band³). In ref 1, a comparison was made to two sets of theoretically determined IR intensities^{4,5} and found very poor agreement between theory and experiment. Since the two theoretical papers failed to address the contributions of electron correlation to the IR intensities, we initially set out to perform a simple study with modest basis sets at various levels of correlation. Subsequent to this, we discovered a paper by Watts *et al.*,⁶ in which the HO₂ radical was characterized at a very high level of correlation (CCSD + triples corrections). The results of Watts *et al.*⁶ indicated a similar level of discrepancy with experiment. This result is quite surprising since these levels of theory are expected to be very accurate, with a discrepancy of at most a factor of 2. Since Watts *et al.* had not intended to thoroughly explore the factors of increasing electron correlation and basis set quality, we expanded our study to address these factors. This work presents the results of our study and the implications for the interpretation of the experimental results.

II. Computational Details

All calculations were performed with the ACES II program system.⁷ The geometry, vibrational frequencies (harmonic approximation), and intensities were calculated at the SCF, MBPT(2), MBPT(3), SDQ-MBPT(4), MBPT(4), and CCSD levels of theory. Four basis sets of increasing quality were used. These were the cc-pVDZ ([3s2p1d/2s1p]),⁸ aug-cc-pVDZ ([4s3p1d/3s1p]),⁹ cc-pVTZ ([4s3p2d1f/3s2p1d]),⁸ and aug-cc-pVTZ ([5s4p2d1f/4s2p1d])⁹ correlation consistent basis sets of Dunning and co-workers. These basis sets were specifically designed to give increasingly better results for correlated calculations. The SCF frequencies and intensities were calculated via analytical second derivatives, while at all other levels of theory the results were obtained via finite difference of the analytical first derivatives. A UHF reference was employed throughout;

spin contamination was found to be negligible. ($\langle S^2 \rangle$ at the SCF level was never larger than 0.77 for any basis set.)

III. Results

The optimized geometries for all basis sets and levels of theory are shown in Table 1. With the cc-pVDZ basis set, improvement of the wave function from the SCF level of theory to the CCSD level gives a continuous increase in the length of the O—O bond. The difference between SCF and CCSD results is only 0.03 Å. For the O—H bond, there is a similar increase from 0.952 to 0.976 Å. In this case, the largest effect of correlation occurs at the MBPT(2) level of theory. A concomitant change in the H—O—O angle is the decrease from 105.90° to 104.21°.

With the aug-cc-pVDZ basis, there is a slight contraction in the bond lengths and a very small increase in the bond angle at the SCF level when compared to the SCF values with the cc-pVDZ basis set. This is to be expected as the aug-cc-pVDZ basis adds diffuse s and p functions, thereby allowing the electrons to localize more effectively in the bonds. The same trends in going from the SCF level to CCSD are found with this basis set as with the cc-pVDZ basis set. The O—O bond is the geometry parameter most susceptible to the change in basis set. Whereas the SCF value for the O—O bond is slightly smaller with the aug-cc-pVDZ basis, this is reversed at the correlated level. At all levels of correlation, the O—O bond is up to 0.01 Å longer. This is in contrast to the O—H bond, which has its largest difference (0.002 Å) between basis sets at the SCF level. Additionally, the O—O—H bond angle differs by at most 0.08° (MBPT(2) level) between basis sets.

For the larger cc-pVTZ basis, there is a continued contraction in the bond lengths relative to the two cc-pVDZ basis sets. As these basis sets were designed for correlated wave functions, it is natural that this is where the largest changes are found. As with the aug-cc-pVDZ basis, the O—O bond undergoes larger changes than the O—H bond. Since both the O—H and O—O bonds are shorter, the O—O—H angle has a greater change (0.34°, CCSD level) between cc-pVTZ and aug-cc-pVDZ. With the aug-cc-pVTZ basis, the progressive improvement in basis sets has essentially reached its limit, at least with respect to geometry. At the CCSD level, the geometry is basically the same as with the cc-pVTZ basis. The angle only differs by 0.11°. Comparing this last result to the highest level calculation of Watts *et al.* (included in Table 1), we find that the bond lengths are all slightly longer with a corresponding decrease in the bond angle. Although CCSD(T) calculations were not performed in our study, the

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TABLE 1: Geometries and Total Energies for the HO₂ Radical (Bond Lengths in angstroms, Angles in degrees, and Total Energy in hartrees)

level of theory	R(O-O)	R(O-H)	θ(O-O-H)	total energy
cc-pVDZ Basis				
SCF	1.303	0.952	105.90	-150.189 913
MBPT(2)	1.314	0.976	104.50	-150.542 530
MBPT(3)	1.315	0.971	104.73	-150.550 827
SDQ-MBPT(4)	1.324	0.975	104.40	-150.558 565
MBPT(4)	1.329	0.977	104.12	-150.567 484
CCSD	1.331	0.976	104.21	-150.561 406
aug-cc-pVDZ Basis				
SCF	1.302	0.950	105.93	-150.204 906
MBPT(2)	1.322	0.977	104.42	-150.586 570
MBPT(3)	1.322	0.971	104.78	-150.593 857
SDQ-MBPT(4)	1.331	0.975	104.40	-150.602 845
MBPT(4)	1.339	0.978	104.06	-150.615 605
CCSD	1.339	0.975	104.18	-150.605 658
cc-pVTZ Basis				
SCF	1.301	0.947	106.11	-150.238 662
MBPT(2)	1.307	0.970	104.66	-150.713 881
MBPT(3)	1.307	0.963	105.03	-150.720 832
SDQ-MBPT(4)	1.315	0.967	104.66	-150.727 702
MBPT(4)	1.322	0.971	104.24	-150.745 734
CCSD	1.321	0.967	104.52	-150.729 443
aug-cc-pVTZ Basis				
SCF	1.301	0.947	106.18	-150.242 328
MBPT(2)	1.307	0.970	104.79	-150.739 156
MBPT(3)	1.307	0.962	105.15	-150.745 766
SDQ-MBPT(4)	1.315	0.966	104.78	-150.752 587
MBPT(4)	1.323	0.971	104.39	-150.772 342
CCSD	1.321	0.966	104.63	-150.754 381
ROHF-MBPT(2) ^a	1.313	0.976	104.53	-150.542 933
ROHF-CCSD ^a	1.332	0.976	104.20	-150.561 283
CCSD(T)/TZ2P ^b	1.333	0.970	104.18	-150.793 523
BP/TZVPD ^c	1.347	0.991	104.8	
experiment ^d	1.331	0.971	104.29	

^a Calculations performed with the cc-pVDZ basis set. ^b Reference 6. TZ2P basis is [5s3p2d1f/3s2p1d]. ^c DFT results of ref 10. ^d Reference 11.

difference in geometries between the SDQ-MBPT(4) and full MBPT(4) results provides a good measure of the change between CCSD and CCSD(T), i.e., the affect of noniterative triple excitations. For the aug-cc-pVTZ basis set these differences are 0.008 Å (O-O), 0.005 Å (O-H), and -0.39°, giving predicted "CCSD(T)" values of 1.329 Å (O-O), 0.971 Å (O-H), and 104.23° (O-O-H). These values agree very well with those of Watts *et al.* and experiment (also given in Table 1). It is readily apparent that at these levels of theory there is excellent agreement between theory and experiment for the geometry of HO₂.

The harmonic frequencies (Table 2) reflect the changes found in the geometry at the various computational levels of theory. With the cc-pVDZ basis, each of the vibrations decreases from the SCF to the CCSD level of theory. The changes are 99 cm⁻¹ for the O-O stretch (ν_3), 142 cm⁻¹ for the O-O-H bend (ν_2), and 362 cm⁻¹ for the O-H stretch (ν_1). Larger decreases are found with the aug-cc-pVDZ basis set: 131, 154, and 395 cm⁻¹, respectively. Consistent with the change in the geometry, the decreases proceed without breaks in the progression of increasing level of theory. The frequencies are smaller at the correlated levels of theory for the aug-cc-pVDZ basis set, while slightly larger at the SCF level. As noted earlier, the O-O bond is the most susceptible to this change in the basis set; hence, the decrease in the CCSD value for the O-O stretch is 25 cm⁻¹ vs 1 and 12 cm⁻¹ for the bend and the O-H stretch, respectively.

For the larger basis sets, similar results are found. The cc-pVTZ basis set leads to larger SCF frequencies than for the cc-pVDZ basis sets. The aug-cc-pVTZ basis has the same trends compared to the cc-pVTZ basis as found for the corresponding cc-pVDZ basis sets. The cc-pVTZ basis set shows decreases in

cm⁻¹ for the O-O stretch, O-O-H bend, and O-H stretch, respectively. With the larger aug-cc-pVTZ basis, these changes are 77, 129, and 393 cm⁻¹, respectively. For the O-H stretch, the CCSD/cc-pVTZ frequency is larger than its CCSD/cc-pVDZ counterpart, whereas this is not found for the CCSD/aug-cc-pVTZ and CCSD/aug-cc-pVDZ pair. The geometry difference (0.009 Å) is the same for both pairs, suggesting that the largest basis set gives a different description of the potential energy surface. Comparing our best results (CCSD/aug-cc-pVTZ) to experiment, we find that the vibrations are overestimated by 85, 81, and 219 cm⁻¹ for the O-O stretch, O-O-H bend, and O-H stretch, respectively. Even the highest level result of Watts *et al.* shows differences of 40, 47, and 260 cm⁻¹. These remaining discrepancies in the frequencies are due mostly to anharmonic corrections.

The infrared intensities show interesting behavior with the cc-pVDZ basis set. Simply going to the MBPT(2) level leads to I_3 doubling in value from the SCF value (94.4 km/mol vs 46.5 km/mol). As the level of perturbation theory is improved, I_3 decreases in value but still remains above the SCF value. At the CCSD level, I_3 falls below the SCF value (31.2 km/mol); however, it is still approximately a factor of 4 larger than the experimentally determined value (see Table 2). For I_2 , the intensity shows a different response to increasing the level of correlation. I_2 decreases from 51.1 to 28.7 km/mol from SCF to MBPT(2), then increases to 38.2 km/mol at MBPT(3), and decreases slightly to 33.0 km/mol at full MBPT(4). The CCSD result is almost identical to the MBPT(3) level, having a value of 38.1 km/mol. The comparison with experiment for I_2 is not quite as bad as for I_3 , being only a factor of 2.9 higher. The intensity for the O-H stretch is the only one which follows a trend with increasing level of theory. I_1 is 71.0 km/mol at the SCF level, which is nearly halved in going to MBPT(2) (39.4 km/mol). This decrease continues until at the CCSD level the value of I_1 is 27.2 km/mol. However, this band has the largest error compared to experiment, being a factor of 6.0 higher.

The aug-cc-pVDZ results for the intensities parallel those found with the cc-pVDZ basis. Comparing between corresponding levels of theory, however, we do not find consistent qualitative changes. For I_3 , the values are smaller at SDQ-MBPT(4) and CCSD. For I_1 , only the SCF value is smaller, whereas at all correlated levels the value is higher. I_2 is the only intensity which is consistent at all levels of theory, being higher. The changes at any level of theory, however, are not very large. The aug-cc-pVDZ values differ from experiment by factors of 3.8, 3.2, and 6.7 for I_3 , I_2 , and I_1 , respectively.

The values of the intensities for the larger cc-pVTZ and aug-cc-pVTZ basis sets do not change very much from aug-cc-pVDZ. The error factors for the cc-pVTZ and aug-cc-pVTZ intensities are 4.3 and 4.1 (I_3), 3.2 and 3.2 (I_2), and 7.6 and 8.0 (I_1), respectively. Even the best theoretical results of Watts *et al.*⁶ differ by factors of 4.7 (I_3), 3.1 (I_2), and 7.0 (I_1). Comparing our best theoretical results to those of Watts *et al.* shows that we have similar values.

Recent work by Dobbs and Dixon¹⁰ has focused on the predictive capability of density functional theory (DFT) for infrared intensities. One of the small molecules they studied was HO₂. The geometries for various DFT calculations are not in as good agreement with experiment as for high level *ab initio* results, but I_1 and I_3 are in significantly better agreement with experiment than our results (or those of Watts *et al.*), with I_2 only slightly better. The best results of Dobbs and Dixon are also displayed in Tables 1 and 2.

IV. Discussion

The continued discrepancy between *ab initio* theory and experiment for the infrared intensities is disturbing. In the current

TABLE 2: Harmonic Frequencies (Intensities) and Total Dipole Moments for the HO₂ Radical (Frequencies in cm⁻¹ and Intensities in km/mol)

level of theory	ν_3	ν_2	ν_1	dipole (D)
cc-pVDZ Basis				
SCF	1245 (46.5)	1599 (51.1)	4042 (71.0)	2.045
MBPT(2)	1235 (94.4)	1459 (28.7)	3680 (39.4)	2.191
MBPT(3)	1203 (74.0)	1495 (38.2)	3760 (34.8)	2.115
SDQ-MBPT(4)	1185 (62.4)	1468 (35.6)	3697 (29.6)	2.126
MBPT(4)	1177 (65.5)	1445 (33.0)	3657 (26.3)	2.130
CCSD	1146 (31.2)	1457 (38.1)	3680 (27.2)	2.160
aug-cc-pVDZ Basis				
SCF	1252 (47.6)	1610 (55.1)	4063 (62.3)	1.953
MBPT(2)	1198 (94.6)	1450 (31.6)	3644 (42.0)	2.159
MBPT(3)	1174 (74.2)	1491 (41.8)	3741 (37.8)	2.089
SDQ-MBPT(4)	1157 (62.1)	1464 (38.3)	3673 (31.5)	2.098
MBPT(4)	1143 (66.3)	1434 (34.9)	3619 (28.3)	2.099
CCSD	1121 (29.9)	1456 (41.5)	3668 (30.0)	2.146
cc-pVTZ Basis				
SCF	1259 (47.4)	1604 (55.3)	4060 (63.0)	2.002
MBPT(2)	1246 (93.9)	1467 (28.9)	3689 (45.6)	2.187
MBPT(3)	1226 (74.0)	1506 (41.2)	3785 (41.7)	2.109
SDQ-MBPT(4)	1211 (62.3)	1482 (38.3)	3725 (35.9)	2.123
MBPT(4)	1195 (67.6)	1451 (33.8)	3665 (32.2)	2.135
CCSD	1184 (33.7)	1476 (41.6)	3720 (34.1)	2.154
aug-cc-pVTZ Basis				
SCF	1260 (46.9)	1602 (54.6)	4048 (62.9)	1.974
MBPT(2)	1240 (91.5)	1460 (29.3)	3618 (47.4)	2.163
MBPT(3)	1224 (72.4)	1503 (41.4)	3718 (44.1)	2.092
SDQ-MBPT(4)	1207 (60.6)	1479 (38.6)	3658 (37.5)	2.102
MBPT(4)	1188 (66.0)	1444 (34.2)	3588 (33.4)	2.114
CCSD	1183 (32.2)	1473 (41.9)	3655 (36.2)	2.138
ROHF-MBPT(2) ^a	1198 (98.6)	1460 (30.5)	3683 (39.0)	2.188
ROHF-CCSD ^a	1146 (30.7)	1457 (38.1)	3680 (27.2)	2.158
CCSD(T)/TZ2P ^b	1138 (36.9)	1439 (39.8)	3696 (31.7)	
BP/TZVPD ^c	1118 (11.8)	1377 (33.8)	3391 (16.8)	
experiment	1098 (7.9 ± 2.0) ^d	1392 (13.0 ± 3.6) ^d	3436 (4.5 ± 1.3) ^d	2.090 ± 0.034 ^e

^a Calculations performed with the cc-pVDZ basis set. ^b Reference 6. TZ2P basis is [5s3p2d1f/3s2p1d]. ^c DFT results of ref 10. ^d Reference 2. ^e Reference 12.

wave function are easily checked. One possibility is that the UHF reference is spin contaminated; however, as mentioned earlier, at no time did $\langle S^2 \rangle$ exceed 0.77 in any of the calculations. To further check this, we performed correlated ROHF based calculations with the cc-pVDZ basis using recently developed techniques.^{13,14} The calculations at the MBPT(2) and CCSD levels revealed no significant differences with their UHF counterparts (see Tables 1 and 2). Another possibility is that the ground state has significant multireference character. An examination of the T_2 amplitudes at the CCSD level gives no indication of a multireference nature of the $^2A''$ ground state (largest $|T_2|$ is 0.031, aug-cc-pVTZ basis). For T_1 , the largest amplitude is 0.127 (corresponding to $1a'' \rightarrow 2a''$ for the β electrons), but this does not necessarily suggest multireference character. Recent work by Lee *et al.*¹⁵ discussed the importance of a T_1 diagnostic as an indicator, which may suggest multireference character and how it can be used to understand differences in molecular properties between CCSD and Brueckner methods. For HO₂, an approximate value of the T_1 diagnostic for open-shell systems¹⁶ is only 0.020, which supports the conclusion that this system does not have significant multireference character. In addition, work by Watts, Urban, and Bartlett¹⁷ on BeO using CCSD and Brueckner methods did not find significant differences between the approaches for the infrared intensity, despite a similarly large CCSD $|T_1|$ of 0.09. It is interesting to note, however, that T_1 may play an important role in the calculated intensity of the I_3 band. Some TZ2P basis set results of Watts *et al.*⁶ for I_3 are 23.1 km/mol (QCISD) and 33.2 km/mol (CCSD). This large difference could be ascribed to the lack of several T_1 terms in the QCISD method. Inclusion of noniterative triples corrections to both QCISD and CCSD brings the I_3 values back into

agreement (29.4 and 30.4 km/mol, respectively).⁶ A discussion of the differences between CCSD and QCISD can be found in ref 18.

There is excellent agreement between theory and experiment for the geometry; however, this property is much less susceptible to changes in the wave function than the intensities. The harmonic frequencies are a second-order property like the intensities. These are in fairly good agreement with experiment. However, the frequencies are a measure of the motion of the nuclei in the potential generated by the electrons. They also may not be as sensitive to changes in the wave function as the intensities. Since the intensities are related to the change in the dipole moment, we examined how well our wave function describes this property. The values of the dipole moment are given in Table 2. Comparing to experiment, in general, the dipole is underestimated at the SCF level. There is a significant increase at MBPT(2) which overestimates the dipole, followed by a smaller decrease at MBPT(3). The MBPT(3) values are all fortuitously within experimental error. Improvement of the wave function up to CCSD leads to a larger dipole moment. Our best result (CCSD/aug-cc-pVTZ) has $\mu = 2.138$ D. This is only slightly (0.014 D) outside the experimental error. Given this excellent agreement for the dipole moment, it is surprising that the intensities are described so poorly.

Recent theoretical work by Thomas *et al.*¹⁹ examined the accuracy of high level calculations on the properties of a number of small closed-shell molecules. They were able to compare their calculated IR intensities with 21 experimentally determined values. With only 3 exceptions, all the calculated intensities were well within a factor of 2 (average is a factor of 1.34, usually overestimated). In fact, the three exceptions all underestimated the experimental values. One of these three was for HCN, and the other two were for NH₃. Thus, the work of Thomas *et al.*

provides no insight as to why the intensities are predicted to be so large for HO₂. Since the highest level of calculations performed by this group were the ones by Watts *et al.*,⁶ this further complicates the picture. At these levels of theory, it is difficult to believe that an RHF wave function will be described any better than an uncontaminated UHF wave function, especially in light of the fact that there is no significant difference between UHF and ROHF results at the CCSD level.

A final consideration is the possibility that the reported experimental values for the intensities are incorrect. An examination of the methods of Zahniser *et al.*¹⁻³ shows that these authors were very thorough in their consideration of possible sources of error. In addition, a second-order property such as the intensities may need even better basis sets than those used here to provide quantitative results. We believe further theoretical work is needed before any substantive comparison can be made with the experimental work.

V. Conclusions

We have presented the results of a systematic study of the effects of increasing basis set quality and level of correlation for ground-state properties of the HO₂ radical. While we were able to accurately describe the geometry and give quite reasonable values for the harmonic frequencies, we did not achieve very good agreement with the experimentally determined infrared intensities. Our results are consistent with previous *ab initio* work on the HO₂ radical. High level calculations on a number of small closed-shell molecules does not help to explain why our results differ so greatly from experiment. Density functional theory describes two of the intensities better than our results but still leaves unanswered the quite fundamental question about the CCSD and CCSD(T) results with high-quality basis sets. Larger basis sets may provide the answer to this discrepancy; however, without a more complete understanding of the behavior of these methods for open-shell systems, it may prove difficult to provide any sort of predictive ability, except for perhaps relative strengths. A systematic study of open-shell molecules for which the infrared intensities are known may provide more insight into the ability of these methods to accurately describe this particular property.

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