5004 *J. Phys. Chem. A* **1997,** *101,* 5004−5009

# Density Functional Study of Hydrogen-Bonded Systems: The Water−Carbon Monoxide Complex

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*Received: November 7, 1996; In Final Form: April 11, 1997*[⊗]

Studies on the abilities of different density functional methods applied to hydrogen-bonded complexes have been carried out on the water−carbon monoxide complex. Various local and nonlocal exchange-correlation functionals have been used in the investigation of the structure, energetics, and vibrational properties of the 1:1 complex. A triple-$\zeta$ basis set, added with diffuse functions and multiple sets of polarization functions (*e.g.*, 6-311++G(2d,2p)), has been used throughout the study. The comparison with the experimental data from the molecular beam measurements and also the results from previous ab initio calculations (second-order Møller-Plesset perturbation theory and coupled cluster with the single, double, and triple excitations) shows good performance of the complex energetics and structural parameters. Especially the hybrid methods mixing the Hartree−Fock exchange with DFT exchange-correlation present their strength for the description of hydrogen-bonded complexes. Additionally, the hybrid methods give good approximations for the vibrational shifts upon complexation comparable to the recent experimental matrix isolation results for the two stable complex structures $H_2O$−CO and $H_2O$−OC.

## Introduction

Molecular complexes are very common in molecular science, and a great amount of experimental and theoretical information has become available.[1−9] The weak interactions are common in atmospheric chemistry, catalytic reactions, surface chemistry, material science, and biological processes. How molecules initially select one of several reaction channels, how molecules bind together in complex biochemical systems, and how they are oriented at surfaces and in small aggregates are all questions that are related to small energetic differences. The fast development of both sensitive experimental methods and efficient computational software and hardware has guided the interest toward weak interactions, which might help us to see deeper into the chemical and physical nature of the matter.

Recently, the second-order perturbation theory (MP2) has become a standard method applied for intermolecular interactions. However, the approach is limited to relatively small systems due to the large computational expense and vast need of computer memory and disk space. In contrast, the density functional method represents an attractive alternative method for the study of electronic structures and vibrational properties of molecular complexes. The DFT approach is not equally computer-demanding as the other advanced correlation methods as the need for computational resources is formally scaled as $N^3$, where $N$ is the number of basis functions. The simplifying factor is that the DFT uses general functionals of electron density to model exchange and correlations. The fast and efficient optimization algorithms have enhanced the possibilities of the DFT approach to be competitive with the widely used traditional ab initio methods.[10]

The interaction between molecules is described by an intermolecular potential energy surface, where small changes in the energy might lead to large distortions. Therefore, calculations with high accuracy are needed. Also, electron correlation plays a very important role in the determination of the structure and properties of the weakly interactive system. Up to now some extensive studies on hydrogen-bonded complexes, using DFT theory, have been performed. The studies by Salahub[11] concentrating mostly on the $H_2O$ dimer, the studies of $H_5O_2^+$ and HF dimer by Latajka,[12] and the DFT studies of various hydrogen-bonded and van der Waals complexes by Hobza et al.[13] have shown that the local density approximation (LDA) is incapable of describing the properties of the hydrogen bond. However, the nonlocal functionals have been noted to result in a closer agreement with experimental and traditional ab initio results.[11−13]

The interaction between water and carbon monoxide represents an ideal model for testing of the DFT functionals. In addition to the weak interaction between the subunits, the electric response properties of CO play a major role in the complexation.[14−16] This poses a challenge for the theoretical capabilities in the case of a hydrogen bond when determining which end of CO is acting as a better proton acceptor. The SCF calculations constantly give the wrong sign for the dipole moment of CO, and only the inclusion of electron correlation is able to ensure the correct sign corresponding to the structure of $C^-O^+$. As the electron density is very nonuniform, the nonlocal (gradient) corrections should play an important role in the proper description of the interaction.

Several computational studies of the $H_2O$−CO complex have been published.[17−24] These studies range from semiempirical calculations to MP2 and coupled cluster calculations with large, multiply polarized basis sets. Experimental structural information has been acquired in the molecular beam experiments with molecular electric resonance spectroscopy,[25] Fourier transform microwave absorption spectroscopy,[25,26] and tunable far-infrared laser studies.[26] Some vibrational properties of the complex have

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

S1089-5639(96)03727-9 CCC: $14.00

**TABLE 1: Calculated Complex Properties of the $H_2O$−CO Complex Using Different DFT Functionals and the 6-311++G(2d,2p) Basis Set**

| | $r(H_a{-}O)$ | $r(O{-}H_b)$ | $r(H_b{-}C)$ | $r(C{\equiv}O)$ | $\alpha_1$(HOH) | $\alpha_2(OH_bC)$ | $\alpha_3(H_bCO)$ |
|---|---|---|---|---|---|---|---|
| HFB | 0.9810 | 0.9816 | 3.0678 | 1.1479 | 104.13 | 182.63 | 187.33 |
| B-VWN | 0.9654 | 0.9670 | 2.6555 | 1.1346 | 104.62 | 188.23 | 187.53 |
| B-VWN5 | 0.9669 | 0.9683 | 2.7039 | 1.1357 | 104.51 | 183.67 | 171.68 |
| B-LYP | 0.9705 | 0.9734 | 2.3914 | 1.1359 | 104.79 | 190.77 | 172.92 |
| B-PL | 0.9675 | 0.9688 | 2.7040 | 1.1362 | 104.56 | 188.12 | 172.31 |
| B-P86 | 0.9699 | 0.9739 | 2.3166 | 1.1359 | 104.45 | 189.00 | 173.50 |
| B-PW91 | 0.9678 | 0.9709 | 2.4130 | 1.1351 | 104.41 | 187.95 | 173.51 |
| Becke3-LYP | 0.9604 | 0.9631 | 2.3779 | 1.1239 | 105.36 | 190.95 | 172.99 |
| Becke3-P86 | 0.9585 | 0.9621 | 2.3093 | 1.1229 | 105.15 | 189.37 | 173.44 |
| Becke3-PW91 | 0.9587 | 0.9615 | 2.4022 | 1.1239 | 105.09 | 188.50 | 173.38 |
| Becke3-LYP(M) | 0.9536 | 0.9554 | 2.4759 | 1.1180 | 105.61 | 190.75 | 187.19 |
| MP2 | 0.9569 | 0.9594 | 2.3406 | 1.1351 | 104.58 | 189.16 | 186.71 |
| CCSD(T) | 0.9580 | 0.9594 | 2.3651 | 1.1337 | 104.36 | 186.34 | 190.12 |

been identified in low-temperature matrices,[27−29] and a conclusive identification of the two complex structures $H_2O$−CO and $H_2O$−OC has recently been done in argon, krypton, and xenon matrices.[24,30] This enables a systematic and wide comparison between the Hartree−Fock-based and experimental results with the widely available family of various density functional methods.

## Details of Calculations

The DFT functionals considered in this paper are separated into exchange and correlation parts. The exchange functional used thoroughly this study is the Becke 88 functional,[31] which includes the Slater exchange along with corrections involving the gradient of the electron density (nonlocal exchange). The Slater type exchange functional[32] corresponding to the free electron gas was omitted from this investigation because it has been shown to be very inefficient to describe weak, long-range interactions.[12,33] Several types of correlation functionals were applied as follows: the Vosko−Wilk−Nusair (VWN) parametrization of the exact uniform gas,[34] the VWN V functional fitted to the Ceperley−Adler solution to the uniform electron gas,[34] the gradient-corrected functionals by Lee, Yang, and Parr (LYP),[35] the local non-gradient-corrected functional by Perdew (PL),[36] the gradient correction of Perdew coupled with his local correlation functional (P86),[37−39] and the Perdew and Wang gradient-corrected correlation functional (PW91).[39]

Recently, Pople and co-workers[40] proposed a notation in which X-C represents the exchange and correlational functionals, respectively. This nomination has also been adopted in this paper, and for example, B-LYP indicates the Becke exchange functional coupled with the Lee−Yang−Parr correlation.

Additionally, we have included in this study the hybrid methods recently suggested by Becke.[41,42] These functionals include contributions from the Hartree−Fock and DFT exchange correlations, and have been determined as three-parameter functionals fitted to various atomic properties. These functionals are designated as the Becke3 functionals and are combined with the LYP, P86, and PW91 correlation functionals.

The last functional considered in this paper is a modification of the Becke3-LYP formulation, where

$$E_{XC} = E_{XC}^{LSDA} + \alpha_0(E_{XC}^{exact} - E_X^{LSDA}) + \alpha_X \Delta E_X^{B88} + \alpha_C \Delta E_C^{P86} \qquad (1)$$

The original parameters of the Becke3 hybrid method ($\alpha_0 = 0.20$, $\alpha_X = 0.72$, $\alpha_C = 0.81$) have been reparametrized to be $\alpha_0 = 0.35$, $\alpha_X = 0.72$, and $\alpha_C = 0.81$, as suggested by Latajka and co-workers in the study of the proton transfer barrier of $(FHF)^-$.[33] This modification is denoted as Becke3-LYP(M).

The applied basis set was the split-valence, triple-ζ, 6-311G-type Gaussian[43] function, added with multiple sets of diffuse[44] and polarization[45] functions to give the 6-311++G(2d,2p) basis set. This basis set has been successfully used in the studies of the complex properties of the $(HF)_2$ dimer[12] and the proton transfer barrier in $(FHF)^-$,[33] employing various DFT functionals. Especially, for the interaction between water and carbon monoxide, when combined with the second-order perturbation theory, this basis set has been noted to give accurate results and a reasonable small basis set superposition error.[23,24]

The binding energies for the $H_2O$−CO complexes were considered as the difference between the total energy of the complex and the separate monomers at infinitive distance. Additionally, the Boys−Bernardi[46] counterpoise correction was applied to give the BSSE-corrected interaction energies. This also gives the opportunity to study the BSSE affecting the interaction energy compared with that of the MP2 level of theory.

All calculations were performed within the framework of the ab initio closed shell approximation using the Gaussian 94 package of computer codes.[47] The gradient procedure was applied for the full geometry optimization of the monomer and complex species. The errors arising from the numerical integration were reduced by the “finegrid” option in the Gaussian 94 program, which corresponds roughly to 7000 gridpoints/atom. All calculations were carried out on the SGI Power Challenge and CRAY C94 supercomputers at the CSC-Center for Scientific Computing Ltd. (Espoo, Finland).

## Results and Discussion

The properties of $H_2O$[11,48] and CO[49−52] monomers have been previously well characterized by DFT, and therefore, we will discuss here only the properties of the complexes.

**Structures.** The optimized complex structures for $H_2O$−CO and $H_2O$−OC are presented in Tables I and 2, respectively. $H_\alpha$ describes the unbound hydrogen, and $H_b$ describes the hydrogen-bonded hydrogen of the water monomer. Experimentally only the carbon-attached $H_2O$−CO complex has been observed with a structure where the intermolecular angle deviates from a linear hydrogen-bonded structure by 11.5°, having an interaction distance of 2.41 Å ($H_b \cdots C$).[27] The $H_2O$−OC has been identified only in low-temperature Kr and Xe matrices, and the low-energy barrier of a few kilojoules per mole between the two energy minima has been addressed upon observing only the lowest-energy structure in the gas phase.[30]

For both the $H_2O$−CO and $H_2O$−OC complexes, the O−H bonds seem to be larger than calculated at the MP2 and CCSD(T) levels of theory. Only the modified Becke3-LYP(M) functional produces O−H bonds shorter than the MP2 and

**TABLE 2: Calculated Complex Properties of the $H_2O$−OC Complex Using Different DFT Functionals and the 6-311++G(2d,2p) Basis Set**

| | $r(H_a{-}O)$ | $r(O{-}H_b)$ | $r(H_b{-}O)$ | $r(O{\equiv}C)$ | $\alpha_1(HOH)$ | $\alpha_2(OH_bO)$ | $\alpha_3(H_bOC)$ |
|---|---|---|---|---|---|---|---|
| HFB | 0.9812 | 0.9812 | 3.4083 | 1.1493 | 104.12 | 177.33 | 172.60 |
| B-VWN | 0.9657 | 0.9658 | 3.1140 | 1.1364 | 104.52 | 177.24 | 174.19 |
| B-VWN5 | 0.9670 | 0.9672 | 3.1390 | 1.1374 | 104.49 | 177.32 | 174.04 |
| B-LYP | 0.9708 | 0.9713 | 2.5019 | 1.1384 | 104.61 | 188.89 | 169.43 |
| B-PL | 0.9677 | 0.9678 | 3.1308 | 1.1380 | 104.48 | 177.26 | 174.76 |
| B-P86 | 0.9702 | 0.9705 | 3.0598 | 1.1383 | 104.24 | 177.31 | 173.36 |
| B-PW91 | 0.9681 | 0.9683 | 3.1459 | 1.1372 | 104.24 | 178.16 | 178.94 |
| Becke3-LYP | 0.9607 | 0.9613 | 2.4048 | 1.1265 | 105.21 | 170.76 | 170.88 |
| Becke3-P86 | 0.9590 | 0.9598 | 2.4389 | 1.1256 | 104.94 | 176.51 | 178.81 |
| Becke3-PW91 | 0.9587 | 0.9591 | 2.6832 | 1.1262 | 104.95 | 176.56 | 179.62 |
| Becke3-LYP(M) | 0.9537 | 0.9542 | 2.4935 | 1.1204 | 105.45 | 180.67 | 188.72 |
| MP2 | 0.9571 | 0.9575 | 2.3213 | 1.1373 | 104.50 | 191.16 | 185.85 |
| CCSD(T) | 0.9580 | 0.9583 | 2.3225 | 1.1357 | 104.39 | 187.50 | 187.27 |

**TABLE 3: Calculated Vibrational Frequencies (in cm$^{-1}$) for the $H_2O$−CO Complex Using Different DFT Functionals and the 6-311++G(2d,2p) Basis Set[a]**

| | $\omega 1$ | $\omega 2$ | $\omega 3$ | $\omega 4$ | $\omega 5$ | $\omega 6$ | $\omega 7$ | $\omega 8$ | $\omega 9$ |
|---|---|---|---|---|---|---|---|---|---|
| HFB | 3657.42 | 3559.52 | 2052.37 | 1600.97 | 189.87 | 105.77 | 37.24 | 34.40 | 25.08 |
| | (53.8) | (7.4) | (66.9) | (51.3) | (104.5) | (64.5) | (1.0) | (12.5) | (5.0) |
| B-VWN | 3814.72 | 3712.76 | 2129.61 | 1639.05 | 272.82 | 168.27 | 55.66 | 53.50 | 46.72 |
| | (82.3) | (31.1) | (67.4) | (47.2) | (89.3) | (77.0) | (7.1) | (5.3) | (5.6) |
| B-VWN5 | 3798.69 | 3698.31 | 2122.22 | 1636.51 | 262.53 | 156.20 | 53.51 | 51.93 | 43.78 |
| | (80.5) | (26.4) | (67.4) | (50.4) | (101.8) | (72.3) | (8.7) | (3.1) | (4.2) |
| B-LYP | 3762.63 | 3652.18 | 2126.58 | 1612.00 | 339.80 | 212.26 | 88.35 | 60.75 | 56.61 |
| | (108.0) | (81.0) | (66.1) | (40.8) | (72.6) | (83.1) | (1.6) | (7.3) | (10.2) |
| B-PL | 3793.01 | 3692.07 | 2119.31 | 1634.11 | 261.65 | 161.85 | 53.08 | 52.78 | 44.20 |
| | (81.1) | (26.0) | (67.4) | (47.6) | (90.3) | (76.6) | (5.4) | (9.1) | (3.3) |
| B-P86 | 3784.30 | 3659.02 | 2135.54 | 1610.24 | 365.34 | 228.79 | 94.38 | 59.03 | 57.85 |
| | (103.9) | (116.6) | (66.9) | (39.4) | (72.4) | (82.1) | (1.3) | (94.4) | (9.3) |
| B-PW91 | 3808.07 | 3690.80 | 2140.26 | 1618.25 | 339.70 | 212.65 | 74.43 | 58.09 | 55.89 |
| | (101.0) | (83.3) | (66.4) | (42.6) | (78.5) | (79.9) | (2.2) | (3.6) | (8.5) |
| Becke3-LYP | 3906.65 | 3797.98 | 2227.12 | 1645.73 | 343.14 | 217.76 | 93.77 | 62.72 | 59.02 |
| | (127.8) | (84.0) | (79.0) | (47.2) | (78.0) | (85.7) | (1.9) | (6.7) | (12.4) |
| Becke3-P86 | 3939.56 | 3818.45 | 2240.28 | 1647.74 | 368.79 | 234.32 | 100.05 | 66.02 | 63.24 |
| | (125.7) | (116.8) | (79.3) | (46.1) | (79.1) | (85.2) | (1.7) | (4.4) | (11.4) |
| Becke3-PW91 | 3939.67 | 3825.01 | 2233.66 | 1649.08 | 341.11 | 216.29 | 81.92 | 66.29 | 62.85 |
| | (120.8) | (85.1) | (79.2) | (48.8) | (84.3) | (82.3) | (3.2) | (3.8) | (10.3) |
| Becke3-LYP(M) | 4000.46 | 3898.25 | 2278.47 | 1681.16 | 314.25 | 201.01 | 81.94 | 63.84 | 58.30 |
| | (128.2) | (57.1) | (91.2) | (53.4) | (86.8) | (84.0) | (3.1) | (6.1) | (13.3) |
| MP2 | 3973.3 | 3849.1 | 2132.6 | 1673.3 | 390.1 | 242.2 | 104.1 | 75.5 | 70.5 |
| | (150.7) | (83.2) | (30.6) | (63.4) | (81.3) | (86.9)‘ | (1.6) | (4.4) | (11.6) |

[a] The numbers in parentheses are the calculated relative intensities (in km mol$^{-1}$).

CCSD(T) calculations. Also, upon formation of a hydrogen bond, the bound O−H bond shows prolongation compared with the unbound O−H bond. This is in accordance with previous reports with $(H_2O)_2$ where the prolongation was found almost constant and not dependent on the functional nor the basis set used.[11,13] However, in the very weak interaction with the oxygen end of CO, the difference between O−$H_\alpha$ and O−$H_\beta$ is almost negligible using noncorrelated functionals, whereas the hybrid functionals tend to show this typical prolongation, nevertheless the weaker interaction.

For the intermolecular distance all functionals are behaving more or less randomly compared with the MP2 and CCSD(T) levels, which show a slight underestimation of the interaction distance compared with the value of 2.41 Å from the molecular jet experiment.[25] For both complex structures the B-LYP functional produces the intermolecular distance quite nicely. The same stands for the B-P86 in the case of the $H_2O$−CO complex. However, all the other nonhybrid functionals show an alarming 0.5−1.0 Å too long intermolecular distance compared with the MP2 and CCSD(T) levels and experimental results. The large variations of the intermolecular distances must be due to the lack of dispersion energy contributions in the functionals, and the well-established electrostatic interaction is not enough to cover the interaction at the level of MP2 and CCSD(T) calculations where the dispersion energy is included. At MP2 level the dispersion energy covers 60% and 80% of the total interaction energy of $H_2O$−CO and $H_2O$−OC complexes, respectively.[23]

Similarly for the hybrid functionals there is a lack of dispersion energy contribution, but the calculated intermolecular distances are better than for the nonhybrid functionals. However, there are a few surprises. Using the Becke3-PW91 functional the intermolecular distance of $H_2O$−CO is overestimated by roughly 0.04 Å compared with the MP2 and CCSD(T) results. Furthermore, for the weaker $H_2O$−OC complex the overestimation is almost 0.4 Å. For the modified Becke3-LYP(M) functional the case is even worse. The intermolecular distance in $H_2O$−CO and $H_2O$−OC is overestimated by 0.14 and 0.17 Å, respectively, compared with the MP2 calculated values. This is mainly due to the improper description of the CO monomer, where the intramolecular bond is predicted to be almost 0.02 Å too short compared with MP2. This is directly reflected on the partial charges of the molecule, as well as the dipole moment, which are much smaller compared with results from all other functionals.

**Vibrational Properties.** The intra- and intermolecular vibrational frequencies together with relative IR intensities for $H_2O$−CO and $H_2O$−OC are presented in Tables 3 and 4, respectively. As concluded for the bond lengths, the intramolecular properties are well reproduced for all functionals.

**TABLE 4: Calculated Vibrational Frequencies (in $cm^{-1}$) for the $H_2O$−OC Complex Using Different DFT Functionals and the 6-311++G(2d,2p) Basis Set**

| | $\omega$1 | $\omega$2 | $\omega$3 | $\omega$4 | $\omega$5 | $\omega$6 | $\omega$7 | $\omega$8 | $\omega$9 |
|---|---|---|---|---|---|---|---|---|---|
| HFB | 3660.98 | 3561.97 | 2041.21 | 1598.84 | 99.44 | 51.33 | 23.08 | 22.30 | 16.58 |
| | (37.9) | (1.7) | (75.4) | (57.7) | (128.9) | (65.4) | (0.1) | (0.1) | (16.7) |
| B-VWN | 3824.79 | 3724.84 | 2114.91 | 1635.92 | 129.49 | 67.83 | 33.74 | 26.54 | 19.59 |
| | (53.0) | (5.0) | (78.7) | (61.0) | (132.0) | (65.0) | (0.0) | (0.4) | (20.3) |
| B-VWN5 | 3809.42 | 3709.46 | 2108.41 | 1623.42 | 126.68 | 66.95 | 32.93 | 25.96 | 20.07 |
| | (51.5) | (4.6) | (78.5) | (60.8) | (131.6) | (65.8) | (0.0) | (0.3) | (19.3) |
| B-LYP | 3778.52 | 3678.84 | 2106.66 | 1607.58 | 176.01 | 101.47 | 49.88 | 38.11 | 30.23 |
| | (82.8) | (13.0) | (84.9) | (53.1) | (103.3) | (80.1) | (0.9) | (14.6) | (10.6) |
| B-PL | 3802.25 | 3702.37 | 2105.13 | 1631.03 | 129.03 | 70.00 | 33.46 | 27.06 | 22.16 |
| | (51.1) | (4.5) | (78.4) | (60.7) | (130.1) | (68.7) | (0.0) | (0.7) | (16.3) |
| B-P86 | 3806.68 | 3703.22 | 2115.59 | 1605.39 | 130.91 | 68.23 | 24.76 | 20.84 | 13.37 |
| | (60.0) | (6.8) | (78.7) | (61.4) | (108.7) | (67.1) | (12.0) | (17.8) | (0.7) |
| B-PW91 | 3827.99 | 3724.73 | 2123.06 | 1613.62 | 129.02 | 64.89 | 21.49 | 17.62 | 10.43 |
| | (58.3) | (6.0) | (78.0) | (61.2) | (116.8) | (65.4) | (0.1) | (14.6) | (20.5) |
| Becke3-LYP | 3921.65 | 3822.10 | 2204.52 | 1641.45 | 199.58 | 119.04 | 65.20 | 40.66 | 31.04 |
| | (108.9) | (21.5) | (102.8) | (59.3) | (105.9) | (88.0) | (0.1) | (13.6) | (9.2) |
| Becke3-P86 | 3954.52 | 3852.19 | 2217.20 | 1645.45 | 211.73 | 131.90 | 54.00 | 36.39 | 32.90 |
| | (102.3) | (24.5) | (103.1) | (68.6) | (128.0) | (81.5) | (0.1) | (6.4) | (7.3) |
| Becke3-PW91 | 3959.98 | 3856.65 | 2213.70 | 1644.39 | 154.58 | 80.73 | 31.76 | 30.80 | 13.61 |
| | (86.2) | (15.8) | (98.2) | (69.2) | (123.2) | (55.3) | (2.9) | (16.7) | (30.6) |
| Becke-LYP(M) | 4011.71 | 3913.45 | 2257.71 | 1678.40 | 190.82 | 106.63 | 53.80 | 31.96 | 25.17 |
| | (104.7) | (21.8) | (114.2) | (69.3) | (134.5) | (80.8) | (0.1) | (3.5) | (11.5) |
| MP2 | 3989.8 | 3871.9 | 2117.6 | 1665.4 | 240.1 | 144.1 | 78.2 | 52.0 | 42.1 |
| | (131.3) | (25.4) | (49.1) | (52.6) | (92.8) | (87.5) | (0.2) | (4.8) | (14.7) |

[a] The numbers in parentheses are the calculated relative intensities (in km $mol^{-1}$).

Therefore, also the intramolecular vibrational modes are close to the values calculated at the MP2 level. Obviously the nonlocal density calculations are in closer agreement with MP2 than local density calculations, but the difference is quite small. For the hybrid methods it should be noted that the deficiency of the Becke3-LYP(M) functional in describing the CO bond properly can also be seen in the calculated monomeric and complexed C≡O stretching frequency. The CO stretching mode is predicted to be about 40 $cm^{-1}$ higher in the complex and about 50 $cm^{-1}$ higher in the monomer that the other hybrid functionals.

The discrepancies between DFT and MP2 for the lower intermolecular frequencies are significantly larger. For the water dimer it was found that the local functionals could differ up to 50%, while the nonlocal functionals could differ up to 28%.[11] This also seems to hold in the case of $H_2O$−CO interaction compared with the MP2 calculations. However, using hybrid functionals these variations may be lowered to 20% and 25%, for $H_2O$−CO and $H_2O$−OC, respectively. The overestimation of the intermolecular distances is, nevertheless, directly affecting the intermolecular frequencies by a lowering effect when the force constants become smaller. The qualitative picture using hybrid functionals is still very promising and supports the use of the functionals in the studies of larger, hydrogen-bonded systems which are beyond current reach of the MP2 level and bigger calculations, due to computer hardware restrictions.

Typically, in hydrogen-bonded complexes, the stretching frequency of the donor associated with the hydrogen bond, in this case the O−$H_\beta$, undergoes a red shift to a lower frequency, compared with the monomer frequency. This is due to the weakening of the hydrogen-bonded O−H bond. On the contrary, the acceptor bond should blue-shift compared with the free monomer. From the results presented in Table 5, it is obvious that both water asymmetric and symmetric stretching modes in $H_2O$−CO show a red shift and the CO stretching mode shows a blue shift.. The water bending mode shows a small blue shift which is typical for hydrogen-bonded bending modes.[53] For the $H_2O$−CO complex the shifts are correctly predicted on all levels of calculation compared with the experimental data from the matrix isolation data. However, the hybrid functionals are showing a larger shift for all the stretching modes than the MP2 level does. The Becke3-LYP(M) functional shows, nevertheless, especially good agreement with the MP2 results. The MP2-calculated and the hybrid DFT-calculated shifts are still larger than the experimental values obtained in the Ar matrix,[24,30] and a factor of 2 or 3 is not an impossible difference. However, in the matrix the surrounding solid rare gas cage perturbs the complex and, therefore, also the vibrational frequencies.

**TABLE 5: Calculated and Experimental Shifts (in $cm^{-1}$) upon Complexation for the Various Monomer Vibrational Fundamentals**

| | $\nu_{as}$(O−H) | $\nu_s$(O−H) | $\delta$(H−O−H) | $\nu$(C≡O) |
|---|---|---|---|---|
| | $H_2O$−CO | | | |
| HFB | −3.08 | −1.28 | 7.77 | 3.27 |
| B-VWN | −8.38 | −9.54 | 10.91 | 4.35 |
| B-VWN5 | −8.91 | −8.59 | 10.02 | 5.31 |
| B-LYP | −16.07 | −25.12 | 14.28 | 5.10 |
| B-PL | −7.69 | −7.93 | 10.01 | 4.31 |
| B-P86 | −22.80 | −44.08 | 15.54 | 5.44 |
| B-PW91 | −18.93 | −32.20 | 14.26 | 5.55 |
| Becke3-LYP | −15.95 | −23.12 | 15.92 | 5.73 |
| Becke3-P86 | −21.24 | −38.25 | 16l.38 | 5.94 |
| Becke3-PW91 | −17.03 | −27.58 | 13.86 | 5.58 |
| Becke3-LYP(M) | −11.79 | −13.57 | 12.74 | 5.91 |
| MP2 | −13.9 | −18.2 | 12.8 | 11.7 |
| experimental[a] | −9.5 | −8.8 | 5.4 | 10.6 |
| | $H_2O$−OC | | | |
| HFB | 0.48 | 1.17 | −3.39 | 1.14 |
| B-VWN | 1.69 | 2.54 | −3.79 | 1.22 |
| B-VWN5 | 1.82 | 2.56 | −3.79 | −7.78 |
| B-LYP | −0.18 | 1.54 | −5.64 | 0.68 |
| B-PL | 1.55 | 2.37 | −4.17 | 1.28 |
| B-P86 | −0.42 | 0.12 | −4.41 | 0.59 |
| B-PW91 | 0.99 | 0.73 | −2.94 | 0.92 |
| Becke3-LYP | −0.95 | 1.00 | −6.68 | 1.45 |
| Becke3-P86 | −6.28 | −4.51 | −6.70 | 3.65 |
| Becke3-PW91 | 3.28 | 4.05 | −6.10 | 0.89 |
| Becke3-LYP(M) | −0.54 | 1.63 | −8.03 | 3.16 |
| MP2 | 2.60 | 4.60 | −2.20 | 3.80 |
| experimental[b] | | | −6.1 | 0.6 |

[a] Ar matrix. [b] Xe matrix.

**TABLE 6: Calculated Energetics of the $H_2O-CO$ and $H_2O-OC$ Complexes Using Various DFT Functionals and the 6-311++G(2d,2p) Basis Set**

| | $H_2O-CO$ | | | $H_2O-OC$ | | | |
|---|---|---|---|---|---|---|---|
| | $E_{tot}$ (au) | $E_{int}{}^{a}$ (kJ mol$^{-1}$) | $E_{int}{}^{b}$ (kJ mol$^{-1}$) | $E_{tot}$ (au) | $E_{int}{}^{a}$ (kJ mol$^{-1}$) | $E_{int}{}^{b}$ (kJ mol$^{-1}$) | $E_{rel}$ (kJ mol$^{-1}$) |
| HFB | −188.961 5600 | −1.612 | −1.215 | −188.961 1678 | −0.583 | −0.292 | 0.923 |
| B-VWN | −191.041 7772 | −2.861 | −2.273 | −191.041 0607 | −0.980 | −0.551 | 1.722 |
| B-VWN5 | −190.571 9014 | −2.578 | −2.003 | −190.571 2631 | −0.902 | −0.460 | 1.543 |
| B-LYP | −189.786 5639 | −5.617 | −4.812 | −189.785 1139 | −1.810 | −1.097 | 3.715 |
| B-PL | −190.561 3223 | −2.603 | −2.057 | −190.560 6742 | −0.902 | −0.506 | 1.551 |
| B-P86 | −189.813 2620 | −5.524 | −4.681 | −189.811 4154 | −0.676 | −0.221 | 4.460 |
| B-PW91 | −189.793 7043 | −3.927 | −3.041 | −189.792 5095 | −0.790 | −0.260 | 2.781 |
| Becke3-LYP | −189.816 4469 | −6.286 | −5.550 | −189.815 0958 | −2.739 | −2.064 | 3.489 |
| Becke3-P86 | −190.228 5574 | −6.430 | −5.692 | −190.226 8445 | −1.933 | −1.107 | 4.585 |
| Becke3-PW91 | −189.733 0279 | −4.778 | −3.918 | −189.731 7480 | −1.417 | −0.689 | 3.229 |
| Becke3-LYP(M) | −190.126 4248 | −4.901 | −4.262 | −190.125 4855 | −2.435 | −1.818 | 2.384 |
| MP2 | −189.461 5907 | | −6.886 | −189.459 8920 | −2.352 | | 4.534 |
| CCSD(T) | −189.430 85 | | −5.293 | −189.429 69 | −3.174 | | 2.119 |

[a] The interaction energy $E_{int}$ is defined as the difference between that of the complex and that of the monomers ($E_{int} = E_{complex} - \sum E_{monomer}$) at infinitive distance. [b] The BSSE-corrected interaction energy.

For the $H_2O-OC$ complex the predicted shifts are not in as striking accordance with the MP2 and experimental results as in the $H_2O-CO$ complex. The $H_2O-OC$ complex is weaker, and the observed perturbations upon complexation are smaller. For the $\nu_{as}$OH mode the MP2-calculated spectrum shows a 2.6 cm$^{-1}$ shift. However, the B-LYP, B-P86, Becke3-LYP, Becke3-P86, and Becke3-LYP(M) functionals all give a blue shift of a few wave numbers. The symmetric OH stretching mode is in better accordance with the MP2 results, as all functionals except Becke3-P86 give a blue shift. The Becke3-P86 functional gives a red shift, which is of almost the right magnitude compared with the MP2 blue shift of 4.6 cm$^{-1}$. The bending mode is earlier for all functionals, and the experimental red shift of 6.1 cm$^{-1}$ is qualitatively reproduced. The surprises are the water bending mode with a red shift and the blue shift of the water stretching modes. This indicates that the CO monomer, indeed, acts as a weak donor instead of an acceptor as in the $H_2O-CO$ complex. This is mainly due to the small negative partial charge residing on the carbon atom instead of the intuitive location at the oxygen atom. The same behavior between oxygen- and carbon-attached CO complexes is observed with HF.[54] Here the CO stretching mode shows a blue shift in HF−CO and a red shift in the HF−OC complex. Qualitatively this same behavior can be observed in the calculated vibrational shifts listed in Table 5. The only exception is the local B-VWN5 functional which shows a shift of −7.8 cm$^{-1}$. The hybrid functionals behave very well, and the sign and the magnitude of the shift of the CO stretching mode in $H_2O-OC$ are nicely reproduced.

**Energetics.** The total electronic energies (in au), the BSSE-corrected and uncorrected interaction energies (in kJ mol$^{-1}$), and the relative energy difference (in kJ mol$^{-1}$) between the two complex structures are given in Table 6.

As noted by Salahub[11] and Hobza[13] earlier, the local and nonlocal exchange functionals predict a weaker interaction than the correlated traditional ab initio methods. For $H_2O-CO$ the hybrid functionals are showing the best performance. The BSSE-corrected interaction energies range from −3.92 (Becke3-PW91) to −5.69 (Becke3-P86) kJ mol$^{-1}$ for $H_2O-CO$ and from −0.69 (Becke3-PW91) to −2.06 (Becke3-LYP) kJ mol$^{-1}$ for $H_2O-OC$. These values are still below the values of −6.89 and −2.35 kJ mol$^{-1}$ for $H_2O-CO$ and $H_2O-OC$, respectively, at the MP2 level. As suggested by Chalasinski and Szczesniak in a recent review article,[55] the CCSD(T) level of theory could reproduce the well depths more reliably than the MP2 level. At the CCSD(T)/6-31++G(d,p) level the interaction energies were −6.03 and −2.95 kJ mol$^{-1}$ for $H_2O-CO$ and $H_2O-OC$, respectively.[23] These results lead to the conclusion that the MP2 results were accurate. However, upon enlargening the basis to the level used in this paper (CCSD(T)/6-311++G(2d,2p)), the $H_2O-CO$ interaction energy dropped down to −5.29 kJ mol$^{-1}$ and the $H_2O-OC$ interaction energy increased to −3.17 kJ mol$^{-1}$. This indicates that the hybrid functionals could give even better results than the MP2 calculations compared with the CCSD(T) level. Even though the intermolecular energetics using DFT are very encouraging compared with the CCSD(T) calculations, it should be remembered that the density functionals do not include dispersive interactions, as pointed out by Hobza and co-workers.[13]

## Conclusions

In this paper studies on the abilities of different density functional methods applied to hydrogen-bonded complexes have been carried out on the water−carbon monoxide complex. Various local and nonlocal exchange-correlation functionals have been used with the 6-311++G(2d,2p) basis set in the investigation of the structure, energetics, and vibrational properties of the 1:1 complex.

On the basis of our results, we note that the local functionals are unreliable even in the case of coupling of nonlocal exchange with local correction form. For those functionals calculated intermolecular distances are overestimated whereas the interaction energies are greatly underestimated. The effect of improvement comes from nonlocal functionals. The large variations of the intermolecular distances are mainly due to the lack of dispersion energy contributions in the functionals, and the well-established electrostatic interaction is not enough to cover the dispersion interaction already included at the MP2 and CCSD(T) levels. It has been shown that at the MP2 level the dispersion energy covers 60% and 80% of the total interaction energy of $H_2O-CO$ and $H_2O-OC$ complexes, respectively.[23] Although for the hybrid functionals there is a lack of dispersion energy contribution, the calculated intermolecular distances are better than for the nonhybrid functionals.

DFT-calculated vibrational frequencies for intramolecular modes are close to the values calculated at the MP2 level. Obviously the nonlocal density results are in closer accord with MP2 than local density results, but the differences are quite small. Less satisfactorily reproduced are the vibrational frequencies for intermolecular modes. Even for the hybrid functionals these variations are ca. 25%.

In our opinion hybrid functionals, even in present forms, are very promising in the studies of larger, hydrogen-bonded complexes which are beyond the current reach of MP2 methods due to computer limitations.

**Acknowledgment.** The CSC-Center for Scientific Computing Ltd. is gratefully thanked for providing excellent computing facilities and generous computing resources.

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