

Ab initio STUDY OF THE POTENTIAL CURVES FOR CO ($X^1\Sigma^+$), CH ($X^2\Pi$) AND OH ($X^2\Pi$)Martina BITTEREROVA^a, Stanislav BISKUPIC^a, Hans LISCHKA^b and Viliam †KLIMO^c^a Department of Physical Chemistry, Slovak Technical University,
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Calculations on spectroscopic properties of the diatomic systems CO, CH, and OH have been carried out by the multiconfiguration SCF, single reference and multireference single and double excitation CI, and average coupled pair functional methods. An evaluation of the different theoretical approaches is performed in order to get better insight into the selection of appropriate procedures for the calculation of the potential energy surface of the H + CO system.

The determination of accurate potential energy surfaces is of great importance for the understanding of the kinetics of chemical reactions. Our goal is to perform an extensive investigation of the formyl radical system HCO and some of its reaction channels. HCO is an important transient species in combustion reactions¹⁻⁸ and many theoretical investigations have been performed⁹⁻¹¹ in order to understand the energetics and the dynamics of that system. The availability of highly accurate energy surfaces (5 kJ/mol or better for dissociation energies and energy barriers) is crucial for the reliability of dynamics calculations. Therefore sophisticated quantum chemical methods and very large basis sets with high angular momentum quantum numbers l (at least up to f and g functions) have to be used for the computation of the potential energies. In order to get a better insight into what accuracy can actually be achieved it is useful to investigate the reaction fragments as well. Spectroscopic quantities like the dissociation energy, equilibrium bond distances, harmonic force constants and anharmonic terms are used as criteria in order to assess the suitability of a given computational approach.

Therefore, in the first step towards our final goal for the computation of the HCO surface, we report a systematic survey of the diatomics CH, OH and CO in their electronic ground states. Even though extensive investigations on those molecules have already been carried out, it is important to investigate and select approaches under the point of view of their applicability to HCO. The most important aspects of our present

work are an evaluation of the quality of basis sets and of wave functions. They should be flexible enough to describe accurately the spectroscopic data for the diatomics but also compact enough so that they can be used in the triatomic system. For that purpose, a series of multiconfiguration SCF (MCSCF), single-reference (SR-CI), MR-CI and averaged coupled pair functional (ACPF) calculations was carried out.

It goes beyond the scope of our work to present a comprehensive review of all previous theoretical publications on the aforementioned diatomic systems. In our survey of the literature we want to restrict ourselves to those calculations which are of direct relevance for our investigation. In case of CH and OH extended calculations on the spectroscopic constants of the first-row and second-row diatomic hydrides by Meyer and Rosmus¹² and full CI calculations by Illas et al.^{13,14} have been reported. For the CO molecule (and other diatomic molecules), fourth-order Møller–Plesset (MP4)¹⁵ has been used by Binkley and Frisch, and SR-CI and coupled-pair-functional (CPF) calculations have been performed by Ahlrichs et al.¹⁶ to study the effect of polarization functions on energies, bond distances and dissociation energies. A similar series of molecules (including CO) has been investigated by Werner and Knowles¹⁷ by means of internally contracted MR-CI and related methods.

CALCULATIONS

The theoretical background of the MCSCF (ref.^{18,19}), MR-CI-SD (ref.²⁰) and ACPF (ref.²¹) methods has been described elsewhere. The COLUMBUS program system^{22,23} was used for all calculations. The reference configurations were obtained from CAS (complete active space) SCF calculations²⁴. For the MR-CI expansion these reference configurations were used to construct all single and double substitutions of the valence orbitals into the complete space of virtual orbitals. In some cases (see below) a selection of the reference configurations (configurations with CI coefficients $|c_i| \geq 0.05$ in the MCSCF wave function were kept) was performed before constructing all single and double substitutions. In order to test the effect of size extensivity MR-ACPF (ref.¹⁸) calculations using the same reference configuration sets as for the CI calculations were performed also. For the purpose of comparison SR-CI and SR-ACPF calculations were performed as well.

Basis set effects on computed spectroscopic properties have been documented extensively by Ahlrichs and coworkers^{16,25} for a selection of A_2 and AB molecules and by Almlöf et al.²⁶ for N_2 . These investigations clearly show the well known slow convergence in l – up to h functions were included in the just mentioned calculations by Almlöf et al. on N_2 . As a minimum requirement at least one set of f functions should be included on the heavy atoms.

We decided to use two recently developed general contraction basis sets: the correlation consistent polarized valence (cc-pVTZ) basis of Dunning²⁷, various contractions of the atomic natural orbital (ANO) basis set of Widmark et al.²⁸ and the ANO basis set

of Almlöf and Taylor²⁹. The primitive sets and contraction schemes for carbon, oxygen and hydrogen are shown in Table I.

In Tables II and III the reference space and the number of reference configurations are given together with the dimension of the CI expansions. For the molecules CH and OH one set of active orbitals constructed from the valence AO's has been chosen for the CAS. For CO several more restricted choices have been used because of the much larger sizes of the CI expansions. It should be pointed out that in the CI and ACPF

TABLE I
Hydrogen, carbon and oxygen basis sets

| Atom | Basis set ^a | Primitive set | Contraction |
|------|------------------------|---------------|-------------|
| H | A | 5s2p1d | 3s2p1d |
| | B | 8s4p3d | 3s2p |
| | C | 8s4p3d | 3s2p1d |
| | D | 8s4p3d | 4s3p2d |
| | E | 8s4p3d3f | 6s3p2d1f |
| C, O | A | 10s5p2d1f | 4s3p2d1f |
| | B | 14s9p4d3f | 4s3p2d1f |
| | C | 14s9p4d3f | 5s4p3d2f |
| | D | 14s9p4d3f | 6s5p3d2f |
| | E | 14s9p4d3f2g | 6s5p3d2f1g |

^a Basis set A originates from ref.²⁷, B, C, and D from ref.²⁸, and E from refs.^{28,29}; f and g functions are taken from ref.²⁹.

TABLE II
The reference and MR-CI wave functions for CH, OH and CO used together with basis A

| Molecule | Active electrons | Active orbitals | Reference configurations | Number of CSF's in MR-CI | |
|----------|------------------|-----------------|--------------------------|--------------------------|----------|
| | | | | Total | Selected |
| CH | 5 | 2σ3σ1π4σ5σ | 11 | 25 892 | 20 473 |
| OH | 7 | 2σ3σ1π4σ5σ6σ | 6 | 104 319 | 39 392 |
| CO | 8 | 3σ4σ1π5σ2π6σ | 14 | 504 223 | 244 093 |

calculations all valence orbitals were considered in the construction of the single and double substitutions by external orbitals. Only the *K*-shell orbitals were kept frozen in the CI wave functions. All calculations have been performed within C_{2v} symmetry only. Quotations of CI dimensions in the text and the Tables II and III refer to this latter symmetry.

Potential energy curves were computed pointwise at appropriately chosen interatomic distances. Spectroscopic constants were obtained using a fitting procedure described in ref.³⁰. The dissociation energy (D_e) was computed as the difference between energy values at a large interatomic separation (50 atomic units) and at the equilibrium distance. In the cases of SR-CI and SR-ACPF calculations dissociation energies were determined as a sum of atomic energies.

RESULTS AND DISCUSSION

Our results are collected in Tables IV – VI and compared to experimental ones and to previous calculations. The MR-CI calculations with basis set A (see Table II) refer to a selected reference configuration set as explained in Calculations. For the computations with basis sets B – E (Table III) no selection restrictions were applied.

We only want to discuss the general trends in our data and refer the reader to an inspection of the tables for more details. The accuracy of the MCSCF results is reasonable but certainly not sufficient for the requirements of dynamics calculations. The harmonic frequencies are off from the experimental values by 50 – 100 cm^{-1} and the

TABLE III

The dimension of the MR-CI wave function for CH, OH and CO as a function of the size of the reference set and the different ANO contraction schemes^a

| Molecule | Active electrons | Active orbitals | Reference configurations | Number of CSF's in MR-CI | | | |
|----------|------------------|-------------------------------------------------------------|--------------------------|--------------------------|-----------|-----------|-----------|
| | | | | B | C | D | E |
| CH | 5 | 2 σ 3 σ 1 π 4 σ | 18 | 11 975 | 31 238 | 47 746 | 76 293 |
| OH | 7 | 2 σ 3 σ 1 π 4 σ | 10 | 17 975 | 47 042 | 72 182 | 113 505 |
| | 4 | 1 π 2 π | 10 | 76 401 | 195 025 | 235 617 | 330 955 |
| CO | 6 | 5 σ 1 π 2 π 6 σ | 19 ^b | 166 237 | 430 221 | 519 397 | 778 811 |
| | 6 | 5 σ 1 π 2 π 6 σ | 55 | 379 233 | 989 145 | 1 197 649 | 1 710 523 |
| | 10 | 3 σ 4 σ 1 π 5 σ 2 π 6 σ | 328 | 1 309 628 | 3 491 780 | 4 203 984 | 6 036 560 |

^a For the definition of the basis sets see Table I; ^b single and double excitations from 5 σ^2 1 π^4 into the 2 π 6 σ orbitals.

anharmonic corrections are wrong by about 10%. For CH and OH the dissociation energies D_e are significantly too small (about 0.5 – 0.9 eV for CH and OH). SR-CI gives better results in some cases. Very satisfactory results are obtained by the SR-ACPF method (only D_e for CO is off from the experimental result). However, both methods are of course not adequate for the calculation of complete potential energy curves. Significant improvements are obtained by the MR-CI calculations. For our most extended calculations (basis sets D and E) R_e values are accurate within 0.003 Å and better and ω_e values are only 14 cm^{-1} and less off from experiment. The maximum

TABLE IV
Calculated and experimental spectroscopic constants for CH ($X^2\Pi$)

| Method | Basis set | R_e Å | B_e cm^{-1} | ω_e cm^{-1} | $\omega_e x_e$ cm^{-1} | α_e cm^{-1} | D_e eV |
|-------------------------|-----------|------------|---------------------------|--------------------------------|------------------------------------|--------------------------------|-------------|
| MCSCF | A | 1.1325 | 14.138 | 2 754.1 | 63.44 | 0.556 | 2.99 |
| | B | 1.1313 | 14.169 | 2 758.5 | 64.49 | 0.566 | 3.11 |
| | C | 1.1314 | 14.165 | 2 763.4 | 65.75 | 0.559 | 3.12 |
| | D | 1.1308 | 14.181 | 2 764.4 | 63.86 | 0.558 | 3.13 |
| | E | 1.1308 | 14.178 | 2 766.1 | 66.34 | 0.557 | 3.13 |
| SR-CI | A | 1.1190 | 14.479 | 2 878.4 | 60.10 | 0.519 | 3.53 |
| | C | 1.1180 | 14.508 | 2 891.5 | 62.67 | 0.519 | 3.44 |
| | E | 1.1169 | 14.537 | 2 895.2 | 62.04 | 0.522 | 3.65 |
| SR-ACPF | A | 1.1221 | 14.403 | 2 840.9 | 63.41 | 0.537 | 3.61 |
| | C | 1.1210 | 14.431 | 2 853.7 | 65.32 | 0.539 | 3.52 |
| | D | 1.1195 | 14.467 | 2 857.1 | 65.14 | 0.540 | 3.54 |
| | E | 1.1198 | 14.458 | 2 856.8 | 63.47 | 0.537 | 3.64 |
| MR-CI | A | 1.1231 | 14.375 | 2 832.8 | 63.06 | 0.532 | 3.52 |
| | B | 1.1241 | 14.349 | 2 829.1 | 62.59 | 0.552 | 3.47 |
| | C | 1.1221 | 14.400 | 2 840.7 | 63.07 | 0.543 | 3.54 |
| | D | 1.1208 | 14.435 | 2 844.1 | 63.12 | 0.544 | 3.57 |
| | E | 1.1211 | 14.427 | 2 845.4 | 63.83 | 0.540 | 3.58 |
| MR-ACPF | A | 1.1233 | 14.370 | 2 831.0 | 63.05 | 0.535 | 3.53 |
| | C | 1.1225 | 14.392 | 2 838.7 | 62.72 | 0.542 | 3.55 |
| | E | 1.1220 | 14.418 | 2 843.2 | 63.23 | 0.538 | 3.60 |
| CEPA ^a | | 1.1220 | 14.39 | 2 841.7 | 64.4 | 0.532 | 3.47 |
| Experiment ^b | | 1.1199 | 14.457 | 2 858.5 | 63.02 | 0.534 | 3.64 |

^a Taken from ref.¹²; ^b taken from ref.³¹.

error in D_e is found to be 0.2 eV in case of CO. The MR-ACPF results are rather disappointing. With our selection of reference configurations this method does not improve results compared to the respective MR-CI data. The changes by MR-ACPF are small and usually tend into the wrong direction.

Basis set effects are documented extensively for the MCSCF, SR-ACPF and MR-CI cases. The series of basis sets investigated extends up to g functions on the heavy atom and up to f functions on hydrogen. At the MCSCF level results are basically converged with basis set D. This is not the case for the SR-ACPF and MR-CI calculations. Significant effects from g functions on C and O and from f functions on H can be readily

TABLE V
Calculated and experimental spectroscopic constants for OH ($X^2\Pi$)

| Method | Basis set | R_e Å | B_e cm^{-1} | ω_e cm^{-1} | $\omega_e x_e$ cm^{-1} | α_e cm^{-1} | D_e eV |
|-------------------------|-----------|------------|---------------------------|--------------------------------|------------------------------------|--------------------------------|-------------|
| MCSCF | A | 0.9706 | 18.877 | 3 684.0 | 98.60 | 0.8025 | 3.65 |
| | B | 0.9733 | 18.774 | 3 675.6 | 97.06 | 0.7846 | 3.66 |
| | C | 0.9735 | 18.764 | 3 671.6 | 94.86 | 0.7789 | 3.68 |
| | D | 0.9729 | 18.786 | 3 667.3 | 93.86 | 0.7773 | 3.68 |
| | E | 0.9730 | 18.784 | 3 665.6 | 90.45 | 0.7715 | 3.69 |
| SR-CI | A | 0.9661 | 19.053 | 3 822.2 | 78.61 | 0.6960 | 4.73 |
| | C | 0.9663 | 19.044 | 3 824.6 | 81.46 | 0.6980 | 4.35 |
| | E | 0.9652 | 19.086 | 3 830.2 | 80.26 | 0.6908 | 4.42 |
| SR-ACPF | A | 0.9702 | 18.893 | 3 749.5 | 84.17 | 0.7255 | 4.84 |
| | C | 0.9707 | 18.872 | 3 747.7 | 87.07 | 0.7285 | 4.46 |
| | D | 0.9687 | 18.949 | 3 754.9 | 86.97 | 0.7330 | 4.49 |
| | E | 0.9698 | 18.908 | 3 751.5 | 85.75 | 0.7226 | 4.52 |
| MR-CI | A | 0.9711 | 18.854 | 3 747.5 | 87.02 | 0.7233 | 4.41 |
| | B | 0.9737 | 18.753 | 3 719.9 | 86.60 | 0.7159 | 4.39 |
| | C | 0.9721 | 18.818 | 3 729.6 | 84.14 | 0.7289 | 4.47 |
| | D | 0.9702 | 18.891 | 3 738.1 | 84.51 | 0.7231 | 4.49 |
| | E | 0.9707 | 18.872 | 3 740.3 | 84.73 | 0.7210 | 4.53 |
| MR-ACPF | A | 0.9723 | 18.811 | 3 738.4 | 84.48 | 0.7136 | 4.46 |
| | C | 0.9735 | 18.763 | 3 717.3 | 85.04 | 0.7208 | 4.51 |
| | E | 0.9721 | 18.816 | 3 725.7 | 84.49 | 0.7183 | 4.58 |
| CEPA ^a | | 0.9710 | 18.85 | 3 743.6 | 84.9 | 0.724 | 4.34 |
| Experiment ^b | | 0.9697 | 18.911 | 3 737.7 | 84.88 | 0.7242 | 4.62 |

^a Taken from ref.¹²; ^b taken from ref.³¹.

observed. Still higher angular momentum functions are necessary in order to get closer to the basis set limit. Our findings confirm very well previous other investigations^{16,25,26} where similar conclusions have been drawn. This well known slow convergence calls for other approaches which explicitly take into account the correlation cusp. Most of the methods suggested so far are extremely time consuming. Very

TABLE VI
Calculated and experimental spectroscopic constants for CO ($X^1\Sigma_g^+$)

| Method | Basis set | R_e Å | B_e cm ⁻¹ | ω_e cm ⁻¹ | $\omega_e x_e$ cm ⁻¹ | α_e cm ⁻¹ | D_e eV |
|-------------------------|----------------|------------|---------------------------|--------------------------------|------------------------------------|--------------------------------|-------------|
| MCSCF | A | 1.1284 | 1.931 | 2 238.7 | 12.25 | 0.0157 | 10.67 |
| | C ^a | 1.1177 | 1.968 | 2 305.1 | 11.67 | 0.0157 | 9.89 |
| | C ^b | 1.1268 | 1.937 | 2 234.9 | 11.92 | 0.0160 | 10.99 |
| | C ^c | 1.1317 | 1.920 | 2 183.4 | 12.49 | 0.0167 | 10.79 |
| | D ^c | 1.1314 | 1.921 | 2 184.4 | 12.52 | 0.0166 | 10.80 |
| SR-CI | A | 1.1225 | 1.951 | 2 276.7 | 11.93 | 0.0160 | 10.58 |
| | C | 1.1202 | 1.959 | 2 276.5 | 13.31 | 0.0167 | 10.06 |
| | D | 1.1196 | 1.961 | 2 278.4 | 13.35 | 0.0167 | 10.07 |
| SR-ACPF | A | 1.1320 | 1.919 | 2 182.2 | 13.12 | 0.0170 | 11.19 |
| | C | 1.1297 | 1.927 | 2 180.7 | 13.52 | 0.0173 | 10.66 |
| | D | 1.1292 | 1.929 | 2 181.7 | 13.18 | 0.0174 | 10.67 |
| | E | 1.1285 | 1.931 | 2 189.9 | 13.32 | 0.0173 | 10.78 |
| MR-CI | A | 1.1342 | 1.911 | 2 165.5 | 12.94 | 0.0173 | 10.95 |
| | C ^a | 1.1295 | 1.927 | 2 187.4 | 13.71 | 0.0178 | 10.93 |
| | C ^b | 1.1316 | 1.920 | 2 163.9 | 13.64 | 0.0178 | 11.04 |
| | C ^c | 1.1328 | 1.916 | 2 156.1 | 13.16 | 0.0174 | 10.96 |
| | D ^c | 1.1323 | 1.918 | 2 157.7 | 13.18 | 0.0173 | 11.03 |
| MR-ACPF | A | 1.1364 | 1.904 | 2 146.1 | 13.18 | 0.0176 | 10.89 |
| | C ^a | 1.1347 | 1.910 | 2 138.3 | 13.45 | 0.0176 | 10.97 |
| | C ^b | 1.1338 | 1.913 | 2 152.7 | 13.25 | 0.0173 | 10.98 |
| | D ^c | 1.1342 | 1.918 | 2 141.1 | 13.43 | 0.0176 | 10.97 |
| MR-CI ^d | | 1.1319 | 1.919 | 2 164.8 | 13.1 | 0.0173 | 11.14 |
| Experiment ^e | | 1.1283 | 1.931 | 2 169.8 | 13.29 | 0.0175 | 11.23 |

^a 10 Configuration reference space; ^b 19 configuration reference space; ^c 55 configuration reference space; ^d taken from ref.¹⁷; ^e taken from ref.³¹.

promising in this respect is the r_{12} method developed by Kutzelnigg³² which has, however, been applied so far to closed shell systems only³³⁻³⁵.

As has already been stated above, bond breaking processes cannot be described by SR methods in general. However, in many examples large portions of energy surfaces are represented rather well by SR approaches as has been demonstrated by Dunning⁹ and by Bowman et al.¹⁰ for the H + CO reaction. Therefore, it is of great practical importance to characterize more quantitatively the range of bond distances for which a SR method is acceptable. For that purpose, in Fig. 1 we compare the SR-ACPF and MR-CI potential energy curves for CO. The shapes of the two curves agree very well up to a distance of 1.45 Å. Depending on the accuracy one wants to achieve one could even go up to a bond distance of ~1.55 Å before serious discrepancies between the two curves arise. This range of bond distances accomodates about 12 to 16 vibrational levels as can be seen from Fig. 1. For CH an analogous analysis shows an acceptable range in the bond distance up to 2 Å (accomodating 8 vibrational levels) and for OH a range up to 1.6 Å (accomodating 6 vibrational levels). With these ranges in bond distances one covers the geometries of all stationary points (minima and saddle points) on the HCO energy surface^{9,10}. Thus, SR-ACPF calculations are certainly a good choice to describe anharmonic effects of that surface well beyond the regions around the minima.

CONCLUSION

High level MR-CI calculations have been performed for CH, OH and CO and a comparison of the MCSCF, SR-CI, MR-CI and ACPF methods was made. Two general conclusions can be drawn from our results. Even though we have used very large basis sets and very flexible wave functions the challenging goal mentioned in the introduction of achieving an accuracy of 5 kJ/mol for energy differences could not be reached. The errors in D_e are still significantly larger. The results for equilibrium bond

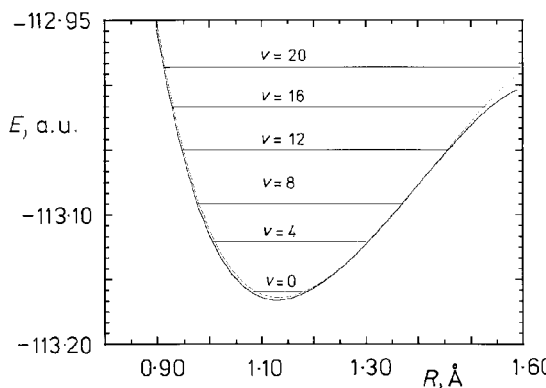


FIG. 1
Potential energy curves for the CO molecule. A comparison of SR-ACPF (dashed line) and MR-CI (solid line) calculations within basis set D (see Table I) and experimental vibrational levels³⁶

distances, harmonic force constants and anharmonic corrections are very satisfactory, even though also there some improvements could be made. Thus, one will still be forced to apply some empirical adjustments to the calculated energy surfaces before using them in dynamics calculations. However, we believe that with our current possibilities energy surfaces for systems like H + CO can be calculated much more accurately than before so that the amount of the empirical adjustments should be significantly reduced.

Our second point refers to the choice one has to make between SR and MR wave functions. In cases where a single configuration dominates the whole section of the potential energy surface one wants to investigate we consider it more profitable to use SR methods (ACPF, or other approaches like coupled cluster methods) instead of the much more time consuming MR-CI methods. The computer time saved is better invested into the possibility to select larger AO basis sets and into the ability to compute more points on the energy surface.

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