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As a first step toward the construction of a single-valued double many-body expansion potential energy surface for CHNO(3A), we have carried out CASSCF and CASPT2 calculations of six diatomic curves, involving a total of nine electronic states. The ab initio curves have been represented analytically using the extended Hartree–Fock approximate correlation energy model. In all cases, the semiempirical curves have been found to agree well with the available spectroscopic RKR data.

1. Introduction

To accurately describe the dynamics of chemical reactions, it is essential to have a good global representation of the involved potential energy surface (PES) or surfaces. In this way, the treatment of a tetraatomic system such as CHNO becomes a formidable task since we deal with a six-dimensional PES. In addition, all fragments which are allowed by the spin– spatial correlation rules must be taken into account to achieve a realistic description of the PES in the asymptotic reactive channels. To represent such a global PES, many analytical approaches have been proposed in the literature.1–6 Among them, the double many-body expansion4,7,8 (DMBE) method offers one of the most intuitive approaches, which has been successfully applied to triatomic4,9–12 and tetraatomic13–15 systems. Moreover, it has the great advantage of assuming the proper functional dependence on the interatomic separation of the long-range interactions, which has been shown to play an important role both in reactive and nonreactive collisions.

In the DMBE method, the molecular potential energy for a $N$-atom system is written as a sum of terms, each dealing with a cluster of $n$ atoms (from one to $N$), in turn partitioned into extended Hartree–Fock (EHF) and dynamical correlation (dc) parts,

$$V(R) = \sum_{n=1}^{N} \sum_{R^l \subset R^g} [V_{EHF}^{(n)}(R^l) + V_{dc}^{(n)}(R^g)]$$  \hspace{1cm} (1)$$

where $R^l$ denotes any set of $[n(n-1)/2]$ coordinates referring to $n$ atoms, which is a subset of $R^g = [R_1, R_2, ..., R_{N(N-1)/2}]$, and the last sum in eq 1 is carried out over all such subsets. Accordingly, $V^{(n)}$ must vanish if any of the $n$ atoms in the cluster is removed from the rest of the $n$-atom subsystem. In order to apply the DMBE method to the CHNO(3A) PES, it is therefore necessary to describe all the diatomic, triatomic, and tetraatomic fragments which correlate with the relevant electronic state of the tetraatomic by the Wigner–Witmer rules. These fragments are listed in Table 1.

The aim of the present work is to provide a reliable description of the diatomic fragments in Table 1. This involves a comparison of the results obtained using five different basis sets in order to reach a reasonable description of the diatomics at an acceptable computational cost since, for consistency, the same level of sophistication should be kept in the calculations referring to the triatomic and tetraatomic fragments. In this work we present also analytical fits of the calculated energies for both the extended Hartree–Fock and the dynamical correlation; the former has been estimated from CASSCF calculations, while the latter has been calculated using the CASPT216 method with the CASSCF wave function as reference.

The plan of the paper is as follows. Section 2 describes briefly the model, while the computational and technical details are given in section 3. In section 4, we present and analyse the results obtained. The conclusions are in section 5.

2. Method

If we restrict ourselves to the diatomic molecules in Table 1, eq 1 becomes

\begin{table}
\centering
\begin{tabular}{|c|c|}
\hline
\textbf{Fragment} & \textbf{Correlation Rules} \\
\hline
HCN(1A') & HCN(1A') + O(3P) \\
HN(1A') & HNO(1A') + C(3P) \\
CNO(1A') & CNO(1A') + H(2S) \\
HCO(1A') & HCO(1A') + N(4S) \\
\textbf{HCN(2A')} & \{HC(X^2\Sigma) + NO(X^2\Pi)\} \\
\textbf{HNO(2A')} & \{HC(a^2\Sigma) + NO(X^2\Pi)\} \\
\textbf{CNO(2A')} & \{HC(X^2\Sigma) + NO(X^2\Pi)\} \\
\textbf{HCO(2A')} & \{HC(X^2\Sigma) + NO(X^2\Pi)\} \\
\hline
\end{tabular}
\caption{Wigner–Witmer Correlation Rules for CHNO(3A) and Associated Fragments}
\end{table}
$V^{(2)} = V^{(2)}_{\text{EHF}}(R) + V^{(2)}_{\text{dc}}(R)$  \hfill (2)

where $V_{\text{EHF}}$ represents the extended Hartree–Fock energy and $V_{\text{dc}}$ is the dynamical correlation term which includes the asymptotic long range dispersion energy; since we deal only with the diatomic fragments, we will drop for simplicity in the following the superscript (2). Thus, the model is commonly referred to by the acronym EHFACE2, after the initials of the authors. Following the above, we now represent the EHF part of the potential energy curve by the form

$$V_{\text{EHF}} = -DR^{-1}(1 + \sum_{\nu=0}^{3} a_{\nu} r^{\nu}) e^{-\gamma r}$$  \hfill (3)

where $r = R - R_0$ is the displacement coordinate from the equilibrium geometry $R_\text{eq}$ and $D$, $\gamma$, and $a_\nu$ are parameters to be determined from a least-squares fit to the calculated $\text{ab initio}$ CASSCF points. However, for the OH($\Sigma^-$) repulsive state, it proved sufficient to use the simpler screened-Coulomb form

$$V_{\text{EHF}} = DR^{-1} \exp(-\gamma R)$$  \hfill (4)

with the parameters $D$ and $\gamma$ being determined in the same way as for eq 3.

The dynamical correlation is in turn represented by

$$V_{\text{dc}} = -\sum_{n=6,10} C_n \chi_n(R) R^{-n}$$  \hfill (5)

where the damping functions $\chi_n$ assume the form

$$\chi_n = [1 - \exp(-A_n R/(\rho - B_n R^2/\rho^3))]^n$$  \hfill (6)

In turn, $A_n$ and $B_n$ are auxiliary functions given by

$$A_n = a_n R^{-a_1}$$
$$B_n = b_n R^{-b_2}$$  \hfill (7)

where $a_n$ and $b_n$ are dimensionless parameters which have been determined from a fit to the $ab$ initio perturbation results for the $\text{H}_2(\Sigma^+)$ interaction: $a_0 = 25.9258$, $a_1 = 1.1868$, $b_0 = 15.7381$, and $b_1 = 0.09729$. Moreover, $\rho = (R_0/2 + 1.25 R_0)$ is a scaling distance written in terms of the equilibrium geometry $R_\text{eq}$ and $R_0 = 2(\langle r^2 \rangle^{1/2} + \langle \delta^2 \rangle^{1/2})$ is the Lé Roy\textsuperscript{18} parameter, which has been suggested to represent the smallest internuclear distance for which the asymptotic series of the dispersion energy is still a good representation of the damped series in eq 5. Note that $\langle r^2 \rangle^{1/2}$ and $\langle \delta^2 \rangle^{1/2}$ are the expectation value of the squared radii for the outermost electrons in atom X($M$);\textsuperscript{19} for a somewhat simpler parametrization in eqs 6 and 7, see ref 20. Finally, following Varandas,\textsuperscript{4} we assume that the values of the $C_6$ and $C_{10}$ dispersion coefficients can be estimated using the universal correlation

$$\frac{C_n}{C_6} = \kappa_n R_0^{a(n-6)/2}$$  \hfill (8)

where $\kappa_6 = 1$, $\kappa_{10} = 1.31$, and $a = 1.54$ are parameters.

To obtain the dispersion coefficients $C_n$ in eq 5, we have adopted the following procedure. First, we subtract, for each grid point, the CASCCF energy value from the calculated total (CASPT2) energy, after removal of the asymptotic CASPT2 and CASCCF energies. We then fit (for $R > R_0$) the dynamical correlation energy so obtained from eq 5, while using eq 8 to estimate the $C_6$ and $C_{10}$ dispersion coefficients.

3. Computational Details

To study the diatomic fragments in Table 1, we have performed both CASSCF and CASPT2 calculations. These calculations have encompassed a grid of 26 different internuclear distances (from 1.4 to 30 $a_0$). The points in the grid were not equally spaced and have been densely distributed in the neighborhood of the minimum of each diatomic. Although our first attempt to the dynamical correlation energy has been to use a configuration interaction approach including all single and double excitations from the full-valence CASSCF reference function, such CASSCF CISD calculations have proved too expensive for the diatoms involving the atoms C, N, and O.

For consistency reasons discussed above, particularly having in mind that similar calculations should be carried out for the triatomic and tetraatomic species, such methodology has been replaced by the more economical CASPT2 one. To perform these CASPT2 calculations, the MOLCAS-3 package\textsuperscript{21} has been employed.

Once the energies have been calculated, they have been fitted to eqs 3 and 5 using the least-squares method as mentioned in section 2. This involves a linear procedure for eq 5, and a mixed nonlinear—linear procedure for eqs 3 or 4. In the latter, the nonlinear parameters have been determined iteratively using the Levenberg–Marquardt\textsuperscript{22} method until convergence was reached, the linear parameters being optimized at every iteration. This procedure consists of using a steepest descent method far from the minimum, while a continuous switch to the inverse Hessian method is employed as the minimum is approached.

In all CASSCF calculations, the active space has been the valence space. For the CASPT2 calculations, all but the 1s electrons have been correlated using the CASSCF wave function as the reference.\textsuperscript{23}

3.1. Basis Sets. Since a major aim of this work has been the search for a reasonable accuracy/computational cost ratio, we have studied five different basis sets of increasing level of sophistication. Of these, we used the largest one as reference, and then compared the results obtained from it with triple-ζ, enlarged double-ζ, and double-ζ basis sets. Specifically, the basis sets employed in this work are (i) the cc-pVDZ 9s4p1d/ [3s2p1d] for C, N, and O and 4s1p/[2s1p] for H basis set of Pierloot\textsuperscript{24} (ii) the D-95 9s5p1d/[4s2p1d] for C, N, and O and 4s2p/[2s1p] for H basis set of Dunning et al.,\textsuperscript{24} (iii) the contracted ANO 10s6p3d/7s6p3d for C, N, and O and 7s3p/ [4s3p] for H basis set of Pierloot et al.,\textsuperscript{26} (iv) the cc-pVTZ 10s5p2d1f/[4s3p2d1f] for C, N, and O and 5s2p1d/[3s2p1d] for H basis set of Dunning et al.,\textsuperscript{24} and (v) the contracted ANO 14s9p4d3f/[5s4p3d2f] for C, N, and O and 8s4p3d/[3s2p1d] for H basis set of Widmark et al.\textsuperscript{27}

4. Results and Discussion

The results obtained for the electronic states of the diatomic molecules listed in Table 1 are summarized in Tables 2–9 for each basis set described in section 3. Tables 2 and 5 give the calculated values of the dissociation energy ($D_0$) and equilibrium geometry ($R_{eq}$), which are also compared with the corresponding experimental values from reference 28.

As might be expected, Tables 2 and 5 show that the best results are obtained with the Widmark ANO [5s4p3d2f] basis set both for the dissociation energy and the equilibrium geometry.
for all diatomic fragments except for CO(1Σ). For the equilibrium geometry, the difference between theory (at the CASPT2 level\(^27\)) and experiment is in all cases but CO(X 1Σ) smaller than 0.02 a₀. On the other hand, it is well-known that the CASPT2 method systematically underestimates all bond energies by \((5 \times 10^{-3})-(1 \times 10^{-2}) E_h\)^\(^{29}\) which explains the observed discrepancies between the CASPT2 values in Tables 2 and 5 and the experimental results. This may also explain the larger discrepancies found for NO(X 2Π) and CO(X 1Σ), since in these cases three electron pairs are formed in the bonding process.

Another important observation from Tables 2 and 5 is that basis set effects are more marked in the CASPT2 calculations.

### Table 2: Values for \(D_e\) and \(R_m\) Obtained for the Ground States of the Diatomic Molecules in Table 1

<table>
<thead>
<tr>
<th>System</th>
<th>Basis Set</th>
<th>(D_e^{CASCF})</th>
<th>(D_e^{CASPT2})</th>
<th>(D_e^{exp})</th>
<th>(R_m^{CASCF})</th>
<th>(R_m^{CASPT2})</th>
<th>(R_m^{exp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(X 2Π)</td>
<td>D-95 dz</td>
<td>0.108 05</td>
<td>0.120 30</td>
<td>0.133 8</td>
<td>2.162</td>
<td>2.140</td>
<td>2.116</td>
</tr>
<tr>
<td></td>
<td>cc-pVDZ</td>
<td>0.105 80</td>
<td>0.118 09</td>
<td>2.177</td>
<td>2.160</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cc-pVTZ</td>
<td>0.108 54</td>
<td>0.126 72</td>
<td>2.152</td>
<td>2.116</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ANO [7s6p3d]</td>
<td>0.108 77</td>
<td>0.122 70</td>
<td>2.147</td>
<td>2.120</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>ANO [5s4p3d2f]</td>
<td>0.108 94</td>
<td>0.128 28</td>
<td>2.149</td>
<td>2.116</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ANO [5s6p3d]</td>
<td>0.134 73</td>
<td>0.160 40</td>
<td>1.848</td>
<td>1.843</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ANO [5s4p3d2f]</td>
<td>0.135 09</td>
<td>0.165 93</td>
<td>1.846</td>
<td>1.846</td>
<td></td>
<td></td>
</tr>
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### Table 3: Values of the Parameters in Equation 3 for the Ground States of the Diatomic Molecules in Table 1. Units as in Table 2

<table>
<thead>
<tr>
<th>System</th>
<th>Basis Set</th>
<th>(D_a)</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(a_3)</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(X 2Π)</td>
<td>D-95 dz</td>
<td>0.233 64</td>
<td>2.527 57</td>
<td>1.866 03</td>
<td>0.592 58</td>
<td>2.040 37</td>
</tr>
<tr>
<td></td>
<td>cc-pVDZ</td>
<td>0.230 31</td>
<td>2.519 21</td>
<td>1.828 61</td>
<td>0.565 10</td>
<td>2.033 37</td>
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<tr>
<td></td>
<td>cc-pVTZ</td>
<td>0.233 53</td>
<td>2.530 76</td>
<td>1.898 03</td>
<td>0.619 21</td>
<td>2.042 85</td>
</tr>
<tr>
<td></td>
<td>ANO [7s6p3d]</td>
<td>0.233 56</td>
<td>2.526 23</td>
<td>1.878 80</td>
<td>0.608 92</td>
<td>2.035 44</td>
</tr>
<tr>
<td></td>
<td>ANO [5s4p3d2f]</td>
<td>0.234 15</td>
<td>2.511 63</td>
<td>1.878 80</td>
<td>0.610 21</td>
<td>2.034 25</td>
</tr>
<tr>
<td></td>
<td>ANO [5s6p3d]</td>
<td>0.230 15</td>
<td>1.116 03</td>
<td>0.135 0</td>
<td>1.996</td>
<td>1.988</td>
</tr>
<tr>
<td></td>
<td>ANO [5s4p3d2f]</td>
<td>0.231 75</td>
<td>0.124 65</td>
<td>1.982</td>
<td>1.971</td>
<td></td>
</tr>
<tr>
<td>OH(X 2Π)</td>
<td>D-95 dz</td>
<td>0.101 63</td>
<td>0.116 03</td>
<td>0.135 0</td>
<td>1.996</td>
<td>1.988</td>
</tr>
<tr>
<td></td>
<td>cc-pVDZ</td>
<td>0.098 45</td>
<td>0.112 68</td>
<td>2.005</td>
<td>1.999</td>
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<tr>
<td></td>
<td>cc-pVTZ</td>
<td>0.102 57</td>
<td>0.123 65</td>
<td>1.986</td>
<td>1.971</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ANO [7s6p3d]</td>
<td>0.103 15</td>
<td>0.119 86</td>
<td>1.983</td>
<td>1.971</td>
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<tr>
<td></td>
<td>ANO [5s4p3d2f]</td>
<td>0.234 56</td>
<td>2.526 23</td>
<td>1.878 80</td>
<td>0.608 92</td>
<td>2.035 44</td>
</tr>
<tr>
<td>NO(X 2Π)</td>
<td>D-95 dz</td>
<td>0.195 58</td>
<td>0.205 87</td>
<td>0.243 0</td>
<td>2.223</td>
<td>2.234</td>
</tr>
<tr>
<td></td>
<td>cc-pVDZ</td>
<td>0.200 11</td>
<td>0.212 79</td>
<td>2.201</td>
<td>2.203</td>
<td></td>
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<tr>
<td></td>
<td>cc-pVTZ</td>
<td>0.206 89</td>
<td>0.227 79</td>
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<td>ANO [7s6p3d]</td>
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<td>0.215 65</td>
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<td>2.192</td>
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<tr>
<td></td>
<td>ANO [5s4p3d2f]</td>
<td>0.206 70</td>
<td>0.224 25</td>
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<tr>
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<td>ANO [5s6p3d]</td>
<td>0.135 09</td>
<td>0.165 93</td>
<td>1.846</td>
<td>1.846</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ANO [5s4p3d2f]</td>
<td>0.135 09</td>
<td>0.165 93</td>
<td>1.846</td>
<td>1.846</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) All quantities are in atomic units: energies in \(E_h\), distances in a₀.
Tables 3 and 6 report the results obtained from the fitting of the \textit{ab initio} CASSCF energies to eq 3 and to eq 4 for OH (\(a^6\Sigma^-\)). It is seen that the values of the linear parameters \(a_i\) and the nonlinear one \(\gamma\) are very similar for all basis sets employed, which reflects the previously mentioned fact concerning the CASSCF calculations. Nevertheless we can appreciate a slight difference in the parameters obtained for the double zeta basis sets (D-95 and cc-pVdz) and those obtained with the larger basis sets (triplet-\(\zeta\) cc-pVTZ and ANO [5s4p3d2f]). Finally, we note that the values determined with the cc-pVdz and ANO [7s6p3d] basis sets and those obtained with the largest basis set employed ([5s4p3d2f]) are very close in all cases except in that of the OH (\(a^6\Sigma^-\)) repulsive state.

Concerning the dynamical correlation, Tables 4 and 7 give the values obtained for the \(C_a\) coefficients in eq 5 following the procedure described in the section 3. First, we observe a more marked influence of the basis set on the reported quantities. Then, we observe from Tables 4 and 7 that the values of the \(C_a\) dispersion coefficients increase with increasing basis set size, which may be attributed to a better reproduction of the dynamical correlation with basis set quality; this leads to a larger difference between the CASSCF (nearly invariant in all basis sets) and the CASPT2 energies, and hence implies higher values of the \(C_a\) dispersion coefficients. Thus, we will assume that the most reliable \(C_a\) values are the largest ones calculated for each diatomic. This corresponds also to the largest basis set [5s4p3d2f] in all cases except in that of CO (\(X^1\Sigma^+\)). Again, this is probably due to the deficiencies of the CASPT2 method in representing this state. In Table 8, we compare our best values (in the sense implied above) obtained for the \(C_a\) coefficient with those available in the literature. Except for the OH dispersion coefficient \(C_a\), all others have been calculated as the geometric average of the dispersion coefficients of the associated homonuclear interactions.\cite{30} In turn, the \(C_a\) OH coefficient has been determined using perturbation theory by Varandas and Voro-

### Table 4: Values of the Parameters in Equation 5 for the Ground States of the Diatomic Molecules in Table 1. Units as in Table 2

<table>
<thead>
<tr>
<th>system</th>
<th>basis set</th>
<th>(D)</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(a_3)</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH((a^6\Sigma^-))</td>
<td>D-95 dz</td>
<td>0.209 242</td>
<td>3.668 29</td>
<td>4.645 14</td>
<td>2.289 56</td>
<td>3.092 52</td>
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<td>cc-pVdz</td>
<td>0.203 158</td>
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<td>cc-pVTZ</td>
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<td>4.809 07</td>
<td>2.427 87</td>
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<td>ANO [7s6p3d]</td>
<td>0.205 901</td>
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<td>ANO [5s4p3d2f]</td>
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<td>3.713 49</td>
<td>4.811 25</td>
<td>2.428 28</td>
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<tr>
<td>OH((a^4\Pi))</td>
<td>D-95 dz</td>
<td>1.979 59</td>
<td>nr</td>
<td>nr</td>
<td>nr</td>
<td>1.010 73</td>
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<td>cc-pVdz</td>
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<td>nr</td>
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<td>nr</td>
<td>0.793 95</td>
</tr>
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<td>ANO [5s4p3d2f]</td>
<td>0.984 67</td>
<td>nr</td>
<td>nr</td>
<td>nr</td>
<td>0.787 53</td>
</tr>
<tr>
<td>CO((a^3\Pi))</td>
<td>D-95 dz</td>
<td>0.370 656</td>
<td>3.672 34</td>
<td>3.934 95</td>
<td>1.453 69</td>
<td>3.365 16</td>
</tr>
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<td>cc-pVdz</td>
<td>0.371 647</td>
<td>3.680 38</td>
<td>3.969 67</td>
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<td>cc-pVTZ</td>
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<td>3.666 09</td>
<td>3.981 03</td>
<td>1.510 92</td>
<td>3.324 02</td>
</tr>
<tr>
<td></td>
<td>ANO [7s6p3d]</td>
<td>0.382 536</td>
<td>3.638 16</td>
<td>3.899 11</td>
<td>1.460 24</td>
<td>3.283 03</td>
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<td>ANO [5s4p3d2f]</td>
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<td>3.991 33</td>
<td>1.516 32</td>
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</tbody>
</table>

\(a^{\star}\) nr = not relevant. See the text.
using the best available semiempirical values for the \( C_n \) have a level of accuracy similar to that reached for the other leading to results for the energy that cannot be considered to and also within the allowed CSFs for the CASPT2 calculation, configuration state functions obtained within the active space diatomic molecule). This reduces drastically the number of p x the \( \text{C}_n \) system basis set \( \ldots \).\footnote{\textsuperscript{31} For all diatomic ground states involving a H atom, the agreement is good. It is only moderate or even poor for the interactions in which both atoms are different from H, which is probably due to the less accurate description of such systems in the CASPT2 approach; note that more than one electron pair can now be formed. Moreover, very poor agreement is found for the \( \Sigma^\ast \) excited states. This may in turn be explained due to the fact that the \( \Sigma^- \) configurations can only be formed by using the \( p_x \) and \( p_y \) orbitals of the heavy atom (\( z \) being the axis of the diatomic molecule). This reduces drastically the number of configuration state functions obtained within the active space and also within the allowed CSFs for the CASPT2 calculation, leading to results for the energy that cannot be considered to have a level of accuracy similar to that reached for the other states.

An alternative approach to the parameters in eq 3 consists of using the best available semiempirical values for the \( C_n \) dispersion coefficients. In this case, the dynamical correlation in eq 5 is set \( a \nobreak\text{priori} \) from those dispersion coefficients and then subtracted from the calculated CASPT2 energies to yield effective EHF energies; these are next used in a way similar to that described above for the true CASSCF points to obtain the parameters in eq 3. This inverse procedure has been used to obtain the coefficients \( a_i \) and \( \gamma \) of eq 3 for the largest basis set (ANO \[5s4p3d2f\]). The results are shown in Table 9. The numerical values obtained using this procedure are in very good agreement with the previously obtained ones. As expected, the larger differences are found when the experimental \( C_n \) coefficient and the calculated one are not in good agreement.

Finally, to calibrate the results obtained with the DMBE method for the diatomic systems, we show in Figures 1–3 a comparison of the results obtained with the ANO \[5s4p3d2f\] basis set with the available accurate RKR spectroscopic data\footnote{\textsuperscript{32}–\textsuperscript{34}} employed the \( C_n \) dispersion coefficients obtained from our fit, obtain the coefficients \( a_i \) and \( \gamma \) of eq 3 for the largest basis set (ANO \[5s4p3d2f\]). The results are shown in Table 9. The numerical values obtained using this procedure are in very good agreement with the previously obtained ones. As expected, the larger differences are found when the experimental \( C_n \) coefficient and the calculated one are not in good agreement.

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and in Figures 4–6 we show the results obtained with the alternative approach which keeps the best available semiempirical values for the $C_n$ dispersion coefficients. Clearly, there is very good agreement for all systems. The slight difference we can appreciate (especially for NO($X^2\Sigma$)) is partly due to the difference between the dissociation energies already reported in Table 2. Such a problem can be overcome by adding a semiempirical correction. This correction$^{32}$ (named SEC from the initials of scaling external correlation) is based on the assumption that the $ab$ initio dynamical correlation is underestimated by the same fraction over the whole range of internuclear distances. Thus, to obtain a realistic description of the dynamical correlation, one just requires to scale it in such a way that the calculated total potential energy (obtained by adding the scaled dynamical correlation to the $ab$ initio extended Hartree–Fock energy) reproduces exactly the known experimental dissociation energy.

5. Conclusions

Five different basis sets have been employed to obtain the potential curves of six diatomics (involving nine electronic states) relevant for building the CHNO PES according to the DMBE strategy. Both the EHF and dynamical correlation parts of the calculated energies have been modelled analytically using forms from the realistic EHF/ACE2 model. The relevant numerical coefficients have been tabulated for the nine studied electronic states. Large differences have been observed between the results obtained from the two smaller basis sets and the biggest one both for the EHF and dynamical correlation energies. Within the larger basis sets, it is worth noting that almost the same result is obtained using the cc-pVTZ [4s3p2d1f] and the ANO [5s4p3d2f] basis sets, while the computational effort required for the first is significantly smaller. Regarding the dispersion coefficients $C_n$, we have found a reasonable agreement with other theoretical results available in the literature. For OH($X^2\Sigma$), the agreement found with the accurate value of Varandas et al.$^{31}$ is particularly good. In summary, the present studies suggest that the cc-pVTZ [4s3p2s1f] basis set is probably the most suited to perform the $ab$ initio calculations of the triatomic and tetraatomic systems necessary for the study of the title potential energy surface. In fact, we have shown that it gives results very close to those obtained by using the largest basis set employed (ANO [5s4p3d2f]) in the present work, while keeping the computational cost at an affordable level.

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References and Notes

(23) The ab initio energies are available upon request from the authors.
(34) Prasad, C. V. V.; Bernath, P. F. J. Mol. Spectrosc. 1992, 156, 327.