# Appendix B

# Kinetic couplings

## B.1 Kinetic coupling terms $T^{(1)}$ of the $A'$ and $A''$ states

In section 3.6 only the kinetic couplings which have been used in the dynamics calculations are shown. All other matrix elements of $T^{(1)}$ and $T^{(2)}$ are depicted in this appendix for the sake of completeness. Furthermore, the smoothed splines of the CI and MO coefficients which have been used for the calculation of the couplings are given.

### B.1.1 Splined curves of the CI coefficients in the case of symmetry $A'$

In the following figures, the original CI coefficients (dots) are shown together with smooth cubic spline approximations (solid lines). Dots in parentheses have not been used in the spline procedure. In the figure captions, standard deviations $s$ in the spline smoothing procedure are given in brackets.
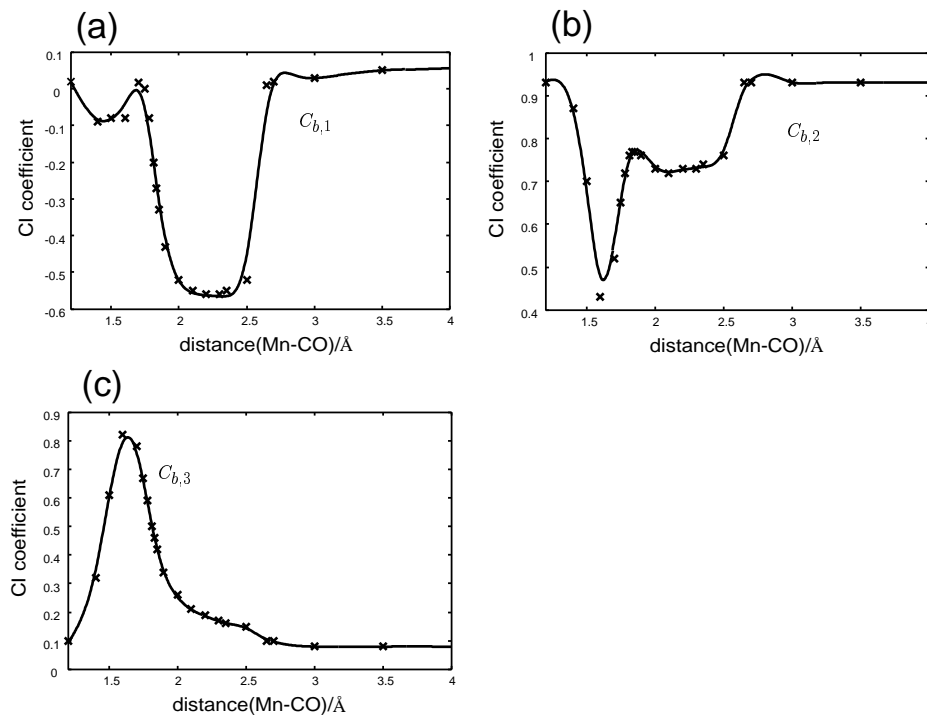
Figure B.1: *CI coefficients: (a)* $C_{b,1}$ *[s=0.021]. (b)* $C_{b,2}$ *[s=0.01]. (c)* $C_{b,3}$ *[s=0.01].* The coefficient $C_{b,4}$ is zero everywhere.
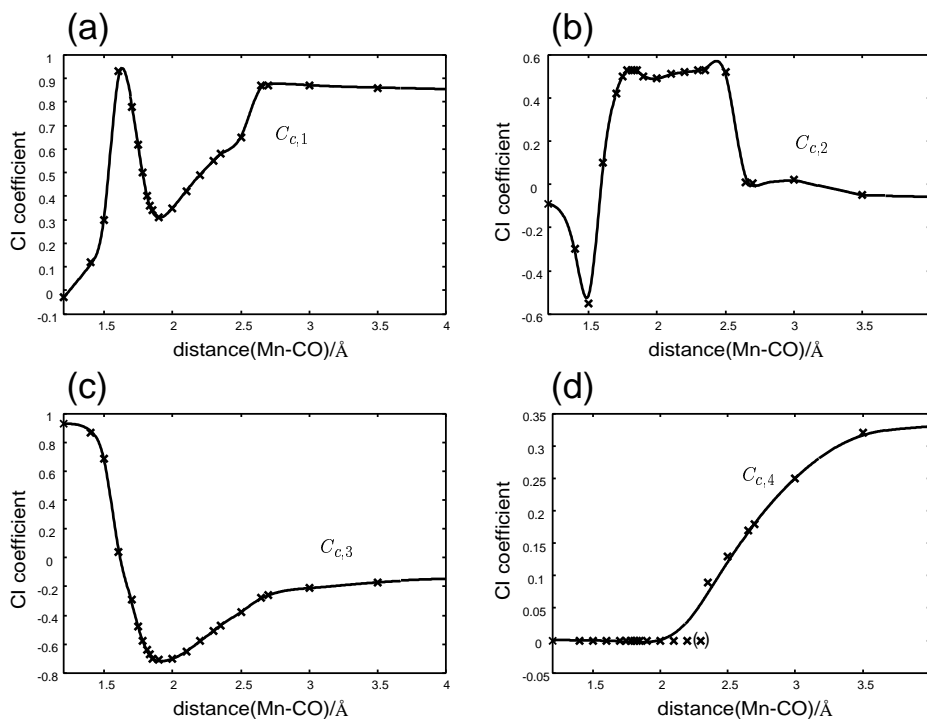


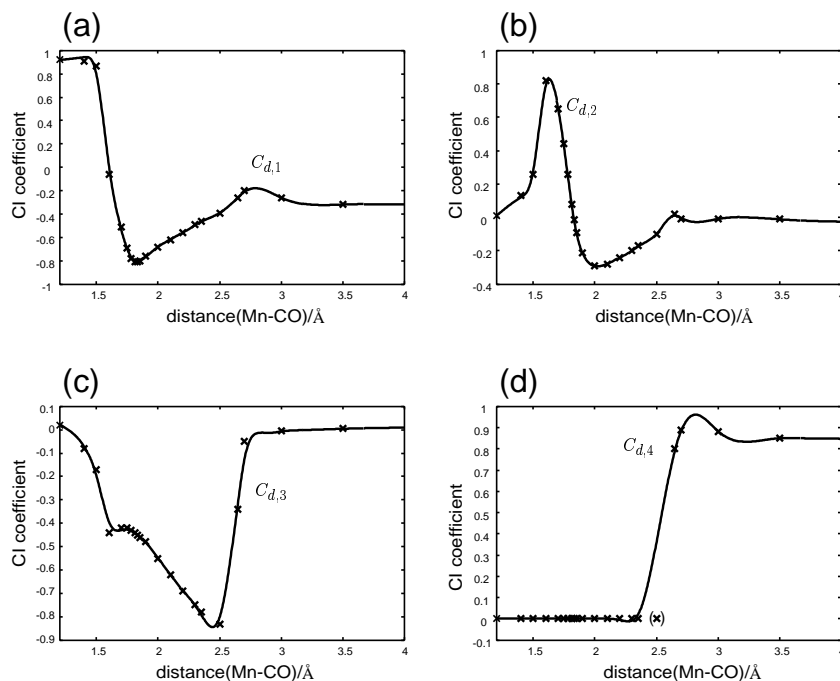Figure B.2: *CI coefficients: (a)* $C_{c,1}$ *[s=0.021]. (b)* $C_{c,2}$ *[s=0.01]. (c)* $C_{c,3}$ *[s=0.01].* (d) $C_{c,4}$ *[s=0.005].*

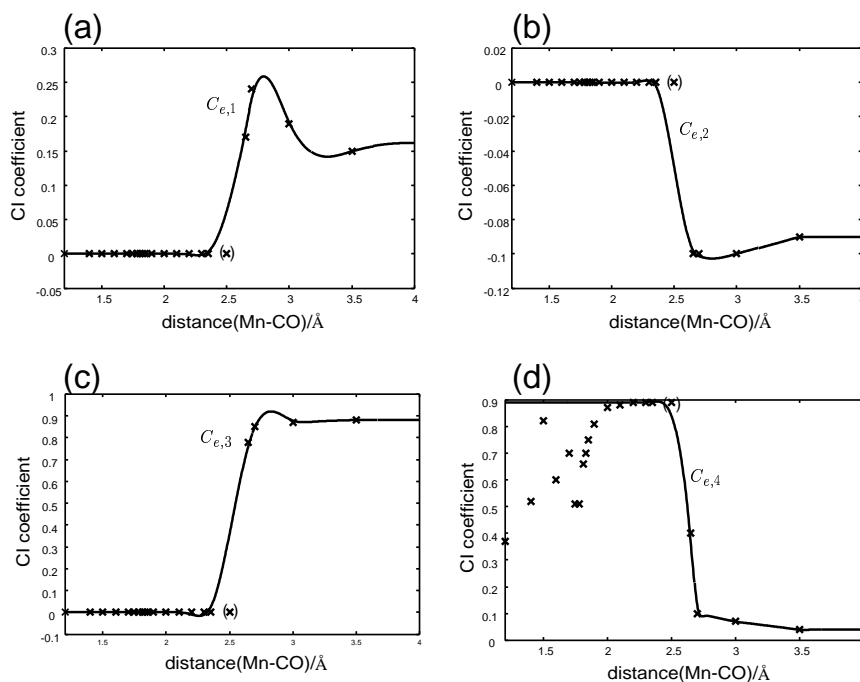Figure B.3: *CI coefficients:* (a) $C_{d,1}$ [s=0.025]. (b) $C_{d,2}$ [s=0.01]. (c) $C_{d,3}$ [s=0.02]. (d) $C_{d,4}$ [s=0.004].



Figure B.4: *CI coefficients:* (a) $C_{e,1}$ [s=0.004]. (b) $C_{e,2}$ [s=0.0005]. (c) $C_{e,3}$ [s=0.005]. (d) $C_{e,4}$ [s=0.005]. The coefficient $C_{e,4}$ has been assumed to be constant at distances below 2.5 Å, since the $e^1 A'$ state has not been converged at these points.

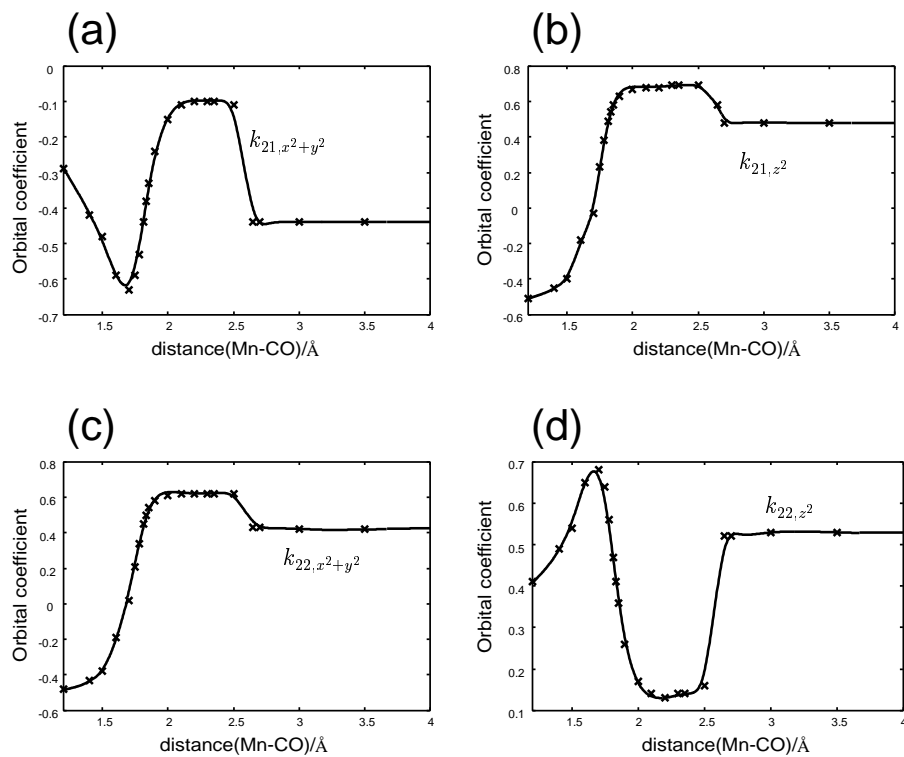## B.1.2   Splined curves of the orbital coefficients in the case of symmetry $A'$



Figure B.5: *Orbital coefficients: Original data (dots) and smooth cubic spline approximation with standard deviation of 0.01 (solid lines): (a) $k_{21,x^2+y^2}$. (b) $k_{21,z^2}$. (c) $k_{22,x^2+y^2}$. (d) $k_{22,z^2}$.*

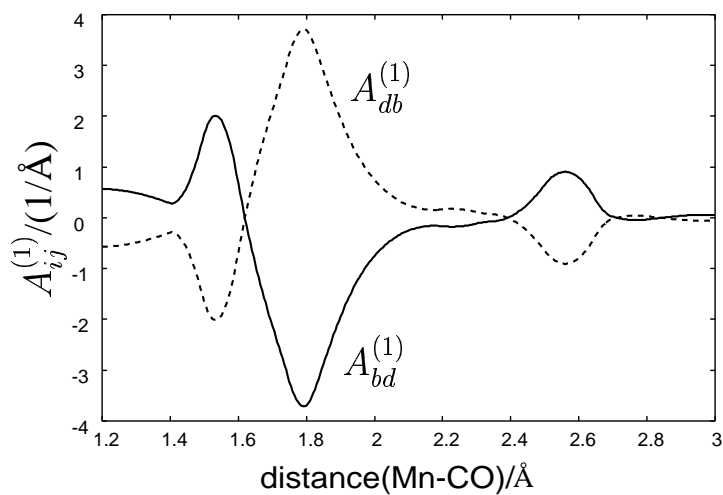## B.1.3   Kinetic coupling term $T^{(1)}$ of the $A'$ states



Figure B.6: *Elements $A_{bd}$ and $A_{db}$ calculated using the CI coefficients according to equation (2.121).*
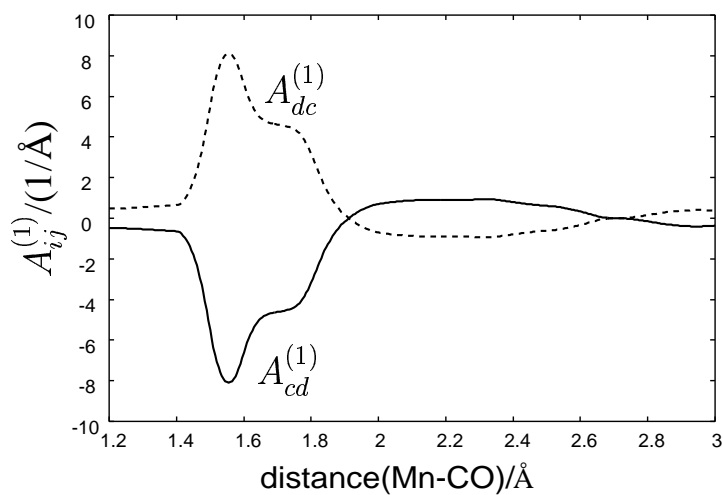


Figure B.7: *Elements $A_{cd}$ and $A_{dc}$ calculated using the CI coefficients according to equation (2.121).*
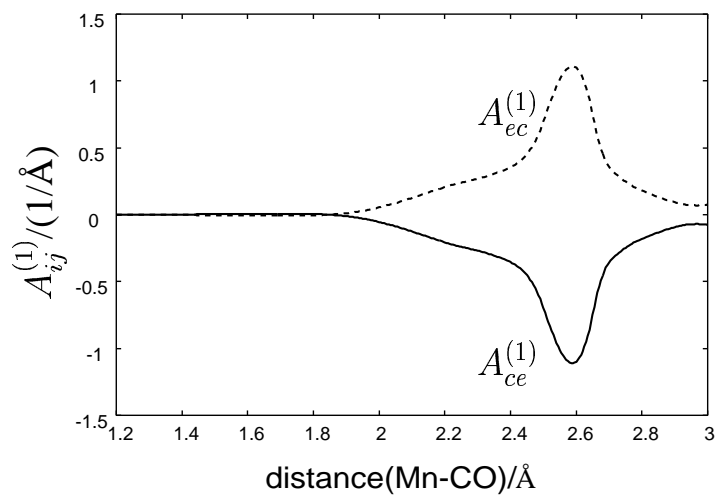
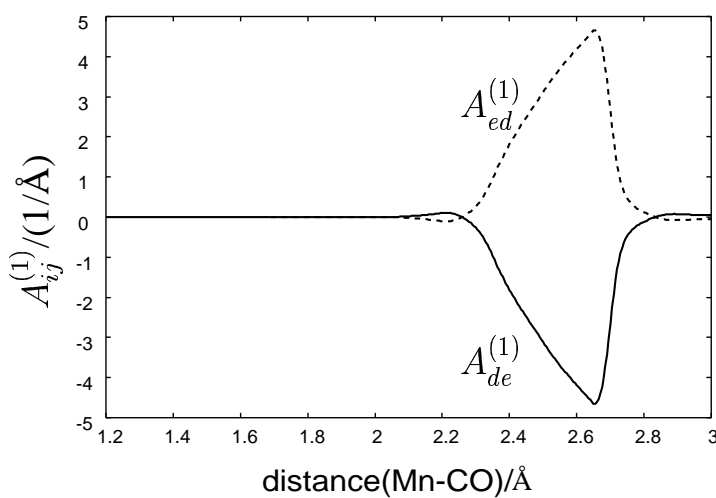Figure B.8: *Elements $A_{ce}$ and $A_{ec}$ calculated using the the CI coefficients according to equation (2.121).*



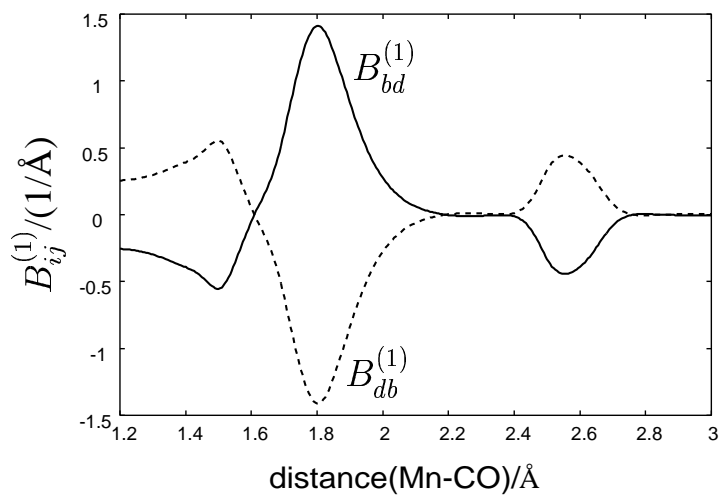Figure B.9: *Elements $A_{de}$ and $A_{ed}$ calculated using the CI coefficients according to equation (2.121).*

Figure B.10: *Elements $B_{bd}$ and $B_{db}$ calculated using the CI coefficients according to equation (2.121).*
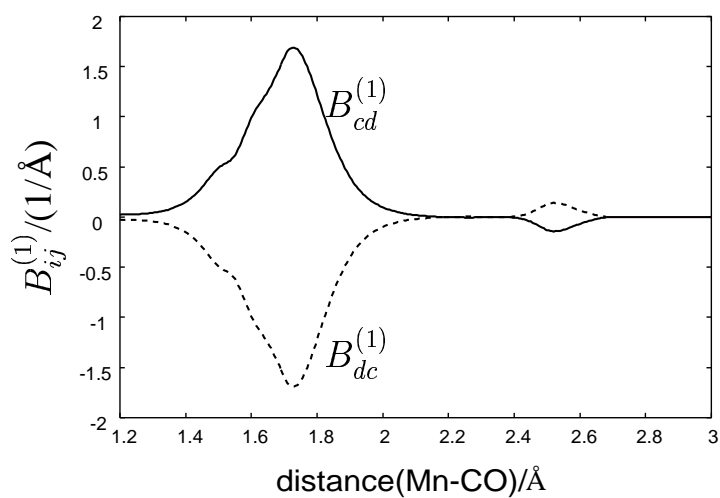


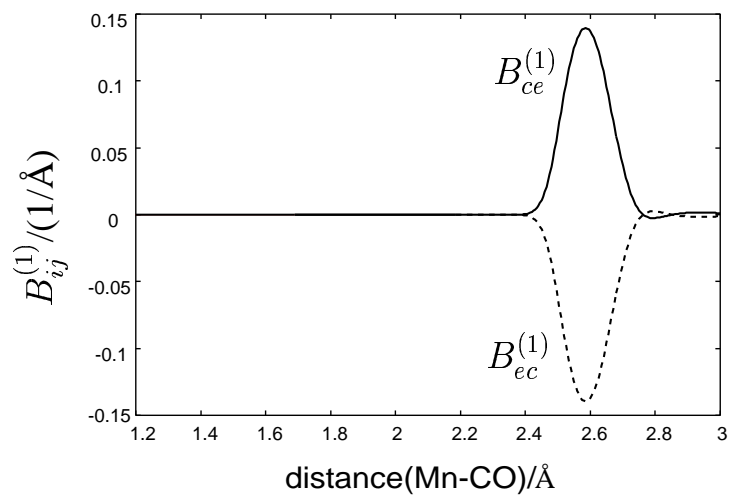Figure B.11: *Elements $B_{cd}$ and $B_{dc}$ calculated using the CI coefficients according to equation (2.121).*

Figure B.12: *Elements $B_{ce}$ and $B_{ec}$ calculated using the CI coefficients according to equation (2.121).*
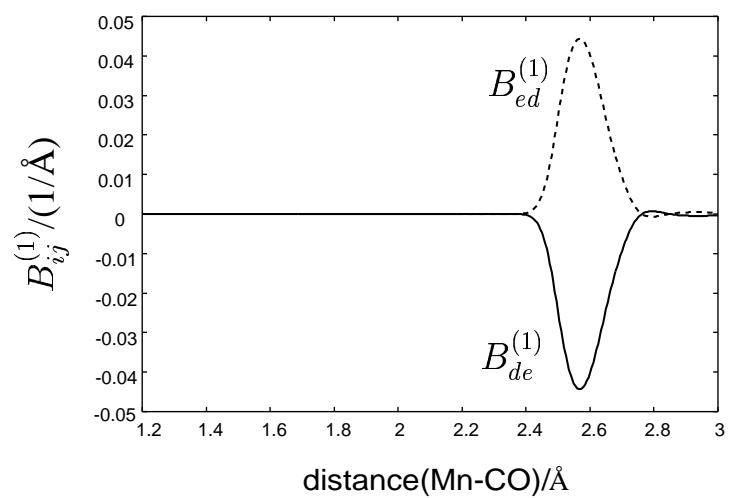


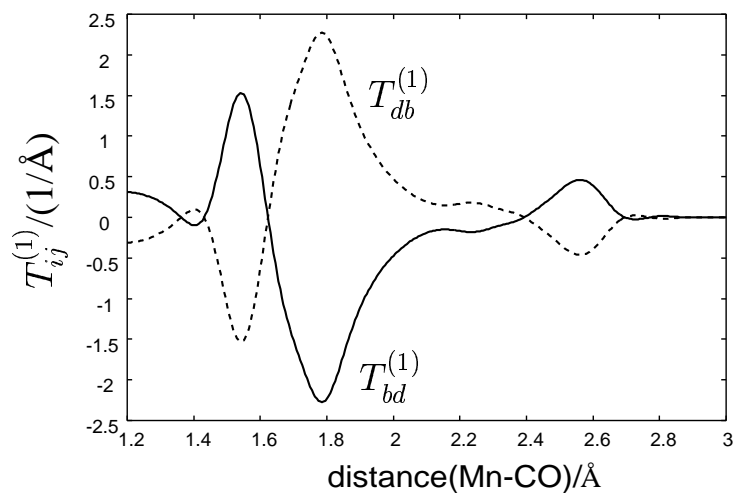Figure B.13: *Elements $B_{de}$ and $B_{ed}$ calculated using the CI coefficients according to equation (2.121).*

Figure B.14: *Coupling element $T_{bd}^{(1)}$ and $T_{db}^{(1)}$ calculated using the CI coefficients according to equation (2.121).*
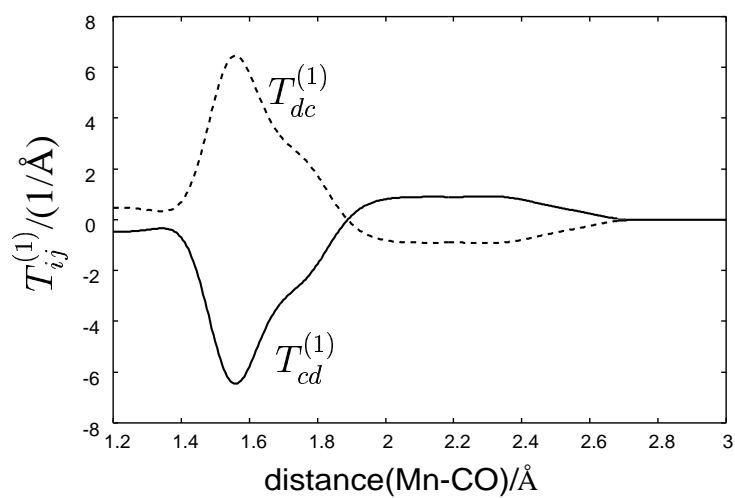


Figure B.15: *Coupling element $T_{cd}^{(1)}$ and $T_{dc}^{(1)}$ calculated using the CI coefficients according to equation (2.121).*
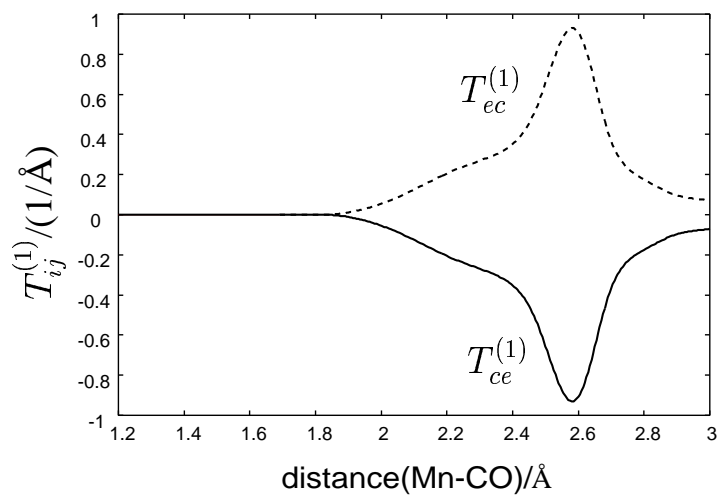
Figure B.16: *Coupling element $T_{ce}^{(1)}$ and $T_{ec}^{(1)}$ calculated using the CI coefficients according to equation (2.121).*
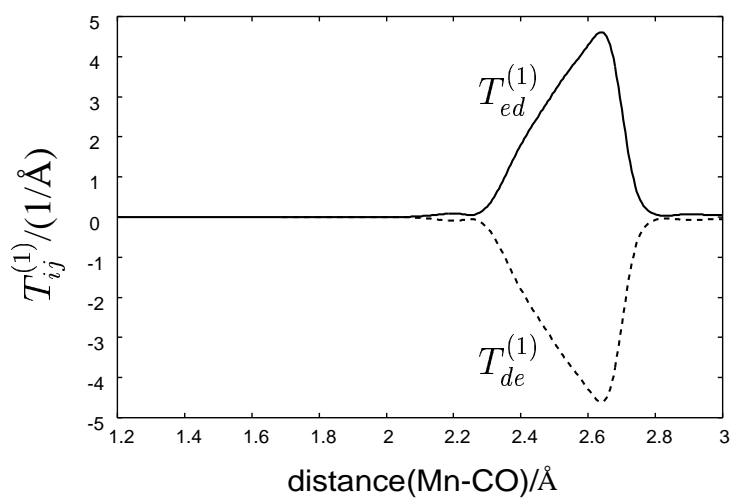


Figure B.17: *Coupling element $T_{de}^{(1)}$ and $T_{ed}^{(1)}$ calculated using the CI coefficients according to equation (2.121).*

## B.1.4 Splined curves of the CI coefficients in the case of symmetry $A''$

In section B.1.1 the CI coefficients of the $A'$ states have been plotted. Here, the original CI coefficients (dots) are shown together with smooth cubic spline approximations (solid lines) for the $A''$ states. Dots in parentheses have not been used in the spline procedure and standard deviations $s$ in the spline smoothing procedure are given in brackets.
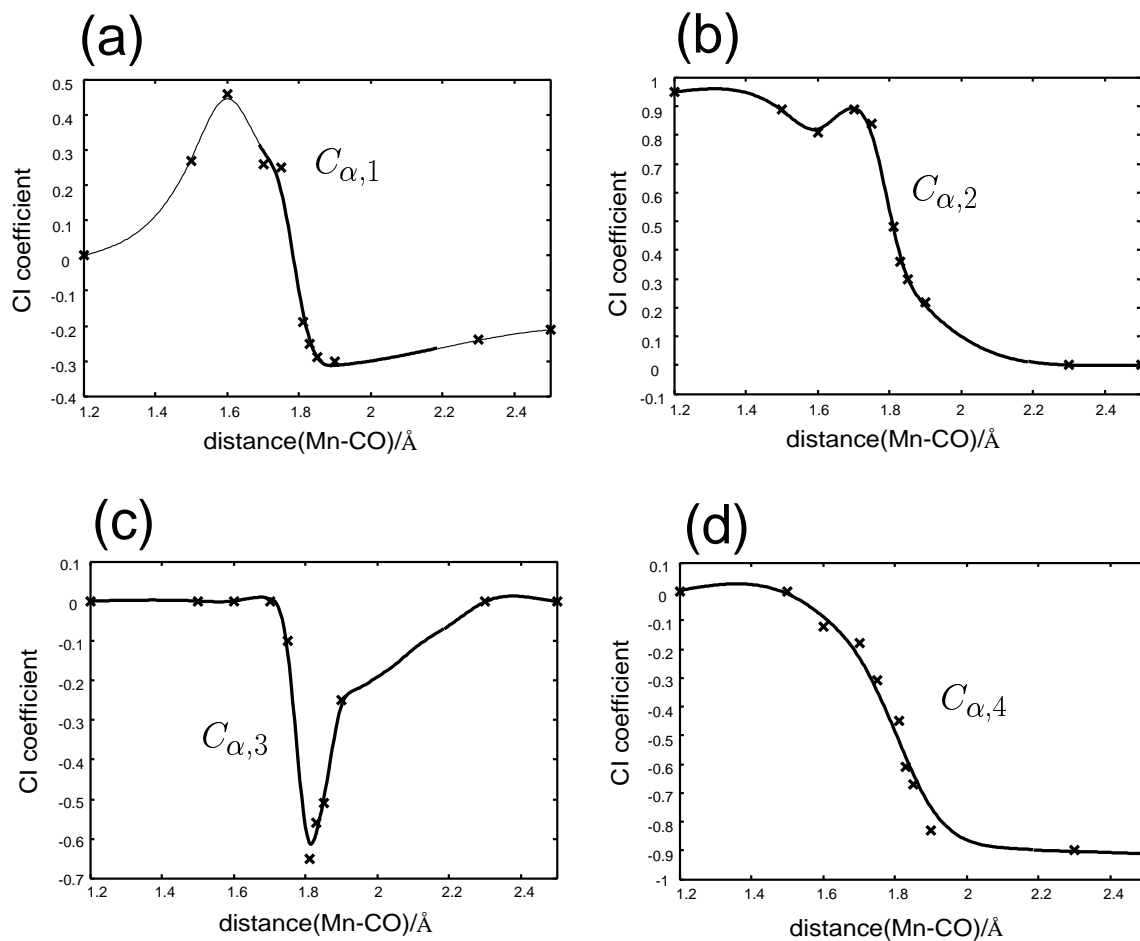


Figure B.18: *CI coefficients: (a) $C_{\alpha,1}$ [s=0.02]. (b) $C_{\alpha,2}$ [s=0.01]. (c) $C_{\alpha,3}$ [s=0.012]. (d) $C_{\alpha,4}$ [s=0.03].*
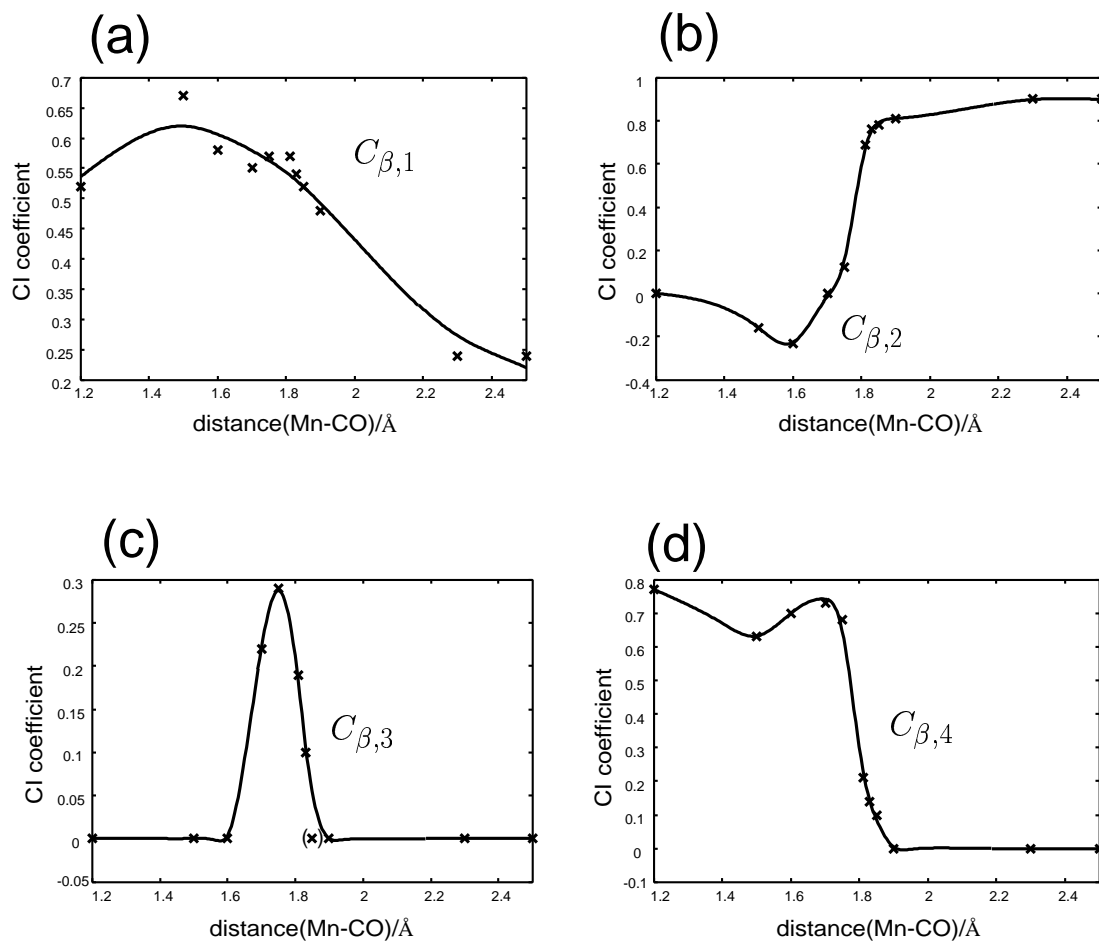
Figure B.19: *CI coefficients:* (a) $C_{\beta,1}$ *[s=0.02].* (b) $C_{\beta,2}$ *[s=0.01].* (c) $C_{\beta,3}$ *[s=0.003].* (d) $C_{\beta,4}$ *[s=0.01].*

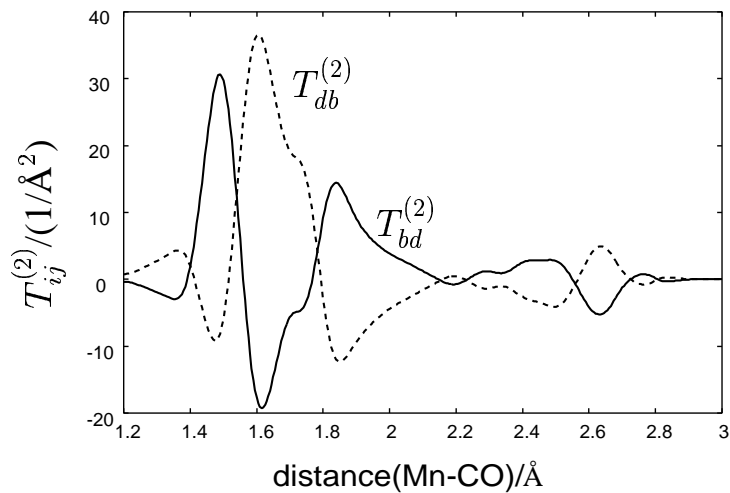## B.2 Kinetic coupling terms $T^{(2)}$ of the $A'$ and $A''$ states



Figure B.20: *Coupling elements $b^1 A' \leftrightarrow d^1 A'$, $T_{bd}^{(2)}$ and $T_{db}^{(2)}$, calculated using the CI coefficients according to equation (2.119).*
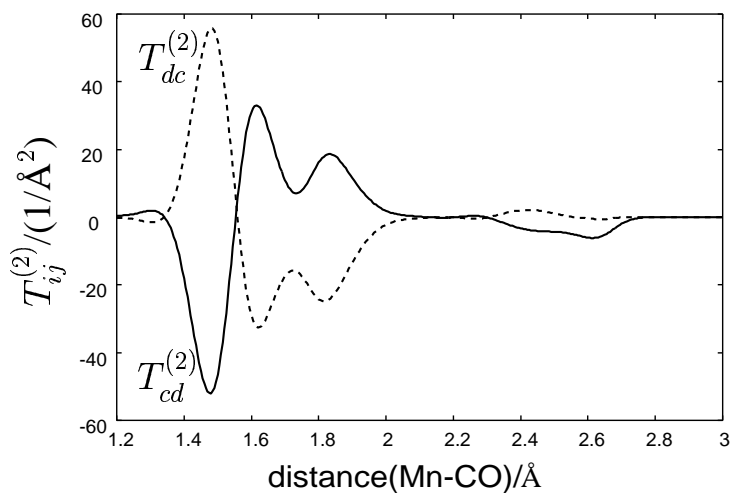


Figure B.21: *Coupling elements $c^1 A' \leftrightarrow d^1 A'$, $T_{cd}^{(2)}$ and $T_{dc}^{(2)}$, calculated using the CI coefficients according to equation (2.119).*
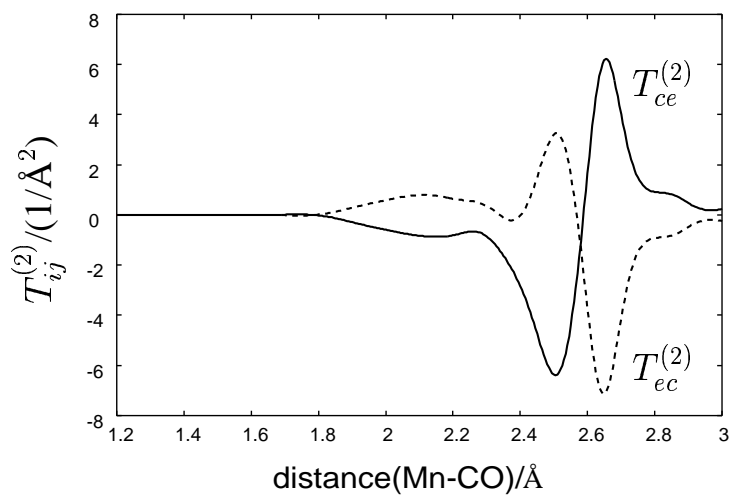
Figure B.22: *Coupling elements $c^1 A' \leftrightarrow e^1 A'$, $T_{ce}^{(2)}$ and $T_{ec}^{(2)}$, calculated using the CI coefficients according to equation (2.119).*
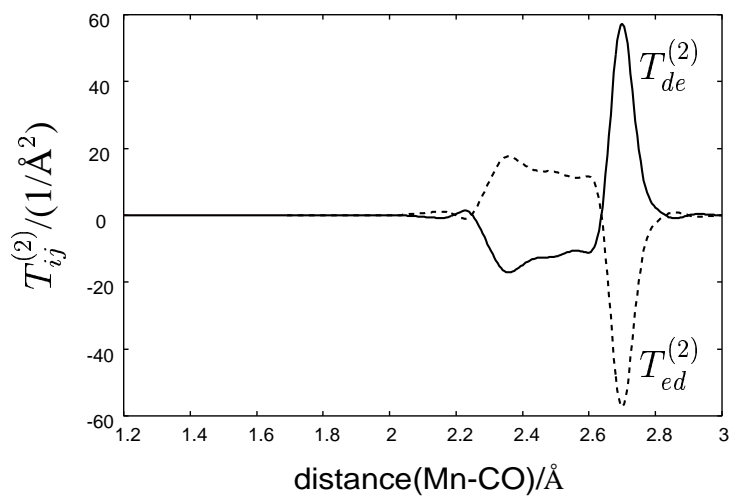


Figure B.23: *Coupling elements $d^1 A' \leftrightarrow e^1 A'$, $T_{de}^{(2)}$ and $T_{ed}^{(2)}$, calculated using the CI coefficients according to equation (2.119).*
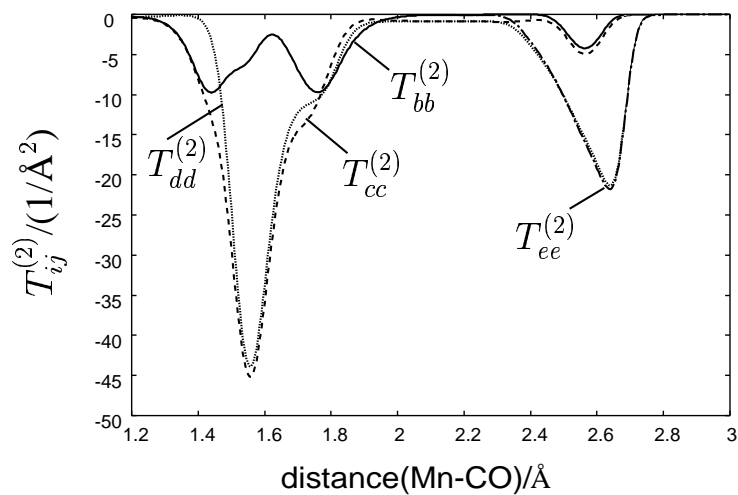
Figure B.24: *A′ states: Diagonal elements of $T^{(2)}$ calculated using the CI coefficients according to equation (2.119).*
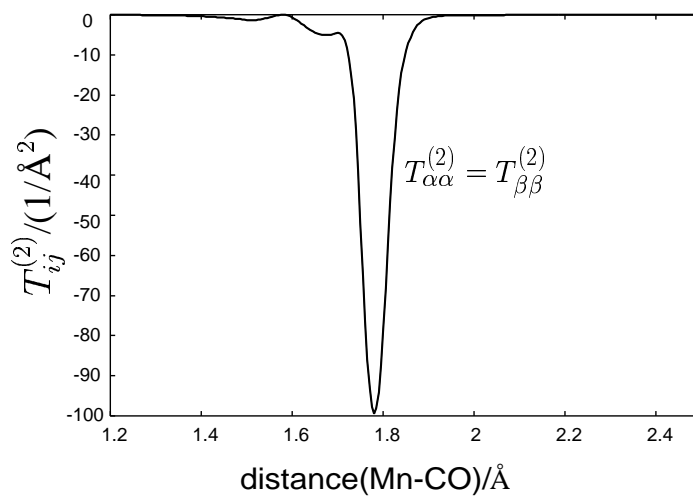


Figure B.25: *A″ states: Diagonal elements of $T^{(2)}$ calculated using the CI coefficients according to equation (2.119).*