Excitation Energies for Transition Metal Compounds from Time-Dependent Density Functional Theory. Applications to MnO_4^-, $Ni(CO)_4$, and $Mn_2(CO)_{10}$

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The first time-dependent density functional theory (TDDFT) calculations on the spectra of molecules containing transition metals are reported. Three prototype systems are considered, of which the assignments are controversial: MnO_4^-, $Ni(CO)_4$, and $Mn_2(CO)_{10}$. The TDDFT results are shown to be comparable in accuracy to the most elaborate ab initio calculations and lead to new insights in the spectra of these molecules. In some cases, the presented TDDFT results differ substantially, in both the ordering and the values for the excitation energies, from the older DFT method for the calculation of excitation energies: the ΔSCF approach. For the $Mn_2(CO)_{10}$ molecule, the presented results are the highest-level theoretical results published so far. Over all, the results show that TDDFT can be a very useful tool in the calculation and interpretation of the spectra of transition metal compounds.

I. Introduction

Although the proposal of the time-dependent density functional equations[1,2] and its theoretical foundation[3] date back quite some time, it has not been until recently that molecular applications of this theory have begun to appear. By now, a whole range of frequency-dependent molecular properties have been obtained from this approach, such as frequency-dependent polarizabilities,[4−7] frequency-dependent hyperpolarizabilities,[8−10] van der Waals dispersion coefficients,[4,11] optical activity,[12] and Raman scattering intensities.[13,14] Perhaps the most popular application of time-dependent density functional theory (TDDFT) in the molecular regime has been the calculation of excitation energies, in which many groups have, by now, been involved.[5,15−33]

The equations from which the excitation energies are obtained are well-established.[18,20,25] They are formally quite similar to the time-dependent Hartree−Fock (TDHF) equations (TDHF is also known as random phase approximation (RPA)) and can be solved efficiently[25] by using iterative techniques, such as the Davidson algorithm.[34−36] The range of molecules for which excitation energies can be calculated with TDDFT is therefore comparable to the range for which a simple self-consistent field (SCF) calculation is possible in DFT. For the SCF calculation, linear scaling techniques have recently been developed in order to be able to handle very large molecules. Those techniques can be applied to the calculation of excitation energies and (frequency-dependent) polarizabilities (almost) without modification, thus further increasing the scope of such calculations to molecules with hundreds of atoms.

Contrary to the TDHF equations, in which only exchange effects are taken into account, the TDDFT equations for the excitation energies are formally exact, including all correlation effects. However, in practical calculations approximations for the occurring exchange-correlation (xc) functionals are required, as in ground state DFT. The appropriateness of the choice for the xc functionals determines the quality of the final results (if technical issues such as basis set selection have been handled properly).

Several issues concerning the accuracy attained in TDDFT excitation energy calculations have already been thoroughly investigated on small (organic) molecules. Furthermore, the applicability of time-dependent DFT applications to large molecules, which forms an important asset in comparison to correlated ab initio approaches, has been shown in calculations on the frequency-dependent hyperpolarizability of the C_{60} molecule,[8] the excitation energies of the higher fullerenes,[22] and the absorption spectra of free base porphin,[26] chlorophyll a,[33] and other large systems,[21] as well as in (hyper)polarizability calculations on quasi-linear conjugated molecular chains.[37,38]

Here, we present time-dependent DFT results on an important class of molecules that has not yet been considered: the compounds containing transition metal atoms. Such compounds represent a difficult case for conventional ab initio approaches, as HF usually provides a very poor starting point. A famous example is given by the equilibrium geometry of ferrocene, for which only very advanced correlated methods, such as coupled cluster calculations provide good results. DFT on the other hand, already yields quite reasonable geometries with the simplest of functionals (such as the Xα functional) and is in good agreement with experiment if the modern generalized gradient approximated (GGA) potentials are applied.[40] For these systems, DFT also has been shown to give good results for vibrational frequencies[40,41] and metal−ligand bond energies,[42] which are competitive in accuracy to advanced ab initio calculations. These DFT successes for transition metal compounds, in combination with the useful accuracy that has been obtained in TDDFT excitation energy calculations so far, make it attractive to apply TDDFT to the calculation of electronic spectra of such systems.

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Our results in this work are compared to the experimental values as well as to high-quality ab initio calculations such as multiconfiguration second-order perturbation theory (CASPT2) and symmetry-adapted cluster configuration interaction (SAC-CI). The assignments obtained by Gray and co-workers,[43−47] on the basis of a variety of experimental and theoretical data, are also discussed. In addition, we present comparisons of our results to previous excitation energy calculations in which an older DFT approach was used, the DFT-ΔSCF approach.[48−50]

The DFT-ΔSCF method uses relaxed Kohn−Sham (KS) orbitals of an excited configuration to evaluate LDA or GGA energies of specific determinantal wave functions (arguments have been put forward in ref 48 to restrict the total energy calculation to electron densities corresponding to single determinants). It is possible, using the "diagonal sum-method" of multiplet theory,[51,52] to resolve many multiplets from these determinantal energies.[48] In the remaining cases, it is possible to mix the DFT and restricted Hartree−Fock types of treatments by explicitly using some two-electron integrals to evaluate a coupling matrix element. Both experimental Racah parameters[53] and explicitly calculated two-electron integrals on the basis of KS molecular orbitals[54] have been used. The use of two-electron integrals has been systematized by Daul using symmetry relations.[55]

Although this DFT-ΔSCF approach is theoretically less well-founded than the TDDFT approach and does not always give a unique final result, we have observed in several cases that the TDDFT and ΔSCF results were close to each other. It is shown here that this is not always the case. In the following, assignments previously suggested in the literature are critically reexamined. In the case of $Mn_2(CO)_{10}$ we provide convincing evidence that the assignments given by Levenson and Gray[46] for the two lowest bands are indeed correct.

II. Theoretical Introduction

In the TDDFT framework (see ref 56 for a recent review) excitation energies can be obtained from the following eigenvalue equation:[5,18,20,25,57]

$$\mathbf{\Omega}\mathbf{F}_i = \omega_i^{\,2}\mathbf{F}_i \tag{1}$$

which, for larger molecules, is usually solved by iterative techniques such as the Davidson algorithm.[34−36] The components of the four-index matrix $\mathbf{\Omega}$ are given by

$$\Omega_{ia\sigma,jb\tau} = \delta_{\sigma\tau}\delta_{ij}\delta_{ab}(\epsilon_{a\sigma} - \epsilon_{i\sigma})^2 + 2\sqrt{(\epsilon_{a\sigma} - \epsilon_{i\sigma})}K_{ia\sigma,jb\tau}\sqrt{(\epsilon_{b\tau} - \epsilon_{j\tau})} \tag{2}$$

where the diagonal components are usually dominated by the squares of the differences between occupied and virtual Kohn−Sham (KS) orbital energies $(\epsilon_{a\sigma} - \epsilon_{i\sigma})^2$ [*a*, *b* refer to unoccupied orbitals and *i*, *j* to occupied ones]. The matrix **K** is the so-called coupling matrix that contains Coulomb and xc parts, of which the latter has to be approximated for practical applications:

$$K_{\mathrm{ia}\sigma,\mathrm{jb}\tau} = \int\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\phi_{\mathrm{i}\sigma}(\mathbf{r})\,\phi_{\mathrm{a}\sigma}(\mathbf{r})\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{xc}}^{\sigma\tau}(\mathbf{r},\mathbf{r}',\omega)\right] \times \phi_{j\tau}(\mathbf{r}')\,\phi_{b\tau}(\mathbf{r}') \tag{3}$$

where the ϕ's are the KS orbitals and f_{xc} is the so-called xc kernel: the functional derivative of the usual xc potential with respect to the density.

In eq 1, ω_i represents the desired excitation energies, while the oscillator strengths are obtained from the eigenvectors $\mathbf{F}_i$.[18] For a spin-restricted calculation, the $\mathbf{\Omega}$ matrix can be split into separate singlet and triplet parts $\mathbf{\Omega}^{\mathrm{S}}$ and $\mathbf{\Omega}^{\mathrm{T}}$, by performing a unitary transformation on the density matrix elements in which spin−flip processes (for the triplet excitation energies) are separated from the processes that keep the total spin unchanged (singlet excitation energies). The singlet and triplet matrices can be diagonalized separately. Here, we restrict ourselves to singlet−singlet excitations.

According to Casida,[18] the eigenvectors $\mathbf{F}_i$ can be used for an approximate description of the excited states. Here one assumes (among other things) that the single determinant of the KS orbitals is a reasonable approximation to the true ground state wave function. The description is therefore based on KS orbitals, which may differ considerably from HF orbitals. This should be kept in mind when comparing to ab initio descriptions of excited states, which are usually based on HF or MCSCF wave functions.

III. Technical Details of the Calculation

All calculations were performed with the RESPONSE module,[58] described in detail in refs 25 and 59, of the Amsterdam Density Functional program (ADF).[60−62] The ADF program uses Slater type orbital (STO) basis sets and contains a density fitting procedure for the efficient evaluation of the Coulomb potential.[60] It further uses an accurate numerical integration scheme[61] and is well parallelized.[62]

Two approximations are made in TDDFT excitation energy calculations. The first one is the approximation for the exchange-correlation potential, which determines the KS orbitals ϕ_i and orbital energies ϵ_i. The second approximation is the approximation for the functional derivative of the exchange-correlation potential with respect to the density: the exchange-correlation kernel f_{xc} in eq 3. In this work we make the Adiabatic Local Density Approximation (ALDA) for the exchange-correlation kernel, in which the frequency-dependence of the kernel is ignored. This approximation has been used in almost all previous TDDFT excitation energy calculations. Calculations on atoms and small molecules in which the ALDA was used for f_{xc} in combination with "exact" (very accurate) xc potentials[17,24] suggest that, at least for those systems, the main error is due to the currently used approximations to the potential and not to approximations to the kernel. This is further supported by the very encouraging results that have been obtained for CO, N_2, and CH_2O with a newly developed approximation for v_{xc}. This new approximation to the xc potential, in combination with the ALDA, provided excellent results for a variety of excitation energies and response properties for these three molecules.[63] This strongly suggests that, for small molecules, especially for the low-lying excitations considered here, the use of the ALDA is not expected to be a significant source of error. On the other hand, if one considers double excitations or states with significant double excitation character, the frequency dependence of f_{xc} will become more important. This makes the validity of the ALDA less clear for highly excited states. For the transition metal complexes investigated in this paper, however, we believe that, for excitations with a dominant single excitation character, the main source of error is in v_{xc}, and not in f_{xc}.

For the exchange-correlation potential we employ generalized gradient approximated potentials (GGAs) by Becke[64] for exchange and Perdew[65] for correlation (BP). Test calculations with the LDA potential showed that the inclusion of a gradient-corrected potential leads only to small changes. Some test calculations with the Van Leeuwen−Baerends potential[66] (LB94) which corrects the LDA xc potential in the outer region of the molecule have also been performed.

TABLE 1: Allowed Excitation Energies of MnO_4^-

excitation	expt[a]	BP/ALDA[a]	LB94/ALDA	SDCI[b]	SAC-CI	ΔSCF[c]	ΔSCF[d]
a^1T_2	2.27	2.82	2.63	2.6	2.57	(2.57)	2.71
b^1T_2	3.47	3.89	3.60	4.2	3.58	(3.42)	4.02
c^1T_2	3.99	4.74	4.52	4.5	3.72	(3.76)	4.22
d^1T_2	5.45	5.84	5.46	6.0	5.82	(5.99)	5.70

[a] Results by Holt and Ballhausen.[80] [b] Singles and doubles Cl.[81]. [c] Dickson and Ziegler,[54] optimized geometries for average of configurations, GGA. The numbers have been given in parentheses as they do not correspond to vertical excitation energies, as do the other theoretical numbers in the table. [d] Stuckl et al.,[68] transition state method, ground state geometry, LDA.

The MnO_4^- and $Ni(CO)_4$ molecules were studied in T_d symmetry. The Mn−O distance in MnO_4^- was taken to be the experimental value of 1.629 Å as in refs 67 and 68. For $Ni(CO)_4$, we used the geometry given in ref 69 with a Ni−C distance of 1.838 Å and a C−O distance of 1.141 Å. For $Mn_2(CO)_{10}$, we assumed, as usual,[70] a D_{4d} symmetry, in which the two sets of equatorial CO's are in a staggered configuration with respect to each other. Three different geometries were used as the results appeared to be strongly geometry dependent. Two of these geometries are experimental,[71,72] while the third was a BP-optimized geometry of ref 70 (Table 6, row 9), which was also used in unpublished ΔSCF test calculations.[73]

Further technical details concern the convergence of the SCF procedure, the numerical integration accuracy, the criterion for neglecting tails of functions in regions of space where they are close to zero, the convergence of the iterative procedure for solving the excitation energy eigenvalue equation (eq 2), and the criterion for the orthonormality of the trial vectors in this procedure. Some tests with very strict values revealed that the default values for these criteria were sufficient for reliable results.

For MnO_4^- and $Ni(CO)_4$, we used the largest available standard Slater type orbital (STO) basis sets in the ADF basis set database.[74] For the C and O atoms this is a valence triple-ζ basis set with a 3d and a 4f polarization function ("basis V"), and a 1s frozen core. For the Mn and Ni atoms, this was a valence (3d, 4s) triple-ζ basis set with one 4p function ("basis IV") and a frozen core up to 2p. For $Mn_2(CO)_{10}$ the reported results correspond to slightly different basis sets used in ref 70. For C and O this was a quadruple-ζ basis with a d polarization function, for Mn it was an extension of the basis used for Mn in MnO_4^-. Additional calculations with the same basis sets for Mn, C, and O as used for MnO_4^- and $Ni(CO)_4$ led to very small changes and are not reported here. It has been tested that, as expected, the use of all-electron calculations, i.e., avoiding the use of frozen core approximations, leads to negligible changes in the excitation energies (typically 0.01 eV).

IV. Results and Discussion

Below we discuss our results for the MnO_4^-, $Ni(CO)_4$, and $Mn_2(CO)_{10}$ molecules. Other TDDFT calculations with the ADF program on transition metal compounds are in progress. Of these, we just mention the TDDFT results for $Cr(CO)_6$,[25,75,76] which reconfirm the assignments based on the CASPT2[69] and DFT-ΔSCF[77] approaches, thus challenging the long-standing assignments by Beach and Gray[43,44] on the nature of the lowest excited states of these systems. The TDDFT results are, in this case, in much better agreement with the experimental and CASPT2 values than the ΔSCF results are.

A. Results for MnO_4^-. The spectrum of MnO_4^- represents a very interesting case for two reasons. First, the assignments of its spectrum have undergone a lot of changes throughout the years, as can be seen from the overview in ref 67. Second, a lot of work has been done on this molecule with the ΔSCF method or related methods,[54,78,79] which represent the main alternatives to TDDFT for the calculation of excitation energies within DFT. For this reason, the permanganate ion can be used to show some important numerical and conceptual differences between ΔSCF and TDDFT approaches to excitation energies.

The experimental spectrum was measured by Holt and Ballhausen[80] (also shown in ref 67). These experimental excitation energies are shown in Table 1, together with theoretical results for the spin- and dipole-allowed excitation energies, which belong to the T_2 irrep of this tetrahedral [T_d] molecule. The four BP/ALDA excitation energies are all shifted upward with respect to the experimental values. The overestimations are +0.52, +0.37, +0.70, and +0.33 eV, respectively. This is remarkable as for some other molecules the BP approximation or other local or gradient-corrected density functionals have led to underestimations of typically 0.3 eV.[20,23] We also performed test calculations with the asymptotically correct (behaving as $-1/r$ for large r) Van Leeuwen−Baerends (LB94) xc potential[66] on this molecule. The results are 0.2−0.4 eV lower than the BP numbers just mentioned. The LB94 potential usually shifts the excitation energies down with respect to LDA or GGA, which in this case leads to improvement (but not always; see $Mn_2(CO)_{10}$ below). The downshift in the LB94 results for MnO_4^- may be related to the improvement of the potential in the outer region of the molecule (especially because we are dealing with a negative ion) but could also be related to the different behavior of the LB94 potential in the inner region of the molecule. The improvement could therefore be accidental (see also the LB94 results for $Mn_2(CO)_{10}$ discussed below). The assignments do not change in going from BP to LB94.

The BP/ALDA results for MnO_4^- imply that those who devise improved functionals should include transition metal compounds in their test set of molecules, as these may display different characteristics than simple organic molecules. The BP/ALDA results should be compared to the values of +0.33, +0.73, +0.51, and +0.55 eV for the SDCI results[81] and +0.30, +0.11, −0.27, and +0.37 eV for the SAC-CI values.

The two sets of ΔSCF results in Table 1 differ substantially. Although the methods used are slightly different (original ΔSCF with two-electron integrals[54] versus a transition state method[68,69]), as are the functionals used, the most likely origin of the difference, in our opinion, is the fact that different geometries were used for ground and excited states in ref 54. For this reason, the results of ref 54 are not directly comparable to the other theoretical results and have been given in parentheses in Table 1. The differences between the ΔSCF and TDDFT results are also important and deserve some discussion. The ΔSCF methods, at least in their original form,[48,78] actually aim at calculating an orbital replacement energy. In cases such as MnO_4^-, where strong mixing occurs between close-lying configurations, it is not straightforward to make a direct correspondence between the excitation energies and the orbital replacement energies. From the TDDFT results on the assign-

TABLE 2: Oscillator Strengths and Assignments of MnO_4^- [a]

state	expt	BP/ALDA[b]	ΔSCF[c]	SDCI[d]	SAC-CI[e]
a^1T_2	strong $1t_1 \rightarrow 2e$, $f = 0.03$[f]	0.0070 $1t_1 \rightarrow 2e$ 88%	$1t_1 \rightarrow 2e$	$1t_1 \rightarrow 2e$	0.0202 $1t_1 \rightarrow 2e$
b^1T_2	weak $1t_1 \rightarrow 7t_2$[e]	0.0011 $6t_2 \rightarrow 2e$ 63% ($1t_1 \rightarrow 7t_2$ 36%)	$1t_1 \rightarrow 7t_2$	$6t_2 \rightarrow 2e$	0.0045 $1t_1 \rightarrow 7t_2$
c^1T_2	strong $6t_2 \rightarrow 2e$, $f = 0.07$[f]	0.0096 $1t_1 \rightarrow 7t_2$ 50% ($6t_2 \rightarrow 2e$ 17%, $6t_2 \rightarrow 7t_2$ 20%)	$6t_2 \rightarrow 2e$	$1t_1 \rightarrow 7t_2$	0.0136 $6t_2 \rightarrow 2e$
d^1T_2	strong $6t_2 \rightarrow 7t_2$[e]	0.0034 $6t_2 \rightarrow 7t_2$ 48%; $6a_1 \rightarrow 7t_2$ 46%	$6t_2 \rightarrow 7t_2$		0.0022 $6t_2 \rightarrow 7t_2$, $6a_1 \rightarrow 7t_2$

[a] Assignments based on all-electron calculation. [b] This work. [c] Ref 54. [d] Ref 81. [e] Ref 67. [f] Ref 47.

ments in Table 2, one can see that strong mixing occurs at the TDDFT level between different orbital replacements. It should be noted that the TDDFT results always refer to the ground state orbitals. The ΔSCF results, however, refer to separately optimized excited state orbitals. One might argue that, in the ΔSCF case, the self-consistent procedure for the excited or transition state should partially account for the mixing between several orbital replacements. As has been detailed in ref 78, orbital relaxation is particularly strong in excited states of MnO_4^-.

All methods gathered in Tables 1 and 2 agree upon the assignment for the first band to an excitation with predominantly $1t_1 \rightarrow 2e$ character. The TDDFT and SAC-CI results are in agreement for the fourth band, which should be assigned to a mix of the $6t_2 \rightarrow 7t_2$ and $6a_1 \rightarrow 7t_2$ orbital transitions. However, the assignments for the second and third bands remain controversial. The SAC-CI and ΔSCF methods assign the second band to a $1t_1 \rightarrow 7t_2$ transition and the third band to $6t_2 \rightarrow 2e$. On the other hand, the TDDFT results are in agreement with the SDCI results, in which these two assignments are reversed. In some further test calculations with other xc functionals recently developed in our group (such as the LB94 potential just mentioned), no changes in assignments with respect to our present TDDFT results were observed. In any case one should take into account that there is a considerable mixing in our results between the configurations responsible for the second and third bands.

An important advantage of the TDDFT approach with respect to ΔSCF techniques, is that oscillator strengths are directly accessible. In Table 2, the TDDFT results can be seen to be in agreement with the experimental finding that the second band is the weakest one. In the SAC-CI calculations, the fourth oscillator strength comes out as the weakest band.

Our permanganate results show that the TDDFT and ΔSCF approaches can certainly not be treated as being roughly equivalent. For this molecule, the use of the ΔSCF approach leads to noticeable quantitative differences with respect to the full TDDFT approach. The ΔSCF results give a different assignment but are (with that assignment) in rather good agreement with experiment. On the basis of the results for the permanganate ion alone, one cannot make statements on the relative accuracy of the ΔSCF and TDDFT approaches to excitation energies. The ΔSCF results are closer to the SAC-CI ones, and the TDDFT results are closer to the SDCI values. Higher level theoretical results are needed to come to definite values and assignments, although, admittedly, the assignments by Ballhausen and Gray,[47] based on indirect evidence from various sources, are consistent with the ΔSCF and SAC-CI assignments. Unfortunately, CASPT2 calculations (which would yield valuable data for comparison) have not yet been performed on this molecule. For this method, the permanganate ion is a difficult system to treat because a (too) large number of active orbitals needs to be considered,[82] in agreement with the analysis of the "weak" metal 3d to oxygen 2p bonding in ref 83.

TABLE 3: All Low-lying Singlet Excitation Energies of MnO_4^- up to 6 eV (Results in eV)[a]

state	TDDFT[b]	SAC-CI[c]	Δ(SAC-CI − TDDFT)[d]
a^1T_1	2.41	2.18	−0.23
a^1T_2	2.83	2.57	−0.26
b^1T_1	3.75	3.33	−0.42
b^1T_2	3.91	3.58	−0.33
a^1A_2	3.99	4.46	+0.47
c^1T_1	4.13	4.12	−0.01
a^1E	4.18	3.41	−0.77
b^1E	4.55	3.54	−1.01
c^1T_2	4.75	3.72	−1.03
c^1E	5.43	5.47	+0.04
d^1T_1	5.49	5.30	−0.19
b^1A_1	5.52	5.41	−0.11
b^1A_2	5.80		
d^1T_2	5.85	5.82	−0.03
e^1T_1	6.15		

[a] Comparison of TDDFT results to SAC-CI results. [b] This work, using BP/ALDA approximations. [c] Ref 67. [d] Difference between CASPT2 (or SAC-CI) excitation energy and TDDFT excitation energy (this work) in eV.

A comparison of all singlet excitation energies (both dipole-allowed and forbidden excitations) up to 6 eV is given in Table 3, where our BP/ALDA TDDFT results are compared to SAC-CI. With a few exceptions, the TDDFT results are higher than the SAC-CI results, as was the case for the allowed excitations. The order of the excitations differs substantially between these two methods, which is hardly surprising in view of the large number of close-lying states. The average difference between the SAC-CI and BP/ALDA results is 0.38 eV. The largest differences occur for the b^1E and c^1T_2 excitations. In both cases the BP/ALDA result is 1 eV above the SAC-CI result, which is in better agreement with experiment for the c^1T_2 excitation.

Finally, we note that the use of the single pole approximation (SPA), developed by Petersilka, Gross, and co-workers[15−17] seems questionable in this case. The SPA is a very cheap way to calculate excitation energies within TDDFT, as it requires the evaluation of a single matrix element only, instead of a complete iterative procedure. It is intended for excitations that are well separated in energy from other excitations and where interconfiguration mixing is limited. In a way, it is an approximation based on the diagonal matrix elements of the $\mathbf{\Omega}$ matrix.

For MnO_4^-, the off-diagonal matrix elements are important, and neglecting them leads to deviations of no less than a few electronvolts with respect to the full TDDFT results (full diagonalization of $\mathbf{\Omega}$) for some excitations. As it is hard to establish the importance of the off-diagonal matrix elements beforehand, the use of the full diagonalization of $\mathbf{\Omega}$ is certainly safer for molecular excitation energies, although one has to pay the price of longer execution times (which are on the order of the execution times needed for an ordinary SCF calculation).

B. The $Ni(CO)_4$ Molecule. Experimentally, the spectrum of $Ni(CO)_4$ has been measured in solution,[84] in a matrix,[85] and recently in the gas phase.[86] As summarized in ref 69, peaks were observed at 6.02, 5.52, and 5.24 eV (in solution), at 5.17 and 4.54 eV (in matrix), and at 4.5, 5.4, and 6.0 eV in the gas phase. These experimental results have been attributed to four main bands in the energy region up to 6.2 eV (the experiments

TABLE 4: Experimental Dipole-Allowed Excitation Energies (in eV) and Theoretical Excitation Energies, Oscillator Strengths, and Assignments for Ni(CO)$_4$

method		property	band I	band II	band III	band IV	band V
expt	solvent[a]	exc en (eV)		5.24	5.52	6.02	
expt	matrix[b]	exc en (eV)	4.54	5.17			
expt	gas[c]	exc en (eV)	4.5	5.4		6.0	
theory	CASSCF[d]	exc en (eV)	7.34	7.49	7.57	7.67	8.16
theory	CASPT2[d]	exc en (eV)	4.34	5.22	5.57	6.28	6.97
theory	SAC-CI[e]	exc en (eV)	4.79	5.51	5.72	5.76	
theory	TDDFT[f]	exc en (eV)	4.70	4.82	5.37	5.84	6.74
theory	CASSCF[g]	assignments	$9t_2 \rightarrow 10t_2$ 92%	$9t_2 \rightarrow 3e$ 92%	$2e \rightarrow 10t_2$ 94%	$9t_2 \rightarrow 2t_1$ 93%	$2e \rightarrow 2t_1$ 88%
theory	SAC-CI[h]		$9t_2 \rightarrow 12t_2$ 54%	$9t_2 \rightarrow 4e$ 48%	$9t_2 \rightarrow 9a_1$ 69%	$2e \rightarrow 12t_2$ 42%	
theory	SAC-CI[h]	assignments	$9t_2 \rightarrow 4e$ 8%	$9t_2 \rightarrow 9a_1$ 20%	$9t_2 \rightarrow 10a_1$ 20%	$9t_2 \rightarrow 3t_1$ 19%	
theory	SAC-CI[h]			$2e \rightarrow 12t_2$ 18%	$9t_2 \rightarrow 3e$ 10%		
theory	TDDFT[f]		$9t_2 \rightarrow 10t_2$ 56%	$9t_2 \rightarrow 3e$ 49%	$9t_2 \rightarrow 2t_1$ 52%	$2e \rightarrow 10t_2$ 51%	$2e \rightarrow 2t_1$ 47%
theory	TDDFT[f]	assignments	$9t_2 \rightarrow 3e$ 35%	$9t_2 \rightarrow 10t_2$ 23%	$2e \rightarrow 10t_2$ 19%	$2e \rightarrow 2t_1$ 37%	$2e \rightarrow 10t_2$ 9%
theory	CASPT2[d]	osc str	0.29	0.38	0.29	0.47	0.83
theory	SAC-CI[e]	osc str	0.0023	0.0067	0.0043	0.0089	
theory	TDDFT[f]	osc str	0.006	0.099	0.123	0.086	1.002

[a] Ref 84. [b] Ref 85. [c] Ref 86. [d] Ref 69. [e] Ref 67. [f] This work, using BP/ALDA approximations. [g] CASSCF wave function taken as reference/ground state wave function. [h] HF wave function taken as reference/ground state wave function. [i] BP used for ground state solution, orbital numbers based on all electron calculation (this work).

did not go beyond this energy value) and are gathered in the upper part of Table 4 where the most reliable ab initio calculations have also been given, including the present TDDFT results at the BP/ALDA level. The excitation energies in Table 4 are the lowest dipole-allowed T_2 excitation energies of this molecule, which has T_d symmetry. We have included the best CASPT2 results of ref 69 and the best symmetry-adapted cluster configuration interaction (SAC-CI) results of ref 87.

Other theoretical treatments of the spectrum of Ni(CO)$_4$ have also appeared in the literature. The first theoretical study used the intermediate neglect of differential overlap in the spectroscopic parametrization model with a subsequent configuration interaction (INDO/S CI).[86] Although an assignment of the experimental values was given on the basis of these results, the agreement with experiment was poor and the assignment is consequently in disagreement with the assignments based on the higher level approaches discussed below.

In ref 87, single-excitation CI (SECI) results are reported next to the SAC-CI ones. The SECI results are too high in energy and much poorer than the SAC-CI results of Table 4. In ref 69, CASSCF results are also reported (based upon CASSCF calculations for the excited states), but they are in quite poor agreement with the experimental values, being typically 2−3 eV too high. The authors of ref 69 attribute this to an active space that is too limited, which, with current computer resources, cannot be helped. The limitations in the size of the active space influence both the CASSCF results and the CASPT2 results, which are based on them. The poor results for excitation energies at the CASSCF level are improved upon considerably by including dynamical correlation with CASPT2. However, other, related quantities, such as the wave function composition and the transition dipoles are not available at the PT2 level and are still based on the CASSCF wave function. So, the amount of interconfiguration mixing in the excited state CASSCF wave function, which is shown in the middle of Table 4, depends on the size of the active space. As the oscillator strengths obtained in both CASSCF and CASPT2 are obtained from dipole matrix elements calculated from CASSCF wave functions, one should also be careful not to overinterpret the "CASPT2" results for these properties in cases where the active space is too limited.

The TDDFT, CASPT2, and SAC-CI approaches in Table 4 all give rise to four dipole-allowed excited states in the energy window of 4.0−6.5 eV, in agreement with experiment. In contrast to this, INDO/S CI[86] yields six of such states, CASSCF[69] yields zero (!), and SECI yields two. Reasonable assignments can be obtained from both the TDDFT, CASPT2, and the SAC-CI approaches, although the assignments in Table 4 show that there are important differences. Before discussing these assignments, we should note that the CASPT2 assignments are based on the CASSCF wave functions for the excited configuration, while the SAC-CI assignments are based on a HF ground state. For our TDDFT results the labeling refers to the one in an all-electron BP calculation, although in the actual calculations we used frozen cores. By using the labeling of an all-electron calculation, the comparison to other work is simplified. If one keeps the caveats mentioned in the Introduction in mind, one can compare the TDDFT assignments to the CASSCF and SAC-CI numbers.

The BP and CASSCF approaches lead to similar assignments, as can be observed in this table, while at the HF level the $10t_2$, $11t_2$, $2t_1$, and 3e levels are Rydberg-like and do not play a role in the low-lying excitations. These Rydberg levels do cause a different labeling of the relevant virtuals in the SAC-CI results, however, because the $10t_2$, $11t_2$, $2t_1$, and 3e orbitals do not appear in the TDDFT and CASSCF low-energy orbital sets. This may be a basis set effect.

The CASSCF interconfiguration mixing is very limited, as can be seen from the high percentages in this table. As was just explained, this could be an artifact of the too limited active space[69] that could be used, but the fact that the CASSCF wave functions are relaxed for each excited state separately could also be of importance. Contrary to this, the TDDFT results always refer to the occupied and virtual ground state KS orbitals.

Apart from the percentages, there is agreement on the assignment for the lowest two excited states, which should be mainly attributed to $9t_2 \rightarrow 10t_2$ and $9t_2 \rightarrow 3e$ orbital transitions, respectively (or $9t_2 \rightarrow 12t_2$ and $9t_2 \rightarrow 4e$ in the SAC-CI case). In the SAC-CI assignments, the $9a_1$ and $10a_1$ virtuals appear, which do not play an important role in the TDDFT calculations. In the CASSCF calculations, these orbitals were not included in the active space and could therefore not become populated. For this reason, the $9a_1$ and $10a_1$ virtuals also do not appear in the CASSCF assignments.

Contrary to the case for the lowest two excitations, there is

TABLE 5: All Low-lying Singlet Excitation Energies of $Ni(CO)_4$ (in eV)[a]

state	TDDFT[b]	CASPT2[c]	Δ(CASPT2-TDDFT)[d]	SAC-CI[e]	Δ(SAC-CI-TDDFT)[d]
a^1T_1	4.36	4.04	−0.32	4.53	0.17
a^1E	4.60	3.58	−1.02	4.52	−0.08
b^1T_1	4.62	4.88	0.26	4.97	0.35
a^1T_2	4.70	4.34	−0.36	4.79	0.09
b^1T_2	4.82	5.22	0.42	5.51	0.69
a^1A_2	4.95	5.15	0.20	6.07	1.12
b^1A_1	4.99	3.72	−1.27	5.41	0.42
c^1T_1	4.99	5.14	0.15	5.25	0.26
b^1E	5.06	5.20	0.14	6.28	1.22
c^1T_2	5.37	5.57	0.20	5.72	0.35
d^1T_1	5.45	6.00	0.55		
b^1A_2	5.60	6.01	0.41		
d^1T_2	5.84	6.28	0.44	5.76	−0.08
c^1E	6.02	6.13	0.11		
e^1T_1	6.04	7.05	1.01		
e^1T_2	6.74	6.97	0.23		
$f\,^1T_2$	6.99				

[a] Comparison of TDDFT results to other theoretical methods. [b] This work, using BP/ALDA approximations. [c] Ref 69. [d] Difference between CASPT2 (or SAC-CI) excitation energy and TDDFT excitation energy (this work) in eV. [e] Ref 67.

no agreement on the assignment of the third and fourth transitions. The TDDFT and CASSCF assignments are reversed with respect to each other (the TDDFT assignment for the fourth band agreeing with the SAC-CI assignment). The SAC-CI assignments of the third band to a $t_2 \rightarrow a_1$ transition cannot be related to any of the assignments with the other methods. The CASSCF and TDDFT assignments are again in agreement for the fifth excitation energy (although the CASSCF mixing is again quite low), for which no SAC-CI result is available.

In the lower part of Table 4, the oscillator strengths are given for the three methods. Surprisingly, the CASPT2 (based on CASSCF dipole moment integrals) and SAC-CI results differ by almost 2 orders of magnitude, while the TDDFT results are somewhere in between. As regards the TDDFT oscillator strengths, the first one is clearly the smallest, in agreement with the small peak observed experimentally. The other three peaks are of comparable magnitude in all three approaches, whereas the 6.0 eV peak is experimentally clearly the strongest one.

Next to the experimentally observable excitation energies, the dipole-forbidden singlet excitation energies have also been calculated with the CASPT2 and SAC-CI methods. We compare our results for all low-lying excitation energies up to 7 eV to the available data from these ab initio calculations in Table 5. For ease of reference, the allowed T_2 excitations, which have already been discussed, are included in this table as well. The differences between the ab initio results and our TDDFT results are also reported.

Although caution is needed in drawing conclusions based on theoretical results alone, a few comments on the results in this table are in order. The CASPT2 excitation energies start at 3.58 eV, which is much lower than the 4.36 eV for our BP/ALDA results and especially the 4.52 eV obtained in SAC-CI. In the cases where CASPT2 is clearly below TDDFT (a^1E 1.02 eV; b^1A_1 1.27 eV), the SAC-CI results are much closer to TDDFT. For the b^1A_1 excitation it is even 0.42 eV higher in energy, which leads to the conclusion that CASPT2 probably underestimates these excitation energies.

In all cases where comparison is possible, the SAC-CI excitation energies are higher than the TDDFT results, with the exceptions of the a^1E and d^1T_2 excitations, which are both slightly lower (0.08 eV). There are three cases where the SAC-CI results are more than 0.5 eV above the TDDFT results: b^1T_2 (0.69 eV), a^1A_2 (1.12 eV), and b^1E (1.22 eV). In all three cases, the CASPT2 results are between the TDDFT and SAC-CI results. The BP/ALDA result for b^1T_2 is almost certainly too low, as is evident from a comparison to both sets of ab initio results and to the experimental results of Table 4. On the other hand, the SAC-CI results for a^1A_2 and b^1E seem to be too high, as the CASPT2 results and TDDFT results are close for these cases and typically 1 eV lower. It has furthermore been argued in ref 69 that the SAC-CI results are too high by roughly 0.4 eV, due to the fact that the metal core 3s and 3p electrons were not correlated in the SAC-CI calculations. Our present comparison is consistent with that conclusion.

On the whole, the TDDFT results seem to be somewhat too low in comparison to the other methods (and also in comparison to the experimental data of the previous table, on average). This is especially true for the excitations in the range 5−7 eV, where all TDDFT results are below the corresponding CASPT2 and SAC-CI results.

For most excitations the discrepancies are much smaller, giving an overall reasonable agreement. For other excitations (such as e^1T_2) there are still considerable discrepancies, but there are insufficient data for statements about the relative accuracy of the methods.

Although the three approaches in Tables 4 and 5 give reasonable agreement with experiment and each other, further theoretical work is clearly needed in order to give definite unambiguous assignments and oscillator strengths, in particular for bands III and IV, as well as for some of the forbidden transitions. It is important to note that all three approaches have at least one weakness. The restrictions of the active space in the CASPT2 calculation have already been mentioned. In the SAC-CI calculations, only a limited number of occupied orbitals has been correlated, which can be expected to be of importance if one considers the significant differences that occur in the results of ref 69 if the metal core 3s and 3p electrons are correlated, in addition to those that are correlated in the SAC-CI calculations. Finally, the approximate nature of the xc functionals in the TDDFT calculations leads to a source of error for which it is hard to give a quantitative estimate.

C. Results for $Mn_2(CO)_{10}$. The experimental spectrum of $Mn_2(CO)_{10}$ has been studied by Gray and co-workers[45,46] in solution. On the basis of a variety of experimental and semiempirical theoretical data, they came to assignments of the main peaks in their spectra. It is summarized here, using the orbital assignments of refs 88 and 89 and the experimental spectral data from Table 3 of ref 46.

TABLE 6: Excitation Energies and Oscillator Strengths for Bands I and II of $Mn_2(CO)_{10}$ in Three Different Geometries

method	geometry	property	band I	band II
TDDFT, BP/ALDA	expt A[a]	excitation energy in eV (cm^{-1})	3.44 (27 700)	4.01 (32 400)
TDDFT, BP/ALDA	expt B[b]		3.35 (27 000)	3.84 (30 900)
TDDFT, BP/ALDA	BP-optimized[c]		3.22 (26 000)	3.76 (30 300)
ΔSCF	BP-optimized[c]		3.07 (24 800)	2.95 (23 800)
Experimental spectrum[d]			3.31 (26 700)	3.69 (29 740)
TDDFT, BP/ALDA	expt A[a]	oscillator strength	0.006	0.252
TDDFT, BP/ALDA	expt B[b]		0.006	0.350
TDDFT, BP/ALDA	BP-optimized[c]		0.007	0.384
Experimental spectrum[d]			weak	strong
TDDFT, BP/ALDA	expt A[a]	assignment	$d_\pi \rightarrow \sigma^*$	$\sigma \rightarrow \sigma^*$
TDDFT, BP/ALDA	expt B[b]		$d_\pi \rightarrow \sigma^*$	$\sigma \rightarrow \sigma^*$
TDDFT, BP/ALDA	BP-optimized[c]		$d_\pi \rightarrow \sigma^*$	$\sigma \rightarrow \sigma^*$
Experimental spectrum[d]			$d_\pi \rightarrow \sigma^*$	$\sigma \rightarrow \sigma^*$

[a] X-ray diffraction.[71] [b] Electron diffraction.[72] [c] Becke−Perdew optimized geometry (ref 70, Table 6, row 9). [d] Experimental results and interpretation from ref 46.

The first strong band (band II) at 3.69 eV (29 740 cm^{-1}) is attributed to a transition between the σ and σ^* orbitals associated with the metal−metal bond. It has a poorly resolved low-energy shoulder at 3.31 eV (26 700 cm^{-1}, band I), which is attributed to a $d_\pi \rightarrow \sigma^*$ ($8e_3 \rightarrow 10b_2$) transition. Band system III, roughly located at 35 000−40 000 cm^{-1} (4.3−5.0 eV), is assigned to a variety of metal−ligand charge transfer (MLCT) transitions. Band IIIB (4.66 eV or 37 600 cm^{-1}) is assigned to $d_\pi \rightarrow \pi^*$ and band IIIA (4.09 eV or 33 000 cm^{-1}) to $\sigma \rightarrow \pi^*$ transitions. Except for the fact that its oscillator strength is equal to 2.6 experimentally, little information is available on the strong band IV (with its maximum at 49 100 cm^{-1} (6.09 eV)), which has the general designation $M \rightarrow \pi^*$. This excitation is believed to be to π^* orbitals with no metal d, s, or p character. According to Levenson and Gray, it is reasonable to assign band IV to a combination of $8e_1 \rightarrow 2a_2$ and $8e_3 \rightarrow 2b_1$, as both terminate in pure π^* ligand orbitals.

In disagreement with the assignments proposed by Levenson and Gray, Mayer and Gaspar[90] argue, in their review of the photochemistry of $Mn_2(CO)_{10}$, that CO loss, which is observed upon irradiation in band II, occurs from a d → d excited state, which implies that this d → d transition should be one of the lowest allowed excitations. In ref 88, ΔSCF calculations were performed to which Levenson and Gray's assignments could also be compared. The focus in these ΔSCF calculations was mainly on the two lowest bands, as these are important for photochemistry; see ref 89. For the lowest two bands the ΔSCF results agree with the $d_\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ character suggested by Levenson and Gray, but the calculated ordering was reversed compared to the one of Levenson and Gray. Subsequent intensity calculations[89] unambiguously proved the $\sigma \rightarrow \sigma^*$ transition to correspond to the very intense band II, the ΔSCF order thus disagreeing with experiment. The problems of the ΔSCF treatment on the lowest two excited states of $Mn_2(CO)_{10}$ provided our main motivation for treating this molecule, the other reason being that only little work has been done on the higher-lying excited states.

Below we discuss our results for the two lowest bands, I and II, and the strong band IV in some detail. Band III is not considered here. It is not as controversial as the other bands, and we have observed in our test calculations that a large number of relatively weak transitions are collectively responsible for this broad band system, in agreement with Levenson and Gray's analysis. It is already apparent from the data in ref 88 that a large number of transitions is present in the energy regime of the band III system.

For our study we employed the three geometries mentioned earlier. Important differences between our results with these geometries were found. For this reason, we present our results for all geometries, to underline the sensitivity of the results on the molecular structure. Our results for the two lowest dipole-allowed singlet excitations are gathered in Table 6.

The theoretical TDDFT results for band I are in the range 3.2−3.4 eV (26 000−27 700 cm^{-1}). They are thus centered around the experimental value of 3.31 eV (26 700 cm^{-1}). For band II, the TDDFT values of 3.76, 3.84, and 4.01 eV are only slightly higher than the position of the experimental band at 3.69 eV. The splitting between bands I and II is therefore also slightly overestimated. In contrast to the excellent agreement with experiment obtained with the TDDFT approach, the ΔSCF values are not so good. The ΔSCF numbers in the table were taken from earlier calculations[73] in which the same BP-optimized geometry was used as is done here. The ΔSCF results for bands I and II are, respectively, 3.07 and 2.95 eV (24 800 and 23 800 cm^{-1}). (This is about 4000 cm^{-1} lower than the published ΔSCF excitation energies in the geometry and smaller basis set of ref 88. In particular the sensitivity to geometry turns out to be large.) The ΔSCF results are too low in comparison to experiment and the ordering is incorrect.

Although for the oscillator strengths the choice of geometry has, again, a significant effect on the absolute values, there is a huge difference in oscillator strengths, in all geometries, between the TDDFT values for bands I and II. The oscillator strength results leave no room for doubt on the assignments of these bands, thus resolving the controversy regarding the original assignment given by Levenson and Gray. This conclusion is further supported by transition intensity results from ΔSCF calculations.[73]

As regards the interpretation of the strong band IV at 6.09 eV, we are not aware of previous theoretical results to which we can compare. We have gathered our results for excitations with large oscillator strengths in the relevant energy regime in Tables 7 and 8. As far as the B_2 excitations are concerned, the seventh up to tenth excitations (g−j^1B2) are located in the energy region around 6.09 eV; for the E_1 transitions the excitations 18 up to 20 (depending on the geometry) are relevant.

Looking at the energies in Table 7, we consider the i^1B_2 and j^1B_2 excitations to be the main candidates for the assignment of the strong band IV, as far as the B_2 excitations are concerned. However, the E_1 transitions are both more intense and closer in energy to the relevant experimental number of 6.09 eV (49 100 cm^{-1}). We therefore attribute band IV to these E_1 transitions,

TABLE 7: Calculated Excitation Energies in eV (and cm^{-1}) and Oscillator Strengths Relevant for Interpretation of Band IV in $Mn_2(CO)_{10}$ in Three Different Geometries

	geometry A[a]	geometry B[b]	BP-optimized geometry[c]
g^1B_2	5.51 (44 500), 0.302	5.31 (42 830), 0.0007	5.37 (43 300), 0.2043
h^1B_2	5.54 (44 700), 0.001	5.44 (43 800), 0.209	5.41 (43 700), 0.008
i^1B_2	5.94 (47 900), 0.139	5.80 (46 800), 0.122	5.77 (46 600), 0.098
j^1B_2	6.73 (54 300), 0.441	6.75 (54 400), 0.442	6.65 (53 700), 0.489
r^1E_1	6.36 (51 300), 0.464	weak	weak
s^1E_1	6.37 (51 300), 0.570	weak	weak
t^1E_1	weak	6.26 (50500), 1.120	6.25 (50 400), 1.126

[a] X-ray diffraction geometry.[71] [b] Electron diffraction geometry.[72] [c] Becke−Perdew optimized geometry (ref 70, Table 6, row 9).

TABLE 8: Assignments of Strong Excitations in the Band IV Energy Region According to Calculations at Various Geometries

	geometry A[a]			geometry B[b]			BP-optimized[c] geometry		
sym	orbitals	chemical name[d]	weight	orbitals	chemical name[d]	weight	orbitals	chemical name[d]	weight
i^1B_2	$6e_2 \rightarrow 8e_2$	$d\delta\ (t_{2g}) \rightarrow \pi^*$	33%	$8e_1 \rightarrow 11e_3$	$d_\pi \rightarrow \pi^*$	34%	$6e_2 \rightarrow 8e_2$	$d\delta\ (t_{2g}) \rightarrow \pi^*$	36%
	$8e_1 \rightarrow 11e_3$	$d_\pi \rightarrow \pi^*$	33%	$6e_2 \rightarrow 9e_2$	$d\delta(t_{2g}) \rightarrow d\delta(e_g)$	27%	$8e_1 \rightarrow 11e_3$	$d_\pi \rightarrow \pi^*$	35%
j^1B_2	$8e_1 \rightarrow 11e_3$	$d_\pi \rightarrow \pi^*$	40%	$8e_1 \rightarrow 11e_3$	$d_\pi \rightarrow \pi^*$	42%	$8e_1 \rightarrow 11e_3$	$d_\pi \rightarrow \pi^*$	39%
	$8e_1 \rightarrow 10e_3$	$d_\pi \rightarrow \pi^*$	24%	$8e_3 \rightarrow 11e_1$	$d_\pi \rightarrow \pi^*$	21%	$8e_3 \rightarrow 11e_1$	$d_\pi \rightarrow \pi^*$	23%
r^1E_1	$8e_1 \rightarrow 2a_2$	$d_\pi \rightarrow \pi^*$	61%						
s^1E_1	$8e_1 \rightarrow 2a_2$	$d_\pi \rightarrow \pi^*$	28%						
	$6e_2 \rightarrow 11e_3$	$d\delta\ (t_{2g}) \rightarrow \pi^*$	25%						
t^1E_1				$8e_1 \rightarrow 11a_1$	$d_\pi \rightarrow \sigma'$	8%	$8e_1 \rightarrow 11a_1$	$d_\pi \rightarrow \sigma'$	8%
				$6e_2 \rightarrow 9e_1$	$d\delta\ (t_{2g}) \rightarrow \pi^*$	14%	$6e_2 \rightarrow 9e_1$	$d\delta(t_{2g}) \rightarrow \pi^*$	14%
				$6e_2 \rightarrow 9e_3$	$d\delta\ (t_{2g}) \rightarrow \pi^*$	12%	$6e_2 \rightarrow 9e_3$	$d\delta(t_{2g}) \rightarrow \pi^*$	12%

[a] X-ray diffraction geometry.[71] [b] Electron diffraction geometry.[72] [c] Becke−Perdew optimized geometry (ref 70, Table 6, row 9). [d] Chemical names were taken from Tables 1 and 2 of ref 88.

although a contribution could certainly come from the i^1B_2 and j^1B_2 excitations, as the experimental band is quite broad.

There is a remarkable effect of the geometry on the E_1 excitation in this energy region. While the results in the optimized geometry and the electron diffraction geometry (geometry B) of ref 72 are quite close, the results in the X-ray diffraction geometry (geometry A) of ref 71 differ from these. There, two excitations, r^1E_1 and s^1E_1, are important instead of the single t^1E_1 transition. These two excitations share roughly the same oscillator strength as the single excitation in the other geometries.

In geometry A,[71] the most important orbital transition is $8e_1 \rightarrow 2a_2$ which has a weight of 61% in r^1E_1 and 28% in s^1E_1. This is consistent with Levenson and Gray's analysis. In the other geometries, the $2a_2$ orbital plays no role of importance however. Instead, the t^1E_1 transition consists of many different orbital transitions of which none has a very large coefficient. In the optimized geometry, for example, we find the transitions $8e_1 \rightarrow 11a_1$, $6e_2 \rightarrow 9e_1$, and $6e_2 \rightarrow 9e_3$, with weights of, respectively, 8%, 14%, and 12% (and many other transitions with small weights). According to the results of ref 88, these transitions should be referred to as $d_\pi \rightarrow \sigma'$, $d_\pi \rightarrow \pi^*$, and $d_\pi \rightarrow \pi^*$, where the virtual orbital has a large amplitude on the equatorial CO molecules for all three transitions. The σ' has much σ -bonding $d_{z^2} + d_{z^2}$ character, and axial CO 5σ character, but is more than 50% equatorial CO π^*. A closer look at the strong j^1B_2 excitation reveals that it has a $d_\pi \rightarrow \pi^*$ character, where the π^*'s are now located on both the equatorial and the axial CO's.

Some test calculations with the LB94 potential in the optimized geometry did not reveal qualitative differences with respect to our BP results as regards the interpretation of the bands. The LB94 excitation energies for the first and second bands were, however, lower in energy, leading to poorer agreement with experiment than obtained above for the BP potential. However, the interpretation of the spectrum remains unchanged if this potential is used.

Our results for the strong band IV do not afford definite assignments, as was possible for the two lowest bands. The geometry effect is too strong to allow for definite statements. In the X-ray diffraction geometry of ref 71, the $2a_2$ virtual orbital plays an important role, which provides some support for the interpretation of Levenson and Gray. However, this orbital is not important in the other geometries and the $2b_1$ orbital is not encountered at all. Evidently, further work is needed on the interpretation of this band. In such future investigations, the geometry effect should certainly be taken into account.

V. Summary and Conclusions

Time-dependent density functional calculations have been performed on three prototype transition metal compounds: MnO_4^-, $Ni(CO)_4$, and $Mn_2(CO)_{10}$. The results are shown to be of very useful accuracy, often competitive with ab initio CASPT2 and SAC-CI calculations, whereas semiempirical, CASSCF, or standard CI treatments sometimes drastically fail for such molecules. Still, all of the sophisticated theoretical methods occasionally exhibit significant deviations from experiment, up to 1 eV. TDDFT calculations will be especially useful if, in the ab initio calculations, one needs to compromise on the size of the basis sets (because of the size of the molecule) or on the size of the active spaces (in case the number of active orbitals exceeds current computer capacity). Due to the efficiency of DFT calculations such compromises are not necessary in DFT calculations for molecules containing up to about 100 atoms. Therefore, TDDFT is especially suited for the treatment of larger systems for which the ab initio methods become prohibitively expensive. It has been shown in this paper that one can be optimistic on the quality of such TDDFT calculations on large molecules containing transition metal atoms.

By these DFT standards, $Mn_2(CO)_{10}$ is still a small molecule. Our calculations on this molecule unambiguously confirm the assignments by Levenson and Gray[45,46] for the two lowest excitation energies. These assignments had previously been put into question in refs 88 and 90. For the strong band at approximately 6.1 eV (50 000 cm^{-1}), our findings are inconclusive as regards the correctness of the Levenson−Gray assignment, due to the strong dependence of our results on the chosen geometry.

For MnO_4^- and $Ni(CO)_4$, SDCI, SAC-CI, and CASPT2 calculations were available in the literature for comparison. Significant differences between the various ab initio results can be observed in several cases. The present TDDFT sometimes support the CASPT2, and sometimes the SAC-CI results. Higher level treatments, or perhaps larger basis sets and active spaces, will be required in the ab initio calculations to resolve the remaining discrepancies between the various theoretical approaches.

In this paper, we hope to have shown that TDDFT can be a very useful tool in the study of electronic excitation spectra, also of molecules containing transition metals.

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