Short Communication

Molecular Geometry and First Electronic Transitions of MnO_3Cl

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The electronic structure of the molecule MnO_3Cl has been investigated by, among others, Jasinski *et al.*[1] and Vliek *et al.*[2] However, the structural parameters of the molecule still appear to be unknown. It was therefore thought worthwhile to perform a small *ab initio* calculation on MnO_3Cl in order to elicit the bond distances. Furthermore, the assignments of the excited states in MnO_4^- have always presented difficulties owing to the fact that the absorption spectra were recorded with MnO_4^- imbedded in an ionic lattice, whereas the calculations were on the free ion.[3] Since MnO_3Cl can be brought into the gas phase a direct comparison of the spectra with the calculation of the excited states can be performed.

Extrapolating from the electronic structure of MnO_4^- we may anticipate that the first excited spin singlets in MnO_3Cl having C_{3v} symmetry are of symmetry ^1E and $^1A_2$. The parentage of these states are of T_1 nature in T_d. The transition A_1 to E is orbitally allowed and the transition A_1 to A_2 is orbitally forbidden. The inherent Jahn–Teller coupling[4] inside the excited ^1E state has not been considered in the present study.

Computational details

The ground-state geometry in C_{3v} symmetry was determined by use of the program system Gaussian 86 in the Hartree–Fock (HF) approximation.[5] The basis set was of STO3G* quality, with the totally symmetric components of the d functions included in all the computations. The bond distances and the valence angle for the ground state were found to be R(Mn–Cl) = 2.08 Å, R(Mn–O) = 1.47 Å and α(Cl–Mn–O) = 106.1° with a total energy of −1814.2654 a.u. The corresponding electric dipole moment was 0.69 D with the polarization $-ClMnO_3+$.

The configuration interaction (CI) studies of the excited states were carried out at the molecular geometry determined at the HF level of approximation for the ground state. The program system PEDICI[6] was used with the integrals obtained from the programs MOLECULE-ALCHEMY.[7,8]

The CI expansions were generated from a multi-reference (MR) space consisting of the HF determinant and the two configuration state functions corresponding to the orbital transition $1a_2 \rightarrow 10e$. Out of the 55 dimensional orbital basis the 21 orbitals corresponding to the lowest orbital energies were kept frozen in the CI calculations, since a large difference in orbital energies was found between the $11a_1$ (−27.50 eV) and 6e (−18.09 eV) orbitals. All singly excited configurations of the three-dimensional reference space were included in the CI treatment, leading to a total of 1232 and 1680 configuration state functions for the singlet and the triplet states. For convenience we refer to the expansion as MR(3)–CIS.

Results and discussion

When Jasinski *et al.*[1] calculated the electronic structure of MnO_3Cl using the SCF–Xα–SW method they used a Mn–Cl distance of 2.10 Å and a Mn–O distance of 1.58 Å, taken over from MnO_3F. The Cl–Mn–O bond angle was 108.7°. Our result of a Mn–O distance of 1.47 Å shows a somewhat smaller Mn–O bond distance in MnO_3Cl than in MnO_3F. The optimized Mn–Cl bond distance of 2.08 Å is certainly comparable with the sphere radii used by Jasinski *et al.* The calculated Cl–Mn–O bond angle of 106.1° is close to the tetrahedral angle of 109.47° and may be compared with the one used in the SCF–Xα–SW study.[1] It is likely that the use of a larger basis set would change this value somewhat.

The results of the CI calculations are summarized in Table 1. First, we observe that the dipole moment is slightly increased to 0.97 D for the $^1A_1$ ground state (compared with a HF value of 0.69 D), despite the fact that the wavefunction is dominated by the HF determinant (92 %). This is due to the exclusion of the main part of the double excited configurations in the CI expansions.

The first allowed transition, $^1A_1$ to ^1E, is found at 1.92 eV, a value which is in good agreement with the observed value for the first band lying[1] between 13 000 and 18 000 cm^{-1}. Experimentally the band is found to be very weak. The same conclusion is obtained from the calculation

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Table 1. Calculated vertical transition energies and transition moments for the first electronic transitions of the MnO_3Cl molecule. All values are obtained from the configuration interaction treatment MR(3)–CIS. The values in parentheses indicate the squared values of the corresponding CI expansion coefficients.

State	Transition energy/eV		Character of transition			Tansition moment (squared) (a.u.)	Dipole moment/D
	Exp.	Calc.					
$^1A_1$	0.00	0.00	Ground state		(RHF 92 %)	–	−0.97
^3E	–	1.34	$1a_2$	→ 10e	(84 %)	–	−1.28
^1E	1.56[a]	1.92	$1a_2$	→ 10e	(83 %)	0.001	−1.20
$^3A_1$	–	3.12	(8e, 9e)	→ 10e	(74 %)	–	−0.68
^3E	–	3.60	(8e, 9e)	→ 10e	(61 %)	–	−0.88
$^3A_2$	–	3.81	$1a_2$	→ $15a_1$	(54 %)	–	−1.85
$^1A_2$	–	4.39	$1a_2$	→ $15a_1$	(68 %)	–	−2.03
$^3A_2$	–	4.81	(8e, 9e)	→ 10e	(52 %)	–	−1.40
^3E	–	4.82	($13a_1$, $14a_1$)	→ 10e	(51 %)	–	−1.94
$^1A_2$	–	5.01	(8e, 9e)	→ 10e	(66 %)	–	−1.27
^1E	2.22[b] 2.34[c]	5.18	(8e, 9e)	→ 10e	(68 %)	0.048	−1.52
$^1A_1$	2.22[b] 2.35[d]	5.25	(8e, 9e)	→ 10e	(85 %)	0.146	−1.72

[a]First band I from absorbtion spectrum (Ref. 1) (12 550 cm^{-1}), including zero-point vibration energy. [b]Second band from Ref. 1 (17 881 cm^{-1}). [c]Ref. 2, 0–0′ transition $^1A_1 \rightarrow {}^1E$. [d]Ref. 2, 0–0′ transition $^1A_1 \rightarrow {}^1A_1$.

since the transition moment is found to be very small. Since this transition correlates with the forbidden transition $^1A_1 \rightarrow T_1$ in T_d this is not unexpected. From the CI expansion coefficients we also observe that essentially the transition is a $1a_2 \rightarrow 10e$ orbital transition, implying a charge transfer from the oxygen atoms to the manganese atom. This is also indicated by the increase of the electric dipole moment.

The second pair of dipole allowed transitions is calculated to be at 5.18 (^1E) and 5.25 ($^1A_1$) eV. Experimentally the second band system is found at 2.3 eV. The large deviation in the values is to be expected owing to the very limited basis set used and the small inclusion of electron correlation in the CI treatment. We observe, however, that the calculated transition moments are much larger for these transitions, in agreement with the observed intense band system.

The present study has aimed at demonstrating what can be achieved using a small basis in an *ab initio* calculation of a transition-metal complex. The outcome shows that it is possible qualitatively to describe the nature of the lowest electronic states and to assign the first transitions in the MnO_3Cl molecule. We hope further to have encouraged an experimental determination both of the electric dipole of the molecule and of the structural parameters.

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