Physical Chemistry

MNDO method for calculations of magnesium clusters

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A new set of parameters for the magnesium atom has been developed within the MNDO method. In contrast to previously published parameters, the new parameters correctly describe molecules with different chemical natures: magnesium halides, organomagnesium compounds and the recently found small magnesium clusters Mg_n (n = 2—8). The average errors in the calculated heats of formation and bond lengths of magnesium compounds, including clusters are: 10.7 kcal/mol and 0.167 Å, respectively.

Key words: quantum chemical calculations, MNDO parameters, magnesium, clusters.

It is well known that magnesium can easily react with different organic compounds producing various Grignard reagents. The mechanisms of these processes are little understood, especially the nature of their intermediates. It has been shown recently, that magnesium aggregates, Mg_n clusters, play an important role in very interesting reactions of disperse magnesium with organic substrates.[1—3] Theoretical modeling of these processes using quantum chemical methods has met with serious difficulties due to two factors.

First, magnesium clusters are weakly bonded van der Waals adducts stabilized *via* dynamic electron correlation; at the Hartree—Fock level the species with $n = 2$ and 3 are not bonded at all, while bonding in the bigger clusters is grossly underestimated.[4] Reasonably accurate results were obtained only with multiconfigurational self consistent field methods, or in extended configuration interaction calculations with perturbation theory corrections. Good results were obtained for isolated Mg_n clusters with some simplified approaches, for example using model Hamiltonians in the valence bond method[5] and the local spin density pseudopotential (LSD-pseudopotential).[6,7]

Second, the Mg_n clusters do not have rigid structures. This means their potential energy surface (PES) has multiple closely spaced local minima, the number of which increases rapidly as the size of the cluster grows. A study of the reactions of magnesium clusters has as a prerequisite many quantum chemical calculations for all these minima. *Ab initio* quantum chemical calculations are very time consuming even for small individual clusters; using them for more complicated systems, consisting of a cluster and a reacting organic molecule, is hardly possible.[8,9]

In modern semi-empirical methods, for example MNDO, the parameters[10] of Mg are not able to describe clusters (Table 1). This is due to the fact that the set of Mg parameters was obtained[10] using as a reference the data on ionic derivatives like halides. In the present communication we suggest within a MNDO method a modified set of parameters for Mg, able to describe correctly classic as well as cluster magnesium compounds.

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Table 1. MNDO calculated heats of formation ΔH_f° (kcal/mol) of reference molecules

Compound	Experiment[15]	Calculations		
		ab initio[4,11]	MNDO - parameters	
			Ref. 10	This work
Mg_2	—	68.8	43.7	64.9
Mg_3	—	87.1	15.1	90.5
Mg_4	—	93.9	97.2	111.6
CH_3MgCl	—	−38.1	−87.8	−50.5
$MgH\cdot$	40.5	—	49.6	44.4
MgH^+	217.1	—	213.8	222.8
$MgCl\cdot$	−10.3	—	−21.5	−21.2
$MgCl_2$	−93.8	—	−101.6	−71.6
$Mg(OH)_2$	−135.0	—	−130.9	−136.6
MgS	62.0	—	48.8	87.3
Average error δ	—	—	8.1	10.7(13.9)[16]

Experimental data on organomagnesium compounds and Mg clusters are practically absent. So for the reparametrization we used the results of high level *ab initio* calculations for Mg_n[4,11] and CH_3MgHal (Hal = F, Cl)[11] that were taken as reference compounds, together with ionic Mg derivatives (Table 1). The parametrization procedure was essentially the same as that described in Refs. 12,13. The goal function[13] S for the set of reference molecules was minimized using a standard Davidon—Fletcher—Powell algorithm:

$$S = \sum_{i,\alpha}(q_{i\alpha}{}^{calc} - q_{i\alpha}{}^{exp})^2 , \qquad (1)$$

where $q_{i\alpha}{}^{calc}$ and $q_{i\alpha}{}^{exp}$ are calculated and experimental dimensionless reference functions, respectively. The index i is the number of the reference molecule, α indicates the physical characteristics (heat of formation: $\alpha = 1$; geometry parameters: $\alpha = 2$) used in optimization. The reference functions $q_{i\alpha}{}^{calc}$ and $q_{i\alpha}{}^{exp}$ are made dimensionless by multiplying them by weighting factors $\omega_{i\alpha}$. For example, for the heat of formation of the i-th molecule it would be $q_{i1} = \omega_{i1}\Delta H_f$.

As a rule[13] the same weighting factors are used for all molecules. However, the molecules of our reference set are different in nature. Thus, the curvature and well depth of the PES are maximum for halides and minimum for clusters. It is known that the experimental heats of the insertion of a Mg atom $\Delta H_r{}^{ins}$ (for diatomic molecules equal to dissociation energies D_0) in the series halides — Grignard reagents — clusters are related approximately as 100:50:10. The same relation should hold for gradients of ΔH_f with respect to geometric variables. This leads to two problems: first, the goal function[13] S, in form (1), is insensitive to changes in the properties (energies and geometries) of clusters; second the significance of the relative error $(\Delta H_f^{calc} - \Delta H_f^{calc})/\Delta H_r{}^{ins}$, in comparison to the absolute error $(\Delta H_f^{calc} - \Delta H_f^{calc})$ for adequate description of weakly bonded clusters is neglected. For these reasons the weighting factors for the molecules, usually chosen quite arbitrarily[13] according to their «chemical» significance, were replaced by normalizing weighting factors $\omega_{i1} = 1.0/\Delta H_r{}^{ins}$, and $\omega_{i2} = 0.1/\Delta H_r{}^{ins}$, that «level up» the terms arising from different structures and eliminate both defects.

The one-center integrals, g_{ss}, g_{pp}, g_{sp}, g_{pp} , h_{sp}, h_{pp}, as well as U_s and U_p, were determined from spectroscopic data[14] for the Mg atom. The optimal values of U_s and U_p were later checked by including them in the minimized function S. So our semi-empirical parameters give a correct description of the terms of free Mg and its ions. These parameters are collected in Table 2 together with those proposed earlier.[10]

In Tables 1 and 3 are presented the energies and geometries of the molecules used in parametrization as

Table 2. Optimized Mg parameters in the MNDO method

Parameter	Ref. 10	This work
U_s	−15.04	−15.035
U_p	−9.264	−10.605
β_s	−2.586	−2.771
β_p	−2.842	−2.268
α	1.813	1.803
ζ_s	1.049	0.744
ζ_p	0.889	1.267
g_{ss}	7.39	7.389
g_{pp}	6.68	6.872
g_{sp}	6.57	6.489
$g_{pp'}$	5.90	6.092
h_{sp}	0.82	0.816
h_{pp}	0.39	0.390
ρ_0	1.841	1.841
ρ_1	2.203	1.903
ρ_2	1.709	1.354
D_1	2.036	1.573
D_2	1.882	1.321

Table 3. MNDO calculated interatomic distances r_e (Å) in reference molecules

Compound	Experiment[15]	Calculations		
		ab initio[4,11]	MNDO parameters	
			Ref. 10	This work
Mg_2	—	3.811	2.563	3.202
Mg_3	—	3.375	2.407	3.184
Mg_4	—	3.234	2.162	3.110
CH_3MgCl				
r_e(Mg—Cl)	—	2.199	2.000	2.135
r_e(Mg—C)		2.080	1.901	1.860
MgH$^\bullet$	—	—	1.557	1.472
MgH^+	1.730	—	1.478	1.501
MgCl$^\bullet$	1.649	—	2.224	2.076
$MgCl_2$	2.199	2.186	2.208	2.123
$Mg(OH)_2$	—	—	1.787	1.624
MgS	1.800	—	1.932	1.811
Average error δ	—	0.012	0.102	0.167

well as the average errors:

$$\delta = \frac{1}{N}\sum_{i=1}^{N}\left|x_i^{calc} - x_i^{\exp}\right|,$$

where N is the number of molecules and x_i is the property. The average errors δ are close to average MNDO method errors for ordinary (not hypervalent) chemical compounds from Ref. 16. Our calculations reproduce fairly well both the energies and geometries of a series of structures representative of magnesium chemistry, thus demonstrating the adequacy of the semi-empirical NDDO scheme for magnesium compounds with different chemical natures.

Since we extensively used the results of *ab initio* calculations for the most important magnesium compounds a systematic lowering of the calculated binding energies due to underestimation of the electronic correlation is possible. We tried to estimate this in calculations of 3 series of cluster structures ($Mg_n{}^i$, n = 2—7, i = 0,−1,+1), that were earlier studied[6] in detail using the local spin density approach with pseudopotential. The energies are given in Table 4, and the geometries of species with $n \le 5$ are presented in Fig.1.

The smallest deviations are found for the energies and the geometries of neutral clusters, which may be explained by the absence of charged species in our reference set. Nonetheless, the calculations correctly reproduced not only the symmetry (including the highest occupied and the lowest unoccupied MO), but also the energies of the minima for the ground electron states of clusters. In addition, in agreement with the results of Ref. 6 we found that the cations and the anions are more stable than the neutral clusters, and the geometrical changes on going to charged species are caused by the Jahn—Teller effect, due to the removal of the degeneracy of the molecular orbitals. The Mg_4 cluster as its sublimation energy shows, (Table 1) has additional stability, though it is less pronounced than in the data of Ref. 6. As for the electron affinity (one of the properties most precisely calculated by LSD), we obtained, in agreement with data from Ref. 6 a uniformly increasing

Table 4. Energies of neutral and charged magnesium clusters calculated by LSD[6] and MNDO (the new parameters for Mg) methods; the structures of the clusters are presented in Fig. 1

Property	Method	Mg_2	Mg_3	Mg_4	Mg_5	Mg_6	Mg_7	δ
$E_{at}(0)$	MNDO	0.110	0.209	0.308	0.362	0.400	0.601	0.085
$E_{at}(0)^a$	LSD[6]	0.108	0.260	0.500	0.500	0.525	0.604	
$E_{at}(-1)^a$	MNDO	−0.007	0.257	0.449	0.520	0.586	0.636	0.220
$E_{at}(-1)^a$	LSD[6]	0.290	0.570	0.740	0.592	0.760	0.810	
$E_{at}(+1)^a$	MNDO	1.089	1.065	0.989	0.921	0.872	0.964	0.134
$E_{at}(+1)^a$	LSD[6]	0.760	0.846	0.832	0.926	0.842	0.900	
IP^b	MNDO	5.69	5.07	4.92	4.85	4.81	5.10	0.80
IP^b	LSD[6]	6.32	5.85	6.28	5.50	5.71	5.57	
EA^b	MNDO	−0.36	0.14	0.56	0.79	1.11	1.31	0.39
EA^b	LSD[6]	0.38	0.90	0.99	1.09	1.40	1.46	
$E_{sub}{}^c$	MNDO	5.10	9.41	13.93	13.45	13.62	41.59	5.83
$E_{sub}{}^c$	LSD[6]	4.84	12.91	28.13	12.22	13.60	25.83	

Note. $E_{at}(q)$ — atomization energy (eV/atom) of a cluster bearing the charge q; q = +1, 0, −1;
$E_{at}(q) = (n-1)E_{atom} + E(q)_{atom} - E_n(q)$, where $E(q)_{atom}$ is the atomic ion energy;
$E_n(q)$ — energy of a cluster of n Mg atoms bearing the charge q.
E_{sub} — sublimation energy: $E_{sub}(n) = E_{n-1} + E_{atom} - E_n$; EA— electron affinity; IP — ionization potential; δ — average error.
^{a} eV/atom ; ^{b} eV; ^{c} kcal/mol.

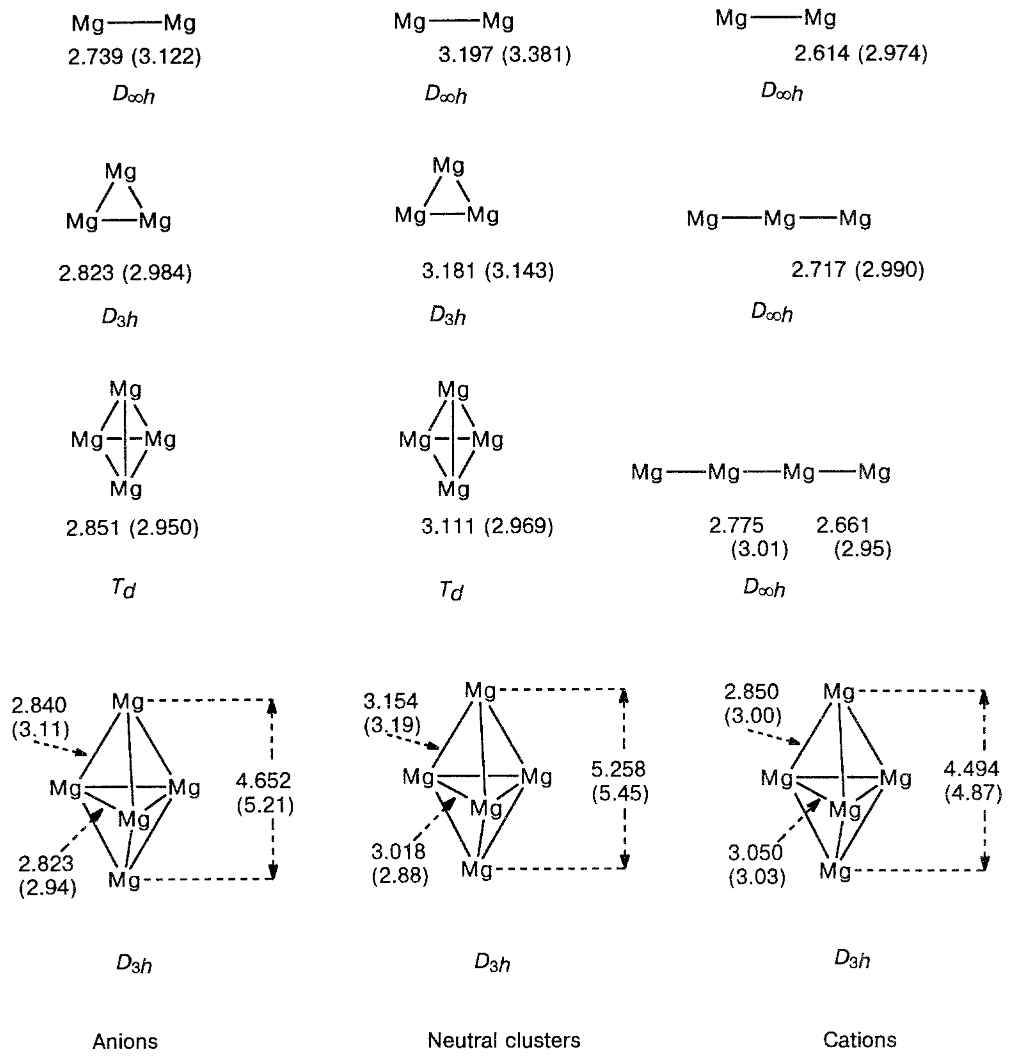

Fig. 1. The structures of neutral and charged Mg_n clusters (n = 2—5), calculated by the MNDO method with the new Mg parameters. Bond lengths are given in Å. The results of LSD[6] calculations are presented in brackets.

series (with the exception of Mg_2), systematically lowered by 0.39 eV.

Thus, by employing the new set of parameters for Mg, the applicability of the semi-empirical NDDO approximation for calculations of various magnesium compounds, including clusters, has been shown. Based on the results of Ref. 13 one would expect that a significant improvement in the Mg atom parameters without deterioration of results for already calculated species cold be obtained by expanding the set of reference molecules. It is evident that not only neutral, but also charged species must be considered. The PM3 method[13] looks promising since in its current version the parameters were also determined[15] without reference to cluster Mg compounds, which resulted in overestimation of their stabilities.

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