On the potential-energy surface of the Mg + CO_2 (C_{2v}) system

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The interaction of magnesium atoms with carbon dioxide molecules leading to the formation of the metastable $MgCO_2$ species has been studied by the *ab initio* methods of quantum chemistry.

The interaction of metal atoms and clusters with small carbon-containing molecules is of interest in investigations of metal–ligand bonding.[1,2] The direct co-condensation of metal atoms with ligands using the matrix isolation technique and spectroscopic detection can be applied to studying the above complexes. Matrix isolation experiments and theoretical works on the reaction of metal (M) atoms with carbon dioxide molecules, have been published.[3–19] In some of them, the C_{2v} symmetry of the MCO_2 species was assumed, in particular, for M = Li,[7] Al[14] and Sc.[16] The theoretically computed binding energies of MCO_2 with respect to M + CO_2 are close to zero for Na and K, and a noticeable binding energy (13–20 kcal mol^{-1}) for η^2-O,O coordination was reported only for Li.[19]

The structure of magnesium complexes with CO_2 was not described in detail, although the interactions of Mg and especially of Mg^+ with other small oxygen- and carbon-containing molecules were characterised theoretically.[20–25] Previously,[26] we described the combined low-temperature matrix isolation and *ab initio* quantum-chemical studies of $MgCO_2$. The complete geometry optimization of the $MgCO_2$ structure performed with the GVB and MP2 approaches with the 6-311G(2d,2p) basis set resulted in the C_{2v} species corresponding to the η^2-O,O coordination mode with slightly elongated CO bonds and a non-linear CO_2 fragment. Calculations of harmonic vibrational frequencies carried out with both GVB and MP2 approaches confirm that this configuration refers to a true minimum of the potential energy surface. The computed high-frequency IR bands of this complex are consistent with the results of matrix-isolation spectroscopy studies (Table 1).

However, a comparison of the energies computed at the MP2/6-311G(2d,2p) level for $MgCO_2$ at this equilibrium point and for the separated species Mg + CO_2 showed that the dissociation limit was lower by more than 10 kcal mol^{-1}. These results could indicate that this structure corresponds to the metastable species actually detected in rare-gas matrices; the species is stabilised due to cage effects. An alternative explanation may consist in a fairly low theoretical level.

In this work, we report the re-computed energy profile for the interaction of Mg + CO_2. These data provide support to the metastable nature of $MgCO_2$. The points on the potential energy surface of the system were calculated using the second-order multiconfigurational quasi-degenerate perturbation theory (MCQDPT2)[27] and the correlation-corrected basis sets d-aug-cc-pVTZ for O and aug-cc-pVTZ for C and Mg.[28] All calculations were performed using the PC GAMESS version[29] of the GAMESS quantum-chemical package.[30] In these calcultions, 12 lowest energy orbitals were assigned to the core, while 13 valence orbitals populated by 10 electrons constituted the active space for the multiconfigurational self consistent field (MCSCF) procedure, as a first stage of the MCQDPT2 approach.

Table 1 The harmonic vibrational frequencies of $MgCO_2$ (cm^{-1}) computed by the MP2/6-311G(2d,2p) method and the bands experimentally detected in the Mg/CO_2/Ar co-condensates by IR spectroscopy.[26]

Assignment	MP2/6-311G(2d,2p)	Experiment
Asym. str(CO)	1699	1594
Sym. str(CO)	1384	1378
Bend(CO_2)	840	862
Str(Mg–CO_2)	432	—
Wag(Mg–CO_2)	431	—
Wag(Mg–CO_2)	280	—

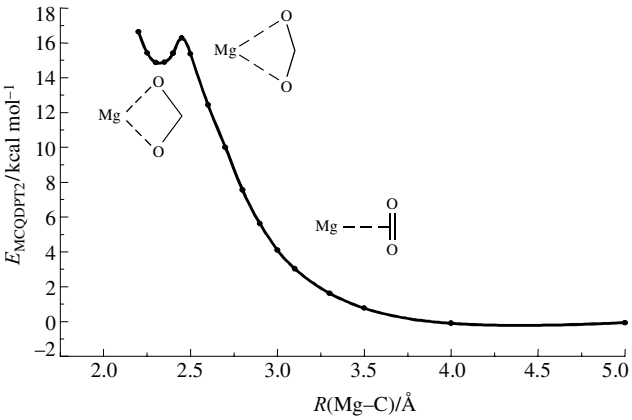

Figure 1 Energy profile of the $MgCO_2$ → Mg + CO_2 reaction path computed at the MCQDPT2/aug-cc-pVTZ level.

The energy profile of the reaction $MgCO_2$ → Mg + CO_2 was constructed as described below. The Mg–C internuclear distance was chosen as a reaction coordinate. At every point along this axis, the non-gradient MCQDPT2 optimization of the C–O bond length and the OCO angle was carried out.

The results of calculations are shown in Figure 1. The shallow minimum in the long-range region around 4 Å refers to a weakly bound van der Waals complex, which is not considered in detail in this work. The inner minimum corresponds to the metastable C_{2v} structure with the equilibrium geometry parameters R(Mg–C) = 2.31 Å, ∠OCO = 125.6°, R(C–O) = 1.26 Å.

In the highest level calculations performed in this work (MCQDPT2/aug-cc-pVTZ), the energy of $MgCO_2$ at the equilibrium point is higher than the dissociation limit of Mg + CO_2 by 14.7 kcal mol^{-1}. Previously,[26] this value was estimated as 10.7 kcal mol^{-1} at the MP2/6-311G(2d,2p) level or 5.5 kcal mol^{-1} at the MCQDPT2/6-311G(2d,2p) level. We believe that the $MgCO_2$ species, detected in the matrix isolation experiments[26] is metastable.

The cusp-like behaviour of the potential curve shown in Figure 1 near 2.5 Å requires an additional discussion. The region of R(Mg–C) within 2.0–2.5 Å represents the part of the curve correlating to the ionic dissociation channel of the $MgCO_2$ complex into Mg^+ and CO_2^-. After passing the point of the sharp barrier, the remaining part of the curve corresponds to the repulsive interaction of neutral Mg and CO_2 particles. The entire diabatic potential curve corresponding to the neutral reactants Mg + CO_2 can be smoothly expanded to the shorter R(Mg–C) distances (less than 2.5 Å by using the MCSCF wavefunctions. However, the curve corresponding to the ionic pair Mg^+ + CO_2^- cannot be smoothly continued to the right from the intersection point. This can be explained by auto-ionisation of CO_2^- for a certain region of the geometry parameters where its energy is higher than the energy of CO_2 and a free electron. The same behaviour of potentials is typical of one-dimensional curves of ionic diatomic molecules, for example, for OH^-/OH.[31] Such a behaviour can be observed for two-dimensional (C_{2v}) potential-energy surfaces of CO_2^-/CO_2, according to the MCSCF calcula-

tions. Therefore, no smooth connection of the inner potential well with the outer region on the energy profile shown in Figure 1 is expected.

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