Matrix Isolation and ab Initio Study of the Reactions of Magnesium Atoms and Clusters with CO_2, C_2H_4, and CO_2/C_2H_4 Mixtures: Formation of Cyclic Complexes

Victor N. Solov'ev,*,† Evgenii V. Polikarpov, Aleksandr V. Nemukhin,* and Gleb B. Sergeev

Chemistry Department, Moscow State University, 119899, Vorobyevy gory, Moscow, Russia

Received: April 18, 1999; In Final Form: June 14, 1999

The products of matrix reactions of magnesium atoms and clusters with carbon dioxide, ethylene, and their mixtures have been characterized by the IR and UV−vis techniques and ab initio methods of quantum chemistry. The structures, binding energies, and vibrational frequencies for the $MgCO_2$, $Mg(C_2H_4)_n$ (n = 1,2), and $MgC_2H_4CO_2$ complexes are reported. We conclude that in the metastable $MgCO_2$ species magnesium is bound to both oxygen atoms forming the four-member ring. The structures of $Mg(C_2H_4)_2$ and $MgC_2H_4CO_2$ correspond to the five-member cycles, and magnesium is responsible for the formation of chemical bonds between the ligands.

Introduction

Metal reactions with light carbon molecules present a significant interest in investigations of metal−ligand bonding, reaction mechanisms, solvation, and adsorption phenomena.[1,2] Direct co-condensation of metal atoms with prospective ligands, combined with matrix isolation techniques and spectroscopic detection, offers a ready route to novel model complexes.

Several important matrix isolation and theoretical studies of the reaction of metal atoms with CO_2 have been described in the literature.[3−10] A variety of reaction routes may occur including the coordination of metal atoms and CO_2 molecules, and the η^1-C, η^1-O, η^2-O,C, and η^2-O,O complexes may be formed depending on the metal.[3−6,9,10] The deeper reactions may lead to carbonates, oxalates, and more complicated polymer structures. Also, spontaneous insertions of metal atom (e.g., Ti, W) into the C−O bond may occur.[7,8] On the other hand, the complexes of metal atoms with ethylene seem to be relatively weak.[11−20] Only Ti atoms react with ethylene forming the insertion compound $HTiCHCH_2$.[20]

The possibility of the conjugate reaction of metal atoms and clusters with CO_2 and C_2H_4 is of particular interest. It was observed that the explosive reaction occurred in the thick (>100 μm) co-condensates of $Mg/CO_2/C_2H_4$ at 100 K.[21] More than 10 reaction products were detected by gas chromatography and mass spectrometry, while only two of them were identified as complex acetales. Recently, the possibility of such reaction was studied with nickel atoms.[22] The results of IR spectroscopic study and ab initio calculations led to the conclusion that the mixed complex $NiCO_2C_2H_4$ in which the metal atom is coordinated to the C−C bond of C_2H_4 and to one of the C−O bonds of CO_2 is formed in the matrix. Further transformations of such a compound were not investigated.

Here, we describe the results of the matrix isolation IR and UV−vis studies of the reactions of magnesium atoms and clusters with CO_2, C_2H_4, and their mixtures CO_2/C_2H_4 supported by ab initio calculations. The work may be viewed as a continuation of our previous studies of the reactions of Mg with CH_3Cl and CH_3Br.[23]

Experiment

Co-condensates were formed on the KBr window mounted on the bottom of a conventional closed cycle refrigerator MSMR-100A-3,2/20 (Omsk Manif. Co.). Temperature was measured by Au−Cu thermocouple and was not higher than 12 K during the deposition The detailed description of the setup may be found elsewhere.[23]

Magnesium of type MG-1 (99.9%) was used in our experiments. Magnesium in pieces was vaporized from stainless steel tube at a temperature 360−380 °C. The condensation rate was about 1−2 μg/min cm^2 according to quartz crystal microbalance.

CO_2 was synthesized from $NaHCO_3$ in accordance with ref 24. Ethylene 99.9% was used without purification.

Gas mixtures were introduced into the cryostat through the needle regulator. Typical deposition rate was about 1 mmol/h.

IR spectra were taken on a grating spectrometer, Specord-M80 (Carl Zeiss Jena), in the region 4000−400 cm^{-1} with spectral slits of 2.5 and 1.5 cm^{-1}. UV−vis spectra were taken in the region 50000−11000 cm^{-1} (200−900 nm) on the Specord M-40 (Carl Zeiss Jena) spectrometer with a spectral slit of 40 cm^{-1}.

Condensation time was varied from 30 min to 4 h depending on the experiment type. After deposition, the sample was gradually annealed at temperatures 24, 30, 35, and 40 K. Spectra were taken after each step. Irradiation by superhigh-pressure mercury lamp with cutoff filters was done in several experiments.

Calculation Details

Full optimizations of geometry parameters without symmetry restrictions for the molecular species considered here followed by the harmonic vibrational analysis have been performed at the MP2/6-311G*(2d,2p) level. For $MgCO_2$, two more approaches, namely, the generalized valence bond (GVB) and the multiconfigurational quasi-degenerate perturbation theory (MP2/

---

* Corresponding author. E-mail: solov@cryo.chem.msu.su; anem@lcc.chem.msu.su. Fax: 7-095-939-0283.

† Present address: The Institute of Chemistry, The Hebrew University of Jerusalem, Givat-Ram, Jerusalem 91904, Israel. E-mail: victor@chem.ch.huji.ac.il. Fax: 972-2-5618033.

10.1021/jp991309b CCC: $18.00

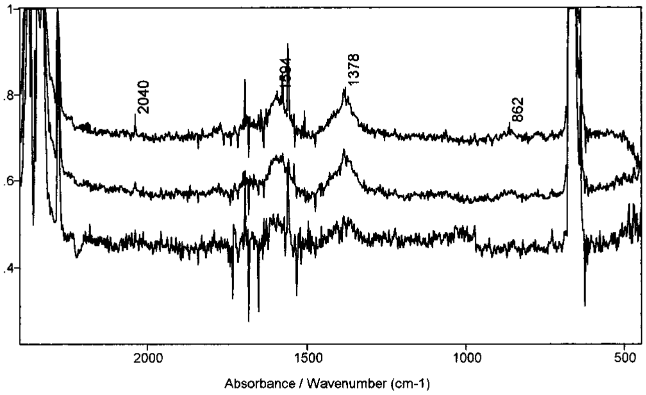

Figure 1. IR spectra of $Mg/CO_2 = 1/150$, obtained at 10 K right after the deposition (bottom curve), after annealing at 35 K (middle curve), and after annealing at 70 K (top curve). Condensation time = 120 min.

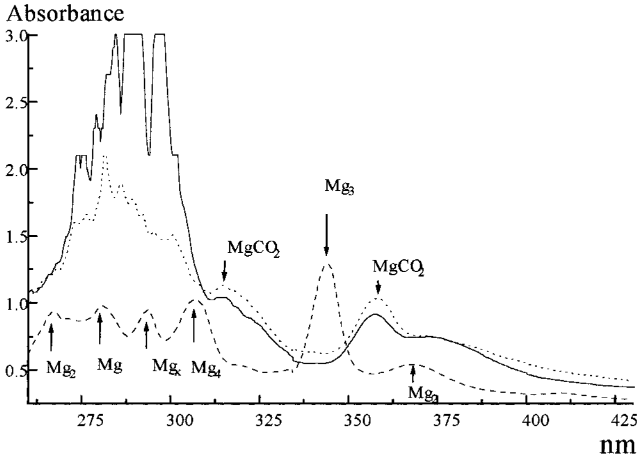

Figure 2. UV−vis spectra of Mg/CO_2 (1/150) condensate after deposition (solid curve) and after annealing at 27 K (dotted curve). Dashed curve corresponds to the spectrum of Mg/Ar (1/200) condensate.

MCSCF) options have been tested as well. The calculations have been performed with the GAMESS program system.[25] No scaling of computed vibrational frequencies or force constants has been employed.

Results and Discussion

1. $Mg-CO_2$. The IR spectra of Mg and CO_2 containing co-condensates are very simple. After the deposition, three new weak absorption peaks at 1594 (C═O st.), 1378 (C−O st.), and 860 (OCO def.) cm^{-1} are visible. Annealing increases their intensity, as can be seen in Figure 1. Variations of CO_2 concentrations and changes in condensation temperature (10 and 80 K) did not influence the spectrum.

The UV−vis spectra of $Mg-CO_2$ condensate in comparison to the spectrum of small magnesium clusters in argon do not show the absorptions from Mg_2, Mg_3, and Mg_4 (Figure 2). The absorptions attributed to the higher aggregates and to the atomic S−P transition are prevailing. Annealing at 27 K led to a complete disappearance of cluster absorptions and decrease of the atomic ones, thus suggesting the higher magnesium cluster reactivity. Two new weak and broad absorptions appear at 318 and 350 nm which grow in intensity during the annealing and may be attributed to the product of Mg and CO_2 interaction. The intensity of new absorptions is low, even in neat CO_2. In the argon-diluted matrix, the band at 352 nm appears only when the absorptions of unreacted magnesium completely cover the ultraviolet region.

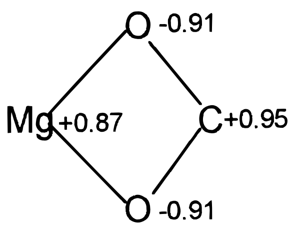

Figure 3. The optimized structure for the $MgCO_2$ complex and the atomic charges.

TABLE 1: Optimized Geometry Parameters of $MgCO_2$ and Energies of the Metastable Minimum Relative to Mg + CO_2

	GVB	MP2	MP2/MCSCF
R(Mg−C), Å	2.23	2.33	2.31
∠OCO, deg	128.7	128.5	127.0
E, kcal/mol	+5.4	+10.7	+5.5

TABLE 2: Internuclear Distances and Bond Orders for the Optimized Structure of $MgCO_2$ Computed at the MP2/6-311G(2d,2p) Level

	internuclear distances (Å)	bond orders
Mg−O	2.11	0.40
C−O	1.25	1.54
Mg−C	2.33	0.56

TABLE 3: Vibrational Frequencies of $MgCO_2$ (cm^{-1})

assignment	GVB	MP2	experiment.
str(CO)	1765	1700	1580
str(CO)	1494	1385	1385
bend(CO_2)	918	840	866
str($Mg-CO_2$)	443	432	
wag($Mg-CO_2$)	436	431	
wag($Mg-CO_2$)	312	280	

Intense absorptions of unreacted magnesium even in neat CO_2 suggest very low reactivity of magnesium atoms and clusters in the ground state in agreement with previous studies.[26]

The geometry optimization of the $Mg-CO_2$ system carried out at GVB, MP2, and MP2/MCSCF levels resulted in the C_{2v} structure with two equivalent Mg−O bonds, slightly elongated (compared to CO_2) C−O bonds and the nonlinear CO_2 fragment. To describe the species in terms of bond orders and effective atomic charges, the natural bond orbital (NBO) analysis [27] has been performed. The optimized structural parameters are given in Tables 1 and 2, and atomic charges are shown in Figure 3. The values of charges suggest this compound can be considered as an ion−radical pair $Mg^+CO_2^-$. The calculated dipole moment of $MgCO_2$ is 2.6 D.

Vibrational frequencies computed at the GVB and MP2 levels compared to the experimental observations are collected in Table 3.

As it is seen in Table 1, the $MgCO_2$ species is a metastable particle according to all calculations. The metastable nature of this species is to some extent consistent with the low (about 10^{-5} s) lifetime of the CO_2^- anion in the gas phase.[28] Apparently, the matrix stabilizes this particle in our experiments. Several ESR and IR studies are known confirming the formation of anion−radical CO_2^-, in various low-temperature matrixes.[29,30] The literature data, presented in Table 4, showing the vibrational bands of previously studied species, which are assigned to the vibrations of the CO_2^- fragment, are also consistent with our findings. Some discrepancy between the observed and calculated frequencies seen in Table 3 should be attributed to matrix effects.

2. Mg and Ethylene. The full MP2/6-311G(2d,2p) optimization of geometry parameters of MgC_2H_4 reveals that only a weakly bound van der Waals complex with a binding energy

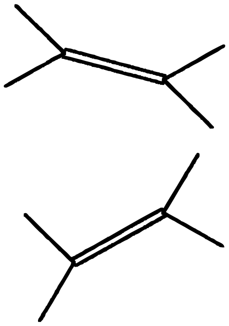

Figure 4. 4. Proposed structure of ethylene dimer.

TABLE 4: Literature Data on the Vibrational Bands of the CO_2-Containing Species

assignment	$AlCO_2$ (ref 5)	$LiCO_2$ (ref 3)	$ScCO_2$ (ref 6)	CO_2^- (ref 30)
str(CO)	1443.5	1574.9	1256	1671
str(CO)	1265.5	1326.6	1074	1424
bend(CO_2)	796.5	798.9	902	849

TABLE 5: Calculated Vibrational Frequencies of MgC_2H_4 and Ethylene and the Shifts of the Frequencies of the C_2H_4 Subunit

assignment	MgC_2H_4	C_2H_4	Δ
str(CH)	3287.6	3288.5	−0.9
str(CH)	3259.5	3260.1	−0.6
str(CH)	3188.1	3189.2	−1.1
str(CH)	3168.5	3169.5	−1.0
str(CC), bend^s(CH)	1679.0	1682.5	−3.5
$\delta^{as}(CH_2)$	1491.1	1491.8	−0.7
bend^s(CH_2), str(CC)	1385.3	1386.8	−1.5
rock(CH_2)	1232.2	1232.9	−0.7
twist	1078.6	1075.7	2.9
wag(CH_2)	976.8	975.7	1.1
wag(CH_2)	926.1	924.3	1.8
rock(CH_2)	835.23	836.22	−0.99
str^s(MgC)	48.5		
tilt	34.9		
str^{as}(MgC)	23.1		

of about 0.8 kcal/mol is formed at the Mg−C distances close to 4 Å. Neither significant frequency shifts (Δ) nor geometry changes of the ethylene species have been found (Table 5).

Experimental studies of the IR spectrum of ethylene at various dilutions in argon matrixes described in ref 31 revealed that ethylene formed relatively stable dimers in the matrix, and the vibrational spectrum consisted of three series which were attributed to monomeric, dimeric, and crystal ethylene.[31] The shifts of vibrational frequencies reached 25 cm^{-1} in the C−H stretch region and 6 cm^{-1} for lower frequency modes. Spectral analysis exhibits the equivalency of ethylene molecules in the dimer, and the proposed dimer structure is shown in Figure 4. Maximum dimer yield was observed at a C_2H_4/Ar ratio of 1:30.

In our opinion, the formation of relatively stable dimer structures in argon matrix should influence the interaction of metal atoms with ethylene, and therefore, we have performed the quantum chemistry modeling of the magnesium complex with two ethylene molecules. Only two studies of this type are known.[18,19] The most stable structures for $Ga(C_2H_4)_2$ and $Ni(C_2H_4)_2$ correspond to the C_{2v} and D_{2d} sandwich-like complexes. However, our calculations show that there is no global minimum associated with the C_{2v} symmetry on the potential energy surface of Mg + $2C_2H_4$. The appropriate structure corresponds to a saddle point with one imaginary frequency of 72i cm^{-1}.

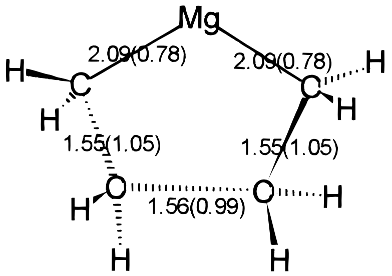

Figure 5. Bond lengths (Å) and bond orders (in parentheses) for $Mg(C_2H_4)_2$.

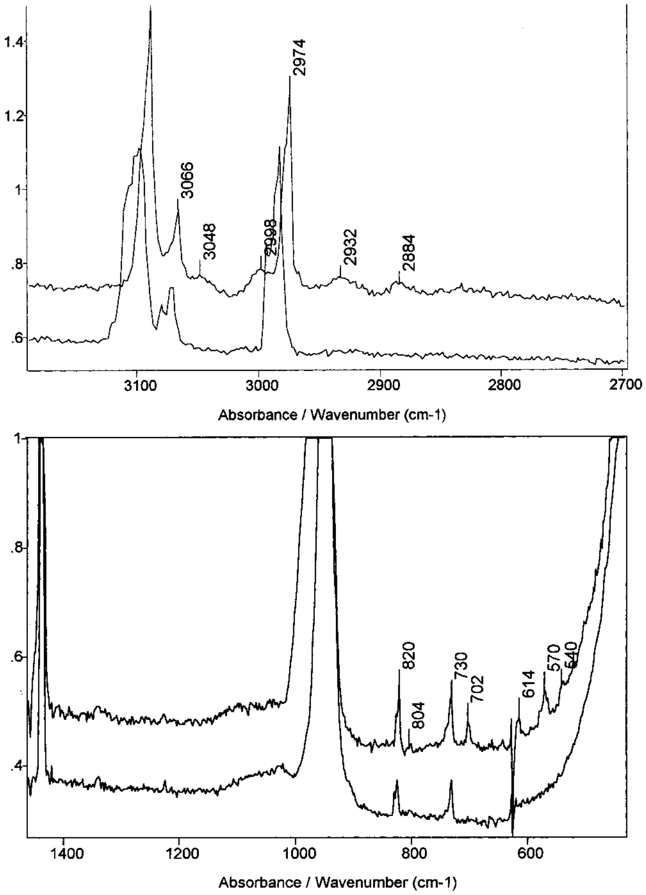

Figure 6. IR spectra of $Mg/C_2H_4/Ar$ 1/10/200 co-condensate: (lower curve) after deposition; (upper curve) after annealing at 40 K. Condensation time = 120 min.

The global minimum at the MP2/6-311G(2d,2p) level corresponds to the five-member cyclic structure (Figure 5) with a binding energy of 21 kcal/mol relative to the separated magnesium and two ethylene molecules.

Experimental studies revealed, that the annealing at temperatures above 30 K led to the appearance of several new absorption lines grouped in the C−H stretch region and in the region below 800 cm^{-1}. The experimental spectra of the $Mg/C_2H_4/Ar$ co-condensates are shown in Figure 6, and a comparison of the calculated vibrational frequencies for the theoretical $Mg(C_2H_4)_2$ structure with the experimental is given in Table 6.

The pairs of bands in the 1400−1500 and 1100−1200 cm^{-1} regions are characteristic for the π-complexes of metals with ethylene and correspond to the coupled $\nu_{C=C}$ and δ_{CH_2} vibration modes of the distorted ethylene molecule.[32] However, no absorption bands were found in the $\nu_{C=C}/\delta_{CH_2}$ region during experimental studies of the Mg/C_2H_4 and MgC_2H_4/Ar co-condensates. On the other hand, the stretching modes of the C−H bonds and those of low-frequency intramolecular motions, which include vibrations of magnesium, are consistent in the

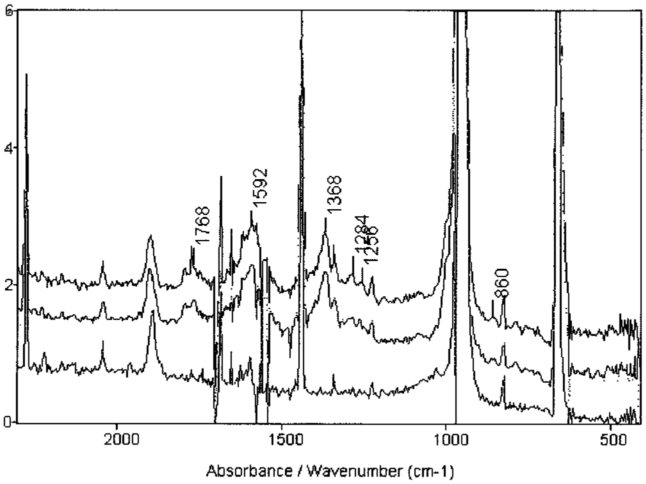

Figure 7. IR spectra of co-condensate $Mg/C_2H_4/CO_2/Ar$ (1/10/10/200), obtained at 10 K after the deposition (bottom curve), after annealing at 35 K (middle curve), and after irradiation (upper curve).

TABLE 6: Comparison of the Calculated and Experimental Frequencies for the $Mg(C_2H_4)_2$ Complex

$Mg(C_2H_4)$ calculated		$Mg/C_2H_4/Ar$ experiment	
ν, cm^{-1}	rel. intensity	ν, cm^{-1}	rel. intensity
2949	0.43	3048	0.7
2890	0.83	2932	0.5
2888	0.35	2886	0.5
2874	0.20		
2837	0.48		
2836	0.37		
1445	0.09		
1158	0.19		
969	0.10	702	0.7
813	0.23	614	0.5
652	1.00	570	1
547	0.55	540	0.4

theoretical and experimental data confirming the formation of the predicted structure $Mg(C_2H_4)_2$.

3. Mixed $Mg/CO_2/C_2H_4$ System. The condensates of magnesium with the $C_2H_4/CO_2/Ar$ (1/1/20) mixtures have been investigated. After the deposition, the IR spectra of the condensate contain only absorptions from CO_2 and C_2H_4. Annealing leads to the appearance and growth of the absorptions at 1768, 1592, 1368, 1284, 1255, and 860 cm^{-1} as can be seen in Figure 7. No changes were noticed in the C−H stretching region. Irradiation by $\lambda > 300$ nm for 30 min does not change the spectrum.

Absorptions at 1592, 1368, and 860 cm^{-1} agree with the values obtained for the $MgCO_2$ complex. Three new bands at 1768 and 1284/1256 cm^{-1} were observed neither in Mg/CO_2 nor in Mg/C_2H_4 co-condensates; therefore, they belong to the product of interaction of all three constituents.

The full-MP2/6-311G(2d,2p) geometry optimization of $MgC_2H_4CO_2$ leads to the five-member cycle as it was in case of $Mg(C_2H_4)_2$. Bond lengths and bond orders for $MgC_2H_4CO_2$ are depicted in Figure 8. It is interesting to compare our results with the proposed structure of the $Ni/CO_2/C_2H_4$ complex.[22]

The natural charge on the Mg atom is +1.6. The binding energy of the complex with respect to the decomposition to Mg + C_2H_4 + CO_2 is estimated as 18 kcal/mol at the MP2 level.

The calculated vibrational spectrum shows that this species has only two intense IR bands at 1222 and 1763 cm^{-1} as can be seen in Figure 9. They are in close agreement with the experimental bands at 1286/1254 and 1768 cm^{-1}.

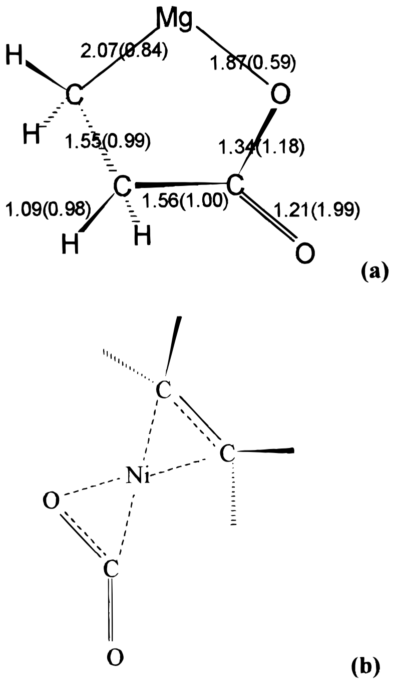

Figure 8. (a) Bond lengths (Å) and bond orders (in parentheses) for $MgC_2H_4CO_2$. (b) Proposed structure of $Ni/CO_2/C_2H_4$ complex.[19]

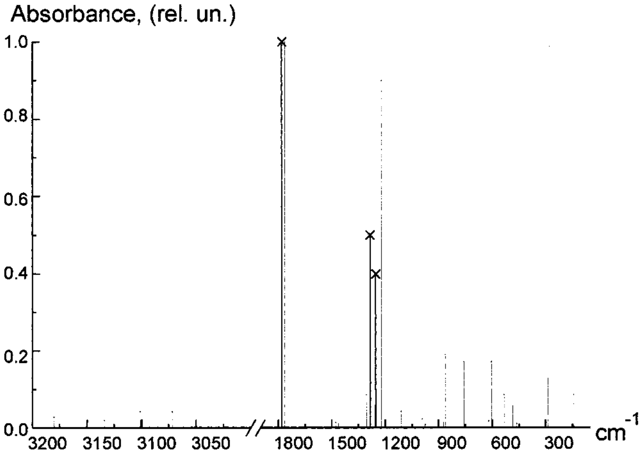

Figure 9. Comparison of experimentally obtained frequencies (*X*) with those calculated for the cyclic $MgCO_2C_2H_4$ compound.

The analysis of the forms of vibrations corresponding to these bands indicates that the band at 1222 cm^{-1} (theoretical spectrum) corresponds to the mixed $\delta_{CH_2}/\nu_{C=O}$ and the band at 1763 cm^{-1} to the mixed δ_{CH_2}/ν_{C-O}. It is important that the experimentally observed bands correspond to the vibrations which include both the CO_2 and C_2H_4 moieties, and therefore, it is highly probable that the theoretically predicted structure adequately describes the experiments.

Conclusions

The main purpose of our work was to analyze the interaction of Mg atom with CO_2 and C_2H_4 by using combined experimental and quantum chemical treatments and to provide an interpretation of the experimental data on the matrix reactions. Our conclusion is that among the reaction products the cyclic complexes are formed: $MgCO_2$ (four-membered ring), $Mg(C_2H_4)_2$, and $MgC_2H_4CO_2$ (five-member rings). In the latter two cases, the complexes are nicely bound with respect to the decomposition into the reactants with the binding energies of

21 and 18 kcal/mol, respectively, at the MP2/6-311G(2d,2p) level. The $MgCO_2$ species corresponds to the metastable particle, which is stabilized by the matrix. These statements are based on a fair agreement within the expected uncertainty limits of the computed IR-active vibrational frequencies and the observed absorption bands.

Acknowledgment. This work was supported in part by the Russian Basic Research Foundation (Grant 98-03-33168). E.V.P. and A.V.N. thank Alex Granovsky for his generous efforts to develop the PC version of GAMESS making these ab initio calculations possible.

References and Notes

(1) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063.
(2) Tanaka, K. *Adv. Inorg. Chem.* **1995**, *43*, 409.
(3) Kafafi, Z. H.; Hauge, R. H.; Billups, W. E. *Inorg. Chem.* **1984**, *23*, 177.
(4) Mascetti, J.; Tranquille, M. *J. Phys. Chem.* **1988**, *92*, 2177.
(5) LeQuere, A. M.; Xu, C.; Manceron, L. *J. Phys. Chem.* **1991**, *95*, 3031.
(6) Sodupe, M.; Branchadell, V.; Oliva, A. *J. Phys. Chem.* **1995**, *99*, 8567.
(7) Papai, I.; Mascetti, J.; Fournier, R. *J. Phys. Chem. A* **1997**, *101*, 4465.
(8) Souter, P. F.; Andrews, L. *Chem. Commun.* **1997**, 777.
(9) Mele, F.; Russo, N.; Illas, F. *Chem. Phys. Lett.* **1998**, *295*, 409.
(10) Fan, H. J.; Liu, C. W. *Chem. Phys. Lett.* **1999**, *300*, 351.
(11) Manceron, L.; Andrews, L. *J. Phys. Chem.* **1986**, *90*, 4514.
(12) Alikhani, M. E.; Hannachi, Y.; Manceron, L.; Bouteiller, Y. *J. Chem. Phys.* **1995**, *103*, 10128.
(13) Gao, J.; Karplus, M. *Chem. Phys. Lett.* **1990**, *169*, 410.
(14) Manceron, L.; Andrews, L. *J. Phys. Chem.* **1989**, *93*, 2964.
(15) Lee, Y. K.; Hannachi, Y.; Xu, C.; Andrews, L.; Manceron, L. *J. Phys. Chem.* **1996**, *100*, 11228.
(16) Parker, S. F.; Peden, C. H. F.; Barrett, P. H.; Pearson, R. G. *Inorg. Chem.* **1983**, *22*, 2813.
(17) McIntosh, D. F.; Ozin, G. A.; Messemer, R. *Inorg. Chem.* **1980**, *19*, 3321.
(18) Bernardi, F.; Bottoni, A.; Calcinari, M.; Rossi, I.; Robb, M. *J. Phys. Chem. A* **1997**, *101*, 6310.
(19) McKee, M. L. *J. Am. Chem. Soc.* **1993**, *115*, 9608.
(20) Lee, Y. K.; Manceron, L.; Papai, I. *J. Phys. Chem. A* **1997**, *101*, 9650.
(21) Sergeev, G. B.; Zagorskaya, O. V. *Vestn. Mosk. Univ. Ser. 2: Chem.* **1987**, *28*, 362.
(22) Galan, F.; Fouassier, M.; Mascetti, J.; Tranquille, M. *Proc. Int. Conf. Low Temp. Chem.*, 5−9 Sept. 1994, Moscow, Russia, 55.
(23) Solov'ev, V. N.; Sergeev, G. B.; Nemukhin, A. V.; Burt, S. K.; Topol, I. A. *J. Phys. Chem. A* **1997**, *101*, 8625.
(24) Karyakin, Yu. V.; Angelov, I. I. *Pure Chemical Substances*; Chemistry: Moscow, 1974; p 302.
(25) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, V.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
(26) Andrews, L.; Yustein, J. *J. Phys. Chem.* **1993**, *97*, 12700.
(27) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(28) Cooper, C.; Compton, R. *Chem. Phys. Lett.* **1972**, *14*, 29.
(29) Knight, L. B.; Hill, D.; Berry, K.; Babb, R.; Feller, D. *J. Chem. Phys.* **1996**, *105*, 5672.
(30) Jacox, M. E.; Thompson, W. E. *J. Chem. Phys.* **1989**, *91*, 1410.
(31) Rytter, E.; Gruen, D. M. *Spectrochim. Acta* **1979**, *35A*, 199.
(32) Aleksanyan, V. T.; Lokshin, B. V. *Mol. Struct. Chem. Bonding* **1976**, *5*, 178 (in Russian).