

AB INITIO CHARACTERIZATION OF MgCCH, MgCCH<sup>+</sup>, AND MgC<sub>2</sub> AND PATHWAYS  
TO THEIR FORMATION IN THE INTERSTELLAR MEDIUM

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## ABSTRACT

A study of Mg-bearing compounds has been performed in order to determine molecular properties which are critical for planning new astronomical searches and laboratory studies. The primary focus of the work is on MgCCH, MgCCH<sup>+</sup>, and the isomers of MgC<sub>2</sub>. Only MgCCH has been identified in laboratory studies. Additional calculations have been carried out on MgH, MgNC, MgCN, and their cations in an effort to evaluate pathways to the formation of MgCCH and MgCCH<sup>+</sup> in the interstellar medium (ISM) or in circumstellar envelopes. Correlated ab initio methods and correlation-consistent basis sets have been employed. Properties including structures, rotational constants, dipole moments, and harmonic frequencies are reported. A transition state between linear MgCC and cyclic MgC<sub>2</sub> has been characterized and was found to yield a minimal barrier (~0.5 kcal mole<sup>-1</sup>), indicating easy interconversion to the cyclic form. Direct reactions in the ISM between Mg or Mg<sup>+</sup> and HCCH are precluded by energetic considerations, but a number of ion-molecule or neutral-neutral exchange reactions between CCH and various Mg-containing species offer plausible pathways to MgCCH or MgCCH<sup>+</sup>. Weakly bound MgH may react with CCH to form MgCCH, but MgH has not been detected. Both MgNC and MgCN have been observed, but reactions with CCH are slightly endothermic by 1-3 kcal mole<sup>-1</sup>. Although MgH<sup>+</sup>, MgNC<sup>+</sup>, and MgCN<sup>+</sup> have not been detected, their reactions with CCH to form MgCCH<sup>+</sup> are all exothermic. With only a small barrier separating linear MgCC and cyclic MgC<sub>2</sub>, the dissociative recombination of MgCCH<sup>+</sup> with an electron is expected to yield cyclic MgC<sub>2</sub> and regenerate Mg and CCH. New astronomical searches for MgCCH, MgCCH<sup>+</sup>, cyclic MgC<sub>2</sub>, MgNC<sup>+</sup>, and MgCN<sup>+</sup> will provide further insight into organo-magnesium astrochemistry.

*Subject headings:* ISM: molecules — molecular processes

## 1. INTRODUCTION

The study of organo-magnesium astrochemistry and the search for Mg-bearing species is an important step toward developing an understanding of the roles and abundances of refractory-element compounds in the ISM and in circumstellar envelopes (CSEs). On the basis of the depletion factors for Si and P in star-forming regions, Turner (1991, 1992) concluded that Mg-bearing compounds, along with those of Na and perhaps Fe and Al, should be abundant enough to be "easily detected." However, only one Mg-bearing species, MgNC and its isomer MgCN, has been observed to date (Guélin et al. 1986; Kawaguchi et al. 1993; Ziurys et al. 1995). As summarized by Turner (1991) and Kawaguchi et al. (1993), various astronomical searches have failed to detect MgO, MgS, and MgH.

In order to identify new candidates for further searches, it is crucial to characterize other species and to evaluate the likelihood of their existence by elucidating viable pathways to their formation. This task can be accomplished by a combination of experimental and theoretical studies. In the case of MgNC, a laboratory study by Kawaguchi et al. (1993) identified the spectra taken from IRC +10216 by Guélin et al. (1986). The subsequent ab initio work of Ishii et al. (1993) offered theoretical predictions for  $B_0$  and  $D_0$  in good agreement with the experimental work and provided further information not easily accessible to laboratory measurement.

The characterization of other Mg-bearing species continues. Anderson & Ziurys (1995) have recently reported the detection of MgCCH in their laboratory, identifying it as a linear radical with a  $^2\Sigma^+$  ground state. In their experiment, Mg vapor was

introduced into a mixture of argon and acetylene and then subjected to an electric current. MgCCH was identified by analyzing the rotational spectrum. They reported a  $B_0$  value of 5010.4 MHz and estimated the  $r_0$  (MgC) bond length to be approximately 2.04 Å based on  $B_0$  and handbook values for the C-C and C-H bond lengths of acetylene. Two possible formation mechanisms leading to MgCCH were postulated,



and



The latter reaction was suggested by the observation that ethynyl radicals were present. Although both reactions may lead to the formation of MgCCH under laboratory conditions, it is unlikely that either process will be efficient under the ambient conditions of the ISM or CSEs. The present work will demonstrate that reaction (1) is highly endothermic for ground-state reactants (see Table 11). Furthermore, large barriers are usually present in neutral-neutral reactions involving two singlet species (Smith 1988). Association reactions such as reaction (2) are often prohibitively slow in a low-density medium with no third body to remove the reaction energy, and radiative stabilization is inefficient for small species (Dalgarno 1987, p. 219).

Reaction (1) is much more favorable if Mg is in an excited state. A bright green glow observed in the Anderson & Ziurys experiment may be indicative of a  $^3P$ - $^3S$  transition. The theoretical work of Chaquin, Sevin, & Papakondylis (1990) and Flores & Largo (1991) has shown that excited state Mg may



react with acetylene to form species such as A-shaped MgC<sub>2</sub>H<sub>2</sub> and linear HMgCCH. MgC<sub>2</sub>H<sub>2</sub> lies about 40 kcal mole<sup>-1</sup> above ground-state Mg + HCCH and thus has little relevance in the present context. Linear HMgCCH can be formed by inserting Mg directly into a CH bond. The Mg-H bond is weak and can be broken to yield MgCCH. However, there is a small barrier to the formation of HMgCCH on the excited state surface that becomes insurmountable on the ground-state surface. Hence, although formation of MgCCH via intermediate HMgCCH is a plausible mechanism for the formation of MgCCH in the Anderson & Ziurys experiment, it is not expected to be important for the ground-state behavior likely to be prevalent under conditions present in the ISM.

Turning elsewhere for viable formation pathways, exchange reactions of the form

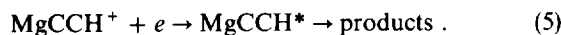


and



are plausible under cold, low-density conditions if they are exothermic and have small or no barriers. In this work, reactions between CCH and MgH, MgH<sup>+</sup>, MgNC, MgNC<sup>+</sup>, MgCN, and MgCN<sup>+</sup> have been considered. Both MgNC and MgCN have been observed, while the concentration of MgH falls below the minimum level for detection. No known searches have been made for MgCN<sup>+</sup>, MgNC<sup>+</sup>, or MgH<sup>+</sup>. The weakness of the Mg-H bond and the implied reactivity of MgH and MgH<sup>+</sup> are consistent with a very low abundance.

Pathways leading to MgCCH<sup>+</sup> have been considered because ion-molecule reactions tend to be much faster than those involving two neutral species. MgCCH<sup>+</sup> is a precursor to MgC<sub>2</sub> species by means of the dissociative recombination reaction



Although the Mg-C bond is weaker than the C-H bond in MgCCH and thus more likely to be broken, H may be ejected to leave linear MgCC (henceforth l-MgCC). However, cyclic MgC<sub>2</sub> (c-MgC<sub>2</sub>) is the more stable isomer. Therefore, it is important to characterize the energetics of the l-MgCC → c-MgC<sub>2</sub> isomerization in order to be able to predict which isomer is most likely to be observed. A low barrier will favor rearrangement to the cyclic form.

In order to evaluate the various reactions described above, the following species have been characterized using exceptionally large basis sets and state-of-the-art correlated ab initio methodology: MgCCH, MgCCH<sup>+</sup>, l-MgCC, c-MgC<sub>2</sub>, the MgC<sub>2</sub> transition state, MgH, MgH<sup>+</sup>, MgNC, MgNC<sup>+</sup>, MgCN<sup>+</sup>, HCCH, CCH, CN, Mg, Mg<sup>+</sup>, and H. For each group of Mg-bearing compounds, a self-contained discussion of the predicted structures, rotational constants, dipole moments, and harmonic frequencies and a comparison to any previous calculations or measurements is presented. The evaluation of proposed formation pathways follows a brief section on bond energies. This work serves the dual purpose of characterizing a number of Mg-bearing compounds while proposing plausible pathways to the formation of MgCCH, MgCCH<sup>+</sup>, and c-MgC<sub>2</sub> in the ISM or in CSEs.

## 2. METHODOLOGY

Correlation-consistent basis sets (Dunning 1989; Kendall, Dunning, & Harrison 1992; Woon & Dunning 1993a, 1994a)

of double (cc-pVDZ), triple (cc-pVTZ), and quadruple (cc-pVQZ) zeta quality have been employed in this work. An extensive series of benchmark calculations (Woon & Dunning 1993b, 1994b; Peterson, Kendall, & Dunning 1993a, b; Peterson, Woon, & Dunning 1994; Woon 1994) on small systems have amply demonstrated the well-behaved convergence patterns associated with the use of these basis sets. This behavior has been exploited in the present work in order to estimate complete basis set (CBS) limits for both structural and energetic properties. A simple exponential function is used (see previous references). The ability to extrapolate to a CBS limit effectively removes the usual ambiguity associated with incomplete one-electron basis sets. Energy differences have been determined by taking the difference of the two CBS limits for the appropriate total energies. Spherical contractions have been used for functions of *d*, *f*, and *g* angular momenta.

The MOLPRO suite of quantum chemistry programs<sup>1</sup> was used exclusively. A substantial fraction of the work utilized the restricted coupled cluster method with full single and double excitations and a perturbative estimate of triple excitations [RCCSD(T)] (Raghavachari et al. 1989; Hampel, Peterson, & Werner 1992; Knowles, Hampel, & Werner 1993; Deegan & Knowles 1994). For linear and cyclic MgC<sub>2</sub> and the intervening transition state (TS), multiconfigurational self-consistent field (MCSCF) calculations were performed. Dynamical correlation was subsequently recovered by means of internally contracted multireference configuration interaction (CMRCI). The multireference Davidson correction (CMRCI + Q) (Langhoff & Davidson 1974) was also applied. In order to allow affordable CMRCI calculations, a limited active space arising from 10 electrons distributed in eight orbitals was selected. This choice was validated by examining larger active spaces and is consistent for both isomers and the TS.

Although multireference methods are critical for describing l-MgCC and the TS, c-MgC<sub>2</sub> falls at the edge of the envelope where the RCCSD(T) method is reliable (on the basis of the so-called T1 diagnostic). Therefore, it was possible to treat the most stable isomer at the same level of theory applied to MgCCH, MgCCH<sup>+</sup>, and the other species. In § 4 it will be demonstrated that RCCSD(T), CMRCI, and CMRCI + Q yield commensurate results for c-MgC<sub>2</sub>. It is advantageous to use RCCSD(T) for bond and reaction energies because it is a size-consistent method: one may directly add or subtract the energies of reactants and products as necessary, which often cannot be done with configuration interaction-based methods.

One of the collections of benchmark calculations cited previously (Woon & Dunning 1994b) includes comparisons of the CMRCI, CMRCI + Q, and RCCSD(T) methods. In the complete basis set limit, the RCCSD(T) and CMRCI + Q methods yield comparable accuracy and similar total energies. Furthermore, in conjunction with CBS extrapolations, all these methods can be used to obtain very accurate bond energies and relative energy differences.

Two variations on the standard cc-pVXZ sets were also used. The aug-cc-pVXZ sets include diffuse functions that are vital to an accurate description of molecular properties such as multipole moments and polarizabilities. Dipole moments have

<sup>1</sup> MOLPRO is a suite of ab initio programs written by H.-J. Werner and P. J. Knowles with contributions by J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. M. Pitzer, A. J. Stone, and P. R. Taylor.

TABLE 1  
MgCCH AND MgCCH<sup>+</sup>: RCCSD(T) RESULTS FOR ENERGETICS AND STRUCTURE

Species	Basis Set	$E_e$ (hartrees)	$r_e$ (MgC) (Å)	$r_e$ (CC) (Å)	$r_e$ (CH) (Å)	$B_e$ (GHz)
MgCCH .....	cc-pVDZ	-276.15052	2.0703	1.2482	1.0823	4.784
	cc-pVTZ	-276.23326	2.0557	1.2298	1.0665	4.877
	cc-pVQZ	-276.25670	2.0544	1.2265	1.0664	4.890
	Estimated CBS limit	-276.26971	2.054	1.225	1.066	4.90
	cc-pCVDZ	-276.39821	2.0639	1.2449	1.0805	4.812
	cc-pCVTZ	-276.60635	2.0427	1.2263	1.0662	4.927
MgCCH <sup>+</sup> .....	cc-pVDZ	-275.88912	1.9681	1.2434	1.0847	5.124
	cc-pVTZ	-275.97126	1.9512	1.2247	1.0689	5.237
	cc-pVQZ	-275.99452	1.9482	1.2211	1.0687	5.257
	Estimated CBS limit	-276.00738	1.947	1.219	1.069	5.27
	cc-pCVDZ	-275.34299	1.9371	1.2211	1.0688	5.297
	cc-pCVTZ	-275.34299	1.9371	1.2211	1.0688	5.297

been computed using aug-cc-pVTZ sets for C and H in conjunction with the cc-pVTZ set for Mg; the standard cc-pVXZ sets are inherently well suited for describing the diffuse character of Mg. In order to assess the effect of core-valence correlation contributions from the 1s electrons of C and the 2s 2p electrons of Mg, calculations were also carried out using sets optimized specifically for this purpose (cc-pCVDZ or cc-pCVTZ). When either aug-cc-pVXZ or cc-pCVXZ sets were used, structures were completely reoptimized. Only valence electrons were correlated in all calculations using cc-pVXZ or aug-cc-pVXZ sets; when cc-pCVXZ sets were used, only the 1s<sup>2</sup> electrons of Mg were excluded. Dipole moments were either computed directly as an expectation value (CMRCI) or with the finite field approximation [RCCSD(T)].

Harmonic frequencies at the RCCSD(T), CMRCI, and CMRCI + Q levels of theory were determined by filling an appropriate collection of points distributed around the minima. The program SURVIBTM (Harding & Ermler 1985; Ermler, Hsieh, & Harding 1988) was used for this task. The potential included all linear, quadratic, and cubic terms, plus even quartic ones. In general, cc-pVTZ sets are sufficient for determining harmonic frequencies and zero-point energies (ZPEs).

### 3. MgCCH AND MgCCH<sup>+</sup>

To date, MgCCH has not been the subject of any detailed computational work, although it was noted in the context of the work on MgC<sub>2</sub>H<sub>2</sub> by Flores & Largo (1991). As mentioned in the introduction, Ziurys & Anderson (1995) have characterized neutral MgCCH as a linear radical with a <sup>2</sup>Σ<sup>+</sup> ground state and  $B_0 = 5.0104$  GHz in their laboratory. The linear MgCCH<sup>+</sup> (<sup>1</sup>Σ<sup>+</sup>) cation has apparently not been the subject of any previously experimental or computational study. Results for both species at the RCCSD(T) level of theory and various

basis sets are presented in Table 1 (equilibrium energies  $E_e$ , bond lengths  $r_e$ , and rotational constants  $B_e$ ) and Table 2 (harmonic frequencies  $\omega$  and zero-point energies ZPE). The CH, CC, and MgC stretches are  $\omega_1$ ,  $\omega_2$ , and  $\omega_4$ , respectively. The doubly degenerate bending frequencies  $\omega_3$  and  $\omega_5$  correspond to the CCH bend (*trans* coupling) and the floppy MgCC bend (*cis* coupling). The dipole moment of MgCCH at the triple zeta level is 1.68 D.

With valence correlation, the estimated CBS limits for the MgC, CC, and CH equilibrium bond lengths are, respectively, 2.054, 1.225, and 1.066 Å for MgCCH and 1.947, 1.219, and 1.069 Å for MgCCH<sup>+</sup>. Removing an electron from Mg reduces the MgC distance by more than 0.1 Å but has little effect on the other bond lengths. Similar trends are exhibited by the stretching frequencies: at the cc-pVTZ level, the CH, CC, and MgC stretches change by -14, +34, and +97 cm<sup>-1</sup>, respectively, when an electron is extracted.

Core-valence correlation effects can be approximated by considering the difference between correlating the valence electrons at the cc-pVTZ level and correlating everything but the 1s<sup>2</sup> electrons of Mg while using the cc-pCVTZ set. The shifts are very similar for the neutral and cationic species: the MgC, CC, and CH bond lengths decrease by 0.0130, 0.0035, and 0.0003 Å in MgCCH and by 0.0141, 0.0036, and 0.0001 Å in MgCCH<sup>+</sup>. When these corrections are added to the valence correlation CBS limits, they yield recommended values for the MgC, CC, and CH bond lengths of 2.041, 1.221, and 1.066 Å for MgCCH and 1.933, 1.215, and 1.069 Å for MgCCH<sup>+</sup>. Although zero-point motion will lengthen the average Mg-C separation, there is still good agreement between the theoretical  $r_e$  (2.041 Å) and the estimated experimental  $r_0$  value (2.04 Å) of Anderson & Ziurys (1995).

The recommended values of  $B_e$  for MgCCH and MgCCH<sup>+</sup> are 4.95 and 5.33 GHz. Similar results are predicted by adjust-

TABLE 2  
MgCCH AND MgCCH<sup>+</sup>: RCCSD(T) HARMONIC FREQUENCIES  
AND ZERO POINT ENERGIES ZPE (cm<sup>-1</sup>)

Species	Basis Set	$\omega_1$	$\omega_2$	$\omega_3 (\times 2)$	$\omega_4$	$\omega_5 (\times 2)$	ZPE
MgCCH .....	cc-pVDZ	3413	1972	648	490	150	3735
	cc-pVTZ	3429	1990	680	496	150	3787
	cc-pCVDZ	3416	1974	656	489	154	3749
MgCCH <sup>+</sup> .....	cc-pVDZ	3403	2000	716	575	149	3854
	cc-pVTZ	3415	2024	748	593	156	3920

ing the valence CBS limits (4.90 and 5.27 GHz, respectively) with triple zeta core-valence corrections of 50 and 60 MHz or by determining  $B_e$  directly from the recommended values of the bond lengths noted above. The computed  $B_e$  value for MgCCH is in good agreement with the experimental  $B_0$  result, differing by only 60 MHz. As reported by Ishii et al. (1993), the difference between  $B_e$  and  $B_0$  is about 60 MHz in MgNC. A similar shift in MgCCH is reasonable. Assuming a similar correction for MgCCH<sup>+</sup> yields a predicted  $B_0$  of 5.39 GHz.

From Table 2 it can be seen that the frequencies change somewhat between the cc-pVDZ and cc-pVTZ sets. Further changes upon improving to the cc-pVQZ level are expected to be minor (see § 4, where cc-pVQZ frequencies are computed). The effect of including core-valence correlation at the double zeta level is almost negligible. Thus, the recommended harmonic frequencies are 3429, 1990, 680, 596, and 150 cm<sup>-1</sup> for MgCCH and 3415, 2024, 748, 593, and 156 cm<sup>-1</sup> for MgCCH<sup>+</sup>. Interestingly, the MgCC bending frequency changes very little between the neutral and cation, while the CCH bending frequency shifts by 68 cm<sup>-1</sup>.

#### 4. THE ISOMERS OF MgC<sub>2</sub> AND THEIR TRANSITION STATE

If the H is removed from MgCCH, linear l-MgCC (<sup>1</sup>Σ<sup>+</sup>) is the initial product. The cyclic isomer c-MgC<sub>2</sub> (<sup>1</sup>A<sub>1</sub>) can be reached in a straightforward manner by bending along a <sup>1</sup>A' surface through the MgCC transition state (TS). The isomers have been the subject of two prior theoretical studies, but both were restricted to single reference methods and small basis sets. Green (1984) reported restricted Hartree-Fock (RHF) calcu-

lations that identified c-MgC<sub>2</sub> as the lowest energy isomer by 20 kcal mole<sup>-1</sup>. A recent correlated restricted singles and doubles configuration interaction calculation (RCISD/6-31G\*) by Ramondo, Sanna, & Bencivenni (1992) obtained an isomerization energy of 24.7 kcal mole<sup>-1</sup>. Neither study characterized the TS separating the two isomers.

The present work has found that l-MgCC and c-MgC<sub>2</sub> both possess significant multireference character, a trait they share in common with MgC (Bauschlicher, Langhoff, & Partridge 1993). In contrast, MgCCH (§ 3) and Mg cyanide and isocyanide compounds (§ 5) do not require a multireference treatment. For MgC<sub>2</sub>, single-reference methods may yield poor results or even lead to a qualitatively misleading description. Unlike most single-reference methods, RCCSD(T) provides a diagnostic parameter to indicate when its use is no longer appropriate. Preliminary calculations showed that RCCSD(T) cannot be reliably used on l-MgCC or the TS, but it can be used for c-MgC<sub>2</sub>. The latter falls close enough to the acceptance threshold, however, to warrant validating the RCCSD(T) results against a multireference treatment. The agreement is good, and no anomalous behavior is apparent. This allows c-MgC<sub>2</sub> to be placed on the same footing as MgCCH and the other species. However, in order to make well-founded conclusions about the isomerization energetics, all three critical points must be treated with the same method. The CMRCI and CMRCI + Q results serve that purpose.

Tables 3, 4, and 5 contain the total energies and equilibrium structural data for l-MgCC, c-MgC<sub>2</sub>, and the MgCC TS, respectively. The harmonic frequencies for all three are col-

TABLE 3  
LINEAR MgCC: ENERGETICS AND STRUCTURE

Method	Basis Set	$E_e$ (hartrees)	$r_e$ (MgC) (Å)	$r_e$ (CC) (Å)	$B_e$ (GHz)
CMRCI .....	cc-pVDZ	-275.45037	2.0542	1.2712	5.237
	cc-pVTZ	-275.51658	2.0353	1.2522	5.355
	cc-pVQZ	-275.53601	2.0331	1.2480	5.374
	Estimated CBS limit	-275.54686	2.032	1.246	5.38
CMRCI + Q .....	cc-pVDZ	-275.46398	2.0549	1.2757	5.224
	cc-pVTZ	-275.53455	2.0354	1.2567	5.342
	cc-pVQZ	-275.55518	2.0334	1.2524	5.361
	Estimated CBS limit	-275.56668	2.033	1.250	5.37

TABLE 4  
c-MgC<sub>2</sub>: ENERGIES AND STRUCTURES

Method	Basis Set	$E_e$ (hartrees)	$r_e$ (MgC) (Å)	$\theta$ (CMgC)	$A_e$ (GHz)	$B_e$ (GHz)	$C_e$ (GHz)
CMRCI .....	cc-pVDZ	-275.46526	2.0743	36.32	50.37	10.83	8.92
	cc-pVTZ	-275.53354	1.0357	36.48	51.86	11.27	0.26
	cc-pVQZ	-275.55350	2.0233	36.60	52.19	11.42	9.37
	Estimated CBS limit	-275.56462	2.016	36.7	52.36	11.51	9.43
CMRCI + Q .....	cc-pVDZ	-275.48180	2.0655	36.63	49.98	10.96	8.99
	cc-pVTZ	-275.55487	2.0259	36.83	51.43	11.40	9.33
	cc-pVQZ	-275.57616	2.0131	36.95	51.74	11.56	9.45
	Estimated CBS limit	-275.58804	2.006	37.0	51.90	11.65	9.52
RCCSD(T) .....	cc-pVDZ	-275.48191	2.0806	36.31	50.10	10.78	8.87
	cc-pVTZ	-275.55835	2.0405	36.53	51.47	11.22	9.21
	cc-pVQZ	-275.58094	2.0272	36.59	51.80	11.33	9.30
	Estimated CBS limit	-275.59355	2.020	36.6	51.98	11.39	9.35
	cc-pCVTZ	-275.93199	2.0236	36.75	51.75	11.42	9.36

TABLE 5  
 MgCC TS: ENERGETICS AND STRUCTURE

Method	Basis Set	$E_e$ (hartrees)	$r_e(\text{MgC})$ (Å)	$r_e(\text{CC})$ (Å)	$\theta(\text{MgCC})$
CMRCI .....	cc-pVDZ	-275.44878	2.0494	1.2771	133°41
	cc-pVTZ	-275.51481	2.0300	1.2575	131.42
CMRCI + Q .....	cc-pVDZ	-275.46268	2.0496	1.2804	136.42
	cc-pVTZ	-275.53318	2.0304	1.2608	134.79

lected in Table 6. In all cases,  $\omega_1$  corresponds to the CC stretch, although there is also an associated C-Mg-C bending motion for c-MgC<sub>2</sub>. For l-MgCC and the TS,  $\omega_2$  is the MgC stretching frequency, and  $\omega_3$  is the bending frequency. The latter is doubly degenerate in l-MgCC and imaginary in the TS. In c-MgC<sub>2</sub>,  $\omega_2$  and  $\omega_3$  correspond to symmetric and asymmetric combinations of MgC stretches, respectively.

There is very little difference between the CMRCI and CMRCI + Q predictions for l-MgCC. The CMRCI estimated CBS limits for the MgC and CC bond lengths are 2.032 and 1.246 Å, with  $B_e = 5.38$  GHz. The Davidson-corrected values show only small variations. The dipole moment (CMRCI/triple zeta) is 4.22 D.

Cyclic MgC<sub>2</sub> was treated with CMRCI, CMRCI + Q, and RCCSD(T). Only small variations are exhibited by the different methods. The estimated CBS limits for the equilibrium MgC bond lengths vary over a range of 0.014 Å, while the C-Mg-C bond angle varies by only 0°4. The largest deviations are in the rotational constants, which vary from 200 to almost 500 MHz. The RCCSD(T) results are comparable to CMRCI and CMRCI + Q, failing closer to the former for most parameters:  $r_e(\text{MgC})$ ,  $\theta(\text{CMgC})$ ,  $B_e$ , and  $C_e$ . As expected, the total energies at the RCCSD(T) and CMRCI + Q levels of theory are very similar, differing by only about 5.5 millihartrees. Core-valence calculations at the RCCSD(T)/cc-pCVTZ level indi-

cate a decrease of 0.017 Å in the MgC distance, only slightly larger than that noted for MgCCH and MgCCH<sup>+</sup>. The bond angle changes by 0°2. The recommended structural parameters for c-MgC<sub>2</sub> are  $r_e(\text{MgC}) = 2.003$  Å,  $\theta(\text{CMgC}) = 36°8$ , and rotational constants of 52.26, 11.59, and 9.50 GHz. The dipole moment (CMRCI) of c-MgC<sub>2</sub> is quite large, 6.17 D.

As in the case of the two isomers, the CMRCI and CMRCI + Q results for the TS are very similar. The MgC bond length (CMRCI/cc-pVTZ vs. CMRCI + Q/cc-pVTZ) differs by only 0.0004 Å, while the CMRCI + Q CC bond length is 0.003 Å longer. The most pronounced difference is the MgCC bond angle, which differs by 3° for the two methods.

The harmonic frequencies show very little change when the basis sets are improved from triple to quadruple zeta quality. The recommended values (CMRCI/cc-pVQZ) are 1900, 496, and 120 cm<sup>-1</sup> for l-MgCC and 1766, 482, and 467 cm<sup>-1</sup> for c-MgC<sub>2</sub>. Variations up to 44 cm<sup>-1</sup> exist between RCCSD(T) and the multireference methods. The net ZPEs are remarkably consistent, especially for c-MgC<sub>2</sub>.

A summary of energy differences is presented in Table 7. The cyclic form is more stable, the same conclusion drawn from two previous studies. The CBS limits for the equilibrium isomerization energy are 11.1 and 13.4 kcal mole<sup>-1</sup> at the CMRCI and CMRCI + Q levels, with very little change when ZPE is added. The extrapolations improve the isomerization energy by 0.5–0.7 and by 0.2–0.3 kcal mole<sup>-1</sup> with respect to the cc-pVTZ and cc-pVQZ results. The barrier height is less sensitive to basis quality, changing by 0.11 kcal mole<sup>-1</sup> or less between the cc-pVDZ and cc-pVTZ sets. The inclusion of ZPE reduces the barrier to only 0.5 and 0.3 kcal mole<sup>-1</sup> for the CMRCI and CMRCI + Q methods, respectively, which indicates that l-MgCC will easily convert to the more stable c-MgC<sub>2</sub> isomer. The dissociative recombination of MgCCH<sup>+</sup> with an electron shown in reaction (5) should provide more than enough energy to eject the H and allow rearrangement to the most stable isomer, c-MgC<sub>2</sub>.

## 5. MgNC, MgCN, AND THEIR CATIONS

MgNC and MgCN are linear radicals with <sup>2</sup>Σ<sup>+</sup> ground states. They have both been detected in IRC + 10216 (Guélin et al. 1986; Kawaguchi et al. 1993; Ziurys et al. 1995) and have recently been studied theoretically by Ishii et al. (1993) with single-reference CI. MgNC, the isocyanide isomer, is more stable, but by less than 1000 cm<sup>-1</sup> (about 3 kcal mole<sup>-1</sup>). The present RCCSD(T) treatment does not differ in any important particulars from the previous work, although the CBS extrapolations remove any uncertainty regarding the sufficiency of the basis sets used by Ishii et al. To date, no one has reported calculations on the <sup>1</sup>Σ<sup>+</sup> states of MgNC<sup>+</sup> and MgCN<sup>+</sup> ions. The results obtained here may assist future laboratory or astronomical work.

TABLE 6

l-MgCC, c-MgC<sub>2</sub>, AND THE MgCC TS: HARMONIC FREQUENCIES AND ZERO POINT ENERGIES ZPE (cm<sup>-1</sup>)

Species	Method	Basis Set	$\omega_1$	$\omega_2$	$\omega_3^*$	ZPE
l-MgCC .....	CMRCI	cc-pVDZ	1871	487	107	1287
		cc-pVTZ	1891	496	120	1313
		cc-pVQZ	1900	496	120	1318
	CMRCI + Q	cc-pVDZ	1840	481	109	1270
		cc-pVTZ	1859	491	113	1288
		cc-pVQZ	1867	490	112	
c-MgC <sub>2</sub> .....	CMRCI	cc-pVDZ	1737	488	412	1319
		cc-pVTZ	1758	488	454	1350
		cc-pVQZ	1766	482	467	1358
	CMRCI + Q	cc-pVDZ	1702	492	436	1315
		cc-pVTZ	1723	499	474	1348
		cc-pVQZ	1731	489	486	1353
	RCCSD(T)	cc-pVDZ	1710	500	395	1302
		cc-pVTZ	1727	520	436	1341
		cc-pVQZ	1736	524	442	1351
MgCC TS .....	CMRCI	cc-pVDZ	1595	572	-127	1083
		cc-pVTZ	1612	588	-137	1100
	CMRCI + Q	cc-pVDZ	1575	565	-123	1070
		cc-pVTZ	1591	580	-130	1086

\*  $\omega_3$  corresponds to the doubly degenerate bending mode in l-MgCC.

TABLE 7  
ENERGY DIFFERENCES FOR LINEAR MgCC AND CYCLIC MgC<sub>2</sub> (kcal mole<sup>-1</sup>)

METHOD	BASIS SET	BARRIER HEIGHT		IZOMERIZATION ENERGY	
		$\Delta E_e$	$\Delta E_0$	$\Delta E_e$	$\Delta E_0$
CMRCI .....	cc-pVDZ	1.00	0.42	-9.34	-9.25
	cc-pVTZ	1.11	0.51	-10.64	-10.53
	cc-pVQZ	...	...	-10.97	-10.86
	Estimated CBS limit	...	...	-11.1	-11.0
CMRCI + Q .....	cc-pVDZ	0.82	0.25	-11.19	-11.06
	cc-pVTZ	0.86	0.28	-12.75	-12.58
	cc-pVQZ	...	...	-13.17	-12.99
	Estimated CBS limit	...	...	-13.4	-13.2

Table 8 contains RCCSD(T) total energies and equilibrium structural data for MgNC, MgNC<sup>+</sup>, MgCN, and MgCN<sup>+</sup>. The valence correlation CBS limits can be taken as the recommended values for the present work. The isomerization energy for MgNC → MgCN is 641 cm<sup>-1</sup>. Ishii et al. (1993) reported values of 899 cm<sup>-1</sup> (singles and doubles configuration interaction [SBCI]) and 510 cm<sup>-1</sup> (SDCI + Q) from single-point calculations at restricted open-shell Hartree-Fock (ROHF) geometries. The full-surface SDCI treatment for MgNC of Ishii et al. yielded  $B_e = 5.883$  GHz. The present RCCSD(T) CBS limit of 5.85 GHz compares well with this value and with the experimental  $B_0$  of 5.967 GHz of Guélin et al. (1986) and Kawaguchi et al. (1993). Anderson, Steimle, & Ziurys (1994) reported a  $B_0$  of 5.0948 GHz for MgCN. The RCCSD(T) CBS limit for  $B_e$  is 5.01 GHz, within 100 MHz of the experiment (as in MgCCH). This discrepancy can be accounted for by incorporating corrections for core-valence effects (+53 MHz at the triple zeta level) and the difference between  $B_e$  and  $B_0$  (nearly 60 MHz in the MgNC study of Ishii et al. 1993). The two cations are essentially isoenergetic in the CBS limit. The CBS predictions for the rotational constants of MgNC<sup>+</sup> and MgCN<sup>+</sup> are 6.26 and 5.41 GHz, respectively.

## 6. OTHER SPECIES INVOLVED IN PROPOSED FORMATION REACTIONS

RCCSD(T) total energies and ZPEs for the ground states of MgH, MgH<sup>+</sup>, Mg, Mg<sup>+</sup>, HCCH, CCH, CN, and H are given in Table 9. Although MgH and MgH<sup>+</sup> have not been observed, they are of interest as precursors in the formation of MgCCH and MgCCH<sup>+</sup> owing to the weakness of Mg-H bonds. To be consistent, all the ZPE corrections in the table are cc-pVTZ values.

## 7. IONIZATION POTENTIALS OF Mg-BEARING SPECIES

Table 10 lists the RCCSD(T) ionization potentials (IPs) for five of the Mg-bearing species considered in this work. The only point of comparison to experiment currently available is the IP of Mg. More than half the intrinsic error of 0.113 eV in this quantity results from the neglect of core-valence correlation: an improvement of 0.072 eV was found at the triple zeta level. The estimated CBS limits for the five species span an interval of about 1 eV, between 6.8 and 7.9 eV, which is strong evidence that the electron in question is always being removed from Mg. The variation with respect to the atomic IP is caused

TABLE 8  
MgNC, MgCN, AND THEIR CATIONS: RCCSD(T) ENERGIES AND STRUCTURES

Species	Basis Set	$E_e$ (hartrees)	$r_e$ (MgX) <sup>a</sup> (Å)	$r_e$ (CN) (Å)	$B_e$ (GHz)
MgNC .....	cc-pVDZ	-292.24004	1.9662	1.2003	5.707
	cc-pVTZ	-292.33458	1.9485	1.1847	5.826
	cc-pVQZ	-292.36322	1.9473	1.1810	5.842
	Estimated CBS limit	-292.37932	1.947	1.179	5.85
MgNC <sup>+</sup> .....	cc-pVDZ	-291.95108	1.8758	1.2082	6.066
	cc-pVTZ	-292.04501	1.8540	1.1921	6.216
	cc-pVQZ	-292.07337	1.8503	1.1884	6.246
	Estimated CBS limit	-292.08932	1.849	1.186	6.26
MgCN .....	cc-pVDZ	-292.23944	2.1036	1.1961	4.910
	cc-pVTZ	-292.33231	2.0869	1.1715	5.002
	cc-pVQZ	-292.36052	2.0870	1.1678	5.011
	Estimated CBS limit	-292.37640	2.088	1.166	5.01
	cc-pCVTZ	-292.70833	2.0740	1.1681	5.055
MgCN <sup>+</sup> .....	cc-pVDZ	-291.95477	2.0031	1.1858	5.256
	cc-pCVTZ	-292.04621	1.9807	1.1708	5.381
	cc-pVQZ	-292.07382	1.9783	1.1668	5.401
	Estimated CBS limit	-292.08933	1.977	1.165	5.41

<sup>a</sup> X = N for MgNC and MgNC<sup>+</sup>; X = C for MgCN and MgCN<sup>+</sup>.

TABLE 9  
 RCCSD(T) TOTAL ENERGIES AND ZERO-POINT ENERGIES OF MISCELLANEOUS SPECIES

SPECIES	$E_e$ (hartrees)				ZPE ( $\text{cm}^{-1}$ )
	cc-pVDZ	cc-pVTZ	cc-pVQZ	Estimated CBS limit	
MgH.....	-200.18471	-200.19719	-200.19981	-200.21015	748
MgH <sup>+</sup> .....	-199.93394	-199.94522	-199.94775	-199.94907	838
Mg.....	-199.64117	-199.64708	-199.64815	-199.64866	...
Mg <sup>+</sup> .....	-199.36482	-199.37046	-199.37140	-199.37184	...
HCCCH.....	-77.11087	-77.19765	-77.20932	-77.22131	5854
CCH.....	-76.40064	-76.46779	-76.48763	-76.49872	3064
CN.....	-92.49066	-92.56637	-92.59045	-92.60410	1025
H.....	-0.49928	-0.49981	-0.49995	-0.50003	...

by the modifying effect of bonding to H, N, or C. Although the Mg-C bond energies in MgCN and MgCCH are very similar (see Table 11), the bonding is different enough to cause a shift of nearly 0.7 eV in the IPs of the two species.

#### 8. ASSOCIATION REACTIONS (BOND ENERGIES)

The top portion of Table 11 is a compendium of bond energies for association reactions leading to MgCCH, MgH, MgNC, MgCN, and their cations. The discussion here will focus on estimated CBS limits at the RCCSD(T) level of theory. The tables provide the computed values for the sequence of basis sets, which allows one to examine the adequacy of the smaller basis sets. The cc-pVTZ sets, for example, typically approach the CBS limits to within 1–3 kcal mole<sup>-1</sup>.

Although association reactions are usually slow under the conditions prevalent in the ISM and in CSEs, the trends in bond energies are interesting and suggestive. The Mg-C bond in MgCCH and MgCCH<sup>+</sup> is of moderate strength (ZPE-corrected values of -74.7 and -83.4 kcal mole<sup>-1</sup>, respectively). The Mg-C and Mg-N bonds in the cyanides and isocyanides are of similar magnitude to each other and to the Mg-C bonds in MgCCH and MgCCH<sup>+</sup>. In contrast, the Mg-H bonds in MgH and MgH<sup>+</sup> are much weaker, -30.8 and -46.0 kcal mole<sup>-1</sup>, respectively. Bonds between Mg and C, N, or H are largely ionic, resulting in the characteristically large dipole moments of Mg-bearing species. However, there is an important source of additional stabilization in the Mg-C and Mg-N bonds that is not present between Mg and H: hyperconjugation or back-bonding of  $\pi$  character into the underutilized 3p orbitals of Mg.

The relative strengths of Mg-X bonds can provide insight into whether exchange reactions are likely to be endothermic or exothermic. As mentioned previously, the weakness of the Mg-H bond makes MgH and MgH<sup>+</sup> obvious candidates for precursors to the formation of MgCCH and MgCCH<sup>+</sup>. On the other hand, the Mg-C bond energy in MgCCH is very similar to that of Mg-C in MgCN or Mg-N in MgNC, which makes it

difficult to predict if reactions with CCH will be exothermic or not. It is interesting to note, however, that the relevant bond energies of the associated cations shift in different directions; i.e., the Mg-C bond is  $\sim 9$  kcal mole<sup>-1</sup> stronger in MgCCH<sup>+</sup> than in MgCCH, but it is 6–7 kcal mole<sup>-1</sup> weaker in the MgNC<sup>+</sup> or MgCN<sup>+</sup> than in their respective neutral species. Thus, on the basis of the cation bond energies, one would expect reactions between MgNC<sup>+</sup> or MgCN<sup>+</sup> and CCH yielding MgCCH<sup>+</sup> to be exothermic, which is verified in the next section.

#### 9. EXCHANGE REACTIONS

The bottom portion of Table 11 gives the energetics for a collection of nine exchange reactions that lead to the formation of MgCCH, MgCCH<sup>+</sup>, or c-MgC<sub>2</sub>. There are several viable candidates for reactions which could occur in the ISM or in CSEs. Others can be excluded.

The reactions between ground-state Mg or Mg<sup>+</sup> and HCCH (reactions 9–10 in Table 11) are highly endothermic. Both require on the order of 50 kcal mole<sup>-1</sup> to form their respective products, not including any barriers that might be encountered. Also endothermic, by about 30 kcal mole<sup>-1</sup>, is the direct reaction (number 11 in Table 11) between Mg and CCH to yield c-MgC<sub>2</sub>. It is assumed that intermediate l-MgCC immediately rearranges to c-MgC<sub>2</sub> owing to the tiny barrier to interconversion (see Table 7 and § 4).

Reactions between MgH or MgH<sup>+</sup> and CCH (reactions 12–13) are strongly exothermic, producing on the order of 40 kcal mole<sup>-1</sup> excess energy. The long-range attraction of the dipole moments of MgH + CCH favors the products MgCCH + H rather than Mg + HCCH, though the latter will be more favorable energetically. One would expect the ion-molecule reaction (reaction 13) to have a higher rate than the neutral-neutral one (reaction 12).

The final four reactions (14–17) involve cyanides and isocyanides. In the CBS limit, the two neutral-neutral reactions (14–15) are both slightly endothermic, but the one involving MgCN is only endothermic by 1–2 kcal mole<sup>-1</sup> and may generate MgCCH if the reactants are hot enough or if there is an opportunity for tunneling. As in reaction (12), the dipole moments are aligned to favor these products rather than Mg and cyanopolyne radical formation. Both ion-molecule reactions (16 and 17) are exothermic.

#### 10. SUMMARY AND CONCLUSIONS

In an effort to expand our understanding of Mg astrochemistry, this work has characterized numerous Mg-bearing

 TABLE 10  
 RCCSD(T) IONIZATION POTENTIALS (eV) OF Mg-BEARING SPECIES

Basis Set	Mg <sup>+</sup>	MgH	MgNC	MgCN	MgCCH
cc-pVDZ.....	7.520	6.824	7.863	7.747	7.113
cc-pVTZ.....	7.527	6.856	7.879	7.785	7.129
cc-pVQZ.....	7.531	6.859	7.887	7.802	7.134
Estimated CBS limit.....	7.533	6.859	7.891	7.812	7.138

\* Experiment: 7.646 eV.



TABLE 11  
 REACTIONS INVOLVING Mg-BEARING SPECIES (kcal mole<sup>-1</sup>)

NUMBER	REACTION	$\Delta E^a$			
		cc-pVDZ	cc-pVTZ	cc-pVQZ	Estimated CBS limit
Association Reactions					
1.....	Mg + CCH → MgCCH	-68.2	-74.3	-75.9	-76.8 (-74.7)
2.....	Mg <sup>+</sup> + CCH → MgCCH <sup>+</sup>	-77.6	-83.5	-85.0	-85.9 (-83.4)
3.....	Mg + H → MgH	-27.8	-31.6	-32.5	-32.9 (-30.8)
4.....	Mg <sup>+</sup> + H → MgH <sup>+</sup>	-43.8	-47.0	-47.9	-48.4 (-46.0)
5.....	Mg + CN → MgNC	-67.9	-76.0	-78.2	-79.4 (-78.3)
6.....	Mg <sup>+</sup> + CN → MgNC <sup>+</sup>	-60.0	-67.9	-70.0	-71.1
7.....	Mg + CN → MgCN	-67.5	-74.6	-76.5	-77.6
8.....	Mg <sup>+</sup> + CN → MgCN <sup>+</sup>	-62.3	-68.6	-70.3	-71.2
Exchange Reactions					
9.....	Mg + HCCH → MgCCH + H	64.2	63.6	63.3	62.9 (57.0)
10.....	Mg <sup>+</sup> + HCCH → MgCCH <sup>+</sup> + H	54.8	54.6	54.1	53.8 (48.3)
11.....	Mg + CCH → c-MgC <sub>2</sub> + H	38.0	35.6	34.5	33.8 (28.8)
12.....	MgH + CCH → MgCCH + H	-40.4	-42.7	-43.4	-43.8 (-43.9)
13.....	MgH <sup>+</sup> + CCH → MgCCH <sup>+</sup> + H	-33.8	-36.4	-37.1	-37.4 (-37.4)
14.....	MgNC + CCH → MgCCH + CN	-0.3	1.7	2.3	2.7 (3.6)
15.....	MgCN + CCH → MgCCH + CN	-0.7	0.3	0.6	0.8
16.....	MgNC <sup>+</sup> + CCH → MgCCH <sup>+</sup> + CN	-17.6	-15.6	-15.9	-14.7
17.....	MgCN <sup>+</sup> + CCH → MgCCH <sup>+</sup> + CN	-15.3	-14.8	-14.8	-14.7

<sup>a</sup> Equilibrium energies are shown, except CBS limiting values in parentheses, which include a ZPE correction based on cc-pVTZ harmonic frequencies.

species including MgCCH, MgCCH<sup>+</sup>, linear MgCC, cyclic MgC<sub>2</sub>, the MgCC transition state, MgNC, MgCN, MgNC<sup>+</sup>, and MgCN<sup>+</sup>. Table 12 summarizes the recommended values of various molecular properties. None of these species have previously been the subject of exhaustive basis set studies, which were made possible here by adopting correlation consistent basis sets.

Where experimental data is available for rotational constants, MgCCH, MgNC, and MgCN, the computed values are within 60–100 MHz of the experiment. The remaining discrepancy is largely a result of the difference between  $B_e$  and  $B_0$

 TABLE 12  
 RECOMMENDED PARAMETERS FOR Mg-BEARING SPECIES

Species	$r_e$ (Å), $\theta$	$A_e$ , $B_e$ , $C_e$	$\mu_e$ (D)
MgCCH .....	$r_e$ (MgC) = 2.041 $r_e$ (CC) = 1.221 $r_e$ (CH) = 1.066	$B_e$ = 4.95	1.68
MgCCH <sup>+</sup> .....	$r_e$ (MgC) = 1.933 $r_e$ (CC) = 1.215 $r_e$ (CH) = 1.069	$B_e$ = 5.33	
c-MgC <sub>2</sub> .....	$r_e$ (MgC) = 2.003 $\theta$ (CMgC) = 36°8	$A_e$ = 52.26 $B_e$ = 11.59 $C_e$ = 9.50	6.17
l-MgCC .....	$r_e$ (MgC) = 2.032 $r_e$ (CC) = 1.246	$B_e$ = 5.38	4.22
MgNC .....	$r_e$ (MgN) = 1.947 $r_e$ (CN) = 1.179	$B_e$ = 5.85	
MgCN .....	$r_e$ (MgC) = 2.088 $r_e$ (CN) = 1.166	$B_e$ = 5.01	
MgNC <sup>+</sup> .....	$r_e$ (MgN) = 1.849; $r_e$ (CN) = 1.186	$B_e$ = 6.26	
MgCN <sup>+</sup> .....	$r_e$ (MgC) = 1.977 $r_e$ (CN) = 1.165	$B_e$ = 5.41	

values. Predictions have been made for structures, rotational constants, harmonic frequencies, and Mg-X bond energies, which may serve as a basis for laboratory or astronomical searches.

A study of reaction energetics demonstrates that MgCCH will not form under cold, low-density conditions from a direct reaction between Mg and either HCCH or CCH. The first is highly endothermic, and the latter would require an unusually efficient radiative association rate. Neutral-neutral or ion-molecule exchange reactions are more plausible candidates for pathways to MgCCH or MgCCH<sup>+</sup>, such as CCH reacting with MgH, MgNC, MgCN, or their cations. In the case of ionic precursors, MgCCH<sup>+</sup> is produced. The dissociative recombination of MgCCH<sup>+</sup> with an electron should lead to a fractional yield of cyclic MgC<sub>2</sub>. Although the linear isomer MgCC is encountered along the reaction surface, the barrier separating it from the cyclic form is very small, on the order of 0.5 kcal mole<sup>-1</sup> or less.

This study, with its dual emphasis on the prediction of molecular properties and evaluation of plausible formation pathways, has laid the foundation for further experimental and astronomical studies. MgCCH, MgCCH<sup>+</sup>, MgNC<sup>+</sup>, and MgCN<sup>+</sup> have been studied theoretically for the first time, and MgC<sub>2</sub> has received the most thorough treatment to date. In evaluating reaction pathways, MgCCH<sup>+</sup> would appear to be easier to form than MgCCH, but the necessary precursors may not be present. If MgCCH<sup>+</sup> is present in IRC +10216 or elsewhere, then dissociative recombination should generate some c-MgC<sub>2</sub> if sufficient free electrons are present.

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