ELECTRONIC SPECTRA OF MgC$_2$H ($n = 1$–$3$) CHAINS IN THE GAS PHASE

H. Ding, C. Apetrei, L. Chacaga, and J. P. Maier

Department of Chemistry, University of Basel, CH-4056 Basel, Switzerland

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ABSTRACT

Electronic transitions of MgC$_2$H ($n = 1$–$3$) have been observed in the gas phase in the visible region. A mass-selective, resonant two-color two-photon ionization technique, coupled with a laser ablation source, was used. Ab initio calculations of the geometries, energies, and vertical electronic excitations have been carried out using hybrid density functional theory and the coupled-cluster approach. The spectra are assigned as the $A$ $^2\Pi \leftrightarrow X$ $^2\Sigma^+$ electronic transition of linear chains. The origin bands are located at 4383, 4453, and 4525 Å for MgC$_2$H, MgC$_4$H, and MgC$_6$H, respectively, and provide a means of detecting such species in astronomical environments.

Subject headings: ISM: general — ISM: lines and bands — ISM: molecules — molecular data

1. INTRODUCTION

Despite the success of ion-molecule chemistry for carbon and other nonrefractory elements, unanswered questions remain concerning the molecular carriers of the cosmically abundant metallic elements, such as magnesium, iron, and sodium (Ziurys et al. 1995). These elements are heavily depleted in molecular clouds, and a small percentage may remain in the gas phase as atoms or incorporated in molecules (Sofia et al. 1994). It is believed, in general, that most of these elements have condensed out onto the surfaces of dust grains. The identification of the molecular carriers containing such metals in the interstellar medium (ISM) would have implications for gas-phase and grain chemistry, ionization balance in dust particles, recycling by shock waves, and constraining models of nucleosynthesis (Anderson & Ziurys 1995b). Carbon chains are abundant molecules and play an important role in the chemistry of the ISM (Herbst et al. 1994; Millar & Herbst 1994; Bettens & Herbst 1997). For example, small carbon chains ($C_2$, $C_3$, $C_5$) were detected in the ISM and circumstellar shells (van Dishoeck & Black 1986; Maier et al. 2001), and larger ones were proposed to be of relevance as carriers of the diffuse interstellar bands (Maier et al. 2002). Monohydrocarbon chains C$_n$H ($n = 2$–$8$) have been measured in the circumstellar envelope of the carbon-rich star IRC +10216 and in dark molecular clouds such as TMC-1 (McCarthy et al. 1997, 2000; Bell et al. 1999). The small even polynye chains HC$_{2n}$H ($n = 2$–$3$) have been observed in the proto–planetary nebulae CRL 618 and CRL 2688 (Cernicharo et al. 2001a, 2001b) and in the atmospheres of planets (Kim et al. 1985). Because the isoelectronic cyanopolynes HC$_{2n+1}$N ($n = 1$–$5$) were detected in the ISM (Broten et al. 1978; Kroto et al. 1987; Bell et al. 1997), the larger HC$_{2n}$H chains are believed to exist there. One thus might wonder if metal-containing carbon chains are also present. Unfortunately, knowledge about the gas-phase abundances and forms of species that contain refractory metals in the ISM is limited (Turner et al. 2005).

Magnesium is one of the most abundant refractory metals in the universe. Molecules MgNC and MgCN have been discovered toward the circumstellar envelopes of IRC +10216 and CRL 2688 (Guélin et al. 1986; Kawaguchi et al. 1993; Anderson & Ziurys 1994, 1995a). Both molecules are present in the outer shell of IRC +10216, where temperatures ($T \sim 10$–$50$ K) and densities ($n \sim 10^3$ cm$^{-3}$) are comparable to those in molecular clouds. In the inner circumstellar shell ($T \geq 1000$ K, $n \sim 10^{10}$ cm$^{-3}$), the more stable metal halide species NaCl, AlCl, KCl, and AlF are abundant (Cernicharo & Guélin 1987; Ziurys et al. 1994). The formation of metal halide species in the inner envelope of IRC +10216 has been explained with equilibrium chemistry (Tsuji 1973; Sharp & Huebner 1990). The synthesis of MgNC and MgCN radicals, however, is more difficult to account for by equilibrium chemistry. Several possible routes have been proposed, such as the radiative association of Mg$^+$ and HCN (or HNC) followed by dissociative electron recombination (Kawaguchi et al. 1993; Anderson & Ziurys 1995a), the reaction Mg$^+$ + CN, and desorption from grain surfaces (Guélin et al. 1993). However, experimental data for these processes are scarce. In order to improve our understanding of interstellar chemistry, studies of other Mg-bearing species have been carried out. For example, MgC$_2$H, a radical isoelectronic with MgCN, has been investigated in the laboratory by millimeter-wave spectroscopy (Anderson & Ziurys 1995a). Electronic spectra of several alkaline earth monoacetylides, MC$_2$H (M = Mg, Ca, Sr), have been investigated experimentally (Bopegedera et al. 1987; Li & Coxon 1996; Corlett et al. 1996, 1997; Dick et al. 2005) and theoretically (Woon & Herbst 1996; Woon 1997). These indicate that the alkaline earth monoacetylides have a linear geometry and $X$ $^2\Sigma^+$ ground-state symmetry. Considering that magnesium and the polynye chains HC$_{2n}$H are both abundant in the ISM, it is to be expected that MgC$_{2n}$H chains may be identified. The abundance and distribution of such MgC$_{2n}$H species as a function of molecular size in the ISM could provide an important clue to the chemistry of magnesium-containing species. Thus, laboratory-based spectroscopic studies are vital.

In this paper, we report the first observations of the gas-phase electronic spectra of MgC$_2$H and MgC$_4$H. The experimental technique uses two-color laser spectroscopy with mass analysis and a laser ablation source. Ab initio calculations on the ground and electronic excited states have been carried out. The electronic structures and bonding nature of these magnesium-containing carbon chains are discussed in view of the spectral analysis.

2. EXPERIMENT

The experimental setup consists of a molecular beam combined with a linear time-of-flight (TOF) mass spectrometer (Ding et al. 2006). The laser ablation of a magnesium rod in a pulsed gas mixture of CH$_4$ (or HC$_2$H) and He (1:100) was used to produce MgC$_4$H and MgC$_6$H. The 532 nm output of a Nd:YAG laser (30 mJ per pulse, 5 ns width) was focused on a rotating and
translating magnesium rod. The vaporization took place within a pulse of the carrier gas with a backing pressure of ~5 bars. The hot plasma flew through a 15 mm long and 3 mm diameter channel, followed by expansion into a vacuum chamber. The resulting supersonic jet was passed through a skimmer. Ions were removed from the beam by a perpendicular electrical field before entering the extraction zone of the TOF. The neutral molecules were then ionized by lasers, and the ions were extracted with a pulsed electrical field. The signal from a multichannel-plate ion detector was fed into a fast oscilloscope, followed by data acquisition.

Resonant two-color two-photon ionization (R2C2PI) spectra of MgC₂H, MgC₂H, and MgC₃H and their vibronic bands were measured over the 360–640 nm range (see Table 1). Excitation photons were provided by an optical parametric oscillator (OPO) system (~3 cm⁻¹ bandwidth) or a dye laser (~0.1 cm⁻¹) pumped by a XeCl excimer laser. The power of the OPO was typically 15 mJ per pulse in the visible and 5 mJ per pulse in the UV region. The wavelength calibration was carried out with a wavemeter. An ArF excimer laser at 193 nm delivered the photons for the ionization.

### 3. THEORETICAL CALCULATIONS

#### 3.1. Ground State

Ab initio studies of MgC₂H at the RCCSD(T) and MRCI+Q levels of theory have been reported previously (Woon 1997). The results indicated that the single-reference RCCSD(T) method yields good results compared with the experimental observations. In this study, the hybrid density functional theory DFT-B3LYP (Becke 1993) and the restricted coupled-cluster RCCSD(T) approach (Watts et al. 1993) were used for calculation of the ground-state electronic structures of MgC₂nH chains with n = 1–8. Dunning’s correlation-consistent basis set aug-cc-pVTZ (Woon & Dunning 1993) was adopted for full geometry optimization and calculations of vibrational frequencies. The resulting Mg−C bond lengths, the harmonic frequencies of the Mg−C stretching mode, rotational constants Bₐ, and dipole moments D for MgC₂H through MgC₆H are given in Table 2. The trends of these values are shown as a function of chain size (MgC₂nH, n = 1–8) in Figure 1. Both the lowest bending frequency (open circles) and Mg−C stretching frequency (filled circles) decrease with the chain size, as has been observed for other carbon-chain systems. The Mg−C bond length (triangles) increases from 2.048 to 2.063 Å on passing from MgC₂H to MgC₁₆H. The calculations also indicate a C−C alternation, with short (~1.23 Å) and long (~1.34 Å) bonds.

#### 3.2. Excited State

A theoretical investigation of the first excited electronic state of MgC₂H has been reported (Woon 1997). The calculated Tₑ of the A 2Π state is 2.81 and 2.88 eV at the RCCSD(T) and MRCI levels, respectively. The observed transition energy of MgC₂H is around 2.83 eV. This indicates that single-reference theoretical methods such as RCCSD(T) provide reasonable predictions. Thus, the RCCSD(T) approach was used for MgC₂H through MgC₆H, and the time-dependent B3LYP theory (TD-DFT; e.g., Stratmann et al. 1998) was used for all MgC₂nH (n = 1–8) molecules, with Dunning’s correlation-consistent basis set cc-pVTZ. The X 2Σ⁺ ground state of linear MgC₂H is dominated by the · · · 4(n + 1)σ²(n + 1)π⁴(4n + 5)σ⁺ electronic configuration, n = 1, 2, 3, ..., 8. Electron promotion from the semioccupied molecular orbital (SOMO), (4n + 5)σ, to the lowest unoccupied molecular orbital (LUMO), (n + 2)π, leads to the first electronic excited state A 2Π, with electronic configuration 4(n + 1)σ²(n + 1)π⁴(4n + 5)σ⁺(n + 2)π⁺. The calculations indicate that the SOMO mainly consists of a 3s orbital of Mg and that the LUMO is dominated by 3pₓ/3px of Mg. The A 2Π − X 2Σ⁺ transition corresponds to the observed spectra.

Vertical electronic excitation energies were calculated in the ground-state geometry for the doublet multiplicity only. These were obtained using TD-DFT for n = 1–8 and the RCCSD(T) approach for n = 1–3. Gaussian 98 (Frisch et al. 1998) and the MOLPRO package (Werner et al. 2002) were used for the calculations. The values are listed in Table 3 and plotted in Figure 2. The calculated A 2Π − X 2Σ⁺ energies at the TD-B3LYP level of theory have a typical error of ~0.06 eV compared with the

![FIG. 1 — Calculated lowest bending vibrational frequencies (1), Mg−C stretching frequency (2), and Mg−C bond lengths (3) in the ground state for MgC₂nH (n = 1–8) as a function of the number of carbon atoms, using TD-DFT theory with cc-pVTZ basis sets.](image-url)
TABLE 3

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>STATE</th>
<th>$T_0$ (eV)</th>
<th>B3LYP</th>
<th>RCCSD(T)</th>
<th>$f$ (B3LYP)</th>
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<tr>
<td>MgC$_3$H</td>
<td>$X^2\Sigma^+$</td>
<td>2.9175</td>
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<td></td>
<td>$A^2\Pi$</td>
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<td>$X^2\Sigma^+$</td>
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<tr>
<td></td>
<td>$A^2\Pi$</td>
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<tr>
<td>MgC$_5$H</td>
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<tr>
<td></td>
<td>$A^2\Pi$</td>
<td>2.8338</td>
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</table>

**Note:** Calculated with cc-pVTZ basis sets.

The transition energies of both the $A^2\Pi \leftrightarrow X^2\Sigma^+$ and $B^2\Pi \leftrightarrow X^2\Sigma^+$ systems decrease with chain size (Fig. 2).

4. RESULTS AND DISCUSSION

4.1. Electronic Spectra

The observed electronic spectra of MgC$_2$H, MgC$_3$H, and MgC$_n$H in the visible region are shown in Figure 3. In the case of MgC$_2$H, the observed excitation energy of the origin band at 2.83 eV is close to 2.87 eV, as predicted by the RCCSD(T) calculation. The transition energies of both the $A^2\Pi \leftrightarrow X^2\Sigma^+$ and $B^2\Pi \leftrightarrow X^2\Sigma^+$ systems decrease with chain size (Fig. 2).

The rotational constants ($B_n$) and dipole moments ($D$) of MgC$_n$H, the calculations predict that the frequencies of the Mg–C stretch are 398 cm$^{-1}$ in the ground state and 460 cm$^{-1}$ in the $A^2\Pi$ state; the observed frequency in the latter is 453 cm$^{-1}$. Thus, the frequency in the $A^2\Pi$ state is 7% higher than in the ground state. For MgC$_2$H a similar behavior is expected. Therefore, the vibrational progression discernible in the spectra of Figure 3 corresponds to the Mg–C stretching motion. The maxima of the detected vibronic bands and their proposed assignments are listed in Table 1.

4.2. Dipole Moment and Oscillator Strength

The rotational constants ($B_n$) and dipole moments ($D$) in the ground state of MgC$_n$H ($n = 1–8$) have been calculated (Fig. 4). The rotational constant $B_n$ has been fitted:

$$\log B_n (\text{MHz}) = 4.47754 - 0.46787N + 0.0418N^2 - 0.00219N^3 + 4.58744 \times 10^{-5}N^4,$$

where $N = 2n = 2, 4, 6, \ldots, 16$. The dipole moment (Fig. 4, open circles) increases monotonically with the size of the chain. This makes the detection of larger MgC$_n$H chains with microwave spectroscopy easier. A similar behavior has been experimentally observed for cyano-substituted carbon chains NC$_{2n+1}$H ($n = 1–5$), which are among the longest interstellar polyynes detected (Broten et al. 1978; Bell et al. 1997) as a consequence of their large dipole moments.

![Fig. 3.](image-url) Electronic R2C2PI spectra of MgC$_n$H ($n = 1–3$).

![Fig. 4.](image-url) Calculated rotational constant (1), plotted as log $B_n$, and dipole moment, $D$ (2), in the ground state for MgC$_n$H ($n = 1–8$) as a function of the number of carbon atoms, using DFT-B3LYP theory with cc-pVTZ basis sets.
curves of the ground and $A^2\Pi$ states of MgC$_2$H as a function of Mg–C bond length using the RCCSD(T)/cc-pVTZ level of theory.

5. CONCLUDING REMARKS

The electronic transitions of magnesium-substituted carbon chains, MgC$_{2n}$H, have a significantly different character compared with highly unsaturated carbon chains such as HC$_{2n}$H. The dipole moment of MgC$_{2n}$H in the ground state increases with the chain’s size, while the oscillator strength of the dipole-allowed electronic transitions decreases. This means that for the larger chains, a measurement of the electronic spectrum becomes more difficult than an observation of their microwave transitions. In a comparison of the laboratory gas-phase electronic spectra of MgC$_2$H, MgC$_4$H, and MgC$_6$H with the catalog of the diffuse interstellar bands from Jenniskens & Desert (1994), no match was found. Nevertheless, the presented laboratory data on electronic transitions of the magnesium-containing carbon species in the visible region may provide a basis for their detection in space. The bonding energy of Mg–C was calculated as $\sim$78 kcal mol$^{-1}$ (3.4 eV), suggesting that MgC$_2$H, MgC$_4$H, and MgC$_6$H may be destroyed by UV light in the gas phase but could remain on the surface of dust grains in molecular clouds.

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