Spectroscopic Properties Relevant to Astronomical and Laboratory Detection of MCH and MCH\(^+\) (M = Al, Mg)

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Abstract

New spectroscopic parameters have been calculated to aid in the laboratory and observational detection of AlCH, AlCH\(^+\), MgCH, MgCH\(^+\), and their deuterated analogs. All species exist in linear geometry except for AlCH\(^+\), which exhibits a bent structure. Rotational frequencies have been calculated and the transition with maximum intensity is discussed for three temperature regions present in space: 100 K for a central circumstellar envelope (CSE), 30 K for an outer CSE, and 3 K indicative of the interstellar medium. Pertinent frequencies range from 25 to 250 GHz, depending on the species. At 30 K, the most intense transition is expected to be \(J = 4 \rightarrow 3\) for all species. The vibrational spectrum of each molecule is expected to be complicated due to the flat nature of the potential energy surface along the bending angle and the presence of anharmonic resonances. Deuteration produces a decrease in vibrational frequency, which may be utilized in experiments to confirm detection of these molecules. The electronic absorption spectrum of both AlCH and MgCH is predicted to be congested and broad. Various high-oscillator-strength transitions are predicted. Upon photoexcitation in the 220–300 nm region, facile dissociation on a repulsive excited state along the Al–C coordinate is predicted to be a source of Al in the colder regions of space. Photodissociation of MgCH requires several nonradiative processes that will control the product state distribution of the fragments.

Unified Astronomy Thesaurus concepts: Interstellar medium (847)

1. Introduction

The detection of many new species, including metal-bearing molecules, in the interstellar medium (ISM), a region originally thought to be devoid of matter, and in the circumstellar envelopes (CSEs) around stars has driven a new appreciation for the chemical complexity present in space. Many of the molecules detected in the past 30 years include aluminum (Higghberger et al. 2001; Ziurys et al. 2002; Tenenbaum & Ziurys 2009, 2010; Kaminski et al. 2013a, 2013b; Decin et al. 2017) or magnesium (Kawaguchi et al. 1993; Higghberger et al. 2001; Cabezas et al. 2013; Agundez et al. 2014; Cernicharo et al. 2019; Ziurys et al. 1995) as their metal; often toward large, evolved stars such as VY Canis Majoris and IRC+10216. The relatively high density of molecules close to these stars causes the creation of novel chemical species through equilibrium and nonequilibrium processes, such as photospheric shocks and photochemistry (Cherchneff 2006; Ziurys et al. 2007). As the molecules move to further reaches of the CSE they experience “freeze-out”, where the abundances stabilize until the molecules reach the outer edge and are bombarded with cosmic radiation (McCabe et al. 1979; Glassgold 1996; Ziurys et al. 2007). Here, new photochemistry and reactions take place.

Aluminum- and magnesium-bearing species have been found in the CSEs of large asymptotic giant branch (AGB) and red supergiant stars IRC+10216 and VY CMa. AINC (Ziurys et al. 2002), AlF, and AICl (Cernicharo & Guelin 1987) have been detected in the carbon-rich CSE of IRC+10216, indicating the presence of free aluminum not locked in dust particles. Additionally, AIC was recently detected in the photosphere of the Sun (Sindhan et al. 2020). Similarly, MgF (Ziurys et al. 1994), MgNC (Kawaguchi et al. 1993), MgCN (Ziurys et al. 1995), HMgNC (Cabezas et al. 2013), MgC\(_3\)N (Cernicharo et al. 2019), MgC\(_4\)N (Cernicharo et al. 2019), and MgCCH (Agundez et al. 2014) have been detected toward IRC+10216. Cosmic abundances do not indicate the existence of metals in a CSE, as metals with similar cosmic abundance to Al (Ca, Ni), and Mg (Fe) are yet undetected. This points to AGB nucleosynthesis and dredge-up as a source of these heavy metals (Ziurys 2006). The high availability of carbon and hydrogen in the stellar photosphere of ICR+10216, along with the presence of free aluminum and magnesium, sets the stage for the possible existence of the triatomic species AlCH and MgCH, as well as their cations.

The C–H bond is found throughout nature and in all biological processes; studying the properties of small molecules that contain this prototypical bond can assist in identifying the pathways that lead to life. Additionally, the CH/CD ratio can be utilized to study the chemical and physical conditions present during the early years of the detection source. Few computational and experimental studies have been performed to explore the chemical and physical properties of the AlCH and MgCH triatomic species. The first such study was done by Fox et al., where they used self-consistent field (SCF) calculations to determine the equilibrium geometry and harmonic frequencies of the ground electronic state (Fox et al. 1980). Following this, Jin et al. further explored AlCH with higher-level configuration interaction and coupled-cluster methods (Jin et al. 1990, 1991). Later, Tyerman et al. (1996) used SCF and second-order Möller–Plesset perturbation theory (MP2) to study MgCH. More recently, Hearne et al. (2019) experimentally characterized the magnetic parameters of MgCH using matrix-isolated electron spin resonance. They
also performed DFT studies of the structure and dissociation energies of MgCH. No past studies were found that predicted spectroscopic parameters for AlCH and MgCH, nor were there any papers that examined the excited states of such molecules.

Many high-level theoretical studies have been conducted on aluminum-bearing triatomic molecules (Ma et al. 1995; Alikhani 2003; Trabelsi & Francisco 2018; Trabelsi et al. 2018; Yousefi & Bernath 2018; Yurchenko et al. 2018; Trabelsi et al. 2019a, 2019b; Esposito et al. 2020). The methods utilized in this work have been adapted from these previous studies.

In this paper, highly accurate spectroscopic parameters are presented to drive the detection of AlCH, MgCH, and their respective cations in the laboratory and via remote observation. Isotopic data is also included. Frequencies of rotational transitions from highly populated rotational states at various rotational temperatures based on a Boltzmann distribution are provided. Additionally, vibrationally corrected rotational constants, permanent dipole moments, anharmonic rovibrational frequencies, and vertical excitation energies are given. Finally, potential energy surfaces (PESs) are calculated for the M–CH dissociation coordinate to investigate the photostability of the electronic excited states of each molecule.

2. Computational Methods

The geometric properties, including optimized geometries, harmonic vibrational frequencies, and rotational constants, of AlCH, AlCH$^+$, MgCH, and MgCH$^+$ are determined by gradient optimization followed by harmonic frequency analysis using the internally contracted multireference configuration interaction method (MRCl; Knowles & Werner 1988; Werner & Knowles 1988) including the Davidson correction (MRCl+Q; Szalay & Bartlett 1993), in conjunction with the large aug-cc-pV(X+d)Z (X = T, Q, 5) basis sets (Dunning 1989; Dunning et al. 2001; Prascher et al. 2011), which include additional tight $d$ functions to properly describe the aluminum and magnesium atoms (Dunning et al. 2001). Additionally, the explicitly correlated multireference configuration interaction (MRCl-F12) method (Shiozaki et al. 2011) is used with the aug-cc-pVXZ (X = T, Q, 5) basis sets. The MRCl calculations are based on a one-state complete active space self-consistent field (CASSCF) reference wave function. The active space in these calculations consists of 15 occupied orbitals where 6 are closed, achieving an active space of 8, 7, 7, 6 electrons in 9 orbitals for AlCH, AlCH$^+$, MgCH, and MgCH$^+$, respectively. In all cases, the 1s and 2s orbitals of carbon were closed as well as the 1s, 2s, and 2p orbitals of the metal atom, resulting in a full valence calculation. Simultaneously, coupled-cluster theory, including single and double excitations and perturbative treatment of triple excitations (CCSD(T)), was used to characterize each molecule and assess its multireference character. In the CCSD(T) calculations, all electrons (AE) and orbitals were included in the active space, with zero frozen core orbitals. These calculations were performed using the second-order Douglas–Kroll–Hess Hamiltonian in conjunction with the contracted relativistic Douglas–Kroll aug-cc-pVXZ-DK (X = T, Q, 5) basis sets to include scalar relativistic and core correlation effects. The equilibrium geometries were then determined at the complete basis set (CBS) limit using the three-point power function extrapolation scheme $E(x) = E_{CBS} + Bx^{-\alpha}$, where $E(x)$ is the ab-initio value for a given basis set, $x$ is the basis set cardinal number, $E_{CBS}$ is the extrapolated parameter, and $B$ and $\alpha$ are fit parameters using a least-squares fitting procedure. A T1 diagnostic value below 0.02 for AlCH, MgCH, and MgCH$^+$ implies a single-reference character of the wave function, indicating the usefulness of CCSD(T)-AE to characterize these molecules’ electronic structure. For AlCH$^+$, a T1 value $>0.04$ indicates that multireference methods are better suited to properly characterize its electronic structure. All calculations are based on ROHF-SCF orbitals.

Following determination of the equilibrium geometries, a three-dimensional potential energy surface (3D-PES) for each isomer is determined by single-point energy calculations at small displacements along both bond coordinates (0.05 Å) and the bending angle (0.4 rad) around the equilibrium value. The 3D-PESs for MgCH and MgCH$^+$ were calculated with the RCCSD(T)-AE level of theory in conjunction with the aug-cc-pwCV5Z-DK basis set. Due to multireference character at values far from equilibrium, AlCH and AlCH$^+$ were studied using the MRCI+Q method. From the 3D-PES, the SURFIT code is utilized to produce a set of spectroscopic constants and rovibrational energy levels for each molecule using the derivatives of the potentials around equilibrium and perturbation theory (Mills 1972; Senekowitsch 1988). During the fitting procedure, first derivatives in all three coordinates of equilibrium were checked to ensure a value of zero. Deuteration is also explored in this step. Vibrationally corrected rotational constants (Kroto 1975) are then calculated using the following formula:

$$X_o = X_r + \Delta X_o,$$

where $X_r$ is the equilibrium rotational constants corresponding to the molecular geometry at the minimum of the Born–Oppenheimer PES. $\Delta X_o$ is the vibrational correction obtained from the following formula:

$$\Delta X_o = -\sum r - \alpha_{\nu} \left(\nu_{\nu} + \frac{1}{2} d \right),$$

where the sum is over all normal coordinates, $r$, and $\alpha_{\nu}$ is the vibration–rotation interaction constants. $\nu_{\nu}$ is the vibrational quantum number of the normal mode and $d$ is the degeneracy factor. Including the vibrational correction to the equilibrium rotational constants accounts for the presence of zero-point vibrational motion in the ground-vibrational state of the molecule.

Using the vibrationally corrected rotational constants and the second-order centrifugal distortion ($D_J$), relative energy level populations and rotational frequencies are calculated for each molecule at different temperatures corresponding to varying regions of space.

Vertical electronic excitation energies, transition dipole moments, and oscillator strengths of each molecule were calculated at the MRCI+Q level of theory. The excited electronic state calculations were performed using the same active space as detailed above. For AlCH and MgCH$^+$, 12 states were averaged in the CASSCF wave function with three states in each of the four irreducible representations. MgCH was also treated with 12 averaged states, including two $A_1$, three $B_1$, three $B_2$, and six $A_2$ states. For AlCH$^+$, the 12 states were split into six $A'$ and six $A''$ states. In addition, permanent dipole moments ($\mu$) and bond-dissociation energies were calculated using the MRCI+Q level of theory. The finite-field procedure as implemented in MOLPRO was used to calculate
Table 1
Spectroscopic Parameters for the Ground Electronic State of Neutral and Cationic AlCH and MgCH

| Parameter | AlCH (X 2Σ−) | AlCD (X 2Σ−) | AlCH+ (X 2A′) | AlCD+ (X 2A′) | MgCH (X 2Σ−) | MgCD (X 2Σ−) | MgCH+ (X 2Σ−) | MgCD+ (X 2Σ−) |
|-----------|---------------|---------------|----------------|----------------|--------------|--------------|---------------|---------------|
| r_e (C–H), Å | 1.9455 | 1.9455 | 1.9238 | 1.9238 | 2.0169 | 2.0169 | 1.9249 | 1.9249 |
| r_e (C–H), Å | 1.0889 | 1.0889 | 1.0971 | 1.0971 | 1.0876 | 1.0876 | 1.0807 | 1.0807 |
| θ, deg | 180.0 | 180.0 | 126.5 | 126.5 | 180.0 | 180.0 | 180.0 | 180.0 |
| θ_e, deg | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| A_p, MHz | 701,429 | 399,047 | 14,616 | 13,180 | 13,183 | 11,476 | 14,393 | 12,480 |
| B_p, MHz | 13,562 | 11,804 | 14,318 | 12,758 | 732,015 | 413,791 |
| C_p, MHz | 13,517 | 11,774 | 14,543 | 13,111 | 14,215 | 12,661 |
| \( \rho_{\text{beat}} \), D | 0.726 | 0.726 | 1.849 | 1.849 | 1.331 | 1.331 |
| B_0, MHz | 0.0239 | 0.0166 | 0.0358 | 0.0296 | 0.0253 | 0.0176 | 0.0229 | 0.0157 |
| D_0, MHz | −0.667 | −1.229 | −1549 | 1549 | 545.5 | 545.5 |
| \( \chi_1 \), cm\(^{-1} \) | 0.1568 | 0.1848 | 0.1680 | −0.2086 | −0.1585 | 0.1895 | −0.1606 | 0.1868 |
| \( \chi_2 \), cm\(^{-1} \) | −0.9876 | −0.9827 | 0.5583 | 0.8452 | 0.9873 | −0.9818 | 0.9870 | −0.9823 |
| \( \alpha_1 \), MHz | 46,402 | 20,142 | −88,684 | −31,713 | −23,295 | −19,110 |
| \( \alpha_2 \), MHz | 63.56 | 65.45 | 18.59 | 12.80 | 49.72 | 54.98 | 58.30 | 62.64 |
| \( \alpha_2 \), MHz | −100.0 | −107.2 | 48.95 | −68.83 | −0.8703 | −21.28 | 126.8 | −14.99 |
| \( \alpha_3 \), MHz | 110.5 | 89.12 | 69.56 | 186.0 | 106.4 | 86.72 | 99.15 | 79.41 |
| \( \alpha_4 \), MHz | 36.34 | 31.57 | 59.50 | −18.61 | 96.75 | 169.7 |
| \( \alpha_5 \), MHz | −68.17 | −36.48 | −68.97 | −37.46 | −65.88 | −34.98 | −61.88 | −32.53 |
| \( \alpha_6 \), MHz | −19.53 | −12.19 | −3.413 | −11.10 | −14.48 | −8.350 | −33.82 | −21.90 |
| \( \alpha_7 \), MHz | −2.178 | −1.899 | −14.77 | 1.977 | 2.877 | 1.871 | 2.092 | 0.9615 |
| \( \alpha_8 \), MHz | 8.075 | 4.422 | −16.14 | −0.8294 | −0.6246 | −0.1611 | 112.7 | 66.67 |
| \( \alpha_9 \), MHz | −2.409 | −0.0316 | −7.383 | −14.05 | −3.583 | −3.798 | −38.26 | −33.56 |
| \( \alpha_{10} \), MHz | −3.824 | −3.603 | −3.391 | −10.75 | −3.264 | −3.103 | −3.731 | −3.530 |
| \( \omega_{a_1} \) cm\(^{-1} \) | 3140.9 | 2316.0 | 3071.7 | 2257.4 | 3140.1 | 2312.6 | 3224.5 | 2378.0 |
| \( \omega_{a_2} \) cm\(^{-1} \) | 239.8 | 184.0 | 583.6 | 461.1 | 446.3 | 342.0 |
| \( \omega_{a_3} \) cm\(^{-1} \) | 672.4 | 652.9 | 688.8 | 644.8 | 626.0 | 607.7 | 751.8 | 728.9 |
| \( \nu_{a_1} \) cm\(^{-1} \) | 2984.0 | 2230.0 | 2863.7 | 2178.0 | 2995.3 | 2235.3 | 3068.0 | 2291.6 |
| \( \nu_{a_2} \) cm\(^{-1} \) | 256.2 | 193.1 | 591.3 | 446.9 | 440.7 | 338.1 |
| \( \nu_{a_3} \) cm\(^{-1} \) | 661.3 | 644.7 | 617.6 | 617.3 | 617.4 | 598.7 | 707.2 | 688.8 |

the permanent dipole moments with field strengths of 0, 0.005, and −0.005 au. Finally, one-dimensional adiabatic PESs were calculated for AlCH and MgCH by elongating the M–C bond and holding all other coordinates fixed at their equilibrium values. All electronic structure calculations were performed using the Molpro2019 software (Werner et al. 2019).

3. Results and Discussion

AlCH and MgCH molecules, as well as their cations, may exist throughout space, from the stellar photosphere and CSE of various stars, to the ISM. The physical environment varies drastically between these regions of space, so the existence of these molecules and potential detectabilities will also vary. To guide experimental characterization and subsequent astronomical detection of the new triatomic molecules AlCH, MgCH, and their respective cations and deuterated analogs, pure rotational transitions, rovibrational data, vertical excitation energies, and other spectroscopic parameters in the electronic ground state have been calculated. The formation mechanisms of triatomic molecules in the CSE of IRC+10216 are not well known, although it is feasible that the closed-shell AlCH may form via local thermal equilibrium in the inner envelope, depending on its stability, or shock waves. MgCH is more likely to form via an ion + neutral reaction or via shock in the outer envelope, although a detailed mechanistic and kinetics study is beyond the scope of this paper. Due to the uncertainty pertaining to the potential detection location in space, three different rotational temperatures (100, 30, and 3 K) have been chosen for predicting rotational-state population based on a Boltzmann distribution to provide a starting point for chemical models and to be used in concert with experimental data. The first two temperatures, 100 and 30 K, are chosen as they represent temperatures in the outer regions of a CSE far from the central star. The latter is representative of the temperature of the ISM. High-energy ionizing radiation will play a part in all three of these regions, increasing the chance of an ion + neutral reaction to produce a neutral triatomic species, as well as ionization of the formed triatomic itself.

The data used to derive the rotational frequencies in Section 3.1, as well as additional spectroscopic parameters, are shown in Table 1. Values of interest include the vibrationally corrected rotational constants (\( A_{\text{rot}} \), \( B_{\text{rot}} \), \( C_{\text{rot}} \)), permanent dipole moment (\( \mu \)), centrifugal distortion constants (\( D_{\text{C}} \), \( D_{\text{D}} \), \( D_{\text{O}} \)), Coriolis coupling constants (\( \zeta \)), vibration–rotation coupling
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Table 2
Rotational Transition Frequencies (in Megahertz) in the Electronic Ground State Using Vibrational Corrected Rotational Constants and Including Centrifugal Distortion

| J   | J'  | AlCH  | AICD  | MgCH  | MgCD  | MgCH⁺ | MgCD⁺ |
|-----|-----|-------|-------|-------|-------|-------|-------|
|     |     |       |       |       |       |       |       |
| 1   | 0   | 27,034| 23,549|       |       |       |       |
| 2   | 1   | 54,068| 47,098|       |       |       |       |
| 3   | 2   | 81,101| 70,647|       |       |       |       |
| 4   | 3   | 108,132| 91,194|       |       |       |       |
| 5   | 4   | 135,160| 117,739|       |       |       |       |
| 6   | 5   | 162,186| 141,283|       |       |       |       |
| 7   | 6   | 189,208| 164,824|       |       |       |       |
| 8   | 7   | 216,227| 188,362|       |       |       |       |
| 9   | 8   | 243,240| 211,897|       |       |       |       |
| 10  | 9   | 270,249| 235,429|       |       |       |       |
| 11  | 10  | 297,252| 258,956|       |       |       |       |
| 12  | 11  | 324,248| 305,997|       |       |       |       |
| 13  | 12  | 351,238| 314,011|       |       |       |       |
| 14  | 13  | 378,220| 329,511|       |       |       |       |
| 15  | 14  | 405,194| 340,331|       |       |       |       |
| 16  | 15  | 432,159| 353,018|       |       |       |       |
| 17  | 16  | 459,115| 366,471|       |       |       |       |
| 18  | 17  | 486,062| 370,357|       |       |       |       |
| 19  | 18  | 512,998| 373,505|       |       |       |       |
| 20  | 19  | 539,923| 404,485|       |       |       |       |
| 21  | 20  | 566,836| 423,503|       |       |       |       |
| 22  | 21  | 593,738| 442,924|       |       |       |       |
| 23  | 22  | 620,627| 453,013|       |       |       |       |
| 24  | 23  | 647,502| 464,269|       |       |       |       |
| 25  | 24  | 674,364| 487,696|       |       |       |       |
| 26  | 25  | 701,211| 611,118|       |       |       |       |

At 3 K, a temperature indicative of the ISM, only the lowest five rotational states will be populated. The lines with peak intensity will be those surrounding Jmax = 1, the J = 1 → 0 transition at a frequency of 27,034 MHz, and J = 2 → 1 at a frequency of 54,068 MHz. Although population is only spread across a few states, making a series of detections difficult, the population in each state will be relatively large, increasing the intensity of the emitted radiation.

The relatively high deuterium abundance in the ISM (Weinberg 2017) increases the likelihood of formation of AlCD. Comparison of AICD and AlCH reveals the effects of deuteration on the many of the forms of spectroscopy. At a temperature of 3 K, the most highly populated state is Jmax = 1, like in AlCH, but the energy of this state is 1.13 K, a decrease of 0.14 K. The presence of a heavy deuterium atom causes a redshift in all rotational frequencies. The highest-intensity J = 1 → 0 transition in AlCD is predicted to occur at 25,549 MHz, a shift of 3489 MHz compared to AlCH. Furthermore, the line spacing of ∼27,000 MHz in AlCH decreases to ∼23,500 MHz in MgCD.

3.1. Rotational Spectroscopy

3.1.1. AICD and AICD⁺

A series of rotational frequencies have been predicted for AlCH, and its deuterated analog, and are shown in Table 2. The small permanent dipole moment calculated for AlCH (0.726 D) will hamper detection, as the intensity of a rotational transition is proportional to the interaction of incoming light with the permanent dipole of a molecule. At Trot = 100K, a temperature representative at ∼10¹⁶ cm in a CSE (Kastner 1991), the most highly populated rotational energy level for AlCH is Jmax = 8, corresponding to an energy of 46.7 K. The transitions surrounding this rotational level are J = 8 → 7 with a frequency of 216,227 MHz and J = 9 → 8 with a frequency of 243,240 MHz. These frequencies are both >200 GHz and will be good candidates for detection via ground-based telescopes.

Contrastingly, much less internal energy is present farther out in the CSE. The most highly populated level of AlCH at Trot = 30 K is Jmax = 4, with an energy of 12.9 K. The rotational transition frequency originating from this level is 108,131 MHz for the J = 4 → 3 transition. This frequency range is difficult for ground-based observation, so weaker lines originating from J > 8 are better suited for use in observational studies. Significant population will still exist in these higher lying states, with J = 8 predicted to have more than half of the population of Jmax, and at least three times the population of the ground state.

3.1.2. AICD⁺ and AICD⁺⁺

Vertical ionization of AlCH to AICD⁺ is predicted to occur with the absorption of 9.761 eV light at the CCSD(T)-AE/aug-cc-pV5Z-DK level of theory. This is in contrast to the MRCl methods which predict vertical ionization to occur at 8.947 and 8.836 eV at the MRCI+Q and MRCI-F12 levels, respectively. The calculated value is 0.8–0.9 eV higher at the CCSD(T)-AE level of theory, which is attributed to coupled-cluster theory missing large multireference effects in the AICD⁺ isomer at linearity. The CASSCF wave function shows multireference effects stemming from the three unpaired...
electrons that were not recovered by the open-shell coupled cluster. The recommended value for the vertical ionization energy is 8.947 eV (138.5 nm) at the MRCl+Q level of theory. Adiabatic ionization, a process describing the minimum energy needed for ionization, is slightly lower than the vertical process at 8.577 eV (144.5 nm). There is relaxation in the ion from the ground-state geometry to equilibrium in the ionic state, with the molecule bending from linearity. Prediction of the rotational spectrum for AICh+ and AlCD+ is more complicated as these molecules have a bent geometry. In this case, the spectroscopic parameters will be discussed instead. AICh+ is calculated to have vibrationally corrected rotational constants of $A_o = 732,015$ MHz, $B_o = 14,543$ MHz, and $C_o = 14,215$ MHz. The permanent dipole moment is predicted to be $1.849$ D, more than twice that of AICh, causing it to have a more intense signal for a similar abundance. Upon deuteration, there is a drastic decrease in the $A_o$ rotational constant to $413,791$ MHz – an almost 56% decrease.

### 3.1.3. MgCH and MgCD

As was done for the aluminum species, the rotational spectrum of MgCH, MgCD, and their deuterated analogs was predicted. The larger, but still relatively small, dipole moment for MgCH ($1.331$ D) will improve the possibility of detection of this molecule, but a weak signal is still anticipated. The rotational transition frequencies are shown in Table 2. Beginning with MgCH, the most highly populated rotational energy levels at 100, 30, and 3 K are $J_{max} = 8, 4, 1$, corresponding to energies of 45.2 K, 12.6 K, and 1.26 K, respectively.

The transition that is predicted to have the highest intensity at 100 K is from $J = 8 \rightarrow 7$ with a frequency of $209.519$ MHz ($6.99$ cm$^{-1}$). The energy of this transition is far below the calculated anharmonic vibrational frequency for the bending mode ($\nu_2$, 440.7 cm$^{-1}$) of MgCH. Because of this large difference, pure rotational transitions are expected to be seen at this energy with little-to-no rovibrational mixing. At 30 K, the highest-intensity transition for MgCH will be seen from $J = 4 \rightarrow 3$ at a frequency of $104.779$ MHz. Again, transitions at this frequency are troublesome because they lie in a frequency region that is difficult to access for ground-based telescopes, so the greatest chance for detection may come from transitions originating from $J > 8$. In the ISM, at 3 K, the rotational states with significant population will be $J = 0$–4, meaning detection will only occur via the first five transitions. The transitions predicted to have the highest intensity are $J = 1 \rightarrow 0$ at $26,196$ MHz or the $J = 2 \rightarrow 1$ transition at $52,392$ MHz. Sensitive satellite telescopes will be needed to detect MgCH in the ISM at these very low frequencies; however, since all the population will be spread across only a few states, the signal intensity is expected to be relatively large at this temperature.

Comparison of MgCD to MgCH at a temperature of 3 K shows the most highly populated state is $J_{max} = 1$, like in MgCH, but the energy of this state is 1.09 K, a decrease of 0.2 K. As is expected, a redshift is seen in all frequencies. The high-intensity $J = 1 \rightarrow 0$ transition in MgCD is predicted to occur at 22,820 MHz, a shift of 3376 MHz compared to MgCH. Furthermore, the line spacing of ~26,200 MHz in MgCH decreases to ~22,800 MHz in MgCD.

#### 3.1.4. MgCH+ and MgCD+

Production of the cation species MgCH+ via photoionization will occur by radiation in the vacuum ultraviolet (VUV) range, similarly to AlCh+. This is light that is readily available in the outer reaches of a CSE and in the ISM. The vertical and adiabatic ionization energies are reported in Table 3 and correspond to 141.7 nm (8.748 eV) and 173.8 nm (7.133 eV), respectively. The 1.615 eV (37.24 kcal mol$^{-1}$) difference in the ionization energies indicates a geometrical change will be seen upon relaxation to the minimum after loss of an electron. These changes can also be seen in Table 3, with shortening of the bond lengths, especially the large change in the Mg–C bond. Inspection of the molecule orbitals (MOs) in Figure B1 reveals electron density in a valence 3s orbital surrounding the Mg atom in MO $7\text{a}_1$. Ionization occurs by removal of the electron from the $7\text{a}_1$ MO, stabilizing the Mg–C bond and causing the large decrease of 0.08 A. The decrease in the bond lengths leads to an overall blueshift in the rotational frequencies of MgCH+. If MgCH+ does exist in appreciable abundance in space, it should be detectable due to its very large permanent dipole moment (6.405 D).

The rotational level with the highest population at 100 K is $J_{max} = 8$ with an energy of 49.2 K. This corresponds to a 4.0 K increase in the energy of the $J = 8$ rotational state upon ionization. The $J = 8 \rightarrow 7$ transition of MgCH+ emits a frequency of 227,809 MHz, 18,289 MHz larger than the corresponding transition in MgCH. Similar, but smaller, trends are seen at a temperature of 30 K. The lower rotational states will be more important at lower temperatures, where less energy is available for the system. The energy of the most highly populated state ($J_{max} = 4$) is 13.7, 1.1 K higher than in MgCH. The resultant frequency from the $J = 4 \rightarrow 3$ transition is 113,922 MHz, 9143 GHz larger than in MgCH. At temperatures present in the ISM (3 K), MgCH+ has peak population in the $J_{max} = 1$ state, corresponding to an energy of 1.36 K. The $J = 1 \rightarrow 0$ transition has a frequency of 28,482, 2286 MHz larger than the same transition in MgCH. A recent spectral survey of IRC+10216 in the 215–285 GHz region published by Tenenbaum et al. detected 12 unidentified transitions, (Tenenbaum et al. 2010) potentially belonging to transitions of the MCH/MCH+ species originating from $J = 7–12$. These transitions would indicate a rotational temperature around 100 K. The large number of unidentified lines indicates the need for additional experimental and observational investigation in this region.

Deuteration to MgCD+ leads to a large decrease in the rotational constant compared to MgCH+. The additional mass at the end of the rotor causes a redshift in the rotational frequencies compared to MgCH+, as was seen for the neutral species. For example, the same $J = 8–7$ transition in MgCD+ is redshifted to a frequency of 198,537 MHz.

Something of chemical interest comes from inspection of the $J_{max}$ values across the aluminum and magnesium species. Within the neutral aluminum species, an increase in $J_{max}$ from 4 to 5 at 30 K and 8 to 9 at 100 K is seen upon deuteration, whereas upon deuteration of the cationic species there is no change in the most highly populated energy level. This behavior can be attributed to the electronic structure changes that occur upon removal of an electron. The small increase in the C–H bond length and small decrease in the Al–C bond length coupled with the angle change to form a bent structure counteracts the increased mass from the deuteration. This can
also be seen in the rotational constants. The $B$ and $C$ rotational constant of AlICH$^+$ only change by $\sim$1000 MHz upon deuteration, while the $B$ constant of AlICH decreases by $\sim$2000 MHz upon the addition of a deuterium atom. This same fact is not seen in the magnesium system, as the cation is a linear structure like the neutral molecule, and similar changes to the rotational constant are seen upon deuteration.

### 3.2. Vibrational Spectroscopy

#### 3.2.1. AlICH and AlICH$^+$

Inspection of the anharmonic vibrational frequencies ($\nu$) in Table 1 shows interesting shifts upon ionization and deuteration of both aluminum and magnesium species. Upon deuteration to AlCD, there is a large decrease in all frequencies. Most notably, there is a 754 cm$^{-1}$ decrease in the asymmetric stretching mode ($\nu_1$) to 2230.0 cm$^{-1}$ from 2984.0 cm$^{-1}$ in AlICH. This amounts to a ratio of 0.747. Along the relatively flat bending mode $\nu_2$, a decrease of 63.1 cm$^{-1}$ is seen, corresponding to a ratio of 0.753.

Upon loss of an electron to form the cation species AlICH$^+$ there is a change in the normal modes due to a change in geometry. As can be seen in Table 3, the bending angle decreases from linear to 124.3°. There is also slight lengthening in the C–H bond and shortening in the Al–C bond. These geometrical changes cause $\nu_1$ to become the pure C–H stretching motion, while $\nu_2$ and $\nu_3$ are the bending motion and Al–C stretch, respectively. Due to these changes, comparison of vibrational frequencies between AlICH and AlICH$^+$ is difficult and will not be undertaken. However, deuteration to AlCD$^+$ results in a large decrease of $\nu_1$, the pure C–D stretch, from 2863.7 to 2178.0 cm$^{-1}$, a ratio of 0.760. The slightly longer C–D bond causes the increased mass to have less of an impact than in the neutral species. Almost no change is seen in $\nu_3$ as this is the Al–C stretch and is unaffected by the mass change at the other end of the molecule due to the involvement of the heavy aluminum atom.

The anharmonic rovibrational energy levels for the aluminum species are expected to be further complicated by the presence of anharmonic resonances.
with MgCH, the asymmetric stretching vibration of the molecule can be made between the two. Like in AlCH, MgCH shows the same impact on the vibrational frequencies of the molecule as the aluminum species. For example, in AlCH, the bending mode combination band ν₁, ν₂, ν₃ is predicted to be 2995.3 cm⁻¹, which decreases dramatically to 2020 cm⁻¹ upon substitution of the heavy deuterium atom in AlCD. Additional decreases are seen in ν₂ and ν₃, with the bending motion experiencing a 102 cm⁻¹ decrease from 440.7 cm⁻¹ in MgCH to 338.1 cm⁻¹ in MgCD.

The anharmonic vibrational frequencies (ν₁) for the magnesium species are reported in Table 1. As expected, deuteration shows the same impact on the vibrational frequencies of the magnesium-bearing species as the aluminum ones; however, because both the neutral and cation molecules are linear, a direct comparison can be made between the two. Like in AlCH, a large frequency ratio between isotopes is seen. Beginning with MgCH, the asymmetric stretching (ν₁) frequency is predicted to be 2995.3 cm⁻¹, which decreases dramatically to 2235.3 cm⁻¹ upon substitution of the heavy deuterium atom in MgCD. Additional decreases are seen in ν₂ and ν₃, with the bending motion experiencing a 102 cm⁻¹ decrease from 440.7 cm⁻¹ in MgCH to 338.1 cm⁻¹ in MgCD.

The loss of an electron to form MgCH⁺ causes minor geometrical changes that can be seen in the vibrational frequencies. The data in Table 3 show a large decrease of 0.08 Å in the Mg–C bond length and a very slight decrease of 0.006 Å for the C–H bond length at the CCSD(T)-AE/CBS level of theory. Shortening of bonds is associated with an increase in the frequency of a molecular vibration due to the strengthening of the bond. Both stretching vibrations in MgCH⁺ increase from the corresponding mode in MgCH. ν₁ has an increase of 72.7 to 3068.0 cm⁻¹, while ν₄, the symmetric stretch, increases by 89.8 to 707.2 cm⁻¹. Examination of the bending mode frequencies for MgCH and MgCH⁺ reveals interesting characteristics in the electronic structure of each molecule. The MgCH harmonic bending mode frequency is 446.3 cm⁻¹, indicative of a deep potential well along the bending angle compared to many tratomic species containing second-row metals (Trabelsi et al. 2018, 2019c; Esposito et al. 2020). Only minor anharmonicity is seen in this mode, with a ~6 cm⁻¹ decrease in frequency to 440.7 cm⁻¹ with anharmonic treatment. Contrastingly, the potential energy is extremely flat along the bending mode of MgCH⁺, making it difficult to characterize with harmonic and VPT2 methods. This difficulty is seen in the disagreement between ab-initio values reported in Table 3 and fit values from SURFIT. The potential energy profile along the bending angle of MgCH⁺ is shown in Appendix C. Due to this, sophisticated variational techniques are needed to properly characterize its shape, as a harmonic oscillator is not a good approximation.

The anharmonic rovibrational spectrum has also been calculated for the magnesium species and is reported in Table 5. The vibrational spectrum of MgCH⁺ is expected to show some complexity as there is the potential for a resonance to occur between the bending mode + symmetric stretch combination band (0,1,1) at 1061.8 cm⁻¹ and the first overtone of the bending mode (0,2,0) at 1075.3 cm⁻¹. This will cause a

### Table 4

Anharmonic Rovibrational Energy Levels of AICH, AICD, AICH⁺, and AICD⁺ in their Electronic Ground State

| AICH (X 1Σ⁻) (ν₁, ν₂, ν₃) | E (cm⁻¹) | AICD (X 1Σ⁻) (ν₁, ν₂, ν₃) | E (cm⁻¹) | AICH⁺ (X 2Σ⁺) (ν₁, ν₂, ν₃) | E (cm⁻¹) | AICD⁺ (X 2Σ⁺) (ν₁, ν₂, ν₃) | E (cm⁻¹) |
|---------------------------|----------|---------------------------|----------|-----------------------------|----------|-----------------------------|----------|
| (0,0,0)                   | 0,0      | (0,0,0)                   | 0,0      | (0,0,0)                     | 0,0      | (0,0,0)                     | 0,0      |
| (0,1,0)                   | 256,2    | (0,1,0)                   | 193,1    | (1,0,0)                     | 591,3    | (1,0,0)                     | 446,9    |
| (0,2,0)                   | 522,3    | (0,2,0)                   | 391,3    | (0,0,1)                     | 617,6    | (0,0,1)                     | 617,3    |
| (0,0,1)                   | 661,3    | (0,0,1)                   | 644,7    | (0,1,1)                     | 1179,8   | (0,1,1)                     | 892,1    |
| (0,1,1)                   | 915,1    | (0,1,1)                   | 837,8    | (0,2,0)                     | 1190,2   | (0,2,0)                     | 1050,1   |
| (0,0,2)                   | 1314,9   | (0,0,2)                   | 1282,2   | (0,0,1)                     | 1213,4   | (0,0,1)                     | 1213,0   |
| (1,0,0)                   | 2984,0   | (1,0,0)                   | 2230,0   | (1,0,0)                     | 2863,7   | (1,0,0)                     | 2178,0   |
| (1,1,0)                   | 3220,7   | (1,1,0)                   | 2410,9   | (1,1,0)                     | 3068,0   | (1,1,0)                     | 2613,7   |
| (1,0,1)                   | 3643,1   | (1,0,1)                   | 2872,8   | (1,1,1)                     | 3173,0   | (1,1,1)                     | 2797,2   |
| (1,1,1)                   | 3877,3   | (1,1,1)                   | 3053,7   | (1,1,1)                     | 3877,3   | (1,1,1)                     | 3173,0   |

### Table 5

Anharmonic Rovibrational Energy Levels of MgCH, MgCD, MgCH⁺, and MgCD⁺ in their Electronic Ground State

| MgCH (X 1Σ⁻) (ν₁, ν₂, ν₃) | E (cm⁻¹) | MgCD (X 1Σ⁻) (ν₁, ν₂, ν₃) | E (cm⁻¹) | MgCH⁺ (X 1Σ⁺) (ν₁, ν₂, ν₃) | E (cm⁻¹) | MgCD⁺ (X 1Σ⁺) (ν₁, ν₂, ν₃) | E (cm⁻¹) |
|---------------------------|----------|---------------------------|----------|-----------------------------|----------|-----------------------------|----------|
| (0,0,0)                   | 0,0      | (0,0,0)                   | 0,0      | (0,0,0)                     | 0,0      | (0,0,0)                     | 0,0      |
| (0,1,0)                   | 440,7    | (0,1,0)                   | 338,1    | (0,1,0)                     | 392,9    | (0,1,0)                     | 247,1    |
| (0,0,1)                   | 617,4    | (0,0,1)                   | 598,7    | (0,0,1)                     | 707,2    | (0,0,1)                     | 666,4    |
| (0,2,0)                   | 869,6    | (0,2,0)                   | 670,6    | (0,2,0)                     | 1061,8   | (0,2,0)                     | 688,8    |
| (0,1,1)                   | 1054,5   | (0,1,1)                   | 933,0    | (0,1,1)                     | 1075,3   | (0,1,1)                     | 902,4    |
| (0,0,2)                   | 1228,2   | (0,0,2)                   | 1191,2   | (0,0,2)                     | 1407,0   | (0,0,2)                     | 1370,6   |
| (1,0,0)                   | 2995,3   | (1,0,0)                   | 2235,3   | (1,0,0)                     | 1706,0   | (1,0,0)                     | 1550,5   |
| (1,1,0)                   | 3421,5   | (1,1,0)                   | 2565,0   | (1,1,0)                     | 1723,3   | (1,1,0)                     | 2291,6   |
| (1,0,1)                   | 3615,5   | (1,0,1)                   | 2835,8   | (1,0,1)                     | 3068,0   | (1,0,1)                     | 2516,8   |
| (1,1,1)                   | 3877,3   | (1,1,1)                   | 3161,8   | (1,1,1)                     | 3773,3   | (1,1,1)                     | 3173,0   |
of the Ground State Neutral and Cation Isomers Calculated at the MRCI Vertical Excitation Energy, Transition Dipole Moment, and Oscillator Strength

besides AlCH

Note. The CCSD(T)-AE/CBS reference geometry was used for all isomers besides AlCH⁺ where the MRCI-F12/CBS geometry was used.

Table 6

| Isomer | State | VEE (nm) | VEE (eV) | μν (D) | f          |
|--------|-------|----------|----------|--------|------------|
| AlCH (X 3Σ⁻) | X 3Σ⁻ | 1 IÎ 935.7 1.325 0.270 0.002 |
|         |       | 2 IÎ 359.0 3.454 0.034 0.000 |
|         |       | 3 IÎ 298.6 4.152 0.749 0.057 |
|         |       | 4 Σ⁺ 245.7 5.045 0.000 0.000 |
|         |       | 5 Δ  245.6 5.048 0.000 0.000 |
|         |       | 6 Σ⁻  226.5 5.473 0.000 0.000 |
|         |       | 7 Σ⁺  222.7 5.566 0.884 0.105 |
| MgCH (X 4Σ⁻) | X 4Σ⁻ | 1 IÎ 391.47 3.167 1.164 0.105 |
|         |       | 2 Σ⁻ 283.94 4.366 0.376 0.015 |
|         |       | 3 IÎ 278.27 4.455 1.092 0.130 |
|         |       | 4 Σ⁻ 257.51 4.815 0.090 0.001 |
|         |       | 5 Δ  256.65 4.831 0.000 0.000 |
|         |       | 6 Σ⁺ 252.18 4.916 0.000 0.000 |
|         |       | 7 Σ⁻ 251.10 4.937 0.419 0.021 |
|         |       | 8 IÎ 219.42 5.650 0.932 0.120 |
| AlCH⁺ (X 2Σ⁺) | X 2Σ⁺ | 1 2Σ⁺ 1593.7 0.778 0.199 0.001 |
|         |       | 2 2Σ⁺  919.2 1.349 0.165 0.000 |
|         |       | 3 2Σ⁺  689.2 1.799 0.163 0.001 |
|         |       | 4 2Σ⁺  486.7 2.548 0.825 0.042 |
|         |       | 5 2Σ⁺  483.6 2.564 0.147 0.000 |
|         |       | 6 2Σ⁺  364.7 3.399 0.271 0.006 |
|         |       | 7 2Σ⁺  343.5 3.610 0.580 0.030 |
|         |       | 8 2Σ⁺  286.4 4.328 0.523 0.029 |
|         |       | 9 2Σ⁺  281.1 4.410 0.036 0.000 |
|         |       | 10 2Σ⁺  256.5 4.834 0.263 0.008 |
|         |       | 11 2Σ⁺  240.5 5.155 0.133 0.002 |
| MgCH⁺ (X 3Σ⁻) | X 3Σ⁻ | 1 IÎ 627.1 1.977 0.440 0.009 |
|         |       | 2 Σ⁻ 262.2 4.728 0.564 0.037 |
|         |       | 3 IÎ 255.4 4.855 0.875 0.091 |
|         |       | 4 Δ  238.2 5.205 0.000 0.000 |
|         |       | 5 Σ⁺  233.9 5.301 0.000 0.000 |
|         |       | 6 Δ  193.3 6.414 0.000 0.000 |
|         |       | 7 IÎ 181.6 6.828 0.600 0.060 |

Note. The CCSD(T)-AE/CBS reference geometry was used for all isomers besides AlCH⁺ where the MRCI-F12/CBS geometry was used.

redistribution of intensity, and each state will experience a perturbation in its energy.

3.3. Electronic Spectroscopy and Photostability

The excited electronic states of AlCH and MgCH were studied to aid in experimental detection of AlCH and MgCH. Vertical excitation energies, transition dipole moments, and oscillator strengths were calculated and are shown in Table 6. The electronic spectrum of both species is very congested. Additionally, differing excited states are in the same energy region across species. For example, the first excited state of MgCH is in the same region as the second excited state of AlCH, and identifying one experimentally may not lead to the correct assignment of the other by experimental analogy.

MgCH is especially congested in the 280–260 nm range, with at least five states located at this energy. Many transitions show large oscillator strengths and will be good for UV absorption studies. The three states with the largest oscillator strength are the 1 4Π, 3 4Π, and 8 4Π. These states lie 3.167 eV (391.5 nm), 4.455 eV (278.3 nm), and 5.650 eV (219.4 nm) above the ground state, respectively.

The absorption spectrum is expected to be broad based on the disbursement of strongly absorbing states at different wavelengths. Figure 1 shows an one-dimensional cut of the PESs of the lowest doublet and quartet excited states along the Mg–C bond coordinate of MgCH. The 8 4Π state is repulsive in the Franck–Condon region, so immediate bond lengthening will occur following vertical excitation. This excitation lies above all four dissociation asymptotes, meaning all product channels will be open. As the Mg–C bond elongates, the 8 4Π state encounters a conical intersection with the 3 4Π state, where population transfer can occur. Once on this state, the molecule can dissociate to form Mg (1S)+ CH (B 3Σ⁻) products or undergo another internal conversion to the 1 4Π state. If this occurs, dissociation will form Mg (1S)+ CH (X 2ΣIII) products. Vertical excitation directly to the 1 4Π state will not lead to direct dissociation as the asymptote lies ~1.5 eV above the vertical excitation. However, there is a curve crossing of the 2 2Π state in the Franck–Condon region where intersystem crossing can take place. Once on this state, two pathways are possible: stabilization in the deep well and subsequent phosphorescence to the ground X 4Σ⁻ state, or internal conversion to the lower 2 2Π state via the strongly coupling conical intersection at R ~2.25 Å. This will lead to formation of ground-state products Mg (1S)+ CH (X 2ΣII). As one can see, depending on the pathway taken, dissociation can form both ground and excited states of Mg, as well as many different forms of CH.

For AlCH, the two transitions with very strong absorption characterized by large oscillator strengths are to the 3 4Π and 6 3Σ⁻ states. Transition to the 3 4Π state has a large oscillator...
All other coordinates were held fixed at their equilibrium value. Strength of 0.057 and lies 4.152 eV above the ground state. The more interesting state is the 6 $^3\Sigma^-$ state that lies 5.473 eV (226.5 nm) above the ground state. This state has the same symmetry as the ground state, making this allowed transition very strong with an oscillator strength of 0.105.

What makes the 6 $^3\Sigma^-$ state interesting is not only its predicted strong absorption, but the topology of the PES. Figure 2 shows an one-dimensional cut of the PES of the Al–C bond coordinate of AlCH. First, one can see that the electronic spectrum will be very complicated from the multitude of electronic states in the 4–6 eV range of the Franck–Condon region. Additionally, these curves show that the ground state follows a barrierless path to the lowest-energy dissociation asymptote to create ground state Al ($^2\Pi$)+ ground state CH ($X$ $^2\Sigma^+$) at 3.977 eV. The 6 $^3\Sigma^-$ state is shown as the purple solid line that correlates to the second dissociation asymptote to create Al ($^2\Pi$)+ CH (a $^4\Sigma^-$), the first quartet excited state of CH.

This is a repulsive state in the Franck–Condon region with a wide, shallow well at long Al–C bond lengths. Upon vertical excitation to this state, the repulsive nature would cause immediate bond elongation until it encounters the conical intersection at $R_{\text{AI-C}} \sim 3.5$ Å. At this point, the molecule can continue on the 6 $^3\Sigma^-$ state to dissociation to form Al ($^2\Pi$)+ CH (a $^4\Sigma^-$). The other available pathway is internal conversion to the ground electronic state leading to dissociation to form Al ($^2\Pi$)+ CH ($X$ $^2\Pi$). The excess energy (VEE – $D_v$) will partition into vibrational excitation of the CH fragment, as well as kinetic energy of both Al and CH fragments. Because the Al atom is almost twice the mass of the CH molecule, and CH has more degrees of freedom, most of the energy is expected to partition into the CH molecule. This will cause the Al to come off cold.

There is also the possibility of other nonradiative processes, such as intersystem crossing (ISC) and internal conversion, occurring prior to dissociation. The 6 $^3\Sigma^-$ state crosses many singlet curves as it follows toward dissociation. Most notably so are the 1$^\Sigma^-$ and 1$^\Pi$ states. If ISC to the 1$^\Pi$ state occurs, the molecule will have enough energy to either surmount or tunnel through the barrier to form ground-state products. Experimental studies of this process would reveal which state the CH cofragment is born in, as well as the kinetic energy release from the dissociation to decipher which pathway is taken.

### 4. Conclusions

Detection of AlCH and MgCH species is expected to be feasible in both carbon- and oxygen-rich CSEs of cool, evolved stars, and the ISM, at rotational frequencies ranging from 25 to 250 GHz. Formation may occur in the outer CSE where subsequent facile ionization may produce significant population of ions. All species are predicted to be linear besides AlCH+, which has an angle of 126.5°. This bent structure will complicate the spectrum of AlCH+. Recent new detection of magnesium-bearing species, coupled with its large permanent dipole moment, make MgCH+ the most promising candidate for detection in space.

Anharmonic rovibrational analysis shows large anharmonicity in the bending motion of each species. Additionally, the existence of resonances may make vibrational characterization of these molecules more complex. Deuteriation of each molecule produced a characteristic reduction in each vibrational frequency of the linear species, with the D/H frequency ratios predicted to be between 0.74–0.76. This ratio may aid in experimental detection via isotope effects.

Many strong electronic transitions in both AlCH and MgCH are predicted to make UV absorption spectroscopy the best means of experimental detection of these molecules. Strong absorptions in the 220–300 nm range may lead to M+C dissociation, producing M+ CH fragments. Product state distribution and energy partitioning will elucidate whether intersystem crossing and internal conversion play a part in dissociation. Electronic excitation of AlCH to the 6 $^3\Sigma^-$ state is expected to lead to dissociation in most cases, making it a potential source of Al in colder regions of space. For MgCH, excitation to the 8 $^4\Pi$ state may lead to dissociation, although many adiabatic processes are needed for that to occur.

The formation mechanism of these molecules is still a mystery and follow up studies should be done to elucidate how they form, whether through collision, reaction on the surface of dust grains, etc. Additionally, collisional stabilization is possible, and may account for the lack of detection of these molecules thus far. Further studies on rotational de-excitation will go far to explain whether this is the case.

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Appendix A
Three-dimensional Potential Energy Surface Fitting

The ground-state spectroscopic constants were calculated by fitting to a three-dimensional potential energy surface (3D-PES). The surfaces were fit to the following equation using a least-squares method:

\[ V(R_1, R_2, \theta) = \sum_{i,j,k} C_{ijk} (R_i - R_{1eq})^i(R_2 - R_{2eq})^j \times (\theta - \theta_{eq})^k, \]

where \( R_{1eq}, R_{2eq}, \) and \( \theta_{eq} \) refer to the equilibrium geometry of the respective isomer, and \( C_{ijk} \) coefficients were optimized during the least-squares procedure. In all isomers, the rms deviations were less than 1 \( \text{cm}^{-1} \).

Appendix B
Molecular Orbitals

Figures B1 and B2 depict the frontier molecule orbitals (MOs) for the four isomers in this study calculated at the CASSCF/aug-cc-pV(T+d)Z level of theory. Orbitals for AlCH, MgCH and MgCH\(^+\) were calculated at the CCSD(T)-AE/CBS equilibrium geometry, while the MRCI+Q/CBS equilibrium geometry was used to AlCH\(^+\). All isomers utilize the same full valence active space of six closed orbitals and nine active orbitals, with only the number of electrons changing. The CASSCF/aug-cc-pV(T+d)Z dominant electronic wave functions are as follows:

\[
\text{AlCH} (X^3\Sigma^-): 0.95 \times (1a_1 - 4a_1)^2(1b_2)^2(1b_1)^2(5a_1)^2(6a_1)^2(7a_1)^2(2b_1)^4(3b_1)^4 \\
\text{AlCH}^+ (X^2A^+): 0.94 \times (1a' - 4a')^2(1a')^0(5a')^2(6a')^2(7a')^2(8a')^2(9a')^4 \\
+ -0.14 \times (1a'-4a')^2(1a')^2(5a')^2(6a')^2(7a')^2(8a')^0(9a')^4 \\
\text{MgCH} (X^4\Sigma^-): 0.98 \times (1a_1 - 4a_1)^2(1b_2)^2(1b_1)^2(5a_1)^2(6a_1)^2(7a_1)^2(2b_1)^4(3b_1)^4(7a_1)^4 \\
\text{MgCH}^+ (X^3\Sigma^-): 0.98 \times (1a_1 - 4a_1)^2(1b_2)^2(1b_1)^2(5a_1)^2(6a_1)^2(7a_1)^2(2b_1)^4(3b_1)^4(7a_1)^0
\]

Figure B1. Frontier molecule orbitals for MgCH and MgCH\(^+\) calculated at the CASSCF/aug-cc-pV(T+d)Z level of theory (isovalue = 0.05) at their CCSD(T)-AE/CBS equilibrium geometry.

AlCH, MgCH and MgCH\(^+\) all exhibit large coefficients for their dominant configuration within the electronic wave function, indicating single-reference character. Alternatively, AlCH\(^+\) has two dominant configurations, explaining the large T1 diagnostic value of 0.04 obtained with coupled-cluster methods.
Appendix C

Potential Energy Profile of MgCH$^+$ Bending Angle

The potential energy profile along the bending angle of MgCH$^+$ is shown in Figure C1 and was calculated at the CCSD(T)-AE/aug-cc-pwCV5Z-DK level of theory with all other coordinates held fixed at their CCSD(T)-AE/CBS equilibrium geometry. The potential surrounding 180° is flat with an increase of only 0.004 eV at 160°. The small gradient in this coordinate proves difficult for the ab-initio and second-order perturbation theory (VPT2) methods utilized in this study. More sophisticated variational techniques are required to properly characterize this coordinate.
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