Abstract

The MgCH$_3$ radical was produced by a laser ablation/photolysis technique in a cold supersonic free-jet expansion and probed by laser induced fluorescence. Rotationally resolved spectra for both spin-orbit components of the $\tilde{A} \ 2E \leftarrow \tilde{X} \ 2A_1$ electronic transition have been recorded. The analysis of these spectra yields the rotational constants of MgCH$_3$ and therefrom a structure for the radical is proposed. A comparison is made among a series of alkyl organometallic radicals.
High Resolution Electronic Spectroscopy of MgCH₃.

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1. INTRODUCTION

The knowledge of organometallic radicals has increased considerably in the last ten years by the application of laser induced fluorescence (LIF) spectroscopy to supersonic free jet expansions of these species. In particular, the study of methyl derivatives of the alkaline earth metals has attracted some interest in the past years and a number of reports regarding the spectroscopy of these radicals have been published.\textsuperscript{1–4}

There are at least three areas in which Mg-containing species are of great interest: extraterrestrial, organic synthesis and biological systems. Mg is the most abundant metal and the seventh most common element overall, but almost no Mg compounds have been spectroscopically observed in astrophysical studies. However, such species have been postulated to be relatively important in a number of environments. Indeed MgCH\textsubscript{3} itself has recently been suggested to play an important role in the atmosphere of Jupiter and perhaps other large gaseous planets.\textsuperscript{5} In the area of organic and inorganic synthesis, Grignard reagents are arguably the most useful and versatile known, making MgCH\textsubscript{3} a particularly interesting object of study. In biological systems Mg-containing compounds such as chlorophyll, play important roles, and the study of free radicals related to such compounds is of intense interest.

In spite of their relevance, very little spectroscopic information is available on Mg radicals. MgH, for which an optical spectrum has long been known,\textsuperscript{6} has also been studied by high resolution Fourier transform spectroscopy\textsuperscript{7} as well as by millimeter-wave spectroscopy.\textsuperscript{8} A moderate resolution spectrum for MgCp (magnesium cyclopentadienyl) was obtained by Robles \textit{et al.}\textsuperscript{9} A small number of Mg radicals have recently been studied by millimeter and sub-millimeter wave spectroscopy: MgNC,\textsuperscript{10–12} MgOH,\textsuperscript{13,14} MgCCH,\textsuperscript{15} MgF,\textsuperscript{16} MgCl.\textsuperscript{17} This work reports and analyzes the first high resolution electronic spectrum of the MgCH\textsubscript{3} radical.

An additional motivation for the study MgCH\textsubscript{3} is to complete the series of moderate and high resolution studies of MCH\textsubscript{3} (M=Ca, Cd and Zn) radicals performed by the Bernath and Miller research groups.\textsuperscript{1–4} We are now able to compare the MgCH\textsubscript{3} spectrum—and therefore
its structure— with the results obtained for CaCH$_3$, ZnCH$_3$ and CdCH$_3$ radicals.

2. EXPERIMENTAL

The MgCH$_3$ radical was obtained by a laser ablation/photodissociation technique$^{18}$. The experimental apparatus and the technique have been described in detail in previous papers.$^{19-21}$ In the ablation/photodissociation technique, a pulsed laser beam simultaneously vaporizes the metal and photolyzes the precursor molecules. Acetone was used as the organic precursor. It was placed in a stainless steel reservoir and maintained at a constant temperature (dry ice-acetone bath, -78$^\circ$C). Helium was passed through the reservoir at a pressure of 200-300 psig, and the acetone vapor/He mixture was flowed through a pulsed valve (General Valve, Series 9) and into the ablation fixture$^{20}$ located on top of the valve. A magnesium rod was mounted inside the ablation fixture, next to the 2 mm channel through which the precursor was flowing. A Lumonics excimer laser with a KrF fill (248 nm) was used as the ablation/photolysis source, with an attenuated output power of 30 mJ/pulse.

The resulting MgCH$_3$ radicals expanded into a low pressure region and were then probed by LIF. A Coherent 699-29 Autoscan continuous wave ring dye laser pumped by an Innova 200 Ar$^+$ laser was used to probe the radical. The output power—using Coumarin 102 dye—was about 100-200 mW with a linewidth of a few MHz. The Te$_2$ spectrum, which was used for absolute frequency calibration,$^{22}$ was taken simultaneously with the sample spectrum. The experimental uncertainty for relative frequency measurements is about 60 MHz and 300 MHz for absolute measurements.

The LIF signal was collected by a f/1 lens, filtered with a Hoya color filter (Y48), and collected with a photomultiplier tube (EMI 9659QB). The signal from the PMT was integrated, amplified, and then digitized by the Coherent Autoscan System version 2.0. The spectra obtained have signal to noise ratios of $\approx 30$ and linewidths of $\approx 150$ MHz, due principally to residual Doppler and power broadening effects.
3. THEORY

MgCH$_3$ presumably belongs to the C$_{3v}$ point group, having $^2A_1$ and $^2E$ ground and first excited states respectively. Expressions for the rotational energy levels for a symmetric top molecule in $^2E$ and $^2A$ states have been derived in detail previously.$^{23-25}$ In Cerny et al.$^3$ the rotational Hamiltonians and their eigenvalues for the MCH$_3$ (M=Cd and Zn) species have been discussed thoroughly, and we will use their notation here. Therefore, only a brief description of the Hamiltonians and basis set used to fit the data follows.

The rotational Hamiltonian for the ground state ($^2A_1$) can be expressed as

$$
\mathcal{H}(^2A) = AN_z^2 + B \left( N_x^2 + N_y^2 \right) + \epsilon_{aa} N_z S_z + \frac{1}{2} \epsilon_{bc} (N_+ S_- + N_- S_+) + \mathcal{H}_{CD}
$$

where $A$ and $B$ are the rotational constants of the molecule and $N$ is the total angular momentum except for the electronic and the nuclear spin angular momenta ($N=J-S$), $J$ being the total angular momentum excluding nuclear spin, and $S$ is the electron spin angular momentum. $\epsilon_{aa}$ and $\epsilon_{bc} (= (\epsilon_{bb} + \epsilon_{cc}) / 2)$ are the spin-rotation coupling constants. $\mathcal{H}_{CD}$ includes the terms for rotational centrifugal distortion,

$$
\mathcal{H}_{CD} = - \left( D_N N^4 + D_{NK} N^2 N_z^2 + D_K N_z^4 \right)
$$

where $D_N$, $D_{NK}$ and $D_K$ denote the usual centrifugal distortion constants. In Endo et al.$^{24}$ a more detailed Hamiltonian for centrifugal distortion can be found, which would be required to reproduce higher precision spectra, e.g. microwave.

The rotational Hamiltonian for the excited state ($^2E$) is much more complicated and can be written as a summation of several terms:

$$
\mathcal{H}(^2E) = \mathcal{H}_{ROT} + \mathcal{H}_{SO} + \mathcal{H}_{COR} + \mathcal{H}_{SR} + \mathcal{H}_{JT} + T_{00}
$$

where $\mathcal{H}_{ROT}$, $\mathcal{H}_{SO}$, $\mathcal{H}_{COR}$, $\mathcal{H}_{SR}$ and $\mathcal{H}_{JT}$ correspond to the rotational, spin-orbit, Coriolis, spin-rotation and Jahn-Teller Hamiltonians respectively, and $T_{00}$ is the transition energy between the vibrationless levels of the two electronic states. The definition for each term is as follows:
$$\mathcal{H}_{\text{ROT}} = AN_z^2 + B \left( N_x^2 + N_y^2 \right) + \mathcal{H}_{\text{CD}}$$  \hspace{1cm} (4)$$

where \( \mathcal{H}_{\text{CD}} \) is the same as in Eqn. 2.

$$\mathcal{H}_{\text{SO}} = a L_z S_z + a_D N_z^2 L_z S_z$$  \hspace{1cm} (5)$$

where \( a \) corresponds to the spin-orbit coupling constant and \( a_D \) to its centrifugal distortion constant and \( L \) is the total electronic orbital angular momentum.

$$\mathcal{H}_{\text{COR}} = -2AN_z L_z + \eta_e N^2 N_z L_z + \eta_k N^3 L_z$$  \hspace{1cm} (6)$$

where \( \eta_e \) and \( \eta_k \) are centrifugal distortion corrections for the Coriolis interaction.

$$\mathcal{H}_{\text{SR}} = \epsilon_{aa} N_z S_z + \frac{1}{2} \epsilon_{bc} (N_+ S_+ + N_- S_-) + \epsilon_1 \left( L_-^2 N_+ S_+ + L_+^2 N_- S_- \right)$$

$$+ \epsilon_{2a} \left[ L_-^2 (N_+ S_+ + S_+ N_-) + L_-^2 (N_+ S_+ + S_+ N_-) \right]$$

$$+ \epsilon_{2b} \left[ L_-^2 (N_+ S_+ + S_+ N_-) + L_-^2 (N_+ S_+ + S_+ N_-) \right]$$  \hspace{1cm} (7)$$

where \( L_+ \) and \( L_- \) are the ladder operators. The last three terms in \( \mathcal{H}_{\text{SR}} \) are higher order contributions to the spin-rotation interaction.

$$\mathcal{H}_{\text{JT}} = h_1 \left( L_-^2 N_+^2 + L_+^2 N_-^2 \right) + h_2 \left[ L_-^2 (N_+ N_- + N_- N_+) + L_+^2 (N_+ N_- + N_- N_+) \right]$$  \hspace{1cm} (8)$$

where \( h_1 \) and \( h_2 \) are parameters to describe the Jahn-Teller interaction.

The basis set used to diagonalize both \( \mathcal{H}(^2A) \) and \( \mathcal{H}(^2E) \), is the Hund’s case (a) basis set,

$$| JPS\Sigma\Lambda; \pm \rangle = \frac{1}{\sqrt{2}} \left[ | + \rangle \langle JPM_J \rangle | S\Sigma \rangle \pm (-1)^{J-P+S-\Sigma} | - \rangle \langle J-PM_J \rangle | S-\Sigma \rangle \right]$$  \hspace{1cm} (9)$$

Here \( P \) is the projection of \( J \) on the top axis and \( M_J \) is the projection of \( J \) on the space fixed axis. The | + \rangle and | - \rangle kets correspond to electronic eigenfunctions with opposite projections of the electronic orbital angular momentum, \( \Lambda \), on the molecule fixed axis. For the \( ^2A \) state, \( \Lambda \) is set to 0, and the linear combination reduces to a single term.
4. RESULTS

In this paper rotationally resolved spectra for the \( ^2E_{1/2} \leftrightarrow ^2A_1 \) (F') and for the \( ^2E_{3/2} \leftrightarrow ^2A_1 \) 00 bands of MgCH\(_3\) are reported. The experimental and the simulated spectra for the F' band are shown in Fig.1, and the spectra for the F' band are given in Fig.2. For each band three subbands corresponding to the \( 2 \leftrightarrow 1, 1 \leftrightarrow 0 \) and \( 0 \leftrightarrow -1 \) \( (K' \leftrightarrow K'') \) transitions were observed, following the \( \Delta K = \pm 1 \) selection rule. Given the \( \Delta J = 0, \pm 1 \) selection rule, P, Q and R branches are present in each subband. The branches with F' upper levels are designated \( P_{1,F''}, Q_{1,F''} \) and \( R_{1,F''} \), where \( F'' \) is either 1 or 2 depending on whether \( J'' \) is equal to \( (N + 1/2) \) or \( (N - 1/2) \) respectively. Similarly, the notation for the F' band is \( P_{2,F''}, Q_{2,F''} \) and \( R_{2,F''} \), and \( F'' \) is defined as above. A stick spectrum for the F' subbands illustrating the branch structure is shown in Fig.3.

Mg has three isotopes, \( ^{24}\text{Mg}, ^{25}\text{Mg} \) and \( ^{26}\text{Mg} \), with natural isotopic abundances of 78.99%, 10.00% and 11.01% respectively. Even though the experimental resolution was adequate to resolve the three isotopes, it was not possible to assign any experimental lines to \( ^{25}\text{MgCH}_3 \). This result can be ascribed to the hyperfine splitting of \( ^{25}\text{Mg} \) – with I equals to \( 5/2 \) – which causes a splitting of each transition into multiple components with a corresponding decrease in the intensities of the transitions. In Fig.4 an enlargement of the experimental spectrum clearly shows the observed isotopic structure for the \( ^{24}\text{Mg} \) and \( ^{26}\text{Mg} \) isotopomers.

SpecSim, a computational program for modelling and fitting spectra, was used to generate the simulated plots in Figs.1-3 and to determine the molecular constants for both isotopes from the spectra.

A few lines that could not be assigned to either \( ^{24}\text{MgCH}_3 \) or \( ^{26}\text{MgCH}_3 \) can be assigned to MgO. The band origins for the (0,0) and (1,1) MgO transitions are at 20003.57 cm\(^{-1}\) and 20043.43 cm\(^{-1}\), overlapping the regions where the F' and F' bands occur.

For \( ^{24}\text{MgCH}_3 \) a total of 71 transitions were fitted for the F' and F' bands. The standard deviation, calculated from the linear least squares fitting, was 80 MHz. Due to the lower intensity of \( ^{26}\text{MgCH}_3 \) lines with respect to the ones for the main isotope, only 54 lines were...
observed and fitted, with a standard deviation of 95 MHz.

It was not possible to determine the A rotational constants for both the ground and the excited states independently because of the $\Delta K$ selection rule. However, since it is possible to determine $\Delta A$, fixing one of the A constants allows the other to be determined. The A value for the ground state was thus fixed at the value of 156.544 GHz, generated in an ab initio calculation. The molecular constants determined for both isotopes are summarized in Table I.

A number of small terms contained in the Hamiltonian, Eqs. 1-8, were found to affect the spectrum less than experimental error. These include rotational distortion terms ($D_N$, $D_{NK}$ and $D_K$), the Coriolis centrifugal distortion terms ($\eta_c$ and $\eta_k$), the high order spin-rotation parameters ($\epsilon_1$, $\epsilon_{2\alpha}$ and $\epsilon_{2\beta}$) as well as the Jahn-Teller parameters ($h_1$ and $h_2$). For the final fits, these were all set equal to zero and are omitted from Table I. The omission of all these terms probably leaves the theoretical model slightly less accurate than the experimental data. However, because of the large number of small but comparable parameters, coupled with the limitation of the observed spectrum to fairly low J values due to the low temperature, it seems imprudent to include these parameters in the fit.

5. DISCUSSION

The first general issue to be dealt with is the identity of the carrier of the spectrum. We have based our assignment to MgCH$_3$ on several grounds. (i) The method of preparation was similar to ones successfully used to prepare the other MCH$_3$ (M=Ca, Zn, Cd) radicals. (ii) All the other MCH$_3$ $A-X$ spectra were very close in absolute frequency to the corresponding MH spectrum and this is likewise the case for the Mg radicals. (iii) While not extensive, the vibrational frequencies seen$^{18}$ in the lower resolution spectrum are consistent with those expected for MgCH$_3$. (iv) Finally, and most importantly, the detailed rotational analysis, in terms of $^{24}$Mg and $^{26}$Mg isotopomers, of well over 100 transitions would seem to remove any residual doubt as to the carrier’s identity.
In Table II all the molecular constants determined from the simulated spectra as well as the structural parameters estimated for MgCH$_3$ are presented. This table also contains the information for the other MCH$_3$ radicals previously studied.\textsuperscript{2,3} We will discuss the results obtained for MgCH$_3$, and compare them with the values determined for the other alkyl organometallic radicals.

A. Spin-rotation, spin-orbit and Coriolis coupling interactions.

The spin-rotation interaction is accounted for by the $\epsilon_{aa}$ and $\epsilon_{bc}$ parameters, i.e. the components of the spin-rotation tensor. Table II shows no values for $\epsilon_{aa}$ in the $\tilde{X}$ state for any of the radicals because it is below the precision of the measurements. On the other hand, $\epsilon_{bc}$ is measured for all the radicals. In the IIA metal methyl radicals, MgCH$_3$ and CaCH$_3$, $\epsilon_{bc}$ is approximately 50 MHz, while for the IIB metals it is about an order of magnitude larger. For either the $\tilde{X}$ or $\tilde{A}$ state the components of the spin-orbit tensor are expected to be dominated by second order cross-terms involving L-uncoupling and spin-orbit coupling. Indeed a comparison among the radicals shows that $\epsilon_{bc}$ qualitatively correlates with the product $B \times a\zeta_e$, but a quantitative relationship cannot be established. In the $\tilde{A}$ state $\epsilon_{bc}$ is still relatively small but again appears to significantly increase for the radicals which have larger spin-orbit coupling.

$\epsilon_{aa}$ in the $\tilde{A}$ state is by far the largest spin-rotation parameter in all the radicals. Again it qualitatively correlates with the magnitude of the spin-orbit coupling but is anomalously large for the IIB metals, presumably as previously noted,\textsuperscript{3} due to the interaction of the $\tilde{A}$ state with another nearby electronic state. Assuming that the sign conventions in the work of Brazier and Bernath\textsuperscript{2} are consistent, their negative $\epsilon_{aa}$ for CaCH$_3$ is quite strange and difficult to explain physically. $E$ symmetry electronic states with a positive spin-orbit coupling ($a > 0$) should have $\epsilon_{aa} > 0$ as is the case for MgCH$_3$, CdCH$_3$, ZnCH$_3$ and CaC$_5$H$_5$.\textsuperscript{3,21} An $\epsilon_{aa} < 0$ is found for an inverted spin-orbit case ($a < 0$), like in CH$_3$O.\textsuperscript{29} In all cases this assumes that the coupling is only to higher-lying $^2E$ states, but it would be surprising if
another $^2E$ perturbing state lies between the $\tilde{A}$ and $\tilde{X}$ states in CaCH$_3$. (Similar questions occur regarding the sign of $\epsilon_{be}$ in CaCH$_3$ but here the arguments are less well formed.)

From fitting the spectra, the Coriolis coupling constant, $A\zeta$, for the $\tilde{A}$ state can be determined. Since we also know the value of the rotational constant $A$, it is possible to calculate the $z$ component of the vibronic angular momentum, $\zeta_t$. The value calculated in this way was 0.86 for MgCH$_3$ as shown in Table II.

Another constant determined from the fitting is the spin-orbit splitting, $\alpha \zeta_e d$. If we assume that $\alpha$, the spin-orbit coupling constant of MgCH$_3$ is similar to that of MgH, it would be possible to determine $\zeta_e d$, the $z$ projection of the electronic orbital angular momentum. Using $\alpha = 35.3$ cm$^{-1}$ for the $A$ $^2\Pi$ state of MgH,$^{30}$ then $\zeta_e d$ would be equal to 0.81, very close to the value of $\zeta_t$ calculated above. If the Jahn-Teller quenching coefficient $d$ is $\approx 1$, then $\zeta_e \approx \zeta_t$, according to the following relationship,

$$\zeta_t = \zeta_e d + \frac{1 - d}{2} \zeta_2$$

(10)

where $\zeta_2$ is the vibrational Coriolis coupling coefficient for the Jahn-Teller active degenerate vibration mode. Such an expression was derived for an $X_3$ molecule$^{31}$ but likely holds well for the MCH$_3$ molecules, where M = Mg, Ca, Zn and Cd.

The same result ($\zeta_e \approx \zeta_t$, $d \approx 1$) was found for the other radicals, with the exception of CdCH$_3$, for which a discrepancy between those two values was encountered. As was indicated by Cerny et al.$^3$, a possible explanation for this would be that the Coriolis coupling constant has contributions from the spin-orbit interaction.

B. Jahn-Teller effect.

Attempts to fit the spectrum varying the Jahn-Teller constants ($h_1$ and $h_2$) were made, but their values were zero within the experimental error. This, in addition to the previous discussion on the values of $\zeta_t$ and $\zeta_e$, led us to conclude that the Jahn Teller interaction is negligibly small in the $\tilde{A}$ state of MgCH$_3$. The same result was found for the other three
C. Geometry

From the observed rotational constants, information about the geometry of the molecule can be obtained. For a MCH$_3$ symmetric-top molecule, three structural parameters are needed to define the geometry: the carbon-hydrogen bond length ($R_{CH}$), the metal-carbon bond length ($R_{MC}$) and the hydrogen-carbon-hydrogen angle of the methyl group ($\theta_{HCH}$). The rotational constant $A$ is a function of $R_{CH}$ and $\theta_{HCH}$ only, whereas the B constant depends on all three parameters. Since we did not have enough independent data, determination of the three parameters is not possible. Attempts to use the $^{24}$Mg and $^{26}$Mg data to independently determine structural parameters proved unsuccessful, as was the case for the isotopomers of ZnCH$_3$ and CdCH$_3$, due to lack of experimental precision. We thus fixed one of these parameters (the carbon-hydrogen bond length) at a theoretical value and then evaluated the other two structural parameters. Following the same procedure that Cerny et al. applied to ZnCH$_3$ and CdCH$_3$ (and that has been applied in some other cases), we determined $\theta_{HCH}$ from the A constant and then calculated $R_{MC}$ from the B rotational constant. The calculated bond lengths and angles obtained by this method for the ground and excited states are presented in Table II.

The change in $R_{MC}$ value, going from the ground to the excited state, has some significance. For MgCH$_3$, as well as for CaCH$_3$, the metal-carbon bond length in the $\tilde{A}$ state is longer than that in the ground state. On the other hand, a change in the opposite direction was found for ZnCH$_3$ and CdCH$_3$ as is shown in Table II. For all these methyl radicals, an increase of about 3-4° was determined for the $HCH$ angle in the $\tilde{A} \leftarrow \tilde{X}$ transition, indicating an opening of the methyl hydrogen umbrella upon excitation.

These structural changes should be viewed in terms of the expected bonding in the radicals. It is useful to consider the radicals to be derived from the corresponding dihydride or dimethyl molecules. The bonding in the ground state of these species is generally thought
to consist of promotion of the two metal s electrons to oppositely-directed, hybrid sp orbitals, each of which gives rise a single σ bond with a H or methyl group. The ground state of the radical is formed by “clipping off” one H or methyl group leaving the unpaired electron in the formerly bonding σ orbital. The excited A state results from excitation of this electron to a pπ orbital, mainly localized on the metal, giving rise to the 2E state. Using this picture, the behavior of the IIB metal methyls is easily understood. The excitation of the electron allows a partial π bond to form via hyperconjugation between the π methyl group orbital, and the metal localized π orbital. This explains both the decrease in M—CH₃ bond length and the “opening” of the methyl umbrella to facilitate the hyperconjugation.

While we believe the essential elements of this picture to be correct, it cannot be the whole story. Clearly the lengthening of the M—CH₃ bond in the A state of MgCH₃ with essentially no change for CaCH₃ requires an additional explanation. It may be that in the smaller IIA metals electronic repulsion is simply too great to tolerate significant shortening of the bond due to hyperconjugation. Correspondingly the reorganization of the hybrid orbitals upon electron excitation may sufficiently weaken the existing σ bond to result in a net lengthening of the bond, despite the effect of hyperconjugation, which still appears the best explanation for the opening of the HCH angle.

It would be useful to see if detailed ab initio calculations can reproduce the observed effects. If so, the resulting eigenfunctions can be studied to provide a chemically intuitive picture of the variation of the bonding in these radicals. Further spectroscopic studies involving deuteriation may also be useful to eliminate the necessity of assuming the C—H bond length in the determination of the experimental structures. Asymmetric deuteriation could also be used to break the degeneracy to the excited 2E state.

D. Isotopic shift

The isotopic shift observed in the origin band is particularly interesting. It was found that the origin for ²⁶MgCH₃ was to the blue of ²⁴MgCH₃ (0.18 cm⁻¹), while one might expect a
red shift for the heavier mass. The contribution to the isotopic shift is
\[ \Delta \nu = \Delta \nu_e + \Delta \nu_v \]  
(11)
where \( \Delta \nu_e \) and \( \Delta \nu_v \) correspond to the electronic and vibrational isotopic shifts respectively. The vibrational isotope shift arises from the difference in the zero-point energies of the Mg-dependent modes, i.e.
\[ \Delta \nu_v = (4\pi)^{-1} \sum_i \left\{ \left[ \left( \frac{\mu_i^{24}}{\mu_i^{26}} \right)^{1/2} \left( \left( k_i''' \right)^{1/2} - \left( k_i'' \right)^{1/2} \right) \right] - \left[ \left( \frac{\mu_i^{26}}{\mu_i^{24}} \right)^{1/2} \left( \left( k_i' \right)^{1/2} - \left( k_i''' \right)^{1/2} \right) \right] \right\} \]  
(12)
where \( \mu_i^{24} \) and \( \mu_i^{26} \) are the appropriate reduced masses for the \( i^{th} \) mode of the \( ^{24}\text{Mg} \) and \( ^{26}\text{Mg} \) containing species, and \( k_i' \) and \( k_i'' \) are the excited and ground state force constants. The quantity containing the reduced masses is clearly positive. Typically the ground state force constant exceeds that of the excited state causing \( \Delta \nu_v \) to be negative. As can be seen from Table II the increased Mg—CH\(_3\) bond length in the \( \tilde{A} \) state is consistent with \( k_i'' > k_i' \), hence we would expect \( \Delta \nu_v \) to be negative for MgCH\(_3\), as usual.

Usually the contribution of the electronic term is negligible. However, a small electronic isotope shift has been found in some molecules, which can be either to the red or to the blue for the lighter isotope. Thus we conclude that either the electronic contribution, \( \Delta \nu_e \), dominates \( \Delta \nu \) or the force constants describing the Mg motion are quite unusual.

6. CONCLUSIONS

The rotationally resolved spectrum of the \( 0^0_0 \) band of the \( \tilde{A}^2E \leftrightarrow \tilde{X}^2A_1 \) electronic transition of MgCH\(_3\) radical has been analyzed. The calculated molecular constants from the simulated spectra allow us to propose a geometrical structure for this radical in both the ground and the first excited electronic states. A comparison with other alkyl organometallic radicals (MCH\(_3\), M= Ca, Cd and Zn) is also made, both in terms of spectroscopic constants and molecular geometries.
7. ACKNOWLEDGMENTS

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28. G. Gawboy (private communication).


### Table 1. Molecular Constants of MgCH$_3$.\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>$^{24}$MgCH$_3$</th>
<th>$^{26}$MgCH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>156.544</td>
<td>156.544</td>
</tr>
<tr>
<td>X $^2A_1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>11.0054 (23)</td>
<td>10.6901 (38)</td>
</tr>
<tr>
<td>$\epsilon_{bc}$</td>
<td>0.0518 (60)</td>
<td>0.0409 (98)</td>
</tr>
<tr>
<td>A</td>
<td>149.666 (17)</td>
<td>149.642 (24)</td>
</tr>
<tr>
<td>B</td>
<td>10.9324 (20)</td>
<td>10.6247 (37)</td>
</tr>
<tr>
<td>$a\zeta_e d$ (cm$^{-1}$)</td>
<td>28.5911 (12)</td>
<td>28.5908 (18)</td>
</tr>
<tr>
<td>$\tilde{A}^2E$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_D\zeta_e d$</td>
<td>- 0.152 (34)</td>
<td>- 0.184 (49)</td>
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<tr>
<td>A$\zeta_t$</td>
<td>129.262 (18)</td>
<td>129.249 (25)</td>
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<tr>
<td>$\epsilon_{aa}$</td>
<td>6.056 (71)</td>
<td>6.02 (10)</td>
</tr>
<tr>
<td>$\epsilon_{bc}$</td>
<td>- 0.118 (88)</td>
<td>-0.11 (21)</td>
</tr>
<tr>
<td>$T_{00}$ (cm$^{-1}$)\textsuperscript{c}</td>
<td>20030.2963 (16)</td>
<td>20030.4770 (37)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}In GHz unless otherwise specified. Numbers in parenthesis indicate one standard deviation.

\textsuperscript{b}Fixed at a theoretical value from Ref. 28.

\textsuperscript{c}The indicated error is statistical only and does not include the uncertainty in absolute frequency calibration of 0.01 cm$^{-1}$.
Table 2. Molecular constants and structural parameters of MCH$_3$ radicals.$^{ab}$

<table>
<thead>
<tr>
<th></th>
<th>$^{24}$MgCH$_3$</th>
<th>CaCH$_3^c$</th>
<th>$^{64}$ZnCH$_3^d$</th>
<th>$^{114}$CdCH$_3^d$</th>
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<tr>
<td>A</td>
<td>156.544$^e$</td>
<td>163.3362 (19)</td>
<td>154.500$^f$</td>
<td>154.598 (49)</td>
</tr>
<tr>
<td>B</td>
<td>11.0054 (23)</td>
<td>7.566042 (66)</td>
<td>9.2864 (60)</td>
<td>7.0166 (50)</td>
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<tr>
<td>$\tilde{X}^2A_1$</td>
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<td>$\epsilon_{bc}$</td>
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<td>0.05462 (13)</td>
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<td>$R_{CH}^g$</td>
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<td>1.100 (20)</td>
<td>1.105$^f$</td>
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<td>$R_{CM}^g$</td>
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<td>2.349 (13)</td>
<td>2.001 (7)</td>
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<td>$\theta_{HCH}^h$</td>
<td>108.163 (12)</td>
<td>105.6 (28)</td>
<td>109.21$^f$</td>
<td>109.18 (150)</td>
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<table>
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<th></th>
<th>A</th>
<th>B</th>
<th>$a\zeta_e d$ (cm$^{-1}$)</th>
<th>$a_D\zeta_e d$</th>
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<td>161.4125 (19)</td>
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<td>81.82 (17)</td>
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<td>0.97613 (13)</td>
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<tr>
<td>$R_{CH}^g$</td>
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<td>1.100 (20)</td>
<td>1.105$^f$</td>
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<td>$R_{CM}^g$</td>
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<td>1.991 (9)</td>
<td>2.184 (8)</td>
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<td>$\theta_{HCH}^h$</td>
<td>111.84 (55)</td>
<td>109.2 (30)</td>
<td>112.56 (150)</td>
<td>112.26 (160)</td>
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$\Delta R_{CM}^g$ $\Delta \theta_{HCH}^h$

|                  | 0.022 (6)       | 0.004 (19)   | -0.010 (11)             | -0.037 (10)   |
|                  | 3.68 (55)       | 3.6 (41)     | 3.35 (150)              | 3.08 (219)    |

$^a$All molecular constants are expressed in GHz, except where otherwise indicated.

$^b$Numbers in parentheses indicate one standard deviation. For the structural parameters ($R_{CM}$ and $\theta_{HCH}$), the uncertainty was calculated by propagation of errors.

$^c$Ref. 2.

$^d$Ref. 3.
Fixed at a theoretical value from Ref. 28.

Fixed, see Ref. 3.

Units are Å.

Units are degrees.
Fig. 1. Experimental and simulated spectra for the $^2E_{1/2} \leftrightarrow ^2A_1$, $0^0_0 (F'_1)$ band of MgCH$_3$. The rotational temperature of the simulated spectrum is 3 K. The peak marked with an asterisk corresponds to a (0,0) rotational transition of MgO. There is considerable variation between the predicted and observed intensities primarily because of both long and short term variation in the MgCH$_3$ production.

Fig. 2. Experimental and simulated spectra for the $^2E_{3/2} \leftrightarrow ^2A_1$, $0^0_0 (F'_2)$ band of MgCH$_3$. The rotational temperature of the simulated spectrum is 3 K. Peaks marked with asterisks correspond to the (1,1) rotational transitions of MgO. There is considerable variation between the predicted and observed intensities primarily because of both long and short term variation in the MgCH$_3$ production.

Fig. 3. Experimental trace of the $^2E_{1/2} \leftrightarrow ^2A_1$ $0^0_0 (F'_1)$ band of MgCH$_3$. Below the experimental spectrum, a stick spectrum is displayed showing the P, Q and R branches originating from the populated $K''$ levels.

Fig. 4. An enlargement of a region of the $^2E_{3/2} \leftrightarrow ^2A_1$ $0^0_0 (F'_2)$ band showing transitions observed for both $^{24}$MgCH$_3$ and $^{26}$MgCH$_3$. 

FIGURES