

Observation of gas phase organometallic free radicals: Monomethyl derivatives of calcium and strontium

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We have observed the organometallic free radicals CaCH_3 and SrCH_3 by the gas phase reaction of Ca or Sr metal vapor with $\text{Hg}(\text{CH}_3)_2$ and several other CH_3 containing oxidants. The positions of the $\tilde{A}^2E-\tilde{X}^2A_1$ and $\tilde{B}^2A_1-\tilde{X}^2A_1$ transitions were determined, as well as several vibrational frequencies. The observation of predissociation in the \tilde{A}^2E state gives an upper limit of 46 kcal/mol (43 kcal/mol) to the bond dissociation energy for CaCH_3 (SrCH_3).

I. INTRODUCTION

Alkyl derivatives of the alkaline earth metals have been known for a very long time. Species of the form RMgX ($X = \text{halide}$) were first prepared by Grignard¹ in 1900 and have since come to be known by his name. Comparatively little research has been performed on the corresponding calcium and strontium species, mainly due to difficulties in preparation.² The use of high purity metal has been found to yield reasonable quantities of the calcium alkyl halides^{3,4} and alkyl strontium iodides have also been produced and isolated.⁵ The organometallic species $\text{M}(\text{CH}_3)_2$ with M an alkaline earth element are easily prepared for both Be and Mg. These solids are found to be chain-like species with the metal atoms linked by bridging methyl groups.⁶ Attempts to produce the analogous calcium and strontium species have proved much more difficult. The first preparation of $\text{Ca}(\text{CH}_3)_2$ and $\text{Sr}(\text{CH}_3)_2$ was reported by Payne and Sanderson⁷ in 1958, but it proved impossible to reproduce their results.⁸ More recently, $\text{Ca}(\text{CH}_3)_2$ and $\text{Sr}(\text{CH}_3)_2$ have been produced from dimethyl mercury and either calcium or strontium.^{9,10} Species of this form have been used as catalysts for ionic polymerization.¹¹

Very few monomethyl species have been observed, and only for the alkali metals are they common. These species are often found in the form of tetramers; for example, the well-known $(\text{LiCH}_3)_4$, which has a tetrahedral arrangement of lithium atoms with a methyl group on each face.¹² This is also the structure of methyl sodium.¹³ Several methyl derivatives of the transition metals have been produced by the matrix isolation technique. Studies of the series of metals calcium through zinc show that Mn, Fe, Co, Cu, and Zn react with methane, while Ca, Ti, Cr, and Ni do not.¹⁴ Reaction of the metals listed above with methane in a pure methane matrix yielded the species HMCH_3 via insertion into the C-H bond. Specific studies of Fe^{15,16} show that this is the only product, while Cu^{17,18} is found to yield copper hydride and methyl copper by photolysis of the initial insertion product. Magnesium is also found to react yielding methyl magnesium hydride when the $^1P-^1S$ transition of Mg is excited.¹⁹

We have produced the species methyl calcium and methyl strontium in the gas phase by reacting a variety of oxidants with calcium or strontium vapor. In all cases, the reaction only proceeded when the $^3P_1-^1S_0$ line of the metal

atoms was excited. Our first observation of methyl calcium was made using azomethane CH_3NNCH_3 , but it was subsequently found that much higher yields could be obtained from the reaction with dimethyl mercury, trimethyl aluminum, or tetramethyl silane. In all cases, significant quantities of the monohydrides, CaH and SrH, were also produced. It is quite likely that the dimethyl, dihydride, or methyl hydride derivatives were also present, but as these do not have electronic transitions in the visible spectral region, they could not be detected by the laser-induced fluorescence technique used in these experiments.

This paper forms part of a continuing series of studies on alkaline earth-containing free radicals. The series began with the monoalkoxide compounds,^{20,21} and has since been extended to hydrocarbon derivatives such as the monocyclopentadienides²² and monoacetylides.²³ Additional derivatives include monocyanates,²⁴ monoalkylamides,²⁵ and monoazides.²⁶

II. EXPERIMENTAL

Methyl calcium and methyl strontium were produced in a Broida-type oven²⁷ by the reaction of metal vapor with a methyl-containing species. The solid metal was resistively heated in an alumina crucible and the vapor entrained in a flow of argon carrier gas. The pressure of argon was typically 1 Torr and a few mTorr of oxidant was added. There was no observable reaction between the ground state metal atoms and any of the oxidants used. However, when the atoms were excited to their 3P_1 states, some reaction was found in all cases. The initial experiments were carried out using calcium and azomethane, CH_3NNCH_3 , prepared from 1,2-dimethylhydrazine using the procedure described by Foster and Beauchamp.²⁸ A weak spectrum, tentatively assigned to CaCH_3 was obtained. In order to improve the signal, other oxidants were considered. It was found that dimethyl mercury yielded about two orders of magnitude more signal. Trimethylaluminum and tetramethylsilane were also used but although these yielded somewhat less signal, they were used for most of the experiments due to the high toxicity of dimethylmercury.

Two broadband dye lasers (1 cm^{-1} bandwidth) operated with either DCM or pyridine 2 dyes were used. Both la-

sers were pumped with either 6 W all lines or 6 W of the appropriate single line from Coherent Innova 90-4 or Innova 20 argon ion lasers. Typical output powers were from 200–1000 mW. The two beams were spatially overlapped and weakly focused into the “flame” (no chemiluminescence was observed). One beam was always tuned to the metal $^3P_1-^1S_0$ atomic line. The other was either scanned to obtain a laser excitation spectrum by recording the emission through a red pass filter to block scattered laser light, or tuned to a specific molecular absorption. The emission was then focused onto the slits of a 0.64 m monochromator and the dispersed fluorescence spectrum recorded using a cooled photomultiplier tube (RCA C31034) and photon counting electronics.

III. RESULTS

The spectrum of CaCH_3 recorded by scanning the laser and recording the total fluorescence through a red pass filter (Schott Glass RG9) is shown in Fig. 1. The ground state of CaCH_3 , by analogy with the previously observed halides,²⁹ CaOH ,^{30–32} and CaOCH_3 ,^{33,21} is 2A_1 , arising from a closed shell ionic core $\text{Ca}^{2+} \text{CH}_3^-$ with one additional unpaired electron in a $4s$ metal-centered orbital, polarized away from the ligand by mixing in some $4p$ character. The low-lying excited states arise from promoting this nonbonding elec-

tron to mixed $4p-3d$ hybrid orbitals. This results in the $\tilde{A}^2\Pi$ and $\tilde{B}^2\Sigma^+$ states for linear ligands which correlate with \tilde{A}^2E and \tilde{B}^2A_1 in the C_{3v} symmetry of CaCH_3 . There is a good discussion of the electronic states of the calcium monohalides by Rice, Martin, and Field³⁴ from a ligand field perspective. As the unpaired electron is centered on the metal, little quenching of the orbital angular momentum in the 2E state by the off-axis hydrogens is expected and thus there should be a spin-orbit splitting of about 66 cm^{-1} similar to CaOH .^{30,32}

At first sight the spectrum shown in Fig. 1 does not appear to match this prediction. The strong band at 6240 \AA could be the $^2A_1-^2A_1$ transition and the doublet at 6330 \AA , split by 75 cm^{-1} the $^2E-^2A_1$ transition. This, however, leaves the strong sequence of five peaks running from $6670-6800 \text{ \AA}$ unassigned. Initially, this was thought to be due to a new 2E state correlating with the $^2\Delta$ state for a linear molecule, which arises from the $(3d)^1$ configuration of Ca^+ . The $^2\Delta-\tilde{X}^2\Sigma^+$ transition is forbidden for a linear molecule and the $^2\Delta$ state has only been located in the BaCl ³⁵ molecule.

Observation of the corresponding SrCH_3 (see Fig. 2) makes the correct assignment for CaCH_3 clear. The spin-orbit splitting in the \tilde{A}^2E state of SrCH_3 is much larger, 273 cm^{-1} (cf 263 cm^{-1} for $\tilde{A}^2\Pi$ state of SrOH ³⁶), and the two sets of vibrational sequence bands are widely separated. The transition to each spin-orbit component consists of a series of bandheads separated by about 65 cm^{-1} . These are sequence bands in the Sr–C–H bending mode. A similar pattern is present in the bands of CaCH_3 between 6700 and 6800 \AA , except that in this case the second band to the blue is much stronger than the first. Due to the fact that the sequence spacing and spin-orbit splitting are almost identical, the 1–1 band of the $\tilde{A}^2E_{1/2}-\tilde{X}^2A_1$ component lies at essentially the same position as the 0–0 band of the $\tilde{A}^2E_{3/2}-\tilde{X}^2A_1$ component for CaCH_3 (Fig. 1).

The ground state vibrational frequencies were determined by exciting individual peaks and resolving the laser-induced fluorescence through a monochromator. The spectrum obtained for CaCH_3 when the 0–0 band of the $\tilde{A}^2E_{1/2}-\tilde{X}^2A_1$ component is excited is shown in Fig. 3. CaCH_3 has six vibrational modes: three of a_1 symmetry (ν_1

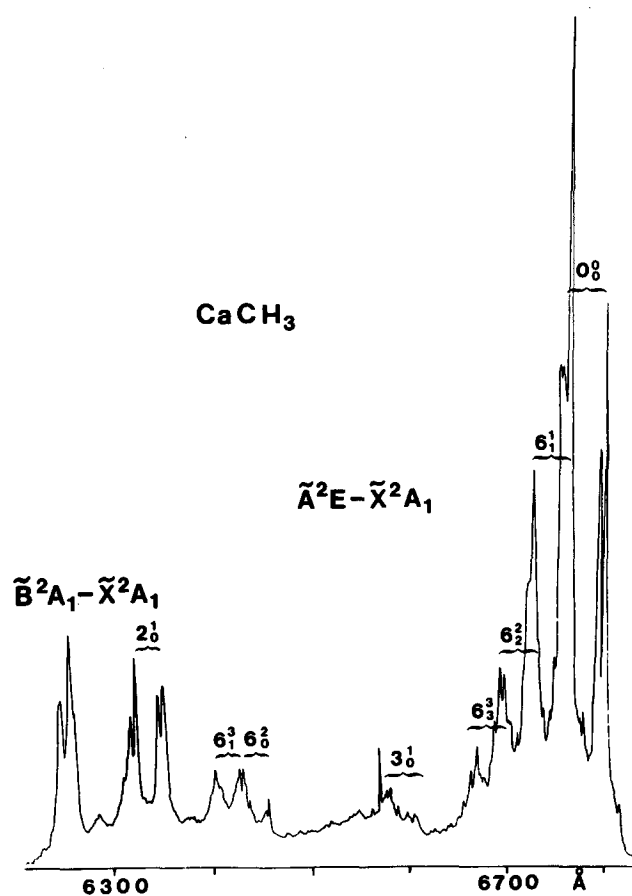


FIG. 1. The $\tilde{A}^2E-\tilde{X}^2A_1$ and $\tilde{B}^2A_1-\tilde{X}^2A_1$ systems of CaCH_3 obtained by scanning the laser and detecting through a red pass filter. The relative intensity of the $\tilde{A}-\tilde{X}$ and $\tilde{B}-\tilde{X}$ systems is distorted by the filter.

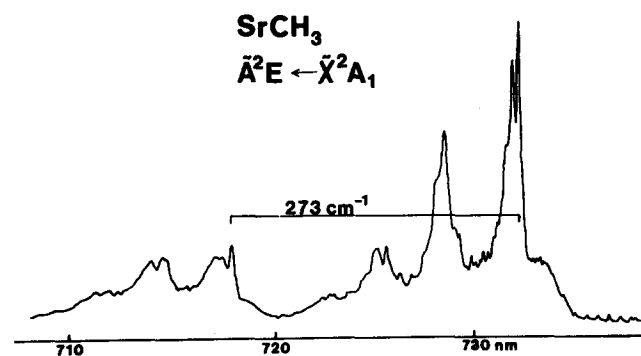


FIG. 2. The $\tilde{A}^2E-\tilde{X}^2A_1$ system of SrCH_3 showing the spin-orbit splitting and the sequence structure due to activity in ν_6 . The $^2E_{3/2}$ component has about the same intensity, but this is distorted by the use of a red pass filter to detect the laser-induced fluorescence.

the symmetric C–H stretch, ν_2 the symmetric H–C–H bend, and ν_3 the Ca–C stretch) and three of e symmetry (ν_4 the asymmetric C–H stretch, ν_5 the asymmetric H–C–H bend, and ν_6 the Ca–C–H bend). Three of these (ν_2 , ν_3 , and ν_6) are seen in the resolved fluorescence spectrum (Fig. 3). The bending mode ν_6 is of e symmetry, and hence is seen only in bands with two quanta, e.g., 6_2^0 . In addition, several weaker bands such as 3_2^0 and combinations such as $2_1^0 6_2^0$ are observed. Each of the strong bands in Fig. 3 has a weak satellite 75 cm^{-1} to lower energy due to collisional relaxation between the spin-orbit components $\tilde{A}^2 E_{3/2}$ and $\tilde{A}^2 E_{1/2}$.

The additional peaks in Fig. 1 can now be assigned as sequence bands and progressions in the same three vibrations and these assignments are indicated in the figure. The vibrational bands to the blue of the $\Delta v = 0$ sequence each contain only two or three peaks, rather than the five seen in the diagonal transition near 6800 Å. This was one of the main reasons for the initial confusion over the assignment. The only reasonable interpretation for the loss of sequence structure is a predissociation in the excited state about 1000 cm^{-1} above the $v = 0$ level. This will be discussed in more detail later in relation to the estimated upper limit to the dissociation energy of the ground state.

The band origins and observed vibrational frequencies are listed in Tables I and II, respectively. The assignment of the 6_2^0 band is confirmed by the difference of 144 cm^{-1} (127 cm^{-1} for SrCH_3) between the 6_2^0 and 6_2^2 bands approximately the same as the separation of the first and third sequence band peaks (6_0^0 and 6_2^2) of 153 cm^{-1} (127 cm^{-1} for SrCH_3).

IV. DISCUSSION

A. Bond dissociation energy

The observation of predissociation in the $\tilde{A}^2 E$ state of both CaCH_3 and SrCH_3 permits the determination of an

TABLE I. Band origins for CaCH_3 and SrCH_3 (in cm^{-1}).

Transition	CaCH_3	SrCH_3
$\tilde{A}^2 E_{1/2} - \tilde{X}^2 A_1$	14 700 ^a	13 653
$\tilde{A}^2 E_{3/2} - \tilde{X}^2 A_1$	14 779	13 962
$\tilde{B}^2 A_1 - \tilde{X}^2 A_1$	16 003	14 777

^a Estimated errors are $\pm 10 \text{ cm}^{-1}$.

upper bound for the ground state bond dissociation energy. The ground $\tilde{X}^2 A_1$ state correlates with the lowest dissociation limit $\text{Ca} (^1S) + \text{CH}_3 (^2A_1 \text{ in } C_{3v} \text{ symmetry, } ^2A_2'' \text{ in } D_{3h})$. The $\tilde{A}^2 E$ and $\tilde{B}^2 A_1$ states both correlate to $\text{Ca} (^3P) + \text{CH}_3 (^2A_1)$ which lies about 15 200 cm^{-1} ³⁷ above the lowest dissociation limit. Two quartet states, 4E and 4A_1 , also arise from this limit but are expected to be repulsive and they will not be discussed further.

At long range, the 2E and 2A_1 states are also likely to be repulsive and only become bonding when they cross over to the strongly bonding ionic potential curves. (See Herzberg³⁸ for a discussion of the diatomic case.) While no *ab initio* theoretical calculations are available for CaCH_3 (or SrCH_3), calculations have been performed for monomeric methyl lithium by Streitwieser *et al.*³⁹ They found that there was essentially no covalent contribution to the bonding in the $\tilde{X}^2 A_1$ state of LiCH_3 . The total charge transfer was found to be about 0.8 of an electron from Li to CH_3 with the remaining contribution to the ground state coming from a nonbonding radical pair configuration with essentially no overlap between Li and CH_3 . The bonding for Ca and Sr is likely to be very similar, particularly in view of the nearly identical electronegativities (Li = 0.98, Ca = 1.00, Sr = 0.95; Pauling's values) for the three metals.

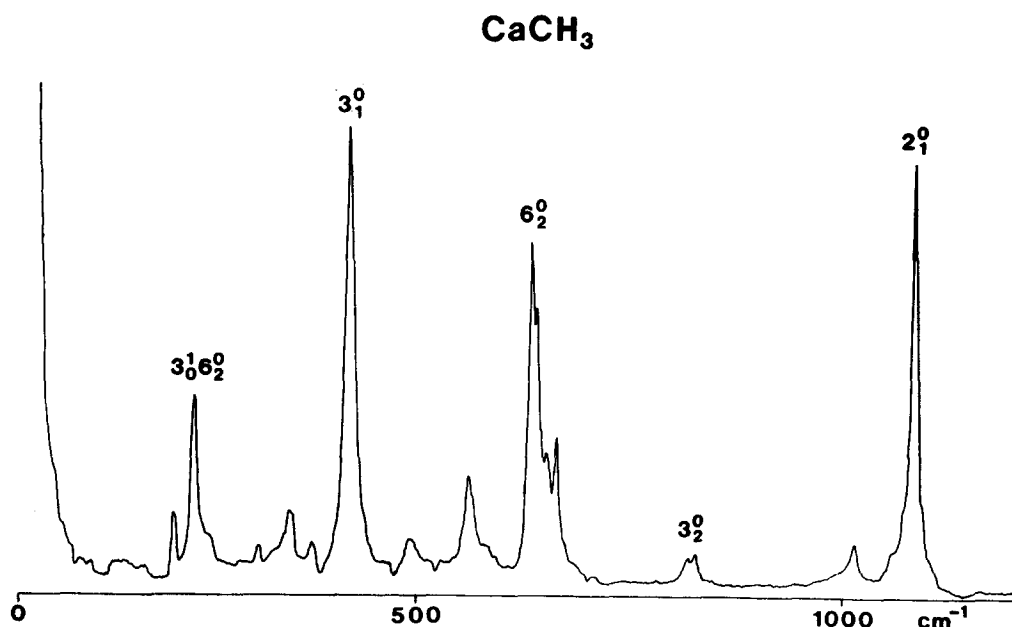


FIG. 3. Resolved fluorescence spectrum for CaCH_3 . The laser is exciting the 0_0^0 band of the $\tilde{A}^2 E_{1/2} - \tilde{X}^2 A_1$ component at 6800 Å, and this point is marked as zero on the x axis. Fluorescence to several excited vibrational levels of the ground state can be seen. The weak bands about 75 cm^{-1} lower in energy from each strong peak are due to collisional relaxation to the $^2 E_{3/2}$ spin-orbit component in the excited state.

TABLE II. Observed vibrational frequencies for CaCH₃ and SrCH₃ (in cm⁻¹).

CaCH ₃		
Mode	\tilde{X}^2A_1	\tilde{A}^2E
ν_2	1085 ^a	1048
ν_3	419	413
$2\nu_3$	834	...
$2\nu_6$	637	781
SrCH ₃		
Mode	\tilde{X}^2A_1	\tilde{A}^2E
ν_2	1072	1054
ν_3	362	373
$2\nu_3$	721	...
$2\nu_6$	557	684
$\nu_2 + \nu_3$	1438	...
$\nu_2 + 2\nu_6$	1625	...

^a Estimated errors are ± 5 – 10 cm⁻¹.

The ionic ground state of CaCH₃ dissociates to Ca⁺ (²S) + CH₃⁻ (¹A₁). This limit is widely separated from the covalent dissociation limit. The ionization potential of Ca is 49 300 cm⁻¹,³⁷ while the electron affinity of CH₃ is only 600 cm⁻¹⁴⁰ leading to a separation of 48 700 cm⁻¹. There will be an avoided crossing between the strongly bound ionic curve and the repulsive covalent curve leading to the ground \tilde{X}^2A_1 state.³⁸ Unfortunately, the picture is far more complicated than this as there are a large number of covalent dissociation limits between the ground state limit and the first ionic one. The ionic curve can interact with many of these and in particular the first excited ²A₁ state is likely to have a strong interaction. Theoretical calculations⁴¹ for CaH predict that the B ²Σ⁺ state has a double minimum which results from an avoided crossing.

Unfortunately, similar theoretical calculations are not available for CaCH₃, but it is not unreasonable to expect a similar type of double minimum curve for the \tilde{B}^2A_1 state. This state must have a normal bound inner well situated almost directly above the ground state as the \tilde{B} – \tilde{X} transition is seen in the laser excitation scans and all of the off-diagonal vibrational transitions are found to have small Franck–Condon factors. The outer well results from the avoided crossing and must lie above the ground state asymptote.

We observe a loss of fluorescent emission from levels more than 1500 cm⁻¹ above the $\nu = 0$ level in the \tilde{A}^2E state of CaCH₃. It does not appear to matter which vibrational mode is excited, all three observed vibrations ν_2 , ν_3 , and ν_6 show the same effect. However, in each case at least one quantum of the Ca–C–H bend ν_6 is excited. This excitation of an *e* symmetry vibration is necessary for a ²E state to interact with a ²A₁ state and for predissociation to occur.

After transferring to the outer well of the \tilde{B}^2A_1 state, the molecule can either transfer to the dissociative part of ground state potential or it may emit at long wavelength down to the bound upper part of the ground state potential. In either case, no fluorescent emission will be observed.

The observed cutoff in emission gives an upper limit for the ground state bond dissociation energy of 16 200 cm⁻¹

(45 kcal/mol). This is considerably less than that for known isoelectronic species CaF⁴² ($D_0^\circ = 124$ kcal/mol) and CaOH⁴³ ($D_0^\circ = 92$ kcal/mol). However, both F and OH have large electron affinities, while CH₃ does not. In comparison, the calculated dissociation energy for LiCH₃ is 24 kcal/mol. The actual dissociation energy for CaCH₃ is probably similar to the value for LiCH₃.

A similar predissociation was observed for SrCH₃, although in this case it was not immediately obvious because the excited state vibrational progressions were much weaker. However, comparison of the emission observed when various vibronic bands were excited proved helpful. For example, excitation of the 6_2^2 band yielded emission from the $\nu_6' = 3$ level due to vibrational energy transfer, while no emission from $\nu_6' = 4$ was observed when the 6_3^3 band was excited. These experiments indicate a loss of fluorescence from the excited state at about 1400 cm⁻¹ above the $\nu = 0$ level, giving an upper limit to the ground state bond dissociation energy of 15 000 cm⁻¹ (43 kcal/mol).

Excited state Ca (and Sr) atoms were found to react with several different methyl-containing oxidants {(CH₃)₂Hg, [(CH₃)₃Al]₂, (CH₃)₄Si, (CH₃)₂N₂}. In no case was a detectable amount of product formed without excitation of the metal atoms. It should be possible to determine the bond dissociation energy from the reaction behavior with different oxidants by a bracketing procedure. However, our oven source operates under multiple collision conditions, making any such determination extremely speculative. Even the excitation energy of the metal atoms is not clear as strong ¹P–¹S emission is observed, indicating significant amounts of ¹P Ca atoms are collisionally produced from ³P₁ Ca. A study of these reactions under single collision conditions using molecular beam techniques could provide an accurate value for the bond dissociation energy. The ion beam methods of Armentrout and co-workers⁴⁴ could also provide an accurate estimate of the dissociation energy.

B. Vibrational structure

There are three active vibrational modes in the spectrum, and two of these involve metal atom motion (ν_3 M–C stretch and ν_6 the M–C–H bend). This is expected because the electronic transition is centered on the metal and hence only those modes associated with the metal are likely to have good Franck–Condon factors. In addition, ν_2 the CH₃ symmetric deformation also appears strongly, as can be seen in Fig. 3. The relative strength of this band may indicate a slight change in the H–C–H bond angle between the ground and excited states.

The Ca–C stretching frequency ($\nu_3 = 419$ cm⁻¹) is substantially less than the Ca–O stretch (606 cm⁻¹) in the heavier isoelectronic CaOH molecule.³⁰ This is indicative of a much weaker bond in the methyl species than the hydroxides. A pseudodiatomic force constant can be evaluated if the ligands are treated as single units. This gives $k = 113$ Nm⁻¹ for CaCH₃ compared with 258 Nm⁻¹ for CaOH. Similar results are obtained for the Sr species. This is consistent with the substantially lower bond dissociation energy determined earlier.

The symmetrical deformation frequency of the CH_3 group has been found to show a consistent variation with the electronegativity of the atom bonded to the carbon.⁴⁵ Each row of the Periodic Table gives rise to a separate correlation, all of them running approximately parallel. More recently, these trends have been extended to the group I and II species, where it was found that the trend is better represented by a curve than a straight line.⁴⁶ If the curves for the third and fourth rows of the Periodic Table are assumed to run parallel to that of the first, then the symmetric methyl deformation frequencies of CaCH_3 and SrCH_3 are predicted to be 1080 and 1040 cm^{-1} , respectively, in reasonable agreement with the observed values of 1085 and 1072 cm^{-1} .

V. CONCLUSION

The organometallic free radicals CaCH_3 and SrCH_3 were found to be produced in the reaction of the metal vapors with a variety of methyl-containing oxidants. These species have C_{3v} symmetry. A full determination of the structure of CaCH_3 by observation of the $\tilde{A}^2E-\tilde{X}^2A_1$ transition at rotational resolution is currently in progress.

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