# Synthesis of CH₃K in the Gas Phase: Structural and Mechanistic Trends for Monomeric, Unsolvated CH₃M and HCCM (M = Li, Na, K)

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**Abstract:** Monomeric, solvent-free $CH_3K$ has been made in the gas phase and its precise structure determined by millimeter/submillimeter spectroscopy, from which the following parameters were deduced: C−K and C−H bond lengths are 2.633 and 1.135 Å, respectively, and the H−C−H angle is 107.0°. The structure completes a series with those reported for $CH_3Na$ and $CH_3Li$, showing the expected decrease in metal−carbon bond length (2.633 to 2.299 to 1.961 Å) ascending the periodic table, but little change in the H−C−H bond angles, which are all near 107°. The latter observation on these simple *monomeric* species clearly differs from the range of 104.8−108.2° reported for *oligomeric* $CH_3M$ samples in the solid phase, which feature several metal−carbon contacts, showing the importance of measurements on monomeric species. Synthetic details for the methyl compounds and HCCM (M = Li, Na, K) are also discussed. Preparation of HCCLi from HCCBr and Li vapor produced LiBr but possible intermediate radical HCC• was not detected, suggesting synchronous reduction of the C−Br bond. The linear structure of HCCM is contrasted with nonlinear structures of LiCCLi (predicted theoretically), NaCN, and KCN, using Coulombic arguments to explain the different molecular geometries.

## Introduction

When the synthetic chemist thinks of the strongest bases at his or her disposal, usually organolithium or other organoalkali reagents come to mind.[1−6] Organoalkali compounds are extremely versatile bases used to make many other bases by deprotonation reactions. Moreover, organoalkali derivatives are excellent nucleophiles, capable of displacing leaving groups on carbon, heteroatoms, and metals. The results of such displacements are the introduction of organic groups and the synthesis of more complex organic and organometallic compounds.

The rate and outcome of many of these reactions depends on the precise structure of the organoalkali compound under the conditions employed. The great difference in electronegativity between carbon and alkali metal typically results in oligomerization of organoalkalis through multicenter bonding. The degree of oligomerization depends on the organic group,

the solvent, and other coligand(s) present. From existing crystal structure data, it is clear that decreasing oligomerization leads to shortening of the metal−carbon bond length.[4,7,8] Although theoretical calculations have been used to predict important structural parameters such as the metal−carbon bond length and bond angles around the metalated carbon, most calculations have treated simple monomeric compounds[9−16] (for exceptions, see refs 14 and 17) without other coligands such as solvent. One major goal of our work reported here is to produce precise structural information on simple organoalkalis in the absence of the complicating influences of oligomerization or solvation, so that direct comparisons can be made between high-level theoretical calculations and experimental results.

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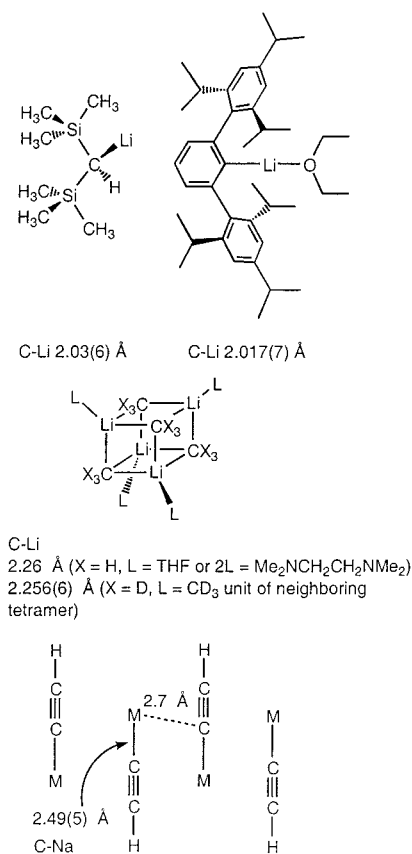
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**Scheme 1**



C-Li 2.03(6) Å         C-Li 2.017(7) Å

C-Li
2.26 Å (X = H, L = THF or 2L = Me₂NCH₂CH₂NMe₂)
2.256(6) Å (X = D, L = CD₃ unit of neighboring
tetramer)

2.7 Å

2.49(5) Å

C-Na

These direct comparisons have been difficult because of the extreme tendency for organoalkalis to oligomerize, a general property which manifests itself in several ways. For example, very large or electronically perturbing substituents have been required to produce monomeric organolithiums. In a series of elegant studies, Power and co-workers have crystallographically characterized monomeric aryllithiums in which the metalated carbon is flanked by large isopropyl or aryl substituents.[18−20] Similarly, $LiCH(SiMe_3)_2$ was prepared and although it is oligomeric in the solid state, when vaporized it becomes monomeric, and its precise structure could be determined using gas-phase electron diffraction.[21] Scheme 1 shows the metal−carbon bond lengths observed in these compounds. The use of bulky groups to block oligomerization probably will be successful only with alkyl and aryl (or vinyl) derivatives, because in alkynyl alkalis R−CC−M, the terminal R group is further removed from the metal center.

As for smaller, simpler organoalkalis such as the parent compounds $CH_3M$, solvent-free tetramers have been characterized by X-ray diffraction.[22−27] For the lithium derivative

(Scheme 1), the C−Li bond length is ∼2.26 Å, but this parameter and H−C−H bond angle data are sensitive to temperature[26] because of changes in interactions between the components of the tetramer and even between tetramers. These behaviors show the difficulty of using condensed-phase data to get an accurate picture of inherent structural trends in $CH_3M$ as a function of the position of M in the periodic table. Solvated tetramers, two examples[28,29] of which are shown in Scheme 1, have also been characterized. Remarkably, attempts to vaporize monomeric $CH_3Li$ or $CH_3CH_2Li$ from the tetramers have failed, instead producing ions such as $[CH_3Li_2]^+$.[30] As far as we are aware, the only way in which monomeric, solvent-free organoalkalis have been made is by the reaction of alkali metal with methyl radicals at 20 K in an argon matrix.[31,32] Under these conditions, the resulting simple methylalkalis could be characterized by infrared spectroscopy, which when combined with assumptions about the matrix shift led to an estimation of 2.1 Å for the C−Li bond length.[31] Finally, solvent-free HCCLi is unknown even in an oligomeric form, but the Na and K analogues have been shown from powder diffraction data to exist as sheet structures (Scheme 1).[33]

In contrast, we have synthesized the title organoalkalis $CH_3M$ and HCCM in the gas phase and determined their structures by millimeter-wave spectroscopy, which yields precision equal to or greater than that obtainable with X-ray diffraction, without the effects of sterically and electronically perturbing substituents.[34] Here, we complete the series of methyl derivatives with the synthesis of $CH_3K$ and its deuterium and ⁴¹K isotopomers and the measurement of their pure rotational spectra. From these data, the structure of $CH_3K$ has been determined and compared with those of $CH_3Li$ and $CH_3Na$, data which show a trend different from that found for oligomeric samples in the solid phase, where multiple metal−carbon contacts complicate the picture. The precise structural data reported allow the first direct comparison of theoretical and experimental data for the six title compounds, the simplest organoalkalis of Li, Na, and K in their monomeric, unsolvated form. In this paper, these experimental results are compared with structures of related molecules, such as LiCCLi and metal cyanides. We also discuss the mechanism of organoalkali formation and comparison to solution-phase chemistry.

## Experimental Section

**General Information.** The millimeter/submillimeter direct absorption spectrometer used to carry out the measurements has been described in detail.[35] The instrument consists of three basic components: a Gunn oscillator/varacter multiplier source, a reaction cell containing a Broida-type oven, and an InSb hot electron bolometer detector. The Gunn oscillator is phase-locked to a 2 GHz synthesizer and serves as the fundamental frequency source (65−140 GHz). Various multipliers are used to double, triple, and quadruple the Gunn frequency to achieve an overall operating range of 65−530 GHz. Spectra are obtained by

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**Table 1.** Summary of Synthetic Technique

| | precursor, method (strength of signals obtained) | | |
| --- | --- | --- | --- |
| molecule | hydrocarbon | haloalkane | (CH$_3$)$_2$Hg or (CH$_3$)$_4$Sn |
| CH$_3$Li | CH$_4$ with dc discharge[a] (weak) | CH$_3$I, no discharge (strong) | either, no discharge (strong) |
| CH$_3$Na | CH$_4$ with dc discharge[a] (weak) | not attempted | either, with dc discharge[a] (strong) |
| CH$_3$K | not attempted | CH$_3$I, with dc discharge[a,b] (strong) | either, with dc discharge[a] (strong) |
| HCCLi | HCCH with dc discharge[c] (strong) | HCCBr, no discharge (very strong) | |
| HCCNa | HCCH with dc discharge[a] (strong) | HCCBr, no discharge (very strong) | |
| HCCK | HCCH with dc discharge[a] (strong) | not attempted | |

[a] Discharge conditions: ~30−80 mA at 250−500V. [b] Not attempted without dc discharge. [c] Discharge conditions: ~750 mA at 20−40 V.

scanning the source in frequency and quasi-optically propagating the radiation through the gas cell, which is a double pass system, using a series of Teflon lenses and a wire grid. Absorption of radiation by molecules created in the cell is monitored by the detector. Phase-sensitive detection is achieved by FM modulation of the Gunn source.

To initially find the spectral signature of the molecules in question, large frequency ranges (~30 GHz) were scanned in 100 MHz increments. Once spectral lines were identified, frequency measurements were carried out using scans 5 MHz in width, in both decreasing and increasing frequency, and one to four pairs of such scans were then averaged. Line widths varied from 200 to 1200 kHz in the frequency range 100−530 GHz, arising presumably from modulation broadening, and typically 20−40 data points were taken over an absorption line. Gaussian fits to the data were used to determine center frequenecies. Experimental accuracy of frequencies is estimated to be ±50 kHz for both HCCM and CH$_3$M.

**CH$_3$M (M = Li, Na, K).** Table 1 summarizes synthetic techniques used for CH$_3$K and the other five organoalkalis examined in this work. In the cell, the organic precursor (3−5 mTorr) was premixed with argon (~20 mTorr) and the resulting mixture was added through the bottom of the Broida oven. Alkali metal vapor (≤1 mTorr) was entrained in the mixture, which flowed out the top of the oven. For CH$_3$M, the organometallics (CH$_3$)$_2$Hg and (CH$_3$)$_4$Sn gave the strongest signals, but in the course of this work, the use of the mercury compound was discontinued because of reports of its extreme toxicity.[36,37] **Caution: (CH$_3$)$_2$Hg is exceedingly toxic and must be handled with great care!** Li vapor appeared to be more reactive than Na, in that the former needed no dc discharge to produce strong signals for CH$_3$Li. To create CD$_3$K, CD$_3$I was used as the precursor under identical conditions. The $^{41}$K isotopomer was observed in the natural isotope abundance ratio relative to $^{39}$K of 7:93, using (CH$_3$)$_4$Sn. To make isotopomers of CH$_3$Li, (CD$_3$)$_2$-Hg and Li enriched in $^6$Li were used; similarly, to make CD$_3$Na, (CD$_3$)$_2$-Hg was employed. Precursor (CD$_3$)$_2$Hg was made from CD$_3$MgI and HgCl$_2$ in refluxing Et$_2$O and was isolated by fractional distillation as a clear, colorless liquid, bp 86−90 °C. $^{13}$C{$^1$H} NMR (CDCl$_3$, 75.46 MHz, $C$DCl$_3$ = 77.00 ppm) δ 20.47 (septet, $J$ = 19.5 Hz) with satellites seen ($J_{Hg-C}$ = 680 Hz). Preparation of the compound has been reported,[23] but without any characterization data. Because of the extreme hazards of using the mercury compound, however, the use of CD$_3$I is strongly preferred. For further details regarding CH$_3$Li and CH$_3$Na, see ref 34a.

Because there was no previous estimates of rotational constants for CH$_3$K, experimental or theoretical, such parameters were estimated from those of CH$_3$Na and CH$_3$Li.[34a] Initially, a large frequency region was searched to find CH$_3$K features, as described above. Once two transitions were identified, other ones could be much more accurately predicted and much smaller regions (100−200 MHz) searched before using scans 5 MHz in range for frequency determinations of individual lines.

**HCCM (M = Li, Na, K).** In the reaction cell, HCCH (30 mTorr) was reacted with metal vapor (≤1 mTorr). Deuterium isotopomers were made using DCCD, and HCC$^6$Li was made using HCCH and Li enriched in $^6$Li. Finally, both of the carbon isotopomers HC$^{13}$CLi and H$^{13}$CCLi could be made employing the very efficient reaction of Li vapor with HCCBr.[38] Intense signals were produced even without a dc discharge and using only a few milliTorrs of HCCBr. For further details, see ref 34b.

### Results and Discussion

**Syntheses.** Although the heavily substituted organolithium (Me$_3$Si)$_2$CHLi could be transformed from a solid polymer to a gaseous monomer,[21] all previous attempts to produce monomers of simple organolithiums such as the title compounds by vaporization of oligomers appeared to have failed.[30] Moreover, calculations of the relative energies of monomers and dimers, trimers, or tetramers of CH$_3$Li suggest that dissociation would require large amounts of energy.[14] Therefore, we sought to directly create monomeric, solvent-free organoalkalis in the gas phase from the vapors of an organic precursor and the appropriate alkali metal.

Metal-exchange reactions were tried first. The first solution-phase synthesis of an organolithium by Schlenk and Holz, reported in 1917,[39] involved the reaction of dialkylmercury compounds with lithium metal in ether. Therefore, inspired by these and later results,[40] we combined either (CH$_3$)$_2$Hg or (CH$_3$)$_4$Sn in argon carrier gas with metal vapor in a reaction cell of 0.5 or 0.7 m in length. In this way, CH$_3$Li could be made directly, but the Na and K analogues required the application of a dc discharge, which may aid in dissociation of the precursor molecule or put the alkali metal atoms in more reactive excited states.[41] The deuterated isotopomer (CD$_3$)$_2$Hg was prepared so as to make CD$_3$M.

Although these procedures gave large amounts of material, as seen by high signal-to-noise ratios, the use of toxic organo-mercury and -tin precursors was required. While this work was in progress, a well-publicized report of the extreme toxicity of (CH$_3$)$_2$Hg[36,37] prompted a search for alternative sources of CH$_3$M. Direct metalation of hydrocarbons would be a very attractive route to organoalkalis. Although some CH$_3$Na could be observed from reaction of CH$_4$ and Na under the influence of a dc discharge, this procedure was not very efficient. In contrast, reaction of HCCH with Li, Na, or K under similar conditions produced satisfactory amounts of HCCM, perhaps because the alkyne is much more acidic than the alkane.

However, the most general synthetic procedure mimics a textbook reaction, the solution-phase preparation of RM from RX (M = Li, Na, K and X = halogen) and 2 mol of M (producing MX byproduct).[1,5,6] In general, it was found that gas-phase reactions of alkali metal vapor and CH$_3$I or CD$_3$I do not require a dc discharge. Moreover, extremely intense signals for HCCLi could be obtained by employing HCCBr and Li vapor. Production of ~1 mol of LiBr was verified by observation of the appropriate absorptions.[42,43] From HCCBr, signal intensities for HCCLi were so high that even from natural abundance

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**Table 2.**  Measured Transition Frequencies (MHz) for Three Isotopomers of CH$_3$K ($\tilde{X}^1A_1$)$^+$

| $J''\rightarrow J'$ | $K$ | CH$_3$K $\nu_{obs}$ | $\nu_{obs}-\nu_{calc}$ | CH$_3$$^{41}$K $\nu_{obs}$ | $\nu_{obs}-\nu_{calc}$ | CD$_3$K $\nu_{obs}$ | $\nu_{obs}-\nu_{calc}$ |
|---|---|---|---|---|---|---|---|
| 35→36 | 0 | 440 783.324 | 0.006 | | | | |
| | 1 | 440 750.164 | 0.009 | | | | |
| | 2 | 440 650.752 | −0.001 | | | | |
| | 3 | 440 485.343 | −0.029 | | | | |
| | 4 | 440 254.406 | −0.039 | | | | |
| | 5 | 439 958.531 | −0.048 | | | | |
| | 6 | 439 598.516 | −0.038 | | | | |
| 36→37 | 0 | 452 913.537 | 0.026 | | | | |
| | 1 | 452 879.525 | 0.008 | | | | |
| | 2 | 452 777.584 | −0.038 | | | | |
| | 3 | 452 608.094 | −0.001 | | | | |
| | 4 | 452 371.385 | 0.004 | | | | |
| | 5 | 452 068.088 | −0.015 | | | | |
| | 6 | 451 699.074 | 0.012 | | | | |
| 37→38 | 0 | 465 034.370 | 0.018 | | | | |
| | 1 | 464 999.541 | 0.008 | | | | |
| | 2 | 464 895.169 | 0.000 | | | | |
| | 3 | 464 721.530 | −0.002 | | | | |
| | 4 | 464 479.089 | 0.007 | | | | |
| | 5 | 464 168.465 | 0.007 | | | | |
| | 6 | 463 790.518 | 0.034 | | | | |
| 38→39 | 0 | 477 145.587 | 0.000 | 470 863.837 | 0.017 | | |
| | 1 | 477 109.934 | −0.018 | 470 829.028 | −0.008 | | |
| | 2 | 477 003.138 | −0.002 | 470 724.776 | −0.001 | | |
| | 3 | 476 825.436 | 0.004 | 470 551.336 | 0.020 | | |
| | 4 | 476 577.323 | 0.024 | 470 309.097 | −0.015 | | |
| | 5 | 476 259.436 | 0.039 | 469 998.750 | −0.053 | | |
| | 6 | 475 872.601 | 0.029 | | | | |
| 39→40 | 0 | 489 246.954 | −0.011 | 482 807.500 | −0.018 | | |
| | 1 | 489 210.521 | 0.001 | 482 771.941 | −0.003 | | |
| | 2 | 489 101.262 | −0.022 | 482 665.336 | 0.021 | | |
| | 3 | 488 919.576 | 0.032 | 482 487.916 | 0.004 | | |
| | 4 | 488 665.807 | 0.025 | 482 240.166 | −0.038 | | |
| | 5 | 488 340.698 | 0.026 | 481 922.917 | 0.068 | | |
| | 6 | 487 945.106 | 0.025 | 481 536.730 | 0.041 | | |
| 40→41 | 0 | 501 338.262 | 0.031 | 494 741.341 | −0.023 | | |
| | 1 | 501 301.001 | 0.015 | 494 705.001 | −0.006 | | |
| | 2 | 501 189.356 | 0.007 | 494 596.063 | 0.006 | | |
| | 3 | 501 003.641 | 0.024 | 494 414.763 | 0.040 | | |
| | 4 | 500 744.281 | −0.001 | | | | |
| | 5 | 500 412.066 | 0.030 | 493 837.210 | −0.023 | | |
| | 6 | 500 007.770 | 0.003 | 493 442.557 | −0.031 | | |
| 41→42 | 0 | 513 419.147 | 0.013 | | | | |
| | 1 | 513 381.079 | −0.018 | | | | |
| | 2 | 513 267.021 | −0.063 | | | | |
| | 3 | 513 077.374 | −0.025 | | | | |
| | 4 | 512 812.546 | −0.003 | | | | |
| | 5 | 512 473.225 | −0.015 | | | | |
| | 6 | 512 060.304 | −0.078 | | | | |
| 45→46 | 0 | | | | | 467 197.971 | 0.039 |
| | 1 | | | | | 467 173.803 | 0.035 |
| | 2 | | | | | 467 101.298 | −0.010 |
| | 3 | | | | | 466 980.664 | 0.012 |
| | 4 | | | | | 466 811.960 | −0.005 |
| | 5 | | | | | | |
| | 6 | | | | | 466 331.482 | −0.007 |
| 46→47 | 0 | | | | | 477 235.733 | −0.026 |
| | 1 | | | | | 477 211.136 | −0.010 |
| | 2 | | | | | 477 137.313 | −0.026 |
| | 3 | | | | | 477 014.453 | 0.012 |
| | 4 | | | | | 476 842.629 | 0.010 |
| | 5 | | | | | 476 622.107 | −0.004 |
| | 6 | | | | | 476 353.238 | 0.018 |
| 47→48 | 0 | | | | | 487 265.923 | −0.009 |
| | 1 | | | | | 487 240.841 | −0.033 |
| | 2 | | | | | 487 165.734 | −0.001 |
| | 3 | | | | | 487 040.605 | −0.014 |
| | 4 | | | | | 486 865.698 | 0.001 |
| | 5 | | | | | 486 641.206 | −0.006 |
| | 6 | | | | | 486 367.467 | −0.006 |
| 48→49 | 0 | | | | | 497 288.299 | 0.012 |
| | 1 | | | | | 497 262.766 | −0.024 |
| | 2 | | | | | 497 186.308 | −0.026 |
| | 3 | | | | | 497 059.044 | 0.020 |
| | 4 | | | | | 496 881.015 | −0.023 |
| | 5 | | | | | 496 652.643 | 0.023 |
| | 6 | | | | | 496 374.081 | −0.008 |
| 49→50 | 1 | | | | | 507 276.736 | 0.006 |
| | 2 | | | | | 507 199.052 | 0.080 |
| | 3 | | | | | 507 069.469 | −0.027 |
| | 4 | | | | | 506 888.465 | −0.015 |
| | 5 | | | | | 506 656.193 | 0.017 |
| | 6 | | | | | 506372.905 | −0.004 |

materials the transitions corresponding to both of the carbon isotopomers HC$^{13}$CLi and H$^{13}$CCLi could be observed. Thus, all six title compounds could be made and characterized.

**Mechanism of Product Formation.** Reduction of halocarbons with metals to produce organometallics is a textbook reaction, yet the precise mechanism is still a matter of research and debate.[44-46] For example, in reaction of RX and a metal, are organic radicals R produced in solution or bound to the metal surface? This question has been debated in the context of the Grignard reaction[44-46] as well as in connection with alkali metal reductions (see especially pages 7 and 8 of ref 1). Our gas-phase studies offer an opportunity to shed light on condensed-phase reactivity. If alkali metal reduction of RX proceeds in a series of two one-electron reductions, we should be able to detect R$^{\bullet}$ from the first step. Although the symmetry of methyl radical precludes its observation in the experiments used in this work, that of HCC$^{\bullet}$ should allow its detection. In fact, in reactions of HCCBr with Li, the $N = 3 \rightarrow 4$ transition for HCC$^{\bullet}$,[47] which consists of several hyperfine components, was absent, whereas several of the known transitions[42] of LiBr (e.g., $J = 14 \rightarrow 15$, $13 \rightarrow 14$, etc.) were clearly visible, as were the transitions for

HCCLi. (It is estimated that lines for HCC$^{\bullet}$ as much as 10% as strong as those for HCCLi could have been detectable.)[48] Therefore, the data suggest that the reduction of HCCBr by 2 mol of Li is a synchronous process. Since there is no metal surface to complicate matters, we need only consider the gas-phase properties of the reactants. Alkali metal dimers, which could efficiently reduce R−X to R−M and M−X, have been observed at atmospheric pressure or above[49] and at pressures on the order of 10$^{-8}$ Torr in the absence of other collisional partners.[50] However, in the experiments reported here, there may be little dimer because the most likely collisional partner for M would be the carrier gas Ar or a reactant gas. One way around this conundrum is to postulate that as the solid alkali metal is vaporized, there is a significant concentration of dimeric species near the solid surface, and it may be here that reaction with haloalkanes takes place.

**Data Reduction.** CH$_3$K has a $C_{3v}$ symmetry axis, making it a symmetric top molecule with a $^1A$ ground electronic state when M is an alkali metal. Hence, the rotational quantum number is $J$ and the quantized projection of rotational angular momentum along the symmetry axis results in a $K$-ladder structure ($J \geq K$) for each transition. Table 2 shows measured

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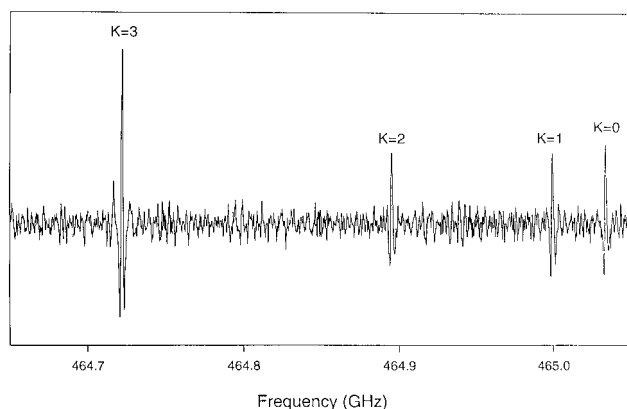(50) Wu, C. H. *J. Chem. Phys.* **1976**, *65*, 3181−3186.

**Figure 1.** Spectrum of the $J = 37-38$ transition of $CH_3K$ observed in this work near 465 GHz, showing the $K = 0$, 1, 2, and 3 components of this symmetric top species. The spacing of the $K$-components follows the expected pattern of 1:3:5. The $K = 3$ line is significantly stronger than the other components because of proton spin statistics. This spectrum covers ~400 MHz in frequency and is a composite of four 100 MHz scans, each lasting 1 min in duration.
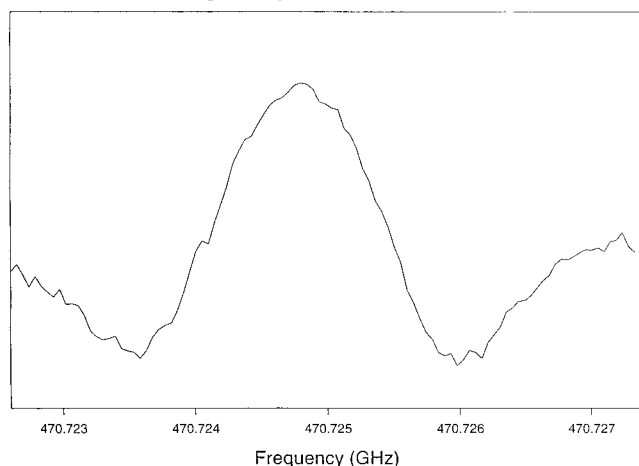


**Figure 2.** Spectrum of the $K = 2$ component only of the $J = 38-39$ transition of $CH_3{}^{41}K$ observed in the natural potassium isotope abundance. This spectrum covers only 5 MHz in frequency and is an average of four 20 s scans.

transition frequencies for the three isotopomers of $CH_3K$. Figure 1 shows a representative portion of the spectrum of $CH_3K$, spanning 400 MHz, ascribed to the $J = 37 \rightarrow 38$ transition near 465 GHz, showing the $K = 0$, 1, 2, and 3 components of this symmetric top species. Figure 2 shows the $K = 2$ component of the $J = 38 \rightarrow 39$ transition of the $^{41}K$ isotopomer, which could be observed at natural abundance (7%), albeit with greater difficulty because of lower signal intensities. This spectrum covers only 5 MHz and required signal averaging. Since $CH_3K$ is a closed-shell species, no fine or magnetic hyperfine structure was present. Nuclear quadrupole interactions involving $^{39}K$ or $^{41}K$ were not seen. The resulting molecular constants for isotopomers of $CH_3K$ are shown in Table 3 and were derived using a $^1A$ Hamiltonian. The rotational constant $B_v$ ($= B_o$), the first-order centrifugal distortion constants $D_{JK}$ and $D_J$, and second-order distortion parameters $H_{KJ}$ and $H_{JK}$ were needed to fit the data within experimental uncertainty, but only $B_o$ was needed to determine the moment of inertia $I_o$ and hence the structure. The structure of $CH_3M$ was considered to be a function

**Table 3.** Molecular Constants for $CH_3K$ Isotopomers[a]

| parameter | $CH_3K$ | $CH_3{}^{41}K$ | $CD_3K$ |
|---|---|---|---|
| $B_v$ | 6149.2895 (40) | 6067.938 (15) | 5106.9575 (69) |
| $D_J$ | 0.0105320 (13) | 0.0102636 (47) | 0.0067862 (15) |
| $D_{JK}$ | 0.48219 (23) | 0.4704 (10) | 0.28110 (39) |
| $H_{JK}$ (10⁵) | 0.8293 (69) | 0.799 (32) | 0.4352 (83) |
| $H_{KJ}$ (10⁴) | 1.003 (22) | 0.977 (40) | 0.299 (22) |
| rms of fit | 0.025 | 0.029 | 0.023 |

[a] In megahertz.

of three variables, the C−M and C−H bond lengths and the H−C−H angle.

Because three isotopomers $^{12}C^1H_3{}^{39}K$, $^{12}C^2H_3{}^{39}K$, and $^{12}C^1H_3{}^{41}K$ were observed, values of the C−M and C−H bond lengths and H−C−H angle (Table 4) could be determined using a partial substitution structure ($r_s$ structure), which assumes the center of mass condition.[51] Such a structure is better than previous $r_o$ calculations done for $CH_3Li$ and $CH_3Na^{34a}$ because some of the zero-point vibrations are accounted for. An identical calculation was consequently carried out for $CH_3Li$, using the spectral data reported earlier, for direct comparison. For the Na analogue, only two isotopomers ($^{12}C^1H_3Na$ and $^{12}C^2H_3Na$) were made, so only an $r_o$ structure is feasible, using an assumed C−H bond length of 1.091 Å from theory.[15] The accuracies of the bond lengths for partial $r_s$ structures are estimated to be on the order of ±0.005 Å, precision rivalling or exceeding that from X-ray or neutron diffraction.

Structural data for HCCM (M = Li, Na, K)[34b] are also given in Table 4 for comparison. For HCCLi, every atom was substituted, so in this case a full substitution structure $r_s$ was determined. Estimated uncertainties in the $r_s$ bond lengths are ±0.0005 Å for a complete subsitution structure.[51]

**Comparison of Geometrical Parameters with Each Other and with Theoretical Predictions.** The derived geometrical parameters are shown in Table 4 along with previously reported values from ab initio calculations. The C−M distances are the shortest ones known for organoalkalis of each metal, certainly a consequence of both the small size of the organic portion and the monomeric, unsolvated nature of the molecules. For example, among organolithiums, the closest examples are the ether-solvated, hindered monomeric aryllithium shown in Scheme 1 [2.017(7) Å][18] and unsolvated LiCH(SiMe₃)₂ [2.03-(6) Å].[21] From inspection of Table 4, for each metal, the C−M bond length is shorter in the acetylide than in the methyl derivative, the difference amounting to 0.071−0.094 Å for the series. The differences between C−M bond lengths in $CH_3M$ and HCCM are similar to differences between C−C bond lengths in hydrocarbons: bonds between sp- and sp³-hybridized carbons are ~0.06 Å shorter than bonds between two sp³-hybridized carbons.[52] As noted previously,[34] for all the compounds examined, experimentally determined C−M bond lengths are somewhat shorter than those predicted by theory. At least some of these discrepancies are probably due to the difficulties in calculations involving highly electropositive or electronegative elements.[53]

The data from our work show the H−C−H angle to vary from 107.2° in $CH_3Li$ to 107.0° in $CH_3K$. (Because one bond distance in $CH_3Na$ was fixed, its structure is not directly comparable.) These measurements suggest a very slight decrease

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**Table 4.**  Comparison of Experimental and Calculated Geometries for $CH_3M$ and HCCM

| molecule | source | basis set | M−C (Å) | C−H or C−D (Å) | C−C (Å) | H−C−H or D−C−D angle (deg) | ref |
|---|---|---|---|---|---|---|---|
| $CH_3Li$ | mm-wave[a] | | 1.961(5) | 1.122(5) | | 107.2(1) | g |
| | IR in matrix | | ∼2.10 | ∼1.12 | | 107.3 or 109.5[b] | 31 |
| | ab initio | STO-4G | 1.969 | 1.122 | | 104.2 | 10 |
| | | SS | 2.032 | 1.092 | | 107.1 | 10 |
| | | SS+d | 2.021 | 1.089 | | 105.8 | 10 |
| | ab initio | various | 2.000 | 1.096 | | 106.8 | 14 |
| | | | ±0.004 | ±0.003 | | ±0.7 | |
| | | MP2/6-311G* | 1.983 | 1.098 | | 106.2 | 14 |
| | ab initio | 6-31G* | 2.0013 | 1.0934 | | 106.2 | 15 |
| | ab initio | 6-31+G* | 2.005 | 1.099 | | 107.3 | 16 |
| $(CH_3Li)_4$ | X-ray | | 2.31(5) | 0.96(5) | | 111(8) | 22 |
| $(CD_3Li)_4$ | neutron diffraction | | 2.256(6), 2.356(6) | 1.072(2) | | 108.2(2) | 24 |
| $CH_3Na$ | mm-wave[c] | | 2.299 | 1.091[d] | | 107.3 | 34a |
| | ab initio | 6-31G* | 2.3236 | 1.0910 | | 107.2 | 15 |
| $(CD_3Na)_{16}$ | neutron diffraction | | 2.528(4)−2.960(19) | 1.094[e] | | 106.2[e] | 27 |
| $CH_3K$ | mm-wave[a] | | 2.633(5) | 1.135(5) | | 107.0(1) | g |
| $(CD_3K)_n$ | neutron diffraction | | 2.947(2)−3.441(3) | 1.082(4), 1.103(2) | | 104.8(2), 105.8(2) | 23 |
| HCCLi | mm wave | | 1.888[c] | 1.061[c] | 1.226[c] | | 34b |
| | | | 1.888[f] | 1.062[f] | 1.227[f] | | 34b |
| | ab initio | STO-4G | 1.862 | 1.070 | 1.213 | | 10 |
| | | SS | 1.921 | 1.056 | 1.219 | | 10 |
| | | SS + d | 1.931 | 1.056 | 1.208 | | 10 |
| | | INDO | 1.842 | 1.099[b] | 1.220[b] | | 11 |
| HCCNa | mm wave[c] | | 2.221 | 1.06[b] | 1.217 | | 34b |
| $(HCCNa)_n$ | powder diffraction | | 2.49(5) | | 1.17(6) | | 22 |
| HCCK | mm wave[c] | | 2.540 | 1.06[b] | 1.233 | | 34b |
| $(HCCK)_n$ | powder diffraction | | 2.87 | | 1.20 | | 22 |

[a] Partial $r_s$ structure. [b] Assumed value. [c] $r_o$ structure. [d] Assumed value (from ref 15). [e] Average of six similar values. [f] $r_s$ structure. [g] This work.

in the H−C−H bond angle as one descends the periodic table. However, the decrease is very small, even experimentally insignificant. The only theoretical comparison of alkali metal compounds $CH_3M$ that we could find[15] would have the H−C−H angles in $CH_3Li$ and $CH_3Na$ differ by 1° (Table 4). This small change is thought to result from electronegativity differences of X in $CH_3X$.[15,54]

The importance of obtaining data on monomeric compounds is highlighted by precise structural data for the solid-phase samples of the $CH_3M$ triad, obtained by neutron diffraction.[23,24,27] First, the bond lengths and angles in these oligomeric samples changed when the samples were observed near 1.5 and 290 K, presumably because of changes in the many intermolecular interactions. For example, for oligomeric $CD_3K$ in which each carbon interacts with six metals,[23] neutron diffraction at 1.35 K showed two different D−C−D angles [two at 104.8-(2)° and one at 105.8(2)°], whereas at 290 K, the data suggested one angle of 108.6(8)°, a difference of at least 3°. Because data from low-temperature experiments have the greatest precision, we compare results near 1.5 K, which showed the average D−C−D angle in the oligomers to vary from 108.2° in $(CD_3$-Li)₄,[24] to 106.2° in $(CD_3Na)_{16}$,[27] and finally to 105.2° in $(CD_3K)_n$,[23] a much greater change than that seen for the monomers in our work and greater than predicted by theory.[15] However, because each $CD_3$ unit in these compounds is associated with more than one metal, it is difficult to predict the effects of several (up to six) carbon−metal interactions on the geometry of the methyl unit. Our data on monomers, free of confusion about metal−carbon contact, reveal a slight, almost experimentally insignificant difference between the angles in $CH_3Li$ and $CH_3K$. In view of the similar Pauling electronegativities of Li and K (0.98 and 0.82) compared with that of C (2.55),[55] it seems reasonable to conclude that the true geometries of the methyl groups in $CH_3Li$ and $CH_3K$ are very similar.

Finally, interesting comparisons between the observed linear geometries of HCCM and nonlinear geometries of closely related molecules can be made. Depending on the basis set employed, LiCCLi is predicted by theory to form either a linear structure or a cross-like structure where the two lithium cations bond to the π electron cloud of the $[C≡C]^{2-}$ group.[56−59] One explanation for the different geometries focuses on different Coulombic attractions in LiCCLi and in MCCH as follows, in the MCCH case, the metal in a linear acetylide experiences less Coulombic attraction to the hydrogen-bearing carbon at the far end. In the case of LiCCLi, the two metals on both sides of the π cloud would experience Coulombic attraction toward the negative charge at both ends of the $[C≡C]^{2-}$ unit. Schleyer essentially advanced the latter explanation for the unusual calculated geometry of LiCCLi.[59] Even more unusual are the alkali monocyanides. These species are thought to exhibit primarily ionic forces in their bonding. The most stable form of LiNC predicted by theory is the linear isocyanide structure,[60] which has been verified by experiment.[61] In contrast, sodium and potassium cyanide form T-shaped molecules, where the metal atom has bonded to the π cloud of the cyanide group.[62−64]

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In fact, it is postulated that the metal atom exists as $M^+$ in these cases and "orbits" the $CN^-$ moiety in a "polytopic", quasi-structureless bond. No known monoacetylide has such a structure, but the presence of the hydrogen atom on one side of the acetylide group likely hinders this configuration. The $C-H$ bond in this case may have enough polarity such that the H atom carries a slight positive charge, which repulses the $M^+$.

## Conclusion

The synthesis of $CH_3K$ completes work on two series of three organoalkalis each, which have been prepared for the first time in the gas phase and structurally characterized by millimeter/submillimeter spectroscopy. Precise measurement of bond lengths and angles for the title molecules is possible for the first time. Completion of the $CH_3M$ series is particularly significant because these molecules feature tetra-hedral carbon, the bond angles around which are a measure of the effects of alkali metal−carbon interaction. The true bond angles in the methyl unit were impossible to evaluate unambiguously from previously obtained data on crystals or powders, because the 3° difference in the $H-C-H$ angle of $(CD_3Li)_4$ and $(CD_3K)_n$ could be due to differences in crystal structure (e.g., intermolecular interactions) as well as to electronegativity differences between Li and K. However, our data on the monomers show an experimentally insignificant difference in $H-C-H$ angle, in line with the similar electronegativities of Li and K.