Infrared Spectral Evidence for Trihalomethyllithium and -sodium Compounds in Solid Argon

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The matrix reaction of alkali metal atoms and perbromochloromethanes produces the trihalomethyl radical followed by a secondary reaction of metal atoms with CX_3 to yield a sufficient concentration of the trihalomethyl alkali metal compounds for infrared spectral study. Use of the five perbromochloromethane precursors with lithium-6, lithium-7, and sodium verifies the molecular identity. Assignments to the antisymmetric carbon–halogen stretching frequencies are 521 and 462 cm^{-1} for the chlorine and bromine species, respectively, while the lithium-6 stretching frequencies are 437 and 391 cm^{-1}, respectively, for the chlorine and bromine molecules. The carbon–halogen frequencies lead to markedly lower force constants than calculated for the carbon tetrahalides which suggests that the CX_3 group has a significant amount of anionic character.

Introduction

There has been a great deal of recent research activity on α-haloalkyllithium compounds or carbenoids.[1] Kobrich[2] has reviewed the chemistry and mechanisms of carbenoid reactions. The reactions of trichloromethyllithium were first thought to go through the carbene intermediate,[3] but later work suggested that the intermediate in reactions of carbenoids is a "carbene–salt complex"[4,5] in contrast to proposed mechanisms using the carbenoid structure itself as the intermediate.[1,2,6]

We have announced the infrared detection of the trichloromethyl radical[7,8] in solid argon using the matrix reaction of lithium and carbon tetrachloride. In the case of reactions of lithium atoms with methyl halides to produce the methyl radical,[9,10] subsequent reaction of lithium atoms with methyl radicals gives methyllithium[11] isolated as the monomer. Thus, the lithium–tetrahalomethane study yields trihalomethyllithium in an argon matrix at 15°K for spectral study. This technique provides a unique opportunity for spectroscopic observations of carbenoids since these compounds decompose exothermally[4,5] at temperatures near −70°. The infrared spectra of the trihalomethyllithium and sodium compounds should provide information about the bonding and structure of these chemically interesting species.

Experimental Section

The 15°K refrigeration system, lithium atom source, experimental technique, chemicals, and purification procedures have been described in detail in earlier publications.[8,12] Samples of tetrahalomethane in argon ($Ar/CX_4 = {}^{200}/_1$ to ${}^{600}/_1$) were simultaneously deposited with an atomic beam of lithium ($Li/CX_4 \approx {}^1/_2$ to ${}^3/_1$) on a CsI window maintained at 15°K.

Infrared spectra were recorded on a Beckman IR-12 filter-grating spectrophotometer in the 200–4000-cm^{-1} region. Frequency accuracy is ±1 cm^{-1} and spectral slit widths were 0.8 cm^{-1} at 900 cm^{-1}, 0.9 cm^{-1} at 700 cm^{-1}, and 2.1 cm^{-1} at 500 cm^{-1}.

Results

Perbromochloromethane Precursors. In the earlier work with CCl_4[8] and CBr_4,[12] absorptions labeled M and L in the 375–525-cm^{-1} spectral region were observed to increase in intensity relative to absorptions owing to the trihalomethyl radical when the lithium concentration was increased. The bands L showed a definite lithium isotopic shift and a shift to longer wavelength as bromine successively replaced chlorine in the parent material. Table I lists the absorptions M and L for the perbromochloromethane and ^7Li and ^6Li parent materials. In several CCl_4 experiments, the relative intensities of the M and L bands remained approximately constant.

Figure 1 contrasts spectra in the 370–590-cm^{-1} spectral region for all of the perbromochloromethane

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(1) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

(2) G. Kobrich, *Angew. Chem. Intern. Ed.*, **6**, 41 (1967).

(3) W. T. Miller, Jr., and C. S. Y. Kim, *J. Am. Chem. Soc.*, **81**, 5008 (1959).

(4) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965).

(5) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

(6) W. T. Miller, Jr., and D. M. Whalen, *J. Am. Chem. Soc.*, **86**, 2089 (1964).

(7) L. Andrews, *J. Phys. Chem.*, **71**, 2761 (1967).

(8) L. Andrews, *J. Chem. Phys.*, **48**, 972 (1968).

(9) W. L. S. Andrews and G. C. Pimentel, *ibid.*, **44**, 2527 (1966).

(10) L. Andrews and G. C. Pimentel, *ibid.*, **47**, 3637 (1967).

(11) L. Andrews, *ibid.*, **47**, 4834 (1967).

(12) L. Andrews and T. G. Carver, *ibid.*, in press.

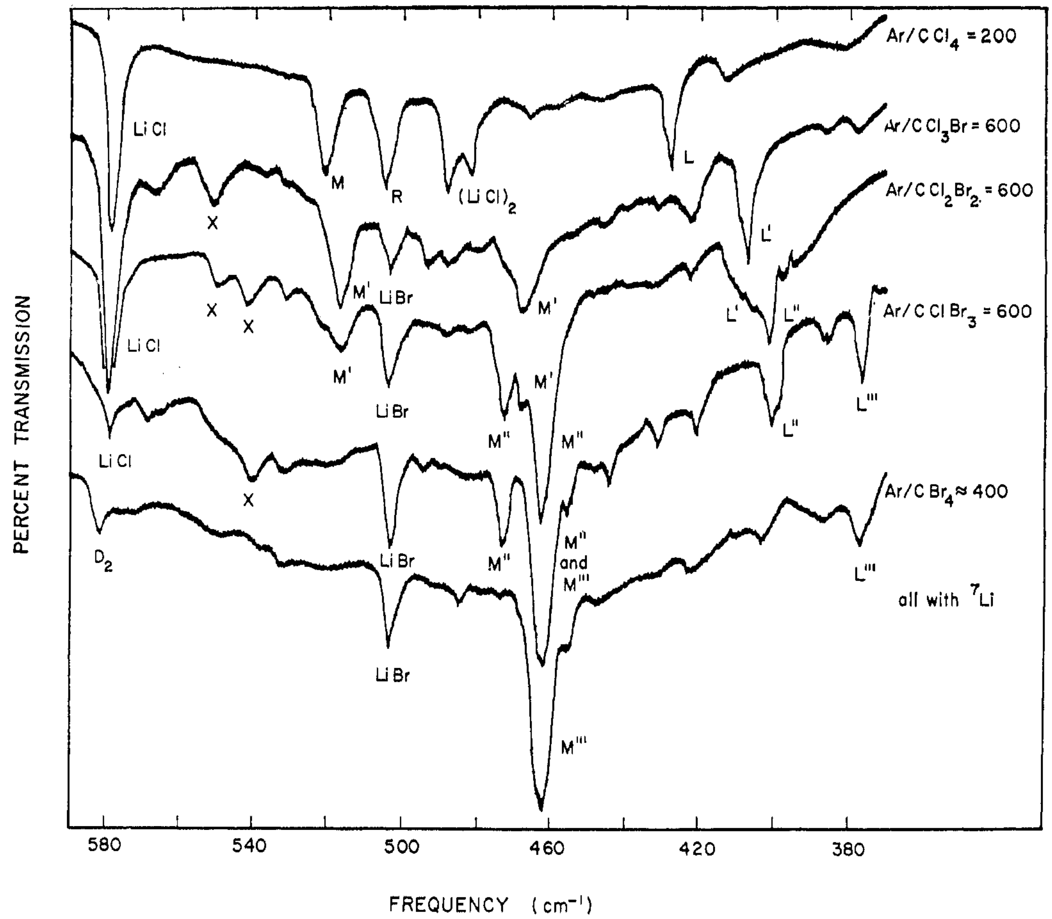

Figure 1. Infrared spectra recorded in the 370–590-cm^{-1} spectral region for samples of CCl$_4$, CCl$_3$Br, CCl$_2$Br$_2$, CClBr$_3$, and CBr$_4$ in argon deposited with lithium-7 at 15°K.

Table I: Absorptions M and L for All Parent Materials Used

Parents	M band, cm^{-1}	L band, cm^{-1}
^{6}Li, CCl$_4$	521	437
^{7}Li, CCl$_4$	521	429
^{6}Li, CCl$_3$Br	517, 468	410
^{7}Li, CCl$_3$Br	518, 469	407
^{7}Li, CCl$_2$Br$_2$	518, 473, 468,[a] 463	407,[a] 401
^{6}Li, CClBr$_3$	473, 463	404, 391
^{7}Li, CClBr$_3$	473, 463	401, 377
^{6}Li, CBr$_4$	462	391
^{7}Li, CBr$_4$	462	377

[a] Shoulder.

parents deposited with ^{7}Li. LiCl and LiBr absorptions are noted. The number of primes on the M and L labels indicates the number of bromine atoms present in the species which will be discussed below.

When CBr$_4$ is deposited with an equimolar mixture of ^{6}Li and ^{7}Li, the L band becomes a doublet with the same ^{6}Li and ^{7}Li components, 391 and 377 cm^{-1}, respectively, observed when the pure isotopic lithium metal was used. Experiments using the 51% ^{13}C-enriched CCl$_4$ sample with ^{7}Li show that the L bands becomes a doublet with components at 729 and 723 cm^{-1}, while with ^{6}Li the L band broadens and shifts 2 cm^{-1} to longer wavelengths from the 437-cm^{-1} frequency observed using natural CCl$_4$.

Upon warming of the deposited sample to 45°K and recooling to 15°K, the M and L bands decrease in intensity to about half of their original value while absorptions of dihalocarbene[13,14] disappear completely and trihalomethyl radicals[8,12] decrease less than one-fourth of their original intensity. These data show that the M and L absorptions are due to a species different from the dihalocarbenes and the trihalomethyl radicals.

Variation of Alkali Metal. Figure 2 illustrates spectra recorded for experiments using sodium with the five perbromochloromethane precursors. Although the same M absorptions within ±1 cm^{-1} were observed using Na as Table I lists for the Li parent, no sodium counterpart of the band L was observed. The M absorptions were markedly more intense relative to the trihalomethyl radical and dihalocarbene absorptions

(13) L. Andrews, *J. Chem. Phys.*, in press.

(14) L. Andrews and T. G. Carver, *ibid.*, in press.

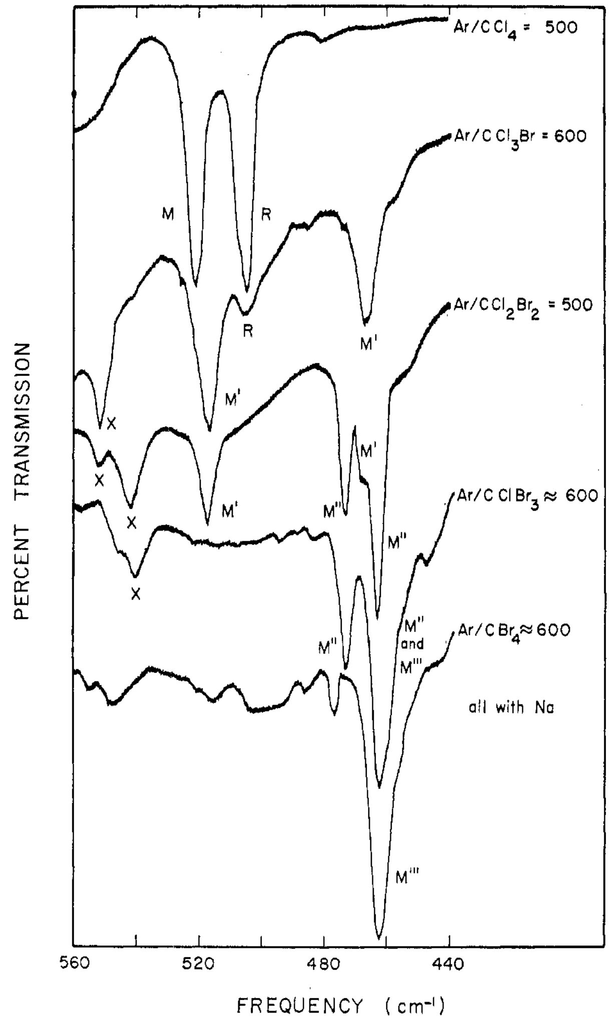

Figure 2. Infrared spectra recorded in the 440-560-cm^{-1} spectral region for samples of the five perbromochloromethanes in argon deposited with sodium at 15°K.

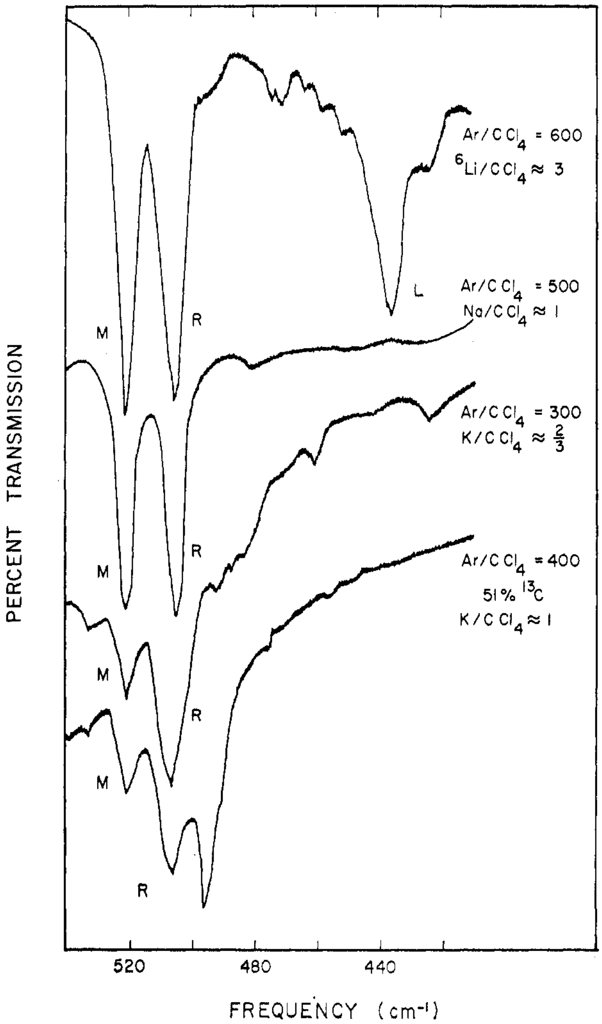

Figure 3. Infrared spectra recorded in the 420-540-cm^{-1} spectral region constrasting the effect of different alkali metal atoms deposited with CCl$_4$ in argon at 15°K.

for the Na parent than for Li, which shows that the M absorber must be still a third molecular species.

Figure 3 contrasts spectra recorded for experiments using ^{6}Li, Na, and K with CCl$_4$. The band labeled M is at 521.0 ± 0.5 cm^{-1} for the three alkali metals, while the R band shifts from 506 to 505 to 507 cm^{-1} as the alkali metal atomic weight increases. The last spectrum recorded for the 51% carbon-13-enriched CCl$_4$ sample with potassium shows a triplet structure with components at 521, 506, and 496 cm^{-1}. The same enriched CCl$_4$ sample deposited with sodium yields a triplet whose components absorb at 521, 505, and 495 cm^{-1}.

Discussion

The purpose of this publication is to identify absorptions which can be assigned to the trihalomethyl alkali metal compounds and to examine these data with regard to structure, vibrational potential function, and bonding in these species.

Species M Identity. Since the M and L absorptions maintain approximately constant relative intensities as concentrations of Li and CCl$_4$ are varied, they are assigned to the same molecular species. The band L doublet in the equimolar lithium isotope experiment shows that species M contains a single lithium atom and suggests that its sodium counterpart likely contains a single sodium atom. The band L in the carbon-13-enriched CCl$_4$ experiments is shifted to lower frequency which indicates that carbon is present in species M.

The spectra illustrated in Figures 1 and 2 show four different sets of M absorptions noted M, M', M'', M''', where the primes note the number of bromine atoms in species M. Single M (521 cm^{-1}) and M''' (462 cm^{-1}) absorptions are observed in the CCl$_4$ and CBr$_4$ experiments, respectively, but when the CCl$_3$Br and CClBr$_3$ precursors are used, additional M' (517 and 468 cm^{-1}) and M'' (473 and 463 cm^{-1}) bands are recorded. These same M' and M'' absorptions are observed in the CCl$_2$Br$_2$ experiments, which suggests that the M and M‴ bands are doubly degenerate and that the M′ and M″ bands result when this degeneracy is broken by mixing bromine with chlorine atoms in species M. The same frequency pattern is observed for the doubly degenerate antisymmetric carbon–halogen stretching vibration in the series of radicals[8] CCl_3, CCl_2Br, $CClBr_2$, and CBr_3 and their haloform[15] counterparts. In the experiments using the three mixed perbromochloromethanes, two different trihalomethyl radicals[8] are produced and their subsequent reaction produces two different trihalomethyllithium or -sodium compounds, which is shown in Figures 1 and 2 by the appearance of two different M (and L) species in the CCl_2Br_2 and $CClBr_3$ experiments.[16]

The fact that four different degrees of chlorine–bromine substitution exist for the species M indicates that three equivalent halogens are present in the M absorber. The presence of carbon is verified by the observed carbon-13 isotopic shifts. Three equivalent halogens imply that species M contains a single carbon atom.

Thus, species M has the formula CX_3Li and is isolated as the monomer, whereas in the sodium experiments, the formula CX_3Na is implied, both presumably with the C_{3v} structure.

Species M Vibrational Assignment. The band L for the trichloromethyllithium compounds shows a lithium isotopic shift from 437 to 429 cm^{-1} which suggests that this vibration involves the lithium atom while the carbon-13 shift shows that the carbon atom participates in the vibration. However, the calculated lithium isotope shift (21 cm^{-1}) assuming a C–Li diatomic molecule is larger than observed which indicates that the vibration is not a pure C–Li stretch so it must partially involve the halogen atoms. This is reasonable in view of the fact that the symmetric halogen stretching mode is expected in this region, and it has the same a_1 symmetry as the lithium stretch in the C_{3v} point group. The band L appears to be nondegenerate on mixing of chlorine and bromine atoms and is assigned to the symmetric stretching mode involving primarily the lithium and carbon atoms, but also the halogen atoms. No assignment is made to the pure C–X symmetric stretching vibration.

In the preceding section we showed that the M and M‴ bands are doubly degenerate and that the M′ and M″ bands result when this degeneracy is broken by mixing of chlorine and bromine atoms. Thus, the M bands are assgined to the doubly degenerate antisymmetric carbon–halogen stretching vibrations of the C_{3v} species.

The absorption labeled R in Figures 1–3 has the same intensity as the M band using Li and Na parents, but its intensity increases markedly over the M band using K. The behavior in the K experiment suggests that the band R is not a fundamental vibration due to species M unless the K atom perturbs the vibration significantly differently than does Li or Na. No bromine counterpart of the absorption R was observed. The R band could be the symmetric C–Cl stretch expected in the 400–550-cm^{-1} region which might be perturbed and made more intense by the K atom. However, a more likely possibility is that the band R is a combination band in Fermi resonance with the band M, since such resonance occurs for ν_3 and $\nu_1 + \nu_4$ for CCl_4 but not for CBr_4.

No other absorptions were observed which could be assigned to bending vibrations of species M owing to their very low intensity and the long wavelength limit of our spectrophotometer.

The bands labeled X in the CCl_3Br and $CClBr_3$ spectra in Figures 1 and 2 were both observed in the CCl_2Br_2 spectra. No CCl_4 or CBr_4 counterparts of the X bands were detected, so no assignment is made.

Species M Force-Constant Calculations. For the C_{3v} geometry for species M, the antisymmetric C–X stretch (e) is the highest frequency in its symmetry class. Using symmetry coordinates, one can factor out the antisymmetric stretching coordinate using Wilson's separation of high and low frequencies.[17] For normal-coordinate calculations we need to estimate the X–C–X bond angle. Since the CX_3 part of species M has a large amount of anionic character, we consider the isoelectronic species NX_3. However, the Cl–N–Cl bond angle for NCl_3 is not known so we use the value of 100° which is near the F–N–F bond angle[18] of 102° in NF_3. Such calculations give $F_r - F_{rr} =$ 1.26 mdyn/Å for CCl_3Li and 1.14 mdyn/Å for CBr_3Li (and their sodium counterparts, since the same halogen stretching frequencies were observed).

The ^{13}C counterpart of the 521-cm^{-1} band M in the CCl_4 experiment is calculated to be at 505 cm^{-1} which coincides with the R absorption. However, if the bands M and R are in Fermi resonance, normal-coordinate calculations could not correctly predict the observed carbon-13 shift. Fermi resonance would shift band M to higher frequency while its carbon-13 counterpart would be displaced to lower frequency since the combination band R lies between the band M frequencies for both carbon isotopes and is expected to show little carbon-13 shift. This is the case for ν_3 and $\nu_1 + \nu_4$ of $^{12}CCl_4$ and $^{13}CCl_4$ where the carbon-12 and carbon-13 fundamental frequencies are shifted apart by Fermi resonance with the intermediate combination bands. Normal-coordinate calculations for

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(15) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

(16) No detectable amount of $LiCCl_3$ was produced in the Li–CCl_3Br reaction possibly owing to the fact that the Li–CCl_3 reaction may favor the carbene product relative to the trihalomethyllithium compound product more than the Li–CCl_2Br reaction.

(17) E. B. Wilson, Jr., *J. Chem. Phys.*, **9**, 76 (1941).

(18) J. Sheridan and W. Gordy, *Phys. Rev.*, **79**, 513 (1950).

ν_3 (788 cm^{-1}) of $^{12}CCl_4$ predict ν_3 of $^{13}CCl_4$ to be 764 cm^{-1} whereas the observed value is 751 cm^{-1}.

Using the C–Li diatomic assumption, for lack of sufficient data prevents a more sophisticated approach, the lithium stretching force constant is calculated to be 0.45 mdyn/Å for $CCl_3{}^6Li$ and 0.48 mdyn/Å for $CCl_3{}^7Li$. The lack of agreement in these two force constants suggests that the vibrational mode involves the chlorine atoms.

Conclusions

The infrared spectra of the trihalomethyl alkali metal compounds are of interest insofar as they provide information on the structure, vibrational potential function, and bonding in these species.

Structure. Observation of a doubly degenerate vibration for the perchloro and perbromo species clearly indicates the presence of threefold symmetry. Presumably the species belong to the C_{3v} point group. This rules out the possibility of the "carbene–salt complex"[4,5] structure for the molecule, but, of course, it cannot preclude this complex as a reaction intermediate.

Potential Constants. A large number of calculations show that the stretch–stretch interaction force constants for chloro and bromocarbon species are small, around 0.30 mdyn/Å. Using this reasonable estimated value for F_{rr} and the calculated values of $F_r - F_{rr}$, we determine $F_{C-Cl} = 1.56 \pm 0.2$ mdyn/Å for CCl_3M and $G_{C-Br} = 1.44 \pm 0.2$ mdyn/Å for CBr_3M. These values are somewhat lower than their tetrahalomethane counterparts as is shown in Table II.

The force constant calculated for the lithium stretching mode is near 0.5 mdyn/Å, which compares to 0.8 mdyn/Å found[11] for F_{C-Li} of CH_3Li. Since the CX_3Li force constant is based on a vibrational frequency which also involves the halogen atoms, we hesitate to attach any significance to the comparison of the CH_3Li and CX_3Li lithium stretching force constants.

Table II: Stretching Force Constants (mdyn/Å) for Anionic Species and Their Neutral Counterparts

CH_4	CCl_4	CBr_4	$GeCl_4$	$SnCl_4$	$SnBr_4$
5.05[a]	3.08[c]	2.45[d]	2.72[e]	2.50[e]	2.02[e]
CH_3Li	CCl_3Li	CBr_3Li	$GeCl_3^-$	$SnCl_3^-$	$SnBr_3^-$
4.32[b]	1.56	1.44	1.09[f]	1.18[g]	1.06[g]

[a] J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 523 (1964). [b] Reference 11. [c] Reference 8. [d] Reference 12. [e] Frequencies from K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963. [f] Frequencies from M. L. Delwaulle, *Compt. Rend.*, **228**, 1585 (1949). [g] Frequencies from L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 407 (1962).

Bonding. Table II also compares stretching force constants for several anions and their neutral counterparts calculated using the separation of frequencies. An X–M–X bond angle of 100° was assumed for the anions since the isoelectronic PCl_3 molecule[19] has a bond angle near this value. The force constants for the three anions are noticeably lower than those for the neutral species, which is expected since repulsions caused by an additional electron present in the anion are not counterbalanced by the attractions of an equal number of protons as in a neutral molecule. The anion force constants are about half of those for their neutral counterparts, the same relationship observed for CX_3Li and CX_4. This comparison suggests that CX_3Li is highly ionic, much more so than CH_3Li whose force constant is near 85% of that for methane. We expect CX_3Li to be more ionic than CH_3Li since the CX_3 group stabilizes negative charge better than the CH_3 group.

Since the same antisymmetric carbon–halogen frequencies were observed for the Li and Na compounds, the same amount of anionic character in the CX_3 group is implied. This is not too surprising in view of the almost identical electronegativities of lithium and sodium.

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(19) P. Kisluik and C. H. Townes, *J. Chem. Phys.*, **18**, 1109 (1950).