Characterisation of Monomeric Methylsodium and Methylpotassium: Infrared Spectra of the Matrix-isolated Molecules

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Co-condensation of CH_3I with sodium or potassium vapour and an excess of N_2 at *ca.* 20 K gives rise to the respective methylmetal monomer CH_3Na or CH_3K which is trapped in the resulting matrix. The i.r. spectrum of the matrix in the region 200—4 000 cm^{-1} discloses all six vibrational fundamentals characterising each of these molecules in C_{3v} symmetry, the assignments being verified by measurements taking in the fully deuteriated as well as the undeuteriated isotopomer. How closely the molecules approximate to the formulation of $CH_3^-M^+$ (M = Na or K) is revealed through fundamentals which are lower in energy than those of any other homoleptic methylmetal compound reported to date. Normal co-ordinate analysis underlines this aspect with M–C stretching force constants = *ca.* 48 N m^{-1} and CH_3 rocking force constants = 10.3 (M = Na) and 7.6 N m rad^{-2} (M = K) which set new standards by their diminutive values.

Compared with organolithium compounds, the organic derivatives of the heavier alkali metals have attracted comparatively little attention.[1] Their reactivity makes them difficult to prepare and manipulate in the pure state, and their susceptibility to decomposition is an added problem. Nevertheless, crystalline methylsodium has been shown to adopt a structure analogous to that of methyl-lithium, being composed of tetrameric $[CH_3Na]_4$ units,[2] whereas the corresponding derivatives of potassium, rubidium, and caesium each assume hexagonal structures of the NiAs-type incorporating what are judged to be 'isolated' methyl carbanions.[3,4] There is but sparse information about the vibrational properties of these compounds,[2,3] and their thermal instability rules out the characterisation of any discrete vapour species, whether monomeric or oligomeric. No attempt seems to have been made to draw on the properties of solid methyl-potassium, -rubidium, or -caesium as a source of information about the CH_3^- anion. Instead, experimental studies of this anion have been more-or-less confined to its formation in the gas phase and detection by u.v.-photoelectron spectroscopy.[5] On the other hand, it has been the subject of numerous theoretical enquiries involving calculations at varying levels of sophistication,[6] and some of which have recently been extended to organometallic derivatives of the type CH_2XM (M = Li or Na; X = H, halogen, CH_3, NH_2, *etc.*).[7]

To meet this type of situation, the techniques of metal-vapour deposition and matrix isolation may be combined to engineer the production and trapping of discrete methylmetal derivatives, i.r. measurements being used to interrogate the resulting solid condensate and identify the product. The feasibility of this approach to organo derivatives of the alkali metals has been demonstrated by Andrews and Pimentel,[8,9] who showed that co-condensation of lithium atoms with CH_3Br or CH_3I in solid argon at *ca.* 15 K affords $CH_3^{\bullet}$ radicals, and that these react with further metal atoms to generate monomeric CH_3Li. In this paper we describe the results of a similar study undertaken to explore the matrix reactions of sodium or potassium atoms with CH_3I. The products include the respective monomeric molecule CH_3Na or CH_3K, which, in its normal and perdeuteriated forms, has been characterised by i.r. measurements. The vibrational properties of the molecules invite comparison, not only with those of CH_3Li[8,9] and related methyl derivatives of the main-group metals,[10] but also with those of a relatively 'electron-deficient' methyl-transition-metal compound like CH_3TiCl_3,[11] which has been the focus of much recent attention through its parentage of at least one system involving 'agostic' Ti$\leftarrow$H–C interactions.[12]

Experimental

The compounds CH_3I (Hopkins and Williams) and CD_3I (Koch–Light) were each dried over P_2O_5 and purified by fractional condensation *in vacuo* with traps held successively at 195, 178, and 77 K. The material collecting at 178 K was shown to be essentially pure iodomethane by reference to its vapour pressure at 273 K[13] and the i.r.[14] and mass spectra of its vapour. On the evidence of their mass spectra, the redistilled samples of CD_3I contained traces of CD_3Cl and CD_3Br, but at concentrations too low to be detected by their i.r. absorptions; no other specific impurity was revealed by the spectroscopic tests. Bromomethane (Matheson) was likewise dried over P_2O_5 and purified by fractional condensation *in vacuo*. Sodium and potassium metals (BDH) were each purified in accordance with the procedure described by Shriver and Drezdzon.[15] For the matrix gases, nitrogen and argon were used as supplied by BOC (both grade 'X').

In the experiments which we report here, a gaseous mixture of iodomethane or bromomethane and the matrix gas (typically in the proportions 1:200—1:300) was co-condensed with a beam of the relevant alkali-metal atoms, admitted *via* a separate inlet tube, on a CsI window cooled to *ca.* 20 K. The sodium- or potassium-atom beam was produced by heating the ampoule containing the metal and the intervening glass pipework up to, and including, a constriction having a direct 'line-of-sight' to the CsI window. The optimum conditions involved sample temperatures of *ca.* 503 and 433 K for experiments with sodium and potassium, respectively. To secure reasonable intensities for the i.r. absorptions characteristic of the products, matrix deposition times of 3—5 h were needed with matrix gas deposition rates of up to 5 mmol h^{-1}. It was difficult to estimate reliably the relative proportions of the reagents, *viz.* metal atoms and halogenomethane, but they were judged to be in the order of 2:1. The CsI window was cooled by means of a two-stage Joule–Thomson refrigerator employing hydrogen as the refrigerant (Air Products AC-2-109 'Cryotip'). The temperature of the window could be varied between 15 and 30 K by decreasing or increasing the hydrogen backing pressure.

Infrared spectra of the matrices were recorded in the range

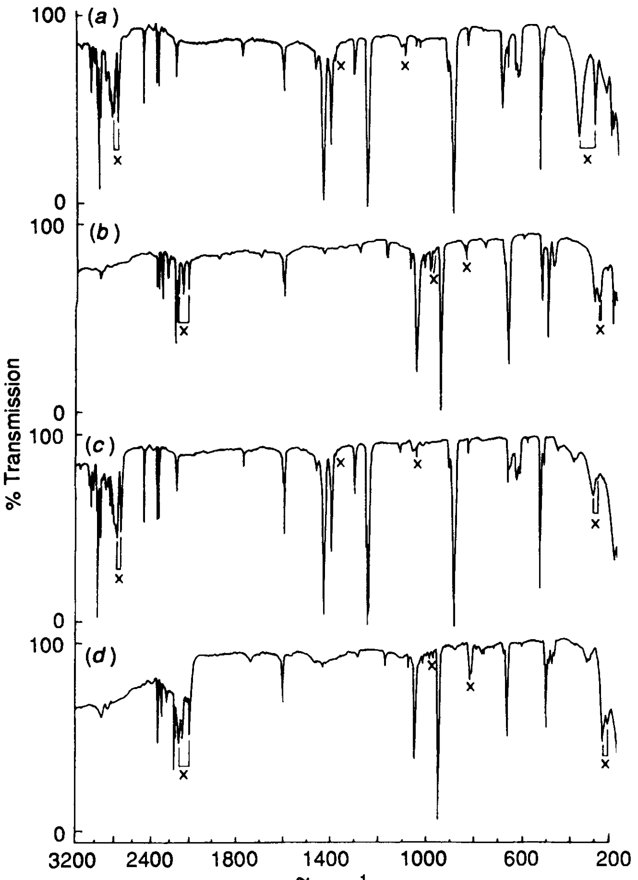

Figure. Infrared spectra of matrices formed by co-condensing (*a*) Na atoms + CH_3I, (*b*) Na atoms + CD_3I, (*c*) K atoms + CH_3I, and (*d*) K atoms + CD_3I, in each case with an excess of N_2 at *ca.* 20 K; proportions typically N_2:CX_3I:M = *ca.* 300:1:2 (M = Na or K; X = H or D). Bands marked 'X' correspond to the methylmetal monomers CX_3M

200—4 000 cm^{-1} on a Perkin-Elmer model 225 double-beam grating spectrophotometer. Calibration was accomplished by reference to the positions of sharp bands in the spectrum of atmospheric H_2O and CO_2. The spectral resolution was typically 0.5 cm^{-1}, and the wavenumbers of bands were determined to an accuracy of ± 1 cm^{-1}.

Normal co-ordinate calculations were carried out on an ICL 1906A digital computer using the normal Wilson *FG* matrix method.[16]

Results

As illustrated in the Figure (*a*) and itemised in Table 1, the i.r. spectrum of the matrix formed by condensing simultaneously a gaseous mixture of CH_3I and N_2 with sodium atoms and having initially the composition N_2:CH_3I:Na = *ca.* 300:1:2 proved to be relatively complicated. Most prominent were the bands attributable to fundamentals or overtones or combinations of these fundamentals for the unchanged CH_3I molecule;[14] in their earlier studies of the interaction of Li atoms with CH_3I under similar conditions, Andrews and Pimentel[8,9] appear mistakenly to have identified some of the weaker bands with 'impurities'. In addition, the spectrum included numerous features whose growth and decay patterns indicated diverse origins (see Table 1). However, a single absorber peculiar to the combination of CH_3I and Na atoms was plainly responsible for a set of six bands having intensities which varied in unison. The wavenumbers (cm^{-1}) and relative intensities (s, strong and w, weak) were as follows: 2 805s, 2 760s, 1 384w, 1 110/1 092w, 362s, and 298s. The bands were observed to grow as the initial matrix concentration of either CH_3I or metal atoms was increased. The circumstances, allied to vibrational properties reminiscent of those of CH_3Li,[9] provide cogent reasons for believing that the absorber in question is the monomeric species CH_3Na formed presumably by the processes (1) occurring

$$\begin{tikzcd} CH_3I + Na \arrow[r] & CH_3^{\bullet} + NaI \arrow[d, "+ Na"] \\ & CH_3Na \end{tikzcd} \qquad (1)$$

either during or after condensation. A broad band of medium intensity near 250 cm^{-1} exhibited the right energy,[17] as well as the right growth characteristics, to be identified with NaI, the co-product of process (1).

Comparison with the results of earlier matrix studies identified both CH_4[18] and C_2H_6[19] as significant by-products whose formation parallelled that of CH_3Na. Despite every endeavour, it was impossible to eliminate all traces of impurity from the matrix, and H_2O,[20] CO_2,[21] and CO[22] could be recognised by their characteristic i.r. absorptions as minor, but adventitious, matrix components. There was also a group of bands, typically of medium intensity, in the region 600—690 cm^{-1} [see Table 1 and Figure (*a*)]. Annealing the matrix at temperatures up to *ca.* 30 K caused these bands to decay with the simultaneous growth of the bands characteristic of C_2H_6.[8,19] The most plausible interpretation is that the absorptions near 600 cm^{-1} represent ν_2, the out-of-plane bending mode, of the $CH_3^{\bullet}$ radical formed, presumably, by the first stage of process (1) and trapped in a variety of matrix cages incorporating more or less strongly interacting dopant molecules, *e.g.* NaI, CH_3Na, or CH_3I.[23,24] The formation of C_2H_6 is then explicable in terms of the facile reaction (2).

$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow C_2H_6 \qquad (2)$$

Two other factors served to complicate the spectrum. First, several of the absorptions were relatively broad or appeared as multiplets, thereby betraying the characteristic signs of matrix-site effects,[25] a problem made more acute than usual by the number of matrix components, as well as the reactivity of some of those components. Secondly, there was the possibility of secondary matrix processes involving aggregation, *e.g.* of Na atoms, CH_3Na, or NaI, or reactions of the resulting aggregates, *e.g.* Na_x ($x \geqslant 2$). Annealing the matrix at temperatures up to 30 K caused significant changes in the low-energy region of the spectrum (200—400 cm^{-1}). Thus, the bands at 362 and 298 cm^{-1} attributed to CH_3Na decayed, with the simultaneous appearance and growth of a band at 263 cm^{-1} associated presumably with an aggregate like $(CH_3Na)_x$ or $CH_3Na \cdots NaI$.

In order to elucidate the interpretation of the matrix spectrum, and fix the assignment of the absorptions belonging to the molecule CH_3Na, we undertook a series of experiments designed to investigate the effects of changing (*i*) the matrix gas, (*ii*) the halogenomethane precursor, (*iii*) the isotopic composition of the iodomethane precursor, and (*iv*) the alkali metal (from sodium to potassium).

(*i*) *Nature of the Matrix Gas.*—Experiments in which nitrogen was replaced by argon as the matrix gas gave results closely similar, in all essential respects, to those outlined above. The only discernible differences were shifts not exceeding 5 cm^{-1} affecting the wavenumbers of the various i.r. features and increases in the multiplicity or band width of several of these

Table 1. Infrared spectra of CX_3I ($X = H$ or D) or mixtures of CX_3I and M atoms ($M = Na$ or K) isolated in nitrogen matrices at *ca.* 20 K

	$\tilde{\nu}$/cm^{-1} and intensity[b]						
Assignment[a]	CH_3I	$CH_3I + Na$	$CH_3I + K$	$CD_3I + K$	$CD_3I + Na$	CD_3I	Assignment[a]
CH_3I, $\nu_4 + \nu_6$	3 938w	3 935w	3 934w				
H_2O (impurity): H_2O, $[H_2O]_x$, or $H_2O \cdots X$ adducts	3 726	3 725	3 726	3 725	3 724	3 726	H_2O (impurity): H_2O, $[H_2O]_x$, or $H_2O \cdots X$ adducts
	3 713	3 713	3 713	3 712	3 712	3 714	
	3 694w	3 694w	3 686w				
	3 632	3 632	3 632	3 630	3 631	3 634	
CH_3I, $\nu_1 + \nu_3$			3 488vw	3 330m	3 331m	3 332m	CD_2I, $\nu_4 + \nu_5$
$H_2O \cdots X$ adduct			3 280vw	3 235w	3 235w	3 238w	CD_3I, $\nu_2 + \nu_4$
$CH_3^{\bullet}$, ν_3		3 143w	3 142vw				
CH_3I, ν_4	3 057m	3 058m	3 058m				
$CH_3I \cdots X$, ν_4		3 045m	3 041m				
CH_4, ν_3		3 012w	3 012w				
C_2H_6, ν_7		2 981s	2 980m				
CH_3I, ν_1	2 969vs	2 969vs	2 969vs				
C_2H_6, ν_5		2 947s	2 943s	2 948w	2 949w	2 944w	CD_3I, $\nu_4 + \nu_6$
C_2H_6, $\nu_8 + \nu_{11}$		2 886m	2 885w				
		2 873vw	2 872vw				
CH_3I, $2\nu_5$	2 848m	2 849m	2 849m				
CH_3I, $\nu_3 + \nu_5 + \nu_6$	2 821m	2 822s	2 822m				
CH_3M, ν_4		2 805s	2 775s				
CH_3M, ν_1		2 760s	2 732s				
CH_3I, $2\nu_2$	2 485s	2 485s	2 485s				
CO_2 (impurity), ν_3	2 348	2 348	2 346	2 347	2 348	2 348	CO_2 (impurity), ν_3
		2 335w			2 332w		
	2 324w	2 327m	2 327m	2 326m	2 326m	2 326m	
CH_3I, $\nu_2 + 2\nu_3$	2 280w	2 281vw	2 281vw	2 283m	2 288m	2 294w	CD_3I, ν_4
				2 235m	2 232m		C_2D_6, ν_7
				2 215w	2 215vw		C_2D_6, $\nu_2 + \nu_6$
				2 187w	2 188vw	2 191w	CD_3I, $\nu_3 + \nu_5 + \nu_6$
				2 153vs	2 153vs	2 153vs	CD_3I, ν_1
CO (impurity)		2 139	2 139	2 136	2 139		CO (impurity)
CH_3I, $\nu_2 + \nu_6$	2 133m	2 132m	2 132m	2 101m	2 123m		CD_3M, ν_4
				2 073s	2 074m	2 074s	CD_3I, $2\nu_5$
				1 994m	2 019m		CD_3M, ν_1
				1 880w	1 880w	1 879w	CD_3I, $2\nu_2$
CH_3I, $2\nu_6$	1 771w	1 771w	1 771w	1 696w	1 698w	1 697w	CD_3I, $\nu_5 + \nu_6$
H_2O (impurity): H_2O, $[H_2O]_x$, or $H_2O \cdots X$	1 603	1 604	1 604	1 603	1 603	1 603	H_2O (impurity): H_2O, $[H_2O]_x$, or $H_2O \cdots X$
	1 597	1 598	1 598	1 597	1 597	1 597	
C_2H_6, ν_8		1 465w	1 466w				
CH_3I, ν_5	1 432vs	1 432vs	1 432vs	1 432w	1 432w	1 433w	CD_3I, $\nu_2 + \nu_3$
CH_3I, $\nu_3 + \nu_6$	1 401s	1 402s	1 402s				
CH_3M, ν_5		1 384w	1 384w				
C_2H_6, ν_6		1 372vw	1 375vw				
CH_4, ν_4		1 303m	1 304m	1 280w	1 280w	1 279w	CD_3I, $2\nu_6$
CH_3I, ν_2	1 247vs	1 249vs	1 249vs	1 169m	1 168m	1 169m	CD_3I, $\nu_3 + \nu_6$
Unknown			1 114w				
CH_3M, ν_2		1 110w,br	1 062w,br	1 071w	1 070m		C_2D_6, ν_6
		1 092w	1 053w				
CH_3I, $2\nu_3$	1 044w	1 044w	1 045w	1 044vs	1 044vs	1 045vs	CD_3I, ν_5
$CH_3I \cdots X$, $2\nu_3$		1 028w	1 025vw	1 013m	1 011m	1 013m	$[CD_3I]_x$, $\delta_{asym.}(CD_3)$
				1 000m			CD_3H, ν_3
				987m	986m	987s	CD_3I, $2\nu_3$
				982m	982m	983m	
				967w	972w		CD_3M, ν_5
$CH_3I \cdots X$, ν_6		909m	910m	946vs	946vs	946vs	CD_3I, ν_2
CH_3I, ν_6	885vs	885vs	884vs				
C_2H_6, ν_9		828w	829w	814m	842w		CD_3M, ν_2
				807m	836m		
				755w	755w	755w	Impurity
$CH_3^{\bullet}$, ν_2		681m		674m(sh)	674m		$CD_3I \cdots X$, ν_6
CO_2 (impurity), ν_2	662	662	662	657vs	657vs	657vs	CD_3I, ν_6
$CH_3^{\bullet}$, ν_2		631m					
		629m	628m				
			625m				
		621m	623m				
		617m					
		614m	614m				
		611m	611m	596w	596w		C_2D_6, ν_9
CH_3I, ν_3	525vs	526vs	526vs		525s		$CD_3^{\bullet}$, ν_2
$CH_3I \cdots X$, ν_3		515m	512m	495vs	495vs	495vs	CD_3I, ν_3

Table 1. (*continued*)

	$\tilde{\nu}$/cm^{-1} and intensity[b]						
Assignment[a]	CH_3I	CH_3I + Na	CH_3I + K	CD_3I + K	CD_3I + Na	CD_3I	Assignment[a]
Unknown[c]			458w	472m	470m		$CD_3^{\bullet}$, ν_2 + $CD_3I \cdots X$, ν_3
$[CH_3K]_x$ or $CH_3K \cdots X$			386[d]	360[d]			
				332[d]			$[CD_3M]_x$ or $CD_3M \cdots X$
CH_3M, ν_6		362s	307m	326w,br	303s		
CH_3M, ν_3		298s	280(sh)	259s	285s		CD_3M, ν_6
$[CH_3M]_x$ or $CH_3M \cdots X$		263[d]	245[d]	237m	278m(sh)		CD_3M, ν_3
NaI		255m,br			260w 250w		NaI
$[CH_3Na]_x$ or $CH_3Na \cdots X$		229[d]		228[d]			$[CD_3K]_x$ or $CD_3K \cdots X$
Matrix feature	220m	220m	218m	220m	220m	220m	Matrix feature

[a] M = Na or K; X denotes some unknown species. [b] s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder. Bands carrying no such label varied irregularly in intensity from experiment to experiment. [c] Some reactive species which decayed when the matrix was annealed at temperatures up to *ca.* 30 K. [d] Band grew when the matrix was annealed at temperatures up to *ca.* 30 K.

features. Not for the first time,[26] then, matrix site effects turned out to be more pronounced with argon than with nitrogen matrices, and for this reason we have based any detailed analysis on the spectroscopic properties of the nitrogen matrices. The experiments with argon matrices were important, none-the-less, for establishing that the nitrogen played no major chemical role in the reactions of sodium atoms with CH_3I. The behaviour of transition-metal atoms like V[27a] and Ni[27b] and of unsaturated species like $M(CO)_5$ (M = Cr, Mo, or W)[27c] testifies that this non-intervention of nitrogen matrices cannot be taken for granted, and indeed the species LiN_2 and Li_2N_4 have been identified as components of matrices formed by the codeposition of Li atoms with nitrogen.[27d]

(*ii*) *Nature of the Halogenomethane Precursor.*—Experiments in which Na atoms were co-condensed with a mixture of CH_3Br and N_2 also gave results very similar to those in which CH_3I was the reagent. Apart from the obvious differences associated with the presence in the matrix of unchanged CH_3Br[14a] and the development of a band not near 250 cm^{-1} but at *ca.* 270 cm^{-1}, which could be identified with the formation of NaBr,[17] the i.r. spectrum resembled closely the one described earlier for the system Na–CH_3I–N_2 [see Figure (*a*) and Table 1]. The six bands believed to originate in CH_3Na maintained the same energies (within ± 3 cm^{-1}) and relative intensities, thereby confirming that they must belong to a common product of the two reactions Na + CH_3I and Na + CH_3Br.

(*iii*) *Experiments with* CD_3I.—The effects of replacing CH_3I by CD_3I in the reaction with Na atoms are illustrated in Figure (*b*), and the results included in Table 1. The most significant finding is that the bands which occurred originally at 2 805, 2 760, 1 384, 1 110/1 092, 362, and 298 cm^{-1} are relocated at the following energies when CH_3I is replaced by CD_3I as the reagent: 2 123, 2 019, 972, 842/836, 285, and 278 cm^{-1}. That these new bands have a common origin is again implied by the constancy of their relative intensities. Other features of the spectrum comply in their behaviour with expectations based on the identities and origins of the appropriate absorbers (see Table 1).

An experiment was also carried out with an equimolar mixture of CH_3I and CD_3I as one of the starting materials. As expected, the resulting matrix gave an unusually rich i.r. spectrum, the details of which were hard to interpret. There was, however, no evidence that the isotopically normal and deuteriated forms of the methylsodium product gave anything more than the two sets of six bands identified in the experiments involving CH_3I and CD_3I separately. This is consistent with the presumption that the product contains only one CH_3 (or CD_3) group.

It would have been interesting to measure the i.r. spectrum of the product derived from the partially deuteriated molecule CHD_2I, so as to gain some knowledge of the 'isolated' C–H stretching frequency, $\nu(CH)^{is}$, thereby minimising problems of Fermi resonance and offering a means of estimating the C–H bond length and H–C–H bond angle.[11,28] On the other hand, the combined experiences of our experiment with the mixture of CH_3I and CD_3I and of earlier experiments with Li atoms and CHD_2I, carried out by Andrews,[9] offer only slender prospects of success, partly because of congestion in the relevant regions of the spectrum, and partly because of the weakness in i.r. absorption of the $\nu(CH)^{is}$ mode of the putative product CHD_2M (M = Li[9] or Na).

(*iv*) *Experiments with Potassium and* CH_3I *or* CD_3I.—Co-condensation of CH_3I with potassium atoms under conditions otherwise similar to those employed for the experiments with sodium yielded a matrix with an i.r. spectrum typically as shown in Figure (*c*) and including the features listed in Table 1. Many of the bands in this spectrum—associated, for example, with unchanged CH_3I, CH_4, C_2H_6, $CH_3^{\bullet}$, and the various impurities—were closely analogous to those displayed by a matrix incorporating Na atoms and CH_3I. The most obvious difference was that the six bands belonging presumably to CH_3Na were replaced by six new bands; centred at 2 775, 2 732, 1 384, 1 062/1 053, 307, and 280 cm^{-1}, respectively, these were mostly displaced somewhat to low energy of, while maintaining more-or-less the same relative intensities as, their CH_3Na counterparts. Substitution of CD_3I for CH_3I caused all six bands to shift, the new locations being 2 101, 1 994, 967, 814/807, 259, and 237 cm^{-1}, respectively. The circumstances of these experiments provide persuasive arguments for believing that the two sets of bands are associated with the molecules CH_3K and CD_3K, each formed presumably as a result of a process akin to process (1). There was no sign in the low-frequency region of the spectrum (200—400 cm^{-1}) of any absorption attributable to KI in either monomeric or oligomeric forms, but, since monomeric KI isolated in an argon matrix is reported[29] to absorb near 170 cm^{-1} and K_2I_2 at even lower frequencies, this need not come as a surprise. On the other hand, the low-frequency region of the spectrum did undergo substantial changes when the matrix was annealed at temperatures up to 30 K. Thus, with matrices containing CH_3I, new bands were observed to grow at 387 and 245 cm^{-1} at the expense of the bands belonging to CH_3K; with matrices containing CD_3I, new bands were observed to grow at 360, 332, and 228 cm^{-1}. The most likely explanation is that

Table 2. Wavenumbers[a] of the vibrational fundamentals and force constants[b] for the matrix-isolated molecules CX_3Na and CX_3K (X = H or D)

Molecule	Symmetry species	CH_3M obs.	CH_3M calc.	CD_3M obs.	CD_3M calc.	Force constant[c]
CH_3Na/CD_3Na	a_1	2 760	2 777	2 019	1 994	$F_{11} = 445$
		1 092	1 095	836	835	$F_{22} = 38$
		298	299	278	284	$F_{33} = 48$
	e	2 805	2 824	2 123	2 102	$F_{44} = 425$
		1 384	1 370	972	991	$F_{55} = 50$
		362	367	285	273	$F_{66} = 10.3$
CH_3K/CD_3K	a_1	2 732	2 746	1 994	1 971	$F_{11} = 435$
		1 053	1 055	807	804	$F_{22} = 35$
		280	275	259	258	$F_{33} = 48.5$
	e	2 775	2 791	2 101	2 077	$F_{44} = 415$
		1 384	1 358	967	983	$F_{55} = 49$
		307	309	237	229	$F_{66} = 7.6$

[a] Wavenumbers in cm^{-1}. [b] f_r in N m^{-1}, $f_{r\alpha}$ in N rad^{-1}, and f_α in N m rad^{-2}. [c] $F_{12} = F_{13} = 0$; $F_{23} = -0.07$; $F_{56} = 0.04$.

thermally induced diffusion encourages aggregation of the CH_3K or secondary reactions involving other matrix components, *e.g.* as in equations (3) and (4).

$$CH_3K + KI \longrightarrow CH_3K\cdots KI \quad (3)$$

$$K_x + CH_3^{\bullet} \longrightarrow CH_3K_x \quad (4)$$

Discussion

The results of our matrix experiments lead us to identify the monomeric molecules CH_3Na and CH_3K as major products of the reactions which take place when CH_3I is co-condensed with a beam of the appropriate alkali-metal atoms. The failure to be able to change the isotopic composition of the metal means that we lack positive evidence that the products are each mononuclear with respect to the alkali metal. On the other hand, the circumstances in which the i.r. bands grow and decay, the number and intensity pattern of these bands, and the obvious parallels with the spectroscopic properties of CH_3Li (the identification of which is validated by $^6Li/^7Li$ isotopic effects)[9] would seem to leave little room for doubt that the molecules each contain a single metal atom. Such a molecule conforms presumably to C_{3v} symmetry and is therefore characterised by six distinct vibrational fundamentals spanning the representation $3a_1 + 3e$ and all of them active in i.r. absorption. The fundamentals involve symmetric and antisymmetric ν(C–H) [ν_1 (a_1) and ν_4 (e), respectively, expected to occur at 2 700—2 820 cm^{-1}],[9] symmetric and antisymmetric $\delta(CH_3)$ [ν_2 (a_1) and ν_5 (e), respectively, expected to occur at 1 000—1 400 cm^{-1}],[9] ν(M–C) [ν_3 (a_1) expected at a wavenumber < 500 cm^{-1}],[9] and $\rho(CH_3)$ [ν_6 (e) expected at a wavenumber < 400 cm^{-1}].[9] In the limit of a system involving a free CH_3^- anion, isoelectronic with NH_3, the last two frequencies, ν_3 and ν_6, would tend to zero.

In order to assign the i.r. spectrum attributable to each of the matrix-isolated molecules CH_3Na and CH_3K, we have drawn on three sources of evidence: (*i*) the energies and relative intensities of the various absorptions, (*ii*) analogies with the spectroscopic properties of related monomethyl derivatives, notably CH_3Li[9] and CH_3TiCl_3,[11] and (*iii*) consideration of the effects of deuteriation. Table 2 summarises the results of our analysis. The energies of all the fundamentals are the lowest of any CH_3M moiety reported to date,[9,10,28] although they conform in this respect to the pattern expected for electropositive M atoms. Particularly striking is the $\rho(CH_3)$ mode, ν_6, which occurs at 362 or 307 cm^{-1} in CH_3Na or CH_3K, respectively, when it would normally be expected to occur in the range 700—900 cm^{-1} for a methyl derivative of a metal or metalloid comparable in mass to either sodium or potassium.[10] There is a parallel here, not only with CH_3Li for which ν_6 408.5 cm^{-1},[9] but also with CH_3TiCl_3 for which $\rho(CH_3)$ 463.7 cm^{-1}.[11] With more-or-less 'normal' ν(C–H) modes at 2 981 and 2 893.5 cm^{-1},[11] however, the titanium compound still differs significantly from the alkali-metal compounds.

Despite differences of frequency amounting in some cases to *ca.* 45 cm^{-1}, there are obvious similarities between the rather sparsely characterised spectra of solid methylsodium[2] and methylpotassium[3] and those of the matrix-isolated monomers, and, as with methyl-lithium,[9] it would seem that the C–H bonds of the methyl groups are affected but marginally by the aggregation attending the switch from the isolated monomer to the solid compound.

Product Rule and Normal Co-ordinate Calculations.—In order to check the vibrational assignments outlined in the preceding section, we have appealed to Product Rule calculations. These depend upon the dimensions of the molecules CH_3Na and CH_3K. Some idea of the C–H bond length has been gained from two sources. First, preliminary calculations have shown that the C–H stretching force constants for both CH_3Na and CH_3K are near 420—430 N m^{-1}; the empirical relationship linking this force constant to the bond length[8] is then used to estimate *r*(C–H). Secondly, we have drawn on another empirical relationship, *viz.* equation (5) involving the 'isolated' C–H

$$r_0(\text{C–H})/\text{pm} = 139.82 - 0.010\,23\nu(\text{CH})^{\text{is}} \quad (5)$$

stretching frequency, $\nu(CH)^{is}$, of the species CHD_2M.[28] In the absence of any measurements, we assume that $\nu(CH)^{is}$ lies somewhere between the limits set by ν_1 and ν_4. Both approaches predict a C–H bond length near 112 pm, in sensible agreement, not only with the distance of 111.3 pm determined by electron diffraction for the molecule $Al(CH_3)_3$,[30] but also with the results of calculations on CH_3^- and CH_3Na.[6,7] The shortest M–C distances in the solid methyl compounds are *ca.* 260 pm (M = Na)[2] and 322 pm (M = K),[3] but these are expected to be appreciably *longer* than the M–C bond lengths in the corresponding monomers. These lengths have therefore been estimated by reference (*i*) to the sums of the relevant covalent radii, with the assumption of a purely 'covalent' M–C bond,[31] (*ii*) to bond length–force constant plots (involving the molecules LiNa, NaF, LiK, and KF),[32,33] and (*iii*) to the ratios of bond lengths in pairs of related molecules (*e.g.* $Al(CH_3)_3:AlF_3$; $CH_3Na:NaF$; and $CH_3K:KF$).[30,32,34] Hence we conclude that

Table 3. Product Rule calculations for the matrix-isolated molecules CH_3M and CD_3M (M = Na or K)

Observed ratio, $\nu_i(H)/\nu_i(D)$	CH_3Na/CD_3Na a_i	CH_3Na/CD_3Na e	CH_3K/CD_3K a_1	CH_3K/CD_3K e
ν_1 or ν_4	1.367	1.321	1.370	1.321
ν_2 or ν_5	1.306	1.424	1.305	1.431
ν_3 or ν_6	1.072	1.270	1.081	1.295
$P_{obs.} = \Pi\left\{\frac{\nu_i(H)}{\nu_i(D)}\right\}$	1.914	2.390	1.933	2.449
$P_{calc.}$	1.923	2.498	1.945	2.517

the bond lengths are probably as follows: *r*(Na–C) *ca.* 230 and *r*(K–C) *ca.* 270 pm. In the case of the sodium compound, there is reassuring agreement between our estimate and the value of 232 pm calculated on the basis of *ab initio* methods.[7] On the other hand, it has proved impossible to arrive at any consistent estimate of the bond angles at carbon, and the H–C–H angle has therefore been set equal to the tetrahedral angle of 109.5°; *ab initio* calculations on CH_3Na [7] give a value of 108.3°.

The results of the Product Rule calculations are presented in Table 3. The proposed assignments give Product Rule factors $P_{a_1} = \nu_1(H)\cdot\nu_2(H)\cdot\nu_3(H)/\nu_1(D)\cdot\nu_2(D)\cdot\nu_3(D)$ and $P_e = \nu_4(H)\cdot\nu_5(H)\cdot\nu_6(H)/\nu_4(D)\cdot\nu_5(D)\cdot\nu_6(D)$ in satisfactory agreement with, but slightly less than, the calculated factors; any alternative assignment of the fundamentals, based on the observed i.r. bands, would give an inferior, or even unacceptable, account of these parameters. The usual effect of anharmonicity, dominated by cubic terms, is indeed to make the observed factors slightly smaller than the calculated ones. Since only with the *e* species do the calculations draw on the dimensions of the molecules, uncertainties affecting these dimensions could contribute to the larger discrepancies between $P_{obs.}$ and $P_{calc.}$ revealed here. However, varying the H–C–H angles over a considerable range produced only marginally better results.

Normal co-ordinate calculations have also been carried out[16] using the assignments for both isotopomers CH_3M and CD_3M to define the potential functions of a quadratic force field. Off-diagonal *F*-matrix elements were first set to zero, and the corresponding diagonal elements calculated for each symmetry block. Interaction force constants F_{23} and F_{56} linking the low-frequency co-ordinates of the a_1 and *e* blocks, respectively, were then introduced to optimise the agreement between observed and calculated frequencies. The results of the calculations are contained in Table 2. The corresponding potential-energy distributions imply that each of the fundamentals is quite well described by the co-ordinate specified earlier, with little or no mixing of these co-ordinates. The principal discrepancies between observed and calculated frequencies are found, as usual, with the ν(C–H) modes ν_1 and ν_4, and may be attributed to the combined effects of anharmonicity and Fermi resonance.[11,28]

Of the force constants calculated for CH_3Na and CH_3K, those governing ν(C–H), ν(M–C), and $\rho(CH_3)$ are most noteworthy. The stretching force constant f_{CH} varies but little in the series CH_3Li, CH_3Na, CH_3K; at 422—432 N m^{-1}, it is substantially smaller than in the halogenomethane molecules CH_3F and CH_3Cl (530[35] and 541 N m^{-1} [36]), CH_3TiCl_3 (479.5 N m^{-1}),[11] or the $CH_3^{\cdot}$ radical (531 N m^{-1}),[37] but not as small as in the CH radical (409 N m^{-1}).[32] The value, which cannot be far removed from that characteristic of the CH_3^- anion, is consistent with a relatively long and weak C–H bond in the molecules CH_3M (M = Li, Na, or K).[28] The force constant f_{MC} is essentially constant for the molecules CH_3Na and CH_3K (*ca.* 48 N m^{-1}), rather larger for CH_3Li (78 N m^{-1}), and much larger for methyl derivatives of more electronegative substituents like $TiCl_3$, Cl, or F (183—567 N m^{-1}). No less conspicuous is the $\rho(CH_3)$ force constant which reaches a new 'low' with the value of 7.6 N m rad^{-2} for CH_3K, almost an order of magnitude less than the corresponding constants for CH_3F and CH_3Cl. Other methyl derivatives of metals or metalloids, *e.g.* $(CH_3)_2Zn$,[38a] $(CH_3)_2Hg$,[38b] and CH_3SiCl_3,[39] are characterised by $\rho(CH_3)$ constants typically in the range 26—42 N m rad^{-2}. There is to our knowledge but one exception, provided by CH_3TiCl_3 with a $\rho(CH_3)$ constant (18.4 N m rad^{-2}) roughly midway between these values and the ones for the methyl-alkali-metal derivatives (7.6—10 N m rad^{-2}). As noted previously, the pliability of alkali-metal molecules of the type CH_3M with respect to the ν(M–C) and $\rho(CH_3)$ co-ordinates testifies to a highly polar M–C bond and to a situation approximating more and more closely to the ion-pair formulation $CH_3^-M^+$ in the series M = Li, Na, K.

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