

generacy of the hyperfine components in the spectrum of TAA<sup>+2</sup> prevents a quantitative interpretation of the line-width variations.<sup>10</sup> Since the spin density at the nitrogen nucleus is high (Table I), one can predict, however, that relaxation contributions due to the <sup>14</sup>N nucleus will be considerably larger than those due to the protons (*cf.* ref 12). The differences in line widths between the three groups of hyperfine components, therefore, can be attributed primarily to terms linear and quadratic in the <sup>14</sup>N nuclear quantum number

$$T_2^{-1} = KM_N^2 + LM_N$$

where  $K$  and  $L$  are constants<sup>10,12</sup> and  $T_2^{-1}$  is the contribution to the line width. The second right-hand term in this expression can be used, together with the observation that the high-field components are broader than the corresponding low-field components, to derive the sign of the <sup>14</sup>N hfs constant.<sup>12-14</sup> Following the arguments which have been presented previously,<sup>12,14</sup> one can show that  $L$ , a constant containing the  $g$ -tensor components and the electron spin-<sup>14</sup>N nuclear spin dipolar interaction component along the trigonal axis of the radical, must be negative. The group with  $M_N = -1$  will, therefore, be broader than the group for which  $M_N = +1$ , so that our experimental finding leads to the conclusion that the <sup>14</sup>N hfs constant must be positive. This is in agreement with the sign derived with the help of the modified Karplus-Fraenkel formula<sup>15</sup> relating the <sup>14</sup>N hfsc to the spin densities on <sup>14</sup>N and its neighboring carbon atoms.<sup>16,17</sup>

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### Vibrational Bands of Alkali Metal Salts in Dimethyl Sulfoxide

Sir:

Recently Edgell and co-workers have reported<sup>1</sup> their observation on the vibrational spectra of Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> salts of Co(CO)<sub>4</sub><sup>-</sup> and Mn(CO)<sub>5</sub><sup>-</sup> anions in tetrahydrofuran solutions. The three salts of the first anion show infrared bands at 407, 190, and 150 cm<sup>-1</sup>, respectively, while the corresponding bands of the Mn(CO)<sub>5</sub><sup>-</sup> salts are shifted to higher frequencies by 20-30 cm<sup>-1</sup>.

We wish to report our observation of the spectra of ammonium and alkali metal salts in dimethyl sulfoxide solutions. The data are given in Table I. It is seen that in our case the absorption band is essentially independent of the nature and the mass of the anion and, therefore, should be due to the interaction of the cation with the solvent molecules.

We made an admittedly very crude assumption that

- (1) W. F. Edgell, A. T. Watts, J. Lyford, and W. M. Risen, Jr., *J. Am. Chem. Soc.*, **88**, 1815 (1966).

Table I. Absorption Band of Alkali Salts in Dimethyl Sulfoxide

Compound	Concn, $M$	$\nu_{\max}$ , cm <sup>-1</sup>
LiCl <sup>a</sup>	0.4	429 ± 2
LiBr	0.4	429 ± 2
LiI	0.9	429 ± 2
LiNO <sub>3</sub>	0.4	429 ± 2
LiClO <sub>4</sub>	0.5	429 ± 2
NH <sub>4</sub> Cl	Satd	214 ± 5
NH <sub>4</sub> Br	0.4	214 ± 4
NH <sub>4</sub> I	0.7	214 ± 4
NH <sub>4</sub> NO <sub>3</sub>	0.4	214 ± 4
NH <sub>4</sub> ClO <sub>4</sub>	0.5	214 ± 4
NH <sub>4</sub> SCN	0.5	214 ± 4
NaCl	Satd	199 ± 5
NaBr	Satd	199 ± 3
NaI	1.0	198 ± 3
NaNO <sub>3</sub>	1.0	206 ± 3
NaSCN	1.0	200 ± 3
NaPh <sub>4</sub> B	0.26	198 ± 3
NaNO <sub>3</sub>	0.60 (in 2:1 C <sub>6</sub> H <sub>6</sub> -DMSO mixt)	205 ± 3
KBr	0.5	153 ± 3
KI	1.0	153 ± 3
KNO <sub>3</sub>	1.0	154 ± 3
KSCN	1.0	153 ± 3
RbI	3.0	129 ± 4
RbNO <sub>3</sub>	0.5	123 ± 5
CsI	Satd	118 ± 6

(~1.5 M)

<sup>a</sup> The Li<sup>+</sup> bands have a shoulder at ~414 ± 2 cm<sup>-1</sup>.

Table II. Calculated and Observed Band Frequencies

Cation	$\nu_{\text{calc}}$ , cm <sup>-1</sup>	$\nu_{\text{obsd}}$ , cm <sup>-1</sup>
Li <sup>+</sup>	335	429
NH <sub>4</sub> <sup>+</sup>	221	214
Na <sup>+</sup>	...	200
K <sup>+</sup>	165	153
Rb <sup>+</sup>	132	125
Cs <sup>+</sup>	120	118

the observed absorption bands are due to a cation-solvent molecule vibration and that the force constants did not change with the change in the cation. Taking the Na<sup>+</sup> band as the standard, we calculated the frequencies of other bands. The results are shown in Table II.

It is, of course, quite evident that the force constants would vary with the nature of the cation and that the alkali metal ions are solvated by several molecules of DMSO. Nevertheless the trends are consistent and seem to indicate the ion-solvent interaction. The large disagreement in the case of lithium salts is to be expected in view of the known coordinating ability of the lithium ion. Further studies of the above and similar systems are now in progress.

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### A Peroxide Fragmentation Reaction

Sir:

Tertiary dialkyl peroxides are normally insensitive to base.<sup>1</sup> We wish to report a unique decomposition of a tertiary peroxide in a basic medium.

When 2-*t*-butylperoxy-2-methylpropionic acid (I) was treated with triethylamine in chlorobenzene at

- (1) N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 205 (1946).