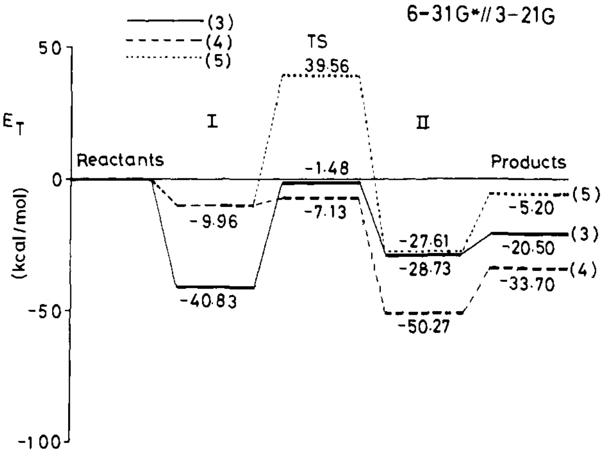

Figure 7. Potential energy profiles of reactions 3, 4, and 5. I and II denote ion-dipole complexes, and TS means the transition state. Energies in the figure stand for the stabilizing (<0) or destabilizing (>0) values relative to those of reactants.

4 and 5 are competitive, holding the intermediate I in common. By the larger kinetic energy, reaction 4 becomes minor as reaction 5 with the larger activation barrier becomes dominant. The large kinetic energy gives either the simple elastic collision (no S_N2) between the methyl hydrogen of $CH_3OCH_2^+$ and NH_3 or reaction 5.

Concluding Remarks

In this work, the kinetics of the three gas-phase reactions, reactions 3, 4, and 5, between methoxymethyl cation and ammonia has been determined at 433 K. The result in Table II shows the similar rate constants where the rank is $k_3 > k_5 > k_4$. An ab initio MO calculation has given the potential energy profile of the three reactions. Reaction 3 consists of the nucleophilic attack of NH_3 to the carbonyl carbon and the 1,3-proton shift from the nitrogen to the oxygen atom. The kinetic efficiency of reaction 3 is ascribed to the substantial stability of the intermediate I (i.e., the long-lived collision complex). Reaction 4 is of the S_N2 type and is not efficient due to the short-lived intermediate I and the pinpoint target of the back-side attack. Reaction 5 is composed of the concerted motion of the proton shift and the ring closure. Although reaction 5 has a large activation barrier, it is more efficient than reaction 4 through the effective conversion[7] of the translation energy to the internal energy and the absence of the methyl hydrogen block.

Reactions 3 and 4 involve the representative mechanisms of organic chemistry. Reaction 5 is a characteristic gas-phase process under the abundant translation energy. The methyl hydrogen may be hardly abstracted in the mild conditions of the aqueous media.

Acknowledgment. We thank the Data Processing Center of Kyoto University for the allotment of the CPU time of the FACOM M-382 computer. Thanks are also due to the Institute for Molecular Science for our use of the HITAC M-200H computer.

Registry No. $MeOCH_2^+$, 23653-97-6; NH_3, 7664-41-7.

Infrared Spectra of Alkali Metal Atom-Ammonia Complexes in Solid Argon

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Abstract: One-to-one complexes between Li, Na, K, and Cs atoms and NH_3 have been studied by using matrix IR spectroscopy. New bands at 1133, 1079, 1064, and 1049 cm^{-1} are assigned to perturbed ν_2 modes, and bands at 3277, 3294, 3292, and 3287 cm^{-1} are assigned to the perturbed ν_1 ammonia submolecule modes of the Li--NH_3, Na--NH_3, K--NH_3, and Cs--NH_3 complexes, respectively. The corresponding bands for K and $^{15}NH_3$, NH_2D, NHD_2, and ND_3 complexes are also assigned. The intensity ratios of ν_1 to ν_2 for the ammonia submolecule modes in the Li, Na, K, and Cs complexes are larger by factors of 15, 20, 30, and 35, respectively, than the corresponding ratio for isolated ammonia. The intensification and position of ν_1 in the complex and the alkali metal-ammonia interaction are consistent with calculations of a very small ammonia → metal charge transfer where the alkali atom acts as a weak Lewis acid for Li and Na. The increased ammonia interaction with K and Cs may suggest a possible acid-base role reversal for the heavier alkali complexes. At higher metal/ammonia concentrations higher aggregate bands of $(M)_n$--NH_3 nature are also observed.

Solutions of alkali metal in liquid ammonia have been the subject of numerous studies dating back more than a century.[1-3] The well-known reactions of alkali metals with liquid water and ammonia are highly exothermic, and solvation of the alkali cation and electron formed provide major contributions to the exothermicity of the reaction. At the molecular level in the gas phase, however, the reactivity is expected to be greatly reduced. Ab initio SCF calculations[4,5] predict a 14.5 kcal/mol binding energy for Li--NH_3 but only 6.0 kcal/mol for Na--NH_3, as compared to 33 and 29 kcal/mol, respectively, for the corresponding ion-molecule complexes Li^+--NH_3 and Na^+--NH_3 observed by high-pressure mass spectrometry in the gas phase.[6] No calculations exist for larger alkali atom complexes, but experimentally measured binding energies decrease steadily going down the series for the cation-ammonia complexes. The ESR spectrum of the Li--NH_3 complex in solid argon indicates a reduced spin density localized in the lithium 2s orbital.[7] Although chemical intuition

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suggests metal → base charge transfer, transfer in the opposite direction can also explain the ESR spectrum. The SCF calculations indicate small base → metal charge transfer and, coupled with the ESR data, provide an explanation for the metal–base interaction where the alkali atom acts as a weak Lewis acid. Matrix infrared studies of the Li--OH_2 complex[8] are consistent with this picture. The present work provides infrared characterization of alkali metal atom–ammonia complexes in solid argon.

Experimental Section

Mixtures of NH_3 and Ar in mole ratios between 1:300 and 1:1000 were codeposited with the alkali metal atoms effusing from a Knudsen cell onto a 12–15 K CsI window; experimental details have been described previously.[9,10] Ammonia (Matheson) and $^{15}NH_3$ and ND_3 (Merck Sharp & Dohme) were used as supplied. Alkali metal atoms were obtained by heating the metals to give vapor pressures of 10^{-4}–10^{-2} torr according to the following temperature ranges: Li, 420–445 °C; Na, 170–240 °C; and K, 140–190 °C. Cs was obtained by the reaction of Li with CsCl at temperatures of 250–290 °C as described previously.[11] For each alkali atom a large number of experiments were conducted in order to unambiguously identify the 1:1 complex with ammonia. Since ammonia aggregates readily in an argon matrix, a large number of experiments at different dilutions had to be carried out to identify bands due to higher NH_3 aggregates as well. Deposition rates of approximately 2 mmol/h were employed for 10-h periods. All data were taken on a Nicolet 5 DXB FTIR spectrometer using 2-cm^{-1} resolution, and band positions are accurate to better than 1 cm^{-1}. All the spectra in absorbance mode were background corrected and normalized to the strongest band of isolated NH_3 at 974 cm^{-1}. Relative intensities of the bands were computed by using ratios of integrated bands; uncertainties in the relative intensities vary depending on the strength of the band, but this is believed to be less than 20%.

Results

Selected spectra for various alkali atom–ammonia/argon mixtures will be presented, and relevant features will be discussed first for Na--NH_3 at different concentrations, then for Li--NH_3, Na--NH_3, K--NH_3, and Cs--NH_3 collectively, and last for K--$^{15}NH_3$ and K--NH_xD_{3-x} (x = 0, 1, 2, 3).

Na and NH_3. Figure 1 shows two regions of the infrared spectra of argon/ammonia (very bottom) and five selected Na–ammonia mixtures deposited at various Knudsen cell temperatures ranging between 170 and 235 °C corresponding to at least a 20-fold increase of Na vapor pressure. The NH_3:Ar mole ratio was varied separately between 1:300 and 1:1000 but is 1:300 for all the spectra presented in the figure. The 3500–3100-cm^{-1} region corresponds to the very weak N–H stretching modes and the 1200–900-cm^{-1} region to the symmetric deformation mode. The absorption scale given in the figure is for the stretching region and must be multiplied by 15 for the bending region. The antisymmetric deformation, ν_4, region around 1640 cm^{-1} is complicated by the presence of water bands and reveals no new bands with alkali atoms at low concentration. Hence, it is not shown. In the spectrum of ammonia, various rotational and aggregate bands are observed and are labeled as such. Also present are the NH_3--H_2O and CO_2 complexes. The relative intensities of the H_2O, CO_2, and aggregate bands are difficult to control and vary from one experiment to another.

Introduction of Na gives rise to two groups of new bands labeled * and ** in both regions. The sharp * bands at 1079 and 3294 cm^{-1} are present even at very low Na concentration and show more or less a linear Na concentration dependence. The broad featureless ** bands show up in all the regions, including the ν_4 region (not shown), and are observable only at higher Na concentrations. Increase of cell temperature to obtain higher Na pressures also causes the various ammonia aggregate and the H_2O and CO_2 complex bands to increase in intensity. Increase of NH_3 concentration causes the ammonia aggregate bands to grow and complicate both the ν_2 and the ν_1 and ν_3 regions.[12] One very noticeable feature in Na--NH_3 spectra, which is actually common to all the alkali atom–ammonia spectra, is that the sharp band labeled * can only be observed in the symmetric stretching ν_1 and symmetric bending ν_2 regions with no sign of their analogues in antisymmetric bending and stretching regions. Furthermore, the relative intensity of the * band in the ν_1 region is greatly enhanced when compared to its ν_2 analogue.

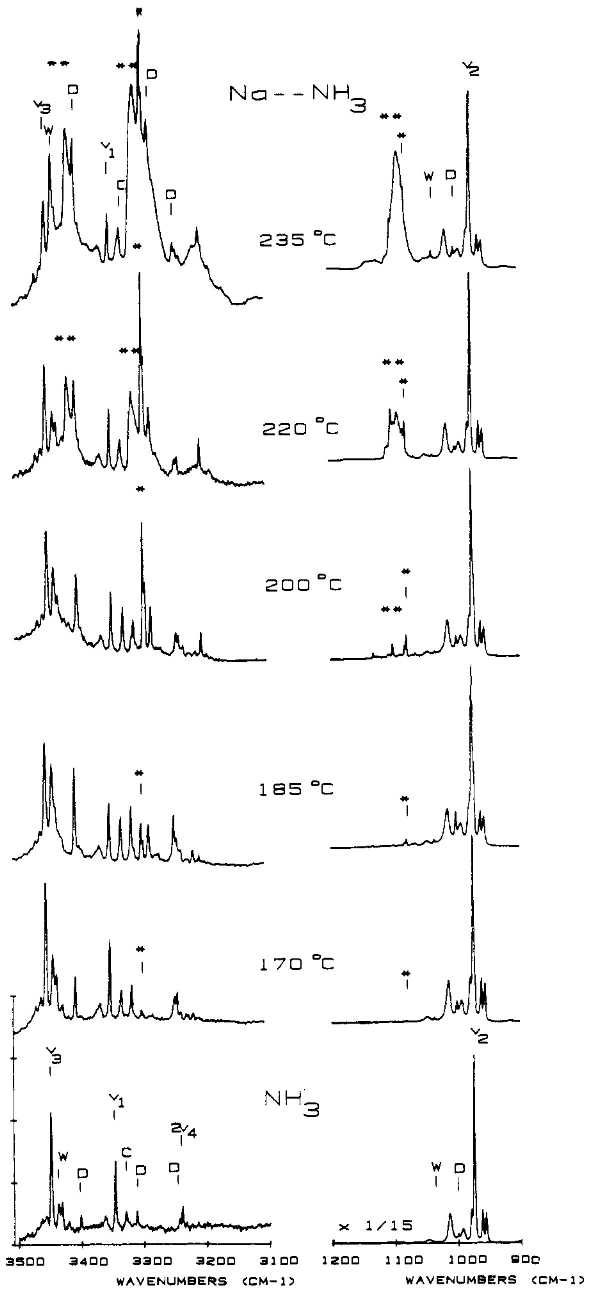

Figure 1. Matrix IR spectra of NH_3 (bottom) and Na--NH_3 complexes taken at various sodium concentrations (Knudsen cell temperatures). All the spectra are normalized to the strongest band of isolated ammonia at 974 cm^{-1}. The absorbance scale refers to the N–H stretching region and must be multiplied by 15 for the bending region. W and C refer to water–ammonia and carbon dioxide–ammonia complex bands, and D refers to ammonia dimer bands. The bands labeled by * and ** are new Na--NH_3 complex bands.

M and NH_3. Figure 2 shows combined spectra of selected Li, Na, K, and Cs ammonia mixtures as well as that of pure ammonia. Again, two groups of bands labeled * and ** are observable in each case, with * bands exhibiting an almost linear metal atom concentration dependence and ** bands appearing only at higher

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Table I. Infrared Absorptions (cm^{-1}) and Relative Intensities for Alkali Metal Atom-Ammonia Complexes

	ν_2		ν_4		ν_1		ν_3	
	ν, cm^{-1}	relative intensity[a]	ν, cm^{-1}	relative intensity[a]	ν, cm^{-1}	relative intensity[a]	ν, cm^{-1}	relative intensity[a]
NH_3	974	100[a]	1639	20	3346	2	3447	4
Li--NH_3	1133	100			3277	30	3379	3
Na--NH_3	1079	100			3294	40		
K--NH_3	1064	100			3292	60		
Cs--NH_3	1049	100			3287	70		

[a] The integrated band intensities normalized to the strongest band of ammonia and complex ν_2 bands.

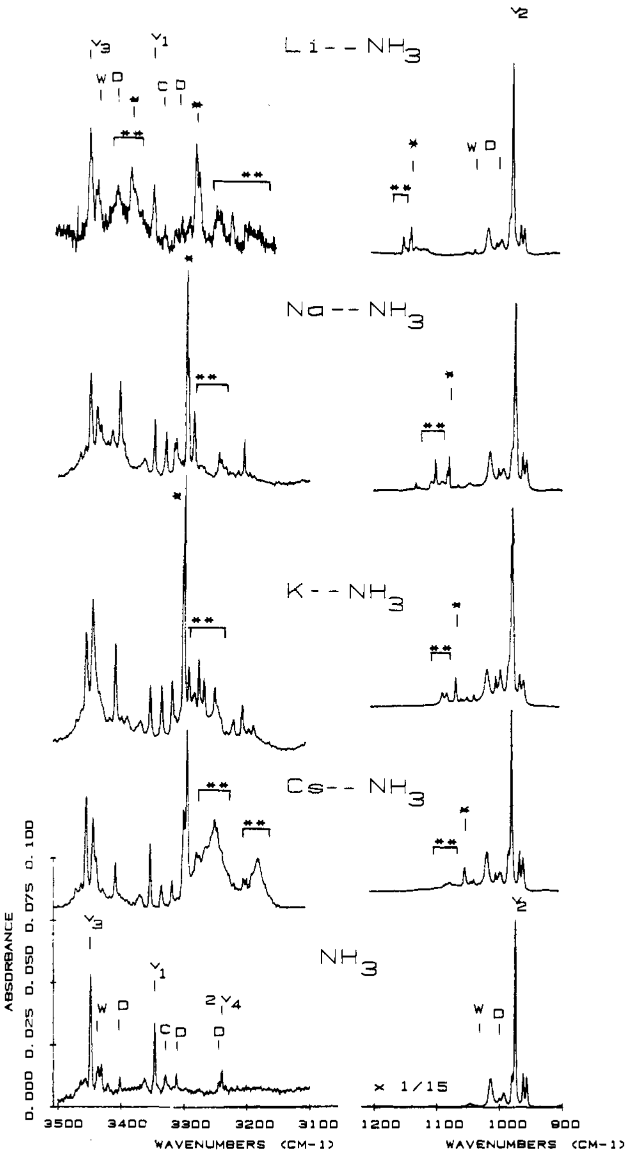

Figure 2. Matrix IR spectra of NH_3 (bottom) and of Li--NH_3 (top), Na--NH_3, K--NH_3, and Cs--NH_3 complexes using the format of Figure 1

concentrations. In all cases the sharp * bands are present in the symmetric regions, and only in the case of Li, an additional sharp * band is observed in the ν_3 region. In all cases the ν_1 analogues of the * bands were greatly intensified with respect to their ν_2 analogues by factors of 15, 20, 30, and 35 (±20%) for Li, Na, K, and Cs, respectively, as compared to the ν_1/ν_2 intensity ratio for isolated ammonia. Band positions and relative intensities for isolated and complexed ammonia are given in Table I. Photolysis by a high-pressure mercury arc lamp caused a slight increase in intensity of ** and ammonia aggregate bands and gave no evidence for new products in each of the alkali-ammonia matrices. Similarly, warming the samples to 20–24 K gave no new bands and only increased the yield of aggregates.

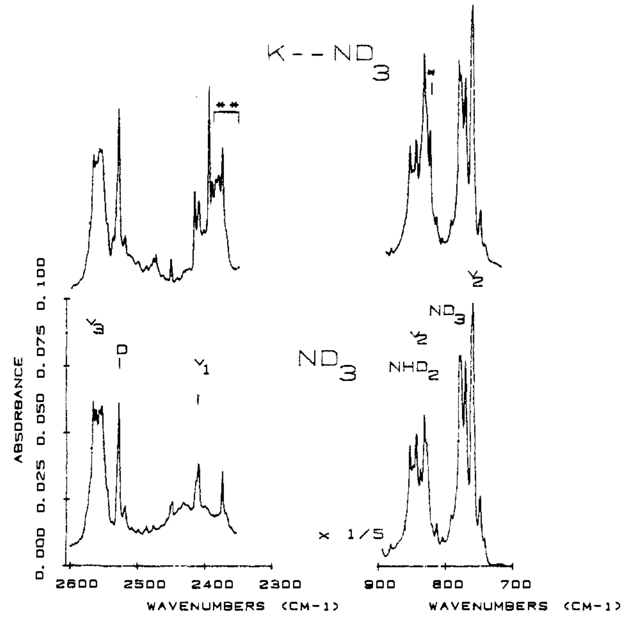

Figure 3. Matrix IR spectra of ND_3 (bottom) and K--ND_3 (top) complexes. The absorbance scale refers to the N–D stretching region and must be multiplied by 5 for the bending region. D refers to the dimer band. Also present is the NHD_2 bending region overlapping with the K--ND_3 complex band.

K and $^{15}NH_3$, NH_2D, NHD_2, and ND_3. Potassium complexes of ^{15}N- and D-substituted ammonia have been studied in detail. The spectrum of K--$^{15}NH_3$ is very similar to that of K--$^{14}NH_3$ with only characteristic red shifts in all the regions. The spectrum of K--ND_3 is complicated due to an enhanced rotational structure and the presence of NH_2D and NHD_2 as a result of exchange with the vacuum system. In all cases complex bands in symmetrical stretching (N–H and N–D) and bending regions are easily identified. Again, the perturbed stretching bands were intensified. Figure 3 shows representative spectra for ND_3 and the K--ND_3 complex, and a stick diagram showing isotopic spectra for stepwise D substitution is displayed in Scheme I. Data for all the isotopic species are collected in Table II.

Discussion

The discussion of these observations will be presented in three separate sections: (i) on the assignment of the * and ** bands, (ii) on the nature of the interaction between ammonia and alkali atom complexes, and (iii) on the relative intensification of the * bands in the symmetric stretching region.

Assignment. Matrix isolation studies of NH_3 complexes with strong acids like HF,[13] HCl, HBr, and HI[14] and weak ones like H_2O[15] reveal a blue shift in the ν_2 symmetric deformation mode of NH_3 depending on the strength of the interaction (120 cm^{-1} for HF and 61 cm^{-1} for H_2O) and smaller red shifts for both symmetric and antisymmetric stretching modes. Similar blue shifts are expected for the ν_2 ammonia submolecule mode in the alkali

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Scheme I

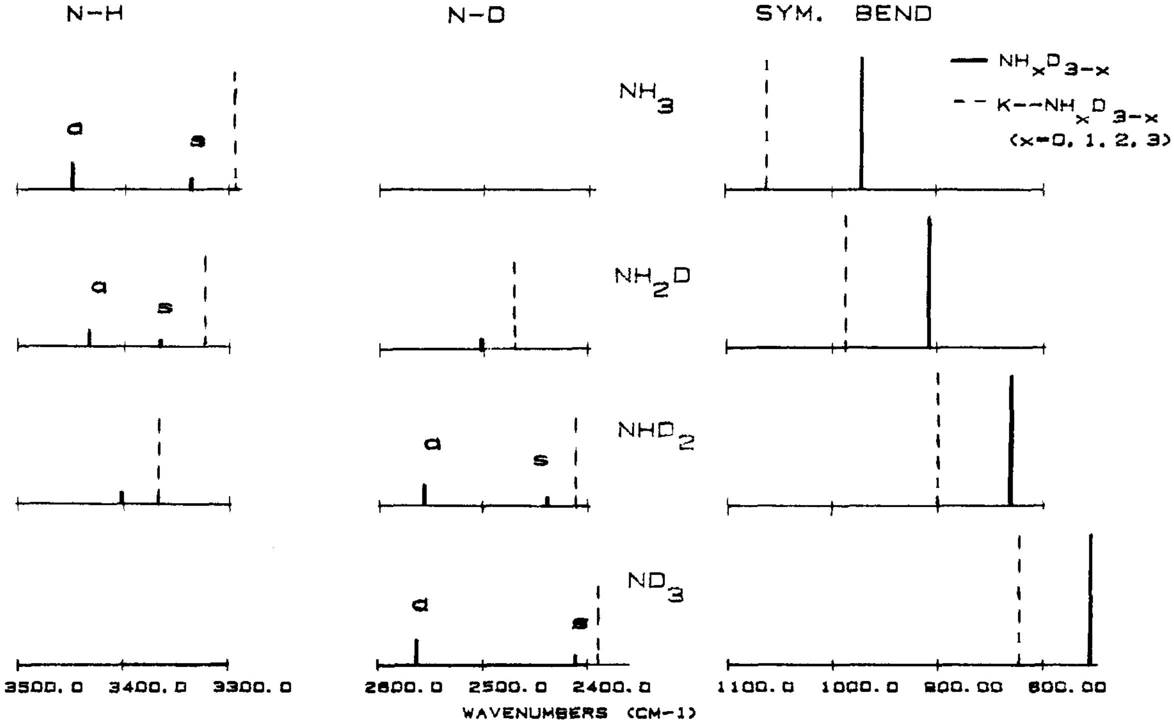


Table II. Infrared Absorptions (cm^{-1}) and Relative Intensities for Potassium and Isotopic Ammonia Complexes

	N–H stretches	N–D stretches	N–H (D) symmetric bend
$^{14}NH_3$	a, 3347 (4)[a]		974 (100)
	s, 3346 (2)		
K--$^{14}NH_3$	a		
	s, 3292 (80)		1064 (100)
$^{15}NH_3$	a, 3439 (4)		
	s, 3344 (2)		970 (100)
K--$^{15}NH_3$	a		
	s, 3290 (80)		1060 (100)
NH_2D	a, 3431[b]	2502[b]	
	s, 3365[b]		908[c] (100)
K--NH_2D	a	2473 (50)	988[c] (100)
	s, 3322 (50)		
NHD_2	3401[b]	a, 2555[b]	830[c] (100)
		s, 2445[d]	
K--NHD_2	3364 (50)	a	900 (100)
		s, 2415 (50)	
ND_3		a, 2553[b] (15)	759[c] (100)
		s, 2416[b] (1)	
K--ND_3		a	
		s, 2394 (60)	830 (100)

[a] Numbers in parentheses refer to relative intensities normalized to the strongest band of each species and are accurate to better than ±25%. [b] From ref 26. [c] The strongest band of the rotational structure. [d] Reference 26 assigns 2480 cm^{-1} for this band. This value, however, does not fit the trend for the otherwise well-observed shift upon complexation with K. Assuming this difference to hold in matrix-isolated NHD_2, we estimate ν_1 to be 2445 cm^{-1}.

complexes, and red shifts in the ν_1 and ν_3 modes follow the example set by the Li--OH_2 complex.[8] The sharp bands designated by * in the figures show blue shifts in the ν_2 region. On the basis of their linear alkali concentration dependence, the bands at 1133, 1079, 1064, and 1049 cm^{-1} are assigned to the 1:1 M--NH_3 complexes for Li, Na, K, and Cs, respectively. Furthermore, the new band observed in the K-$^{15}NH_3$ spectrum at 1060 cm^{-1} shows exactly the same shift of –4 cm^{-1} as in the uncomplexed ν_2 band of ammonia and provides further support for this assignment. Blue shifts of 75–160 cm^{-1} are not unexpected for the bending mode of complexed NH_3. Furthermore, decrease of the shift with increasing size of the metal atom is also reasonable. Theoretical calculations give 2.07 and 2.75 Å for the metal–ammonia distance in Li and Na complexes;[5] hence a larger perturbation is expected for the Li complex with progressively less perturbation going down the series. Similarly, the new * band at 823 cm^{-1} in the K--ND_3 spectrum superposed on the NHD_2 impurity is assigned to the perturbed ν_2 mode, which exhibits a similar relative isotope shift with respect to unperturbed ν_2. For K--NH_2D and K--NHD_2 the corresponding bands are assigned at 988 and 900 cm^{-1}, respectively. The shift decreases progressively from 90 for K--NH_3 to 80 for K--NH_2D to 70 for K--NHD_2 and finally to 64 cm^{-1} for K--ND_3 and is in very good agreement with the expected H/D ratio.

The assignment of the sharp bands in the N–H and N–D stretching regions is less straightforward. The ν_3 band in uncomplexed ammonia is stronger than ν_1 both in the gas phase and in an argon matrix; hence it is possible to assign the single observed sharp bands to the perturbed ν_3 mode in the complex. However, crucial experimental information suggests otherwise. Firstly, the perturbed bands are closer to ν_1 than ν_3 in all complexes. Secondly, the ^{14}N–^{15}N shift in the K--NH_3 complex, 2 cm^{-1}, is exactly the same as that of the uncomplexed ammonia ν_1 mode, as opposed to the 8-cm^{-1} shift observed for the ν_3 band as shown in Table II. Furthermore, in the Li--NH_3 complex two * bands were observed to be shifted by exactly the same amount from the uncomplexed ν_3 and ν_1 bands, with ν_1 being stronger. Finally, the complex bands in K--NH_2D, K--NHD_2, and K--ND_3 follow exactly the same pattern as those of the uncomplexed ammonia isotopes as shown in Scheme I. It is important to note that this mixed H and D isotopic data show that coupling of the different N–H (or N–D) modes is not altered upon complexation, which precludes any direct metal--hydrogen interaction. The strong N–H and N–D bands assigned to symmetric stretching modes for the K--NH_2D, K--NHD_2, and K--ND_3 complexes are compiled in Table II.

Accordingly, the corresponding perturbed ν_1 modes for all the four alkali metal complexes can easily be identified with the * bands red shifted from the 3346-cm^{-1} band of NH_3 to 3277, 3294, 3292, and 3287 cm^{-1} for Li, Na, K, and Cs, respectively. The variations in the shifts are more difficult to interpret, but Li shows the largest perturbation, as expected. The ν_3 analogues of the * bands either are very weak or show no significant perturbation except for the Li complex. Similarly, no corresponding ν_4 analogues were observed. The remaining features in the spectra labeled ** are due to higher aggregates, $(M)_n$- -$(NH_3)_m$ with n and m larger than 1,[16] and are observed in all four regions. However, no attempt was made to identify values of *n* and *m* in this complicated system.

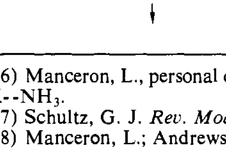
Nature of the Interactions. Theoretical calculations[4,5] and ESR studies[7] indicate a weak charge-transfer interaction, ammonia → metal, for the Li- -NH_3 and Na- -NH_3 complexes. The calculated charge transfer is 0.059 and 0.030 e, and the dipole moment enhancement is 4.05 and 3.33 D for the Li and Na complexes, respectively. The electron affinities of Li and Na are 0.62 and 0.54 eV, respectively,[17] which are not sufficiently different to account for the almost doubling of calculated charge transfer on going from Li to Na. The perturbation on ν_1 is the largest for Li and increases slightly within the Na, K, and Cs subseries. Both calculations and infrared spectra show that the Li- -NH_3 interaction is stronger than the interaction between sodium and ammonia. This is parallel to recent findings from this laboratory on alkali metal complexes with C_2H_2 and C_2H_4,[18,19] which suggests involvement of lithium 2p orbitals in bonding to first-row atoms. Although no calculations exist for heavier metal atoms, we expect a steady decrease in charge transfer to the alkali atom going down the series. The increased shift in ν_1 for the Cs and K complexes, as compared to Na, is surprising based on electron affinities, but it does follow the relative intensification of ν_1 as will be discussed in the next section. The infrared data reveal an increased Cs- -NH_3 interaction as compared to Na- -NH_3 and open the possibility for a reversal in metal → ammonia charge transfer for the heavier alkali complexes. The perturbations on ν_2 show a steady decrease with alkali size, and this can be explained by repulsions between the ammonia hydrogens and the closer, smaller alkali atom in the M- -NH_3 complexes.

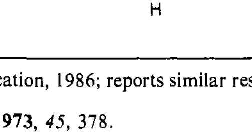
Intensification of the ν_1 Mode. Changes in relative intensities of the bands upon complex formation in IR spectroscopy have been the subject of numerous investigations. This phenomenon has been reported and used for identification of hydrogen bonding. The accepted experimental observation[20] for hydrogen bonding is that "the bending modes are blue shifted and stretching modes are red shifted and intensified".

Intensification of IR bands in charge-transfer complexes[21,22] and hydrogen-bonded complexes[23] has been interpreted by using Mulliken's charge-transfer theory. Accordingly, the ground state of a charge-transfer complex is written as a linear combination of a no-charge-transfer state (DA) and a complete-charge-transfer state (D^+A^-), i.e.

$$\psi(\mathrm{GS}) = a\psi(\mathrm{DA}) + b\psi(\mathrm{D^+A^-})$$

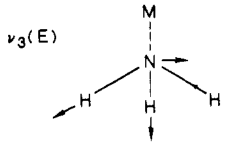
with the normalization condition $a^2 + b^2 = 1$. The amount of charge transfer is proportional to $(b/a)^2$ and is critically dependent on the separation between the submolecules of the complex. Vibrations involving the D–A coordinate, as a result, are expected to show fluctuations in the *b:a* ratio and would exhibit charge fluctuations; hence they are expected to be intensified. Such a model has recently been used to successfully interpret the intensity variation of the Li- -H_2O complex.[8] We expect this phenomena to be applicable to ammonia complexes as well. The complex ν_1 and ν_2 modes both involve the M- -N coordinate as indicated below.

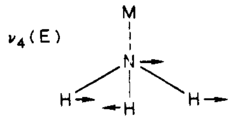




Hence an intensification (as well as a frequency shift) is expected for the ν_1 and ν_2 modes. The ν_1 mode is definitely intensified relative to the ν_2 mode in the complex. But whether the ν_2 mode is also intensified upon complexation is very difficult to answer since there is no experimental way of quantifying the relative amounts of NH_3 and metal–NH_3 complexes.

Both the $\nu_3(E)$ and $\nu_4(E)$ modes involve the N motions as indicated below. Since the M–N distance is already very large (theoretical predictions give ≈2.75 Å for the Na–NH_3 complex), these vibrations are not expected to change the *b:a* ratio to induce any intensity changes in accordance with the experimental findings. The failure to observe ν_3 in some and ν_4 in any of the complexes is also related to this point since they would be very weak and the least shifted. The broad ** bands arise for the ν_3 and ν_4 modes only at very high metal concentrations and can always be identified as aggregates, presumably due to higher $(M)_n$- -NH_3 complexes.





Intensificaton of the ν_1 mode in the infrared spectrum of the alkali metal–ammonia complex can be taken as an indication of charge transfer. Relative variations within the series, however, are difficult to explain. Charge transfer involving the larger, more polarizable, softer alkali atoms causes a higher intensification than interaction with the smaller, less polarizable, harder ones. The intensity of a specific mode is, of course, determined by the derivative of the dipole moment and not the moment itself. This may be the reason that, although calculations predict a larger dipole moment enhancement for the Li complex, it is not reflected in the relative intensities.

In order to quantify the vibrational mode perturbations as well as the infrared intensity changes upon complex formation one clearly needs to take into account the role of the ammonia lone-pair electrons. Polarization of the N–H bonding and lone-pair electrons may be additive or subtractive depending on the symmetry of the vibration. Such analyses have been carried out for ammonia using experimental gas-phase intensities[24] and ab initio calculations[25] and are definitely needed for the alkali atom–ammonia complexes.

Conclusions

Alkali metal atoms interact with NH_3 in solid argon and form definite 1:1 molecular complexes in contrast to the well-known ionic solutions in liquid ammonia. The strength of this interaction is comparable to hydrogen bonding as evidenced by perturbations of the ammonia submolecule vibrational frequencies. Some weak charge transfer in the complexes is suggested by intensity variations among the normal modes of ammonia upon complexation; the smaller alkali metal atoms appear to act as weak Lewis acids although the acid–base role could be reversed with the heavier alkali atoms. The ratios of perturbed ammonia symmetric stretching to bending vibrations in the complexes were typically 15–35 times more intense compared to the corresponding ratio for isolated ammonia in the matrix. Lithium exhibits the strongest interaction of the alkali metals with ammonia. At higher metal–ammonia doping concentrations bands of $(M)_n$- -NH_3 were observed. These studies provide help in understanding the ammonia–alkali atom pair interaction, which is part of the complex problem of ammonia–metal solutions.

Acknowledgment. We thank L. Manceron for correspondence on unpublished results and N.S.F. for financial support.

Registry No. NH_3, 7664-41-7; O_2, 7782-39-0; ^{15}N, 14390-96-6; Li, 7439-93-2; Na, 7440-23-5; K, 7440-09-7; Cs, 7440-46-2; Ar, 7440-37-1.

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