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R. M. Coates,* R. A. Conradi, D. A. Ley
Department of Chemistry, University of Illinois
Urbana, Illinois 61801

A. Akeson, J. Harada, S.-C. Lee, C. A. West*
Department of Chemistry, University of California
Los Angeles, California 90024

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Direct Observation by Raman Spectroscopy of the Coexistence of a Variety of Ion-Paired Species in Liquid Ammonia Solutions of Alkali Metal Salts

Sir:

Spectroscopic studies have provided indirect evidence[1] for the existence, in electrolyte solutions, of contact, solvent-shared and solvent-separated ion-pairs.[2] It has further been suggested that the relative concentration of each type of ion-pair is determined by the bulk dielectric constant, ϵ, of the solvent.[3,4] For liquid ammonia ϵ is in the region within which the different types of ion-pair may coexist.[4] We present the first direct evidence, from the Raman spectra of multiatomic anionic species, that various types of ion-pair do coexist in liquid ammonia solution. We illustrate this evidence by giving some details of the spectra of sodium and potassium cyanide solutions and the way they change with changing concentration, temperature, and cation. The spectra of other anions which show comparable changes are discussed briefly.

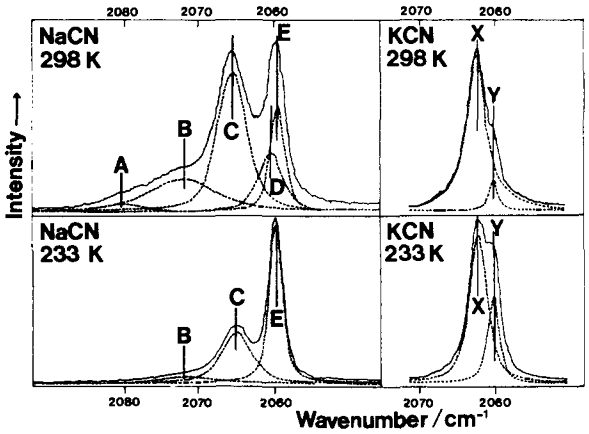

Figure 1. Resolved bands in the C–N stretching region of the Raman spectra of liquid ammonia solutions of NaCN and KCN (parallel polarization).

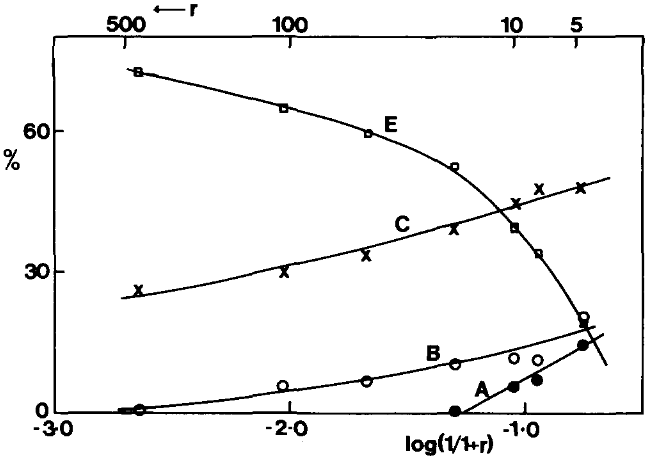

Figure 2. The variation with concentration (expressed as $\log(1/(1+r))$ of resolved component areas (expressed as percent of the total band area) for liquid ammonia solutions of NaCN at 233 K.

The isolated cyanide ion should give a single Raman-active band at ca. 2050 cm^{-1} corresponding to the C–N stretching vibration. The most striking feature of the solution spectra is that more than one band is observed in all cases. Resolved spectra for one concentration of each of the salt solutions at two different temperatures are illustrated in Figure 1.

At least four (polarized) components (not necessarily all visible in the same spectrum) are clearly required to obtain a satisfactory fit of the anion's spectrum with sodium cyanide solutions. These appear at ca. 2083 (A), 2072 (B), 2067 (C), and 2059 (E) cm^{-1}, and all are comparatively sharp.[5] The half-width, w, is between 2 and 9 cm^{-1} and is much less than is observed for comparable bands with aqueous salt solutions. The variation of relative intensity of each component with changes in concentration and temperature are shown in Figures 2 and 3. (r = number of moles of solvent/number of moles of solute). With decreasing concentration components A, B, and C decrease in intensity with respect to E, the lowest frequency component. E becomes the predominant feature of the spectrum at lowest concentration. Similar intensity-concentration trends occur at all temperatures studied. The effect of decreasing temperature is similar to the effect of decreasing concentration and E is the predominant feature of the spectra obtained at the lowest temperature.

The Raman spectra of KCN solutions are simpler, and can be resolved into only two components, X at ca. 2062 and Y at ca. 2060 cm^{-1}. Similar concentration and temperature trends apply to the intensities, with the component at the lower frequency, Y, becoming the more dominant feature at low tem-

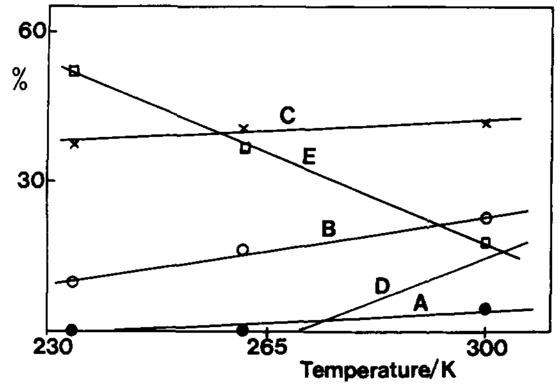

Figure 3. The variation with temperature of resolved component areas (expressed as percent of the total band area) for liquid ammonia solutions of NaCN at $r = 19.3$.

perature and/or concentration. The frequencies of Y and E are identical. The frequency of X is the same as that of D, but this may be coincidental as D is not firmly characterized by the spectra.

Solutions of alkali metal salts of nitrates, nitrites, thiocyanates, azides, and perchlorates also give unexpectedly complex Raman bands which change form with changes of concentration, temperature, and counterion. Bands of these anions have been resolved into components as follows. (Na$^+$ and Li$^+$) NO$_3^-$: ν_1, 2 components; ν_3, 3; ν_4, 2. K$^+$NO$_3^-$: ν_1, 1; ν_3, 2; ν_4, 1. Na$^+$NO$_2^-$: ν_1, 3; ν_2, 4. K$^+$NO$_2^-$: ν_1, 2; ν_2, 2. Na$^+$N$_3^-$: ν_1, 3; $2\nu_2$, 3. K$^+$N$_3^-$: ν_1, 3; $2\nu_2$, 2. (Na$^+$ and Li$^+$)SCN$^-$: ν_1, 3; ν_3, 3. (K$^+$ and Cs$^+$)SCN$^-$: ν_1, 2; ν_3, 2. (Na$^+$ and K$^+$)ClO$_4^-$: ν_1, 1; ν_2, 1; ν_4, 1.[6]

It is possible to present a satisfactory individual anion-specific explanation for many multicomponent bands. Thus, linkage isomerism of contact ion-pair species is possible for NO$_2^-$,[8] NCS$^-$,[8] and CN$^-$.[9] Alternatively, solvent–anion interaction through hydrogen bonding is possible, and has indeed been proposed for the NCS$^-$ ion in liquid ammonia.[10] A similar mechanism has been suggested to account for the ν_3 region of the NO$_3^-$ spectrum, where hydrogen bonding lifts the degeneracy of the asymmetric N–O stretching vibration.[10] In ammonia the corresponding band is much less broad than in water, though we consider the band to be more complex than has been suggested.[10-12]

Contrary to these specific explanations are the trends, common to all anions studied, that: (i) the component at lowest frequency increases in relative intensity as concentration and temperature are decreased; (ii) solutions with K$^+$ as counterion mostly give less complex spectra than solutions with Na$^+$ as counterion. While not excluding the possibility that some anion-specific effects are operative, we propose an explanation which is common to all anions studied. That is, that the resolved components of a complex band are directly attributable to discrete forms of contact, solvent-shared, solvent-separated ion-pairs and unpaired, solvated, "free" anions.

In a solution as concentrated as those considered in these studies, and particularly where $r < 20$, a high degree of short-range ordering of ions and solvent molecules into quasi-lattice structures must be expected. Within such a framework it is highly probable that an anion may be found in a variety of locally structured groups.[1] The proportion of such ion-aggregates would be expected to be concentration, cation, and temperature dependent.

Assignment of band-components to individual ion-paired species is not possible at the present time, since we cannot measure spectra from solutions sufficiently dilute to permit unambiguous assignment for the "free" anion. The lowest concentration that we have been able to study satisfactorily is $r = 1017$ (KCN solution) which is still far above the acceptable upper concentration limit for electrochemical studies of ion-pairing. It is also clear from such studies on liquid ammonia systems[13] that even at a concentration of $r \simeq 10^6$ the solute is still substantially in an ion-paired form. Thus we can confidently assign the lowest frequency component within each band only to the least associated anionic species. Nevertheless, the correlation of bands E, C, B, and A in the NaCN solution spectra with the "free" ion, solvent-separated, solvent-shared, and contact ion-paired species would be consistent with the presently available evidence.

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P. Gans,* J. B. Gill,* M. Griffin
Department of Inorganic and Structural Chemistry
The University
Leeds LS2 9JT, England
Received March 30, 1976

The Role of Water in the Rhodium(I) Catalyzed Reduction of Nitric Oxide by Carbon Monoxide. An Isotope Labeling Study

Sir:

It has previously been reported that the complex [RhCl$_2$(CO)$_2$]$^-$ in aqueous acidic ethanol catalyzes the carbon monoxide reduction of nitric oxide according to eq 1 under mild conditions.[1,2]

$$2NO + CO \rightarrow N_2O + CO_2 \qquad (1)$$

In this environmentally important reaction, water was found to be cocatalytic and intimately related to product formation.[2] Based on the CO reduction of Rh(III) to Rh(I)[3] and the known decomposition of hyponitrous acid,[4] we proposed that water is both consumed in the production of CO$_2$ and regenerated in the formation of N$_2$O. We now report an isotope labeling study which proves this contention by showing that the oxygen in the product CO$_2$ is derived from water in the reaction medium, and not directly from the nitric oxide reactant. Thus water serves as the means by which oxygen is transferred in this stoichiometrically simple, but mechanistically complex reaction. Our study also reveals that intermediate I in reaction 2 exhibits virtually no tendency for back reaction and exchange