Infrared Matrix and Theoretical Studies of the Reduction of Molecular Nitrogen by Lithium Atoms

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Abstract: The 15°K matrix codeposition of lithium atoms and nitrogen molecules produces new absorptions at 1800 and 1535 cm^{-1} which exhibit small lithium isotopic shifts and nitrogen-15 shifts appropriate for N–N fundamental vibrations. The use of nitrogen isotopic mixtures indicates that the 1535-cm^{-1} feature is due to a species containing two equivalent N_2 units, each with inequivalent nitrogen atoms. Concentration studies suggest the assignments to the molecules LiN_2 and $N_2Li_2N_2$. Molecular orbital calculations suggest that the Li–N_2 union requires a surface reaction and that the most likely source of $N_2Li_2N_2$ is dimerization of LiN_2 formed in adjacent matrix sites.

Molecular nitrogen undergoes very few reactions at room temperature, the two most prominent being its reduction by metallic lithium to form Li_3N and with nitrogen-fixing bacteria to produce NH_3. The nitrogen-fixation process is thought to involve the coordination of nitrogen to transition metal complex ions which has been the subject of several recent reviews.[1-3] In contrast to the high temperature–high pressure Born–Haber catalytic process, the lithium metal–N_2 gas reaction proceeds following adsorption of N_2 gas at room temperature and atmospheric pressure on the lithium metal surface.

Spectroscopic investigation of reduced N_2 species has been confined primarily to the transition metal complexes where N–N vibrations near 2000 cm^{-1} have been reported.[1] Quite recently, the Raman spectra of N_2^- ions in KCl, KBr, and KI lattices have produced bands at 1836, 1821, and 1807 cm^{-1}, respectively.[4] From this work the frequency of the isolated N_2^- ion was predicted to be near 1760 cm^{-1}.

In recent work in our laboratory, lithium atom–oxygen molecule reactions have been studied using the matrix reaction technique. The LiO_2 molecule so produced[5,6] was described in terms of predominantly ionic binding in the species $Li^+O_2^-$, based on the near agreement of O–O stretching frequencies for LiO_2 and O_2^-. Lithium atom–nitrogen molecule reactions have been similarly studied by depositing lithium atoms into nitrogen matrices at 15°K. The infrared spectroscopic evidence and theoretical justification for two new lithium–nitrogen species are presented here.

Experimental Section

The 15°K refrigeration system, vacuum vessel, lithium atom source, and experimental techniques have been described in an earlier paper.[7] Isotopically enriched samples of lithium metal 99.99% ^{7}Li and 95.6% ^{6}Li, 4.4% ^{7}Li (ORNL), sodium (J. T. Baker, lump), potassium (Baker and Adamson, lump), and rubidium (Alfa Inorganics) were used without purification. Cesium atoms were produced by the reaction of liquid lithium and ground CsCl at 325° in a Knudsen cell. Natural isotopic nitrogen gas (Air Products, ultra high purity) was passed slowly through a copper coil immersed in liquid nitrogen before use. Argon (Air Products, 99.995%), nitrous oxide (Matheson, 98%), isotopically enriched water D_2O (Diaprep, 99.8%), and nitrogen gas (Isomet, 31% ^{15}N) were used without purification. Isotopically enriched nitrogen (Bio-Rad, 95% ^{15}N) was freed from oxygen impurity by slowly passing the gas through 2 ft of oxygen-free copper coil packed with copper wire and heated to 450–600° by sandwiching nichrome resistance wire between two layers of asbestos tape wrapped around the copper coil. A liquid nitrogen trap was connected to the coil *via* a stainless steel junction silver soldered to the copper. Temperatures were monitored by a copper–constantan thermocouple in contact with the copper coil.

Samples of nitrogen gas (natural isotopic, 31% ^{15}N or 95% ^{15}N enriched) were simultaneously deposited with atomic beams of lithium (^{6}Li, ^{7}Li, or ^{6}Li–^{7}Li mixture at 450–500°), sodium (235°), potassium (165°), rubidium (135°), or cesium atoms (325°) on a cesium iodide window cooled to 15°K. The ^{15}N enriched matrices were recovered by recondensing in a stainless steel tube immersed in liquid helium. Sample deposition times ranged from 20 to 27 hr.

Infrared spectra were recorded during and after sample deposition on a Beckman IR-12 filter-grating infrared spectrophotometer in the 200–4000-cm^{-1} spectral region. The spectrophotometer was calibrated using vibration–rotation bands of standard molecules.[8] High-resolution spectra were recorded in all experiments using either 8 or 3.2 cm^{-1} per minute scanning speeds and either 20 or 10 cm^{-1} per inch scale expansions. Wave number accuracy is ±0.2 cm^{-1} below 2000 cm^{-1} and ±0.5 cm^{-1} above. Spectral slit widths were 1.5 cm^{-1} at 600 cm^{-1} and 0.9 cm^{-1} at 1200 and 2200 cm^{-1}.

Results

Nitrogen Matrices. Table I lists the frequencies of bands observed for reactions of lithium atoms with four different isotopic combinations of nitrogen molecules. The top spectrum of Figure 1 shows an intense absorption (0.55 o.d.) at 1534.9 cm^{-1} which was observed in a reaction between ^{7}Li and natural isotopic N_2 deposited at 15°K. The upper trace of Figure 2 illustrates bands observed in the 1720–1820-cm^{-1} region for the same reaction with the most intense component appearing at 1799.5 cm^{-1} (0.09 o.d.). In a similar reaction with ^{6}Li, these bands shifted 2.1 and 0.8 cm^{-1}, respectively, to 1537.0 and 1800.3 cm^{-1}. Also observed in these experiments were two broad absorption features centered near 1750 and 1780 cm^{-1} in the ^{7}Li experiment. Since these latter bands were not observed in any of the mixed isotope work, no firm conclusions about them can be reached; they

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Table I. Major Infrared Absorptions Produced by Reactions of Lithium Atoms and Nitrogen Molecules Deposited at 15°K[a]

^{6}Li + N_2[b]	^{7}Li + N_2[b]	^{6}Li + $^{14}N^{15}N$[c]	^{7}Li + $^{14}N^{15}N$[c]	^{6}Li + $^{15}N_2$[d]	^{7}Li + $^{15}N_2$[e]
1800.3 (0.08)	1799.5 (0.09)				
1784.5 (0.04)	1783.6 (0.05)				
1778 (0.04)	1776 (0.04)				
1750 (0.02)	1748 (0.02)				
				1754.2 (0.03)	
				1739.6 (0.06)	1739.9 (0.03)
1537.0 (0.41)	1534.9 (0.55)	1536.5 (0.15)	1535.0 (0.19)		1535.3 (0.02)
		1524.3 (0.20)	1522.8 (0.24)		
		f	1521.7 (0.21)		
		f	1512.1 (0.09)		
		1511.6 (0.10)	1510.2 (0.13)		
		1510.3 (0.12)	1508.9 (0.17)		1508.7 (0.16)
		1499.5 (0.05)	1497.8 (0.08)		
		1498.4 (0.07)	1496.5 (0.09)		
		1486.6 (0.02)	1485.0 (0.02)	1486.6 (0.17)	1485.0 (0.31)

[a] Optical densities are given in parentheses. [b] Natural isotopic N_2. [c] 9.6% $^{15}N_2$, 42.8% $^{14}N^{15}N$, 47.6% $^{14}N_2$; N_2/N_2O = 400/1. [d] 90.25% $^{15}N_2$, 9.5% $^{14}N^{15}N$, 0.25% $^{14}N_2$; N_2/N_2O = 400/1. [e] 74% $^{15}N_2$, 8% $^{14}N^{15}N$, 18% $^{14}N_2$. [f] Not resolved.

may be different trapping sites of the 1800-cm^{-1} feature. Finally, in the ^{7}Li experiment sharper absorptions were superimposed on the 1780-cm^{-1} feature, the most intense component appearing at 1783.6 cm^{-1}.

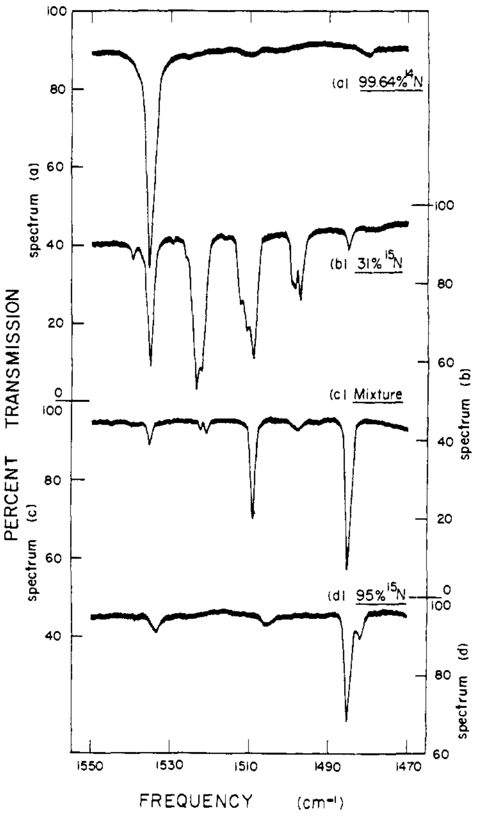

Figure 1. Infrared spectra recorded in the 1470–1550-cm^{-1} spectral region following lithium atom–nitrogen molecule matrix reactions: (a) ^{7}Li and natural isotopic N_2; (b) ^{7}Li and 31% ^{15}N-enriched N_2 gas (9.6% $^{15}N_2$, 42.8% $^{14}N^{15}N$, 47.6% $^{14}N_2$); (c) ^{7}Li and a mixture of N_2 isotopes (74% $^{15}N_2$, 8% $^{14}N^{15}N$, 18% $^{14}N_2$); and (d) ^{6}Li and 95% ^{15}N-enriched N_2 gas (90.25% $^{15}N_2$, 9.50% $^{14}N^{15}N$, 0.25% $^{14}N_2$).

The same band pattern was observed in the ^{6}Li experiment, but the most intense component was shifted slightly to 1784.5 cm^{-1}. In addition, a broad, intense band (as great as 32-cm^{-1} half-width and 0.50 o.d.) was observed at 2300 ± 4 cm^{-1} when lithium atoms were deposited into pure nitrogen matrices.

^{15}N-Enriched Nitrogen Matrices. Spectrum b of Figure 1 shows the results of the deposition of ^{7}Li with 31% ^{15}N-enriched N_2 and a small amount of N_2O (mol ratio (M/R) = 400/1). Notice the four new features present: two partially resolved doublets at 1496.5 and 1497.8 cm^{-1} for the lower duet and 1521.7 and 1522.8 cm^{-1} for the upper pair, a triplet having absorptions at 1508.9, 1510.2, and 1512.1 cm^{-1}, and a weak band at 1485.0 cm^{-1}. These bands showed 1–2-cm^{-1} shifts to higher frequency in the ^{6}Li experiment as is indicated in Table I. Unfortunately, the individual components of the multiplets were not as well resolved as their ^{7}Li counterparts. The second spectrum of Figure 2 shows that the isotopic counterparts to the bands in the 1720–1820-cm^{-1} region of the $^{14}N_2$

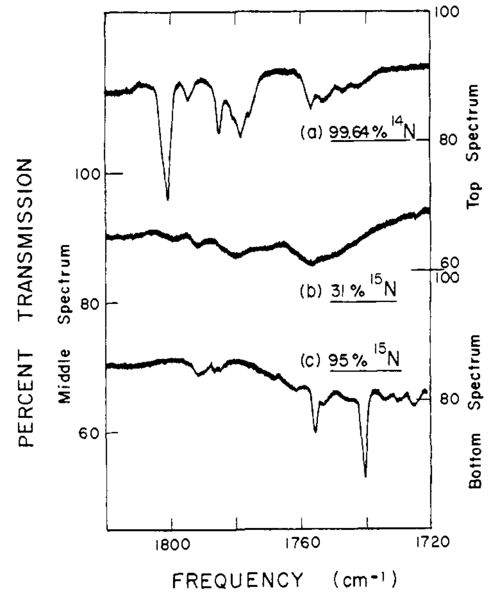

Figure 2. Infrared spectra recorded in the 1720–1830-cm^{-1} spectral region following lithium atom–nitrogen molecule matrix reactions: (a) ^{6}Li and natural isotopic N_2; (b) ^{7}Li and 31% ^{15}N-enriched N_2 gas (9.6% $^{15}N_2$, 42.8% $^{14}N^{15}N$, 47.6% $^{14}N_2$); (c) ^{6}Li and 95% ^{15}N enriched N_2 gas (90.25% $^{15}N_2$, 9.5% $^{14}N^{15}N$, 0.25% $^{14}N_2$).

experiment were too weak to be observed in the 31% ^{15}N-enriched N_2 experiment.

The third spectrum of Figure 1 illustrates the results obtained when ^7Li was codeposited with a mixture of 74% $^{15}N_2$, 8% $^{14}N^{15}N$, 18% $^{14}N_2$, and a small amount of N_2O (M/R = 400/1). Three bands were observed in the 1500-cm^{-1} region at 1485.0, 1508.7, and 1535.3 cm^{-1} and the 1799.5-cm^{-1} band was shifted about 60 cm^{-1} to 1739.9 cm^{-1}. None of the other components in the 1720–1820-cm^{-1} region were observed.

Spectrum d of Figure 1 and the lower trace of Figure 2 show the reaction of ^6Li with a 90% $^{15}N_2$ nitrogen sample. The 1537- and 1800-cm^{-1} bands shifted approximately 50 and 60 cm^{-1}, respectively, to 1486.6 and 1739.6 cm^{-1}. The only other feature observed was a weak band near 1754 cm^{-1} which is probably the isotopic counterpart to one of the bands near 1780 cm^{-1} in the $^{14}N_2$ experiment.

The 2200-cm^{-1} spectral region in the isotopic nitrogen experiments revealed isotopic components of the 2300-cm^{-1} band using natural isotopic N_2 matrices. A broad band was observed near 2265 cm^{-1} in the lithium $^{14}N^{15}N$ (31% ^{15}N enriched) matrix reaction and at 2222 cm^{-1} in the $^{15}N_2$ (95% ^{15}N enriched) matrix reaction.

Nitrogen Matrices Doped with Small Molecules. Many experiments were doped with impurity molecules to determine their effects on the 1800- and 1535-cm^{-1} bands. Most frequently used was nitrous oxide[9] in concentrations from 1 to 0.06%. The general effect of the nitrous oxide was to double or triple the 1535-cm^{-1} band intensity. In some experiments this band was split into two absorptions, the 1535-cm^{-1} component being three times as intense as its 1528-cm^{-1} partner in one experiment and about the same intensity in another Li–N_2 reaction. The N_2O in the reaction mixture had a slight hindering effect on the intensities of the bands in the 1720–1820-cm^{-1} region. An equal mixture of ^6Li and ^7Li was codeposited with N_2 containing 1% N_2O. Unfortunately, the 1800- and 1535-cm^{-1} bands were not sufficiently sharp to resolve intermediate components for these small lithium isotopic shifts.

Both H_2O and D_2O were doped into the nitrogen matrix to show that the 1800- and 1535-cm^{-1} bands were not due to water absorptions. Neither of these features showed deuterium isotopic shifts, thus eliminating water as a contributor to these bands. However, with H_2O and/or D_2O present the band intensities of the absorptions between 1740 and 1800 cm^{-1} were doubled. Particularly effective was one D_2O, N_2O doped experiment with ^6Li in which the optical densities of the 1800- and 1776-cm^{-1} bands increased to 0.23 and 0.19, respectively. Conversely, the 1535-cm^{-1} band intensity was not measurably affected by the presence of D_2O.

The catalytic roles that N_2O and H_2O play in the reaction are not understood. Using $^{14}N_2O$, $^{15}N_2O$, and $N_2{}^{18}O$ isotopes did not shift the bands discussed here; only when ^{15}N was substituted in the matrix was an isotopic shift observed for the 1800- and 1535-cm^{-1} features. Traces of D_2O or H_2O enhanced the 1800-cm^{-1} feature relative to the 1535-cm^{-1} band. Perhaps the role of impurities is primarily to affect the crystallization pattern of the nitrogen matrix which could influence the production of these two molecular species.

Another interesting effect was noted in two reactions between Li and CH_2Br_2 in nitrogen matrices.[10] Both the 1535- and 1800-cm^{-1} bands were produced, but they were much weaker and of comparable intensity (0.05 o.d.), in contrast to the aforementioned reactions in which the intensity ratio of the 1535-cm^{-1} band to that of the 1800-cm^{-1} absorption was typically 6/1 in pure N_2, 20/1 with N_2O impurity, 40/1 with N_2O and a fivefold increase in Li, and 2.5/1 with D_2O and no N_2O.

Heavier Alkali Metals Reacting with Nitrogen Matrices. The 1530-cm^{-1} band was also observed in Cs and K experiments in N_2 matrices but it did not appear in similar reactions with Na or Rb. In the K reaction the molecule absorbed at 1537.4 cm^{-1} (0.15 o.d.) and in the Cs reaction the band was observed at 1531.4 cm^{-1} (0.08 o.d.). The higher frequency absorption near 1800 cm^{-1} was not seen in any of the heavy alkali metal atom reactions. From these results it is apparent that the metal atom has little effect on the 1530-cm^{-1} vibration, although changing from ^6Li to ^{133}Cs does reduce the frequency by about 6 cm^{-1}.

Argon Matrices. Three experiments were performed reacting lithium atoms with N_2 in argon matrices at the following concentrations: $Ar/N_2 = 200/1$, $Ar/N_2/N_2O = 100/10/1$, and $Ar/N_2 = 2.4/1$. The 1535- and 1800-cm^{-1} absorptions were not observed in any of these argon matrix experiments. However, in the most concentrated experiment where 30% N_2 in argon was reacted with lithium atoms, a weak, broad absorption was observed at 1532 cm^{-1}, which might be the argon matrix counterpart of the 1535-cm^{-1} nitrogen matrix feature.

Discussion

We wish to identify the molecular species responsible for these new absorptions using isotopic substitution and rationalize their production with the aid of molecular orbital calculations.

Identification of New Li–N_2 Species. Lithium Composition. The matrix reaction of lithium atoms and nitrogen molecules produces two new absorptions which are illustrated in Figures 1 and 2. Both features show small but measurable lithium isotopic shifts indicating the presence of lithium in each absorber. Unfortunately, the lithium isotopic shifts were too small to resolve each isotopic feature in the mixed ^6Li–^7Li experiment. However, two other comparisons suggest that the 1535-cm^{-1} feature contains more Li than the 1800-cm^{-1} absorber. A fivefold increase in Li concentrations in N_2/N_2O experiments doubles the intensity of the 1535-cm^{-1} feature relative to the 1800-cm^{-1} band. By adding the markedly more reactive molecule CH_2Br_2 to the N_2 samples, the Li concentration is effectively reduced by the faster reaction with CH_2Br_2. In this experiment the 1800- and 1535-cm^{-1} bands are reduced in intensity and their relative intensities are 1 to 1. Hence, the 1535-cm^{-1} feature is more sensitive to changes in Li concentration which indicates a "higher order" reaction in Li. We conclude that the 1535-cm^{-1} absorber likely contains two lithium atoms and that the 1800-cm^{-1} feature is probably a single lithium species.

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No absorptions were observed which could be assigned to lithium–nitrogen stretching modes. In marked contrast, very intense lithium–oxygen modes have been observed.[6] Apparently, lithium–nitrogen vibrations are much weaker infrared absorbers than their oxygen counterparts.

Nitrogen Composition of the 1535-cm^{-1} Absorber. That these features involve fundamental N–N vibrations is graphically indicated by the large ^{15}N isotopic shifts which are in accord with pure N–N vibrations. The molecular formula of the intense feature near 1500 cm^{-1} was revealed by experiments using isotopic mixtures. Figure 1c shows the spectrum of the nitrogen isotopic mixtures 74% $^{15}N_2$, 8% $^{15}N^{14}N$, 18% $^{14}N_2$ deposited with ^7Li atoms. The $^{14}N_2$ and $^{15}N_2$ isotopic counterparts were observed as before at 1535.3 and 1485.0 cm^{-1}, respectively; a sharp, intense intermediate component appeared at 1508.7 cm^{-1}. This sharp intermediate component is clearly due to a molecular species containing one $^{14}N_2$ and one $^{15}N_2$ molecule, based on statistical weights and observed intensities. The fact that a single intermediate component is observed indicates that the two N_2 molecules are equivalent (inequivalent N_2 molecules would produce two intermediate spectral features).

The orientation of the nitrogen atoms in each nitrogen molecule is revealed by the scrambled isotopic mixture (31% ^{15}N enriched N_2 gas, 9.6% $^{15}N_2$, 42.8% $^{15}N^{14}N$, 47.6% $^{14}N_2$), which was used for the ^7Li reaction whose spectrum is shown in Figure 1b. The $^{14}N_2$ and $^{15}N_2$ isotopic components were observed as sharp bands at 1535.0 and 1485.0 cm^{-1}; however, three intense multiplets appeared between these pure isotopic bands. The second and fourth absorptions were partially resolved doublets appearing at 1522.8, 1521.7 and 1497.8, 1496.5 cm^{-1}, respectively, whereas the third band is a partially resolved triplet with peaks at 1512.1, 1510.2, and 1508.9 cm^{-1}, the latter being the most intense. The multiplets observed in this experiment indicate that the two equivalent N_2 molecules are arranged such that the N atoms are not equivalent. (Equivalent N atoms in two equivalent N_2 molecules would produce a sextet.)[11] Hence, the doublet at 1522 cm^{-1} is due to the species 14–15—14–14 and 15–14—14–14 and the doublet at 1497 cm^{-1} arises from the isotopes 14–15—15–15 and 15–14—15–15. Statistics predict four unique arrangements of isotopes for the central component; only three were resolved here. The most intense feature at 1508.9 cm^{-1} is due to 14–14—15–15, which is also seen at 1508.7 cm^{-1} in the $^{14}N_2$–$^{15}N_2$ experiment (Figure 1c). The two other resolved components plus one more not resolved are due to the three unique orientations of pairs of $^{14}N^{15}N$ molecules in this new lithium–nitrogen molecule.

Nitrogen Composition of the 1800-cm^{-1} Absorber. Unfortunately, it was not possible to observe mixed isotopic counterparts of the weaker 1800-cm^{-1} feature which would indicate the nitrogen stoichiometry and structure. The Raman fundamental of N_2^- in KCl, KBr, and KI hosts at 1836, 1821, and 1807 cm^{-1}, respectively, predicts the isolated N_2^- frequency to be about 1760 cm^{-1}.[4] The agreement between the Raman fundamental for N_2^- and the 1800-cm^{-1} infrared band observed here suggests the assignment of the 1800-cm^{-1} feature to the N–N stretching mode in LiN_2. Furthermore, the bonding implication is that the species LiN_2 is ionic ($Li^+N_2^-$) like LiO_2.[5,6] In the MO calculations to follow the isosceles triangular geometry for LiN_2 is predicted to be the most stable structure.

Broad Nitrogen Matrix Absorption. The broad feature, observed near 2300 cm^{-1} in lithium atom–natural nitrogen matrix reactions, was observed near 2265 cm^{-1} in the lithium $^{14}N^{15}N$ (31% ^{15}N enriched) matrix reaction. This feature shows a 78-cm^{-1} isotopic shift from $^{14}N_2$ to $^{15}N_2$, in excellent agreement with a diatomic harmonic oscillator. Since the O_2 fundamental vibration has been observed in the infrared spectrum of pure oxygen matrices,[12] it is conceivable that this broad feature might be due to the N_2 fundamental made allowed by lattice defects or perturbations due to the presence of impurity molecules in the matrix. The broad N_2 matrix band at 2300 cm^{-1} is slightly below the N_2 fundamental at 2331 cm^{-1}. At present, the broad feature can be tentatively assigned to the N_2 fundamental, which has been made allowed by perturbations due to impurity molecules in the matrix. It should be noted that 40–50 mmol of nitrogen was examined in these spectroscopic studies; hence, impurity molecules might indeed cause sufficient perturbation on the N_2 fundamental to produce observable infrared intensity.

Molecular Orbital Calculations. We undertook a molecular orbital exploration of the energy surface of the systems LiN_2, LiN_4, and Li_2N_4, which might account for the observed infrared absorptions discussed above. The program CNINDO by Pople and Dobosh, distributed by the Quantum Chemistry Program Exchange,[13] was the basis of all computations. Only the "Huckel" mode of the program (no SCF iteration) was used, for economic reasons. The approximations and applicability of this MO method have been thoroughly discussed elsewhere;[14] in general we can expect reliable predictions of bond angles but poorer estimates of bond lengths. In our search for equilibrium geometries we assumed bond lengths consistent with Badger's rule for the N_2 fragments and made estimates from model compounds for the Li–Li and Li–N bond lengths: $R_{\mathrm{Li-N}}$ (1.9), $R_{\mathrm{N-N}}$ (1.25), and $R_{\mathrm{Li-Li}}$ (2.6 Å). Dissociation was correctly described in all the Li_xN_{2y} systems studied.

Of all geometric forms of molecular LiN_2, an isosceles triangular species is computed to be most stable. The LiN_2 molecule is symmetry forbidden (in the sense of Woodward and Hoffmann) to dissociate to Li (^2S) and N_2 ($^1\Sigma$) and, therefore, is kinetically stable, even though LiN_2 is energetic relative to its dissociation products. By the principle of detailed balance,[15] there is a substantial energy barrier to the formation of LiN_2 from ground-state Li and N_2, as represented at the right of Figure 3. LiN_2 would not be expected to form in the gas phase. The symmetry analysis by Maltz[16] of the H-Cl_2 system can be applied without

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(15) R. C. Tolman, "Statistical Mechanics," Oxford University Press, Oxford, 1938, p 163 ff.

(16) C. Maltz, *Chem. Phys. Lett.*, **9**, 251 (1971).

change to predict a repulsive interaction between Li and N_2 in the gas phase.[17] Population of a p orbital of Li is necessary for gas-phase broadside addition to occur, which is energetically costly. The symmetry barrier could be obviated after adsorption of Li on the nitrogen matrix, either by a forced close approach of Li to a molecule of N_2 or by the effect of surface states of appropriate symmetry.

The infrared data indicate the existence of a species containing two equivalent N_2 fragments, in which the nitrogen atoms are nonequivalent. The number and symmetry relation of the lithium atoms of this species are not unequivocally established. We have examined two stoichiometries, LiN_4 and Li_2N_4, in an attempt to determine the structure of the four-nitrogen system.

The symmetry relations among nitrogens allow some restriction on the geometry type of LiN_4. For example, a regular square pyramid with Li at the apex is excluded because all nitrogen atoms would be symmetry equivalent. In fact, such an arrangement is Jahn–Teller unstable, and even after distortion is energetic relative to other LiN_4 arrangements.

Colinear N_2–Li–N_2 is also Jahn–Teller unstable and would distort in a way specified by two angles α, β. The angle α is a measure of the departure of the two N_2 fragments from colinearity, while β indicates the degree of relative rotation of the N_2 fragments about the N–Li–N axis. (See Figure 3, at the top.) If $\alpha \neq 0$, then β may vary from 0 (cis configuration) to 90° (trans configuration). The equilibrium geometry has $(\alpha, \beta) = (30, 30°)$. This species occupies a local minimum in the energy surface and is kinetically stable; however, the system Li + LiN_4 is thermodynamically unstable relative to its dissociation products and to a pair of LiN_2 molecules as well. We surmise that if a limited amount of Li is deposited on a nitrogen matrix, LiN_2 will be formed in preference to LiN_4. If more Li is forced into the system, LiN_4 is even less likely to be formed.

We invoked the surface of the nitrogen matrix in order to rationalize the formation of LiN_2; yet we argue that LiN_4 is not an important species. The contradiction is only apparent, however, since the interaction of LiN_2 with N_2 is very probably a poor model of the interaction of LiN_2 with a surface of a nitrogen matrix. In analogous lithium–oxygen reactions, LiO_2 has been isolated as LiO_2 monomer in an O_2 matrix.[6]

If a pair of LiN_2 molecules is formed in adjacent matrix sites, they will dimerize readily according to our computations. Symmetry arguments parallel to those of Woodward and Hoffmann, as well as the symmetry relations deduced from the infrared data, rule out the formation of a D_{2h} Li_2N_4 molecule by the formation of a Li–Li bond. However, the oblique coupling shown at the left of Figure 3 is possible. We stress the dimerization route to the most stable Li_2N_4 geometry, since its direct formation from Li_2 and two N_2 is symmetry forbidden; although formation of Li_2N_4 from Li and LiN_4 is symmetry allowed, the requisite formation of LiN_4 is energetically unlikely, relative to the formation of two nearby LiN_2 molecules.

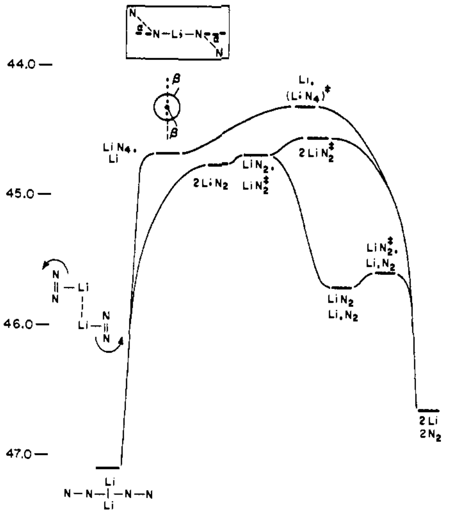

Figure 3. Possible routes from two Li atoms and two N_2 molecules to the species Li_2N_4 are shown. The species marked by a double dagger (‡) represent "activated complexes." Geometries of the LiN_4 molecule are specified by two angles α and β defined at the top of the diagram and the bond distances quoted in the text. The lowest energy path involves the independent formation of two LiN_2 species and their dimerization to Li_2N_4. The formation of isosceles-triangular LiN_2 is symmetry forbidden; presumably the formation can be catalyzed by surface states of the matrix. The dimerization can avoid a symmetry barrier by the oblique approach and rotation indicated at the left.

The bonding in the equilibrium Li_2N_4 species can be roughly characterized as follows. The Li–Li σ bond is diffuse and polarizable; it provides a weak, symmetric bridge between the N_2 fragments. Its influence is slight, since it contains two electrons initially. A more significant couple is made possible by the π virtual orbital of the Li_2 lying in the molecular plane, vacant in the isolated Li_2, but exerting a stabilizing influence on the antisymmetric combinations of occupied N_2-fragments orbitals. Finally, the π orbital of Li_2 stabilizes the symmetric combination of antibonding π MO's of $(N_2)_2$. The necessary promotion of charge to this antibonding N_2 level accounts in part for the resistance of this molecule to dissociation and the relatively low frequency for this N–N fundamental vibration. The present bonding situation nicely illustrates Pearson's generalization,[18] associating strong bonding with large overlap between a vacant orbital of one molecule with an occupied orbital of another.

Conclusions

The nitrogen isotopic shifts observed here for the 1800- and 1535-cm^{-1} features certainly identify these absorptions as fundamental nitrogen–nitrogen vibrations. The 1535-cm^{-1} feature is definitely due to a species containing two N_2 molecules while the 1800-cm^{-1} band is likely due to a single N_2 unit. Lithium atom concentration studies suggest that these new species are LiN_2 and $N_2Li_2N_2$, which we will call lithium supernitride and lithium disupernitride.

We wish to emphasize that the mechanism for these lithium–nitrogen reactions is not well understood. We

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[17] It is of some interest to note that the gas-phase broadside addition of Li to O_2, which requires a similar promotion of charge from Li(s) to Li(p), proceeds without a large barrier even though the reaction is symmetry forbidden, according to *ab initio* SCF calculations. See, for example, F. P. Billingsley, II, and C. Trindle, *J. Chem. Phys.*, in press.

[18] R. G. Pearson, *Theor. Chim. Acta*, **16**, 107 (1970); *J. Amer. Chem. Soc.*, 91, 1252, 4947 (1969).

believe that the observations are best explained by postulating the matrix reaction between Li and N_2 to form LiN_2. It must be noted that this reaction is much slower and less energetically favorable than the Li and O_2 reaction.[5,6] The $N_2Li_2N_2$ species is most likely made by the union of two LiN_2 molecules produced in adjacent matrix sites.

The LiN_2 and $N_2Li_2N_2$ species postulated here are of chemical interest as reduced N_2 species. N–N stretching fundamentals reported for N_2 complexes[1] fall near 2000 cm^{-1}. The N–N modes observed here at 1800 and 1535 cm^{-1} are clearly lower than any N_2 complexes discussed in recent reviews.[1-3] Hence, the lithium–nitrogen species contain N_2 which is *more reduced* than in the usual N_2 complex compounds. Close agreement between the N–N modes of N_2^- and LiN_2 suggests that the species LiN_2 is $Li^+N_2^-$; the valence electron of lithium becomes antibonding in the N_2 molecular orbital scheme and the vibrational frequency is decreased from the free N_2 value (2331 cm^{-1}). The bonding in N_2LiN_2 leading to a still lower N–N frequency is not so readily explained.

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Chemically Induced Dynamic Nuclear Polarization. General Solution of the CKO Model. Applicability to Reactions Run in Low Magnetic Fields[1]

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Abstract: CIDNP is currently attributed to the dynamic behavior of associated radical pairs. In an approximation intended for reactions carried out in high magnetic fields, the CKO model has been used by several workers. For reactions carried out in fields of a few to a few hundred gauss, no clearly justifiable approximate solution of the CKO model is available. Moreover, some of the other approaches to the theory of CIDNP, based on perturbation treatments, fail to provide methods of calculating polarization arising from low-field reactions. For the CKO model, and (in principle) for related diffusion models, this difficulty is overcome by solving the equations describing the model without approximation. The general solution for the CKO model has been programmed for a digital computer in series with other calculations which simulate the polarized nmr spectra of the reaction products. For high-field reactions, the calculations agree with those based on the high-field approximate CKO model. Sample calculations for low-field reactions are presented. For a one-proton radical pair, the intersystem crossings leading to product polarization are examined. The relative contributions from $T_\pm \rightarrow S$ and $T_0 \rightarrow S$ crossings are strongly dependent on the reaction magnetic field, and they vary in a surprising manner. The consequences of these variations are considered in the light of the mechanism and kinetics of reactions of alkyl halides with sodium naphthalene, for which the $T_0 \rightarrow S$ contribution to product polarization is entirely suppressed. The predictions of the theory agree with the experimentally observed polarization patterns, but an effective value of J, the radical pair electronic singlet–triplet splitting parameter, different from zero must be assumed. The field dependence of low-field polarization may provide a useful test of radical pair models and parameters.

While the earliest CIDNP experiments involved reactions run in magnetic fields of thousands of gauss,[3,4] it was soon discovered that the phenomenon persists for reactions run in lower fields, even in zero field.[5,6] In fact, at least one group of reactions has been discovered for which CIDNP can be detected *only* if they are run in low, nonzero magnetic fields, a few to a few hundred gauss.[7-9]

The high-field phenomena have been successfully accounted for, in nearly every detail, by the radical pair theory of CIDNP[10a,11] which seems to have displaced the earlier Overhauser-analog theory.[12,13] Cal-

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[1] Portions of this work were presented at the Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970, paper ORGN 415, and at the 162nd National American Chemical Society Meeting, Washington, D. C., Sept 1971, paper ORGN 77.

[2] National Institutes of Health Postdoctoral Fellow, 1970–1971.

[3] See H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969), and works cited therein.

[4] H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

[5] H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *ibid.*, 91, 4928 (1969).

[6] M. Lehnig and H. Fischer, *Z. Naturforsch.*, *A*, **24**, 1771 (1969).

[7] These are reactions of some alkyl halides with sodium naphthalene in DME. Included are 1,4-diiodobutane, 1,4-dibromobutane, 1,4-dichlorobutane,[8] isopropyl chloride,[9] and *n*-propyl chloride.

[8] J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *J. Amer. Chem. Soc.*, **92**, 5761 (1970).

[9] J. F. Garst, F. E. Barton, II, and J. I. Morris, *ibid.*, **93**, 4310 (1971).

[10] (a) G. L. Closs, *ibid.*, **91**, 4552 (1969); (b) G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183 (1970).

[11] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

[12] J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch.*, *A*, **22**, 1551 (1967); J. Bargon and H. Fischer, *ibid.*, *A*, **22**, 1556 (1967).