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Infrared spectrum of the NH_4-d_n^+ cation trapped in solid neon

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The NH_4^+ cation has been stabilized in solid neon in sufficient concentration for the identification of both of its infrared-active vibrational fundamentals, which appear within a few wavenumbers of the gas-phase band centers. Systematic alteration of the concentrations and positions of introduction of NH_3 and H_2 in the discharge sampling experiments demonstrated that the highest yield of NH_4^+ resulted when both the NH_3 and the H_2 were introduced downstream from a discharge through pure neon. In this configuration, each of these molecules can be ionized by excited neon atoms and their resonance radiation (16.6 eV to 16.85 eV), but fragmentation is minimized. Both infrared-active vibrational fundamentals of ND_4^+ and several fundamentals of each of the partially deuterium-substituted isotopomers of NH_4^+ were also identified. Evidence is presented for complexation of NH_4^+ with an H atom or with one or more H_2 molecules.

I. Introduction

Because of the chemical and biological importance of the ammonium cation, NH_4^+, there have been many observations of its infrared absorption spectrum in the strongly interacting environments of ionic crystals and polar solvents. In contrast, studies of its spectroscopic behavior in the absence of these interactions are sparse. The first gas-phase observations of NH_4^+ were concurrent studies by Crofton and co-workers[1,2] and by Schäfer and co-workers,[3,4] which yielded the assignment of the infrared-active stretching fundamental, ν_3. The other infrared-active fundamental of gas-phase NH_4^+, ν_4, was later observed in diode laser studies.[5,6] Crofton and co-workers[2] also analyzed the ν_3 band of ND_4^+, and, in a study of the zero-kinetic-energy photoelectron spectrum of ND_4, Signorell and co-workers[7] obtained the rotational constant of ground-state ND_4^+ with an uncertainty of 0.004 cm^{-1}. Except for the analysis of one vibrational fundamental of NH_3D^+ by Nakanaga and Amano,[8] there have been no experimental studies of the partially deuterium-substituted ammonium cations. The CCSD(T)/cc-pVTZ *ab initio* calculations, including anharmonic corrections, by Martin and Lee[9] of the vibrational fundamentals of NH_4^+ and all of its deuterium-substituted isotopomers provide tentative information regarding the spectroscopic properties of these species.

Experiments in this laboratory have led to the stabilization of a number of small molecular ions in concentration sufficient for infrared identification.[10] In the study of the infrared spectrum of NH_3^+,[11] a weak absorption appeared near the position of the ν_4 fundamental of gas-phase NH_4^+, 1447.22 cm^{-1}.[5,6] In order to determine whether this peak was indeed contributed by NH_4^+ and, if so, to optimize the conditions for NH_4^+ production, further studies were conducted using several different sampling configurations and introducing additional H_2 into the system. As will be shown in the following discussion, not only did these studies confirm the identification of NH_4^+, but they yielded the first spectroscopic identification of ν_4 of ND_4^+ and of many of the vibrational fundamentals of the partially deuterium-substituted isotopomers.

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II. Experimental details[12]

The ammonia samples used for these studies were the same as had been used for the previous series of experiments[11] concerned with the identification of isotopomers of NH_3^+. These samples were freed of relatively volatile impurities by freezing at 77 K and pumping on the resulting solid. The H_2 and D_2 (Matheson Gas Products, Inc.), HD (97%, Cambridge Isotope Laboratories, Inc.), and neon (Spectra Gases, Inc., Research Grade, 99.999%) were used without further purification. Sample mixtures were prepared using standard vacuum procedures. A number of initial experiments were conducted in order to establish optimal conditions for the stabilization of NH_4^+ and its isotopomers. For these studies, the concentrations of the reactants were varied. The concentrations which will be given in the description of the initial experiments were representative. The optimum Ne : H_2 : NH_3 mole ratio was found to be 400 : 6 : 1. After this had been established, more detailed isotopic substitution studies were conducted at a Ne : H_2-d_m : NH_3-d_n mole ratio of 400 : 6 : 1 or 400 : 5 : 1.

Isotopically enriched ammonia undergoes significant isotopic exchange with ammonia which has previously been adsorbed on the walls of deposition line. The extent of isotopic enrichment improved as a series of experiments on a given isotopically enriched sample proceeded. Flowing some of the sample mixture through the deposition system and cell before the cell was cooled for the experiment enhanced the extent of isotopic enrichment.

A Helitran (APD Cryogenics. Inc.) continuous transfer liquid helium cell maintained at 4.3 K was used for all of the experiments. The deposition configuration has previously been described,[13] as has been the setup used for microwave excitation.[14] In typical ion production experiments, pure neon is subjected to a microwave discharge while it passes through a quartz tube that has a coarse pinhole in the end. The molecule of interest, mixed with a large excess of neon, is introduced into the cell slightly beyond the discharge tube, and the excited neon atoms and their resonance radiation interact with the molecule outside the pinhole and on the cryogenic surface. In some of the preliminary experiments, the two deposition lines were interchanged, so that the ammonia-containing mixture passed through the microwave discharge and additional neon was introduced into the sample without exposure to the discharge.

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In a few experiments, a small concentration of H_2 was added to the neon sample flowing through the discharge tube.

The absorption spectra of the sample deposits were obtained using a Bomem DA3.002 Fourier transform interferometer with transfer optics that have been described previously.[15] Observations were conducted with a resolution of 0.2 cm^{-1} between 400 and 5000 cm^{-1} using a globar source, a KBr beamsplitter, and a wide-band HgCdTe detector cooled to 77 K. Data were accumulated for each spectrum over a period of at least 15 min. The resulting spectrum was ratioed against a similar one taken without a deposit on the cryogenic mirror. Under these conditions, the positions of the prominent, non-blended atmospheric water vapor lines between 1385 and 1900 cm^{-1} and between 3620 and 3900 cm^{-1}, observed in a calibration scan, agreed to within 0.01 cm^{-1} with the high-resolution values reported by Toth.[16,17] Based on previous investigations, with this experimental configuration the standard uncertainty (type B) in the determination of the positions of absorption maxima for molecules trapped in solid neon is ± 0.1 cm^{-1} (coverage factor, $k = 1$, *i.e.*, 1σ).

Information on photoinduced changes in the matrix sample was obtained by exposing the deposit to various wavelength ranges of visible and ultraviolet radiation. For a few studies, a tungsten background source was used with a 780 nm (Schott glass type RG780) or a 630 nm (Corning glass type 2403) short-wavelength cutoff filter. Since no changes were detected in the product spectra under those irradiation conditions, most of the sample irradiations were conducted using a medium-pressure mercury arc with a filter of Corning glass type 3384, 3389 or 7740 or without a filter to provide a short-wavelength cutoff of approximately 490, 420, 280 or 250 nm, respectively.

III. Results and discussion

A. Stabilization of NH_4^+

The initial experiments were focused on determining the conditions that produce the greatest intensity of the product absorption which was previously detected[11] at 1442.5 cm^{-1} when a Ne : NH_3 sample was codeposited with a beam of discharged neon atoms. The results of these experiments are summarized in Fig. 1. The initial strategy was to pass the Ne : NH_3 mixture, rather than pure neon, through the microwave discharge and, to improve the isolation of the products in the solid deposit, diluting the discharged material with an approximately equal amount of pure neon that had not been excited in the discharge. Similar conditions have been used in many laboratories to produce molecular fragments for spectroscopic study. As is shown in trace (a), a weak absorption at 1442.5 cm^{-1} resulted. When a mixture with a greater concentration of NH_3 was used, as in trace (b), a somewhat more intense product absorption appeared. Since the isolation properties of the neon matrix would be likely to degrade at still higher concentrations of NH_3, the introduction of H_2 was next tried. The first such study, shown in trace (c), involved passing a Ne : H_2 : NH_3 = 400 : 4 : 1 mixture through the microwave discharge. Further enhancement of the 1442.5 cm^{-1} absorption resulted. When, as in trace (d), a still higher concentration of H_2 was present in the sample mixture, the 1442.5 cm^{-1} peak and satellite absorptions at 1441.2 and 1440.9 cm^{-1} grew still more. In the experiments of traces (b) through (d), a new absorption at 3357.5 cm^{-1} appeared and grew in prominence. It was not feasible to increase the H_2 concentration in the mixture passed through the discharge tube beyond about 2.5%, the value employed for the experiment of trace (d); at higher concentrations spontaneous warmups of the deposit frequently occurred. The experiment of trace (e) more closely followed the procedure which has typically been used for ion production studies in this laboratory. The Ne : NH_3 mixture was introduced into the system downstream from the discharge region. A Ne : H_2 = 39 mixture was passed through the microwave discharge, providing a source not only of excited neon atoms and their resonance radiation but also of H atoms and undissociated H_2. Although care had been taken to match the sample size and deposition time in the other experiments in this comparison, only a limited amount of liquid helium was available to conduct the experiment shown in trace (e). Despite the smaller sample size, both the absorption pattern near 1442.5 cm^{-1} and that near 3357.5 cm^{-1} were more prominent than in the earlier studies. Finally, an experiment was conducted using an undischarged Ne : H_2 : NH_3 = 400 : 6 : 1 sample mixture and passing pure neon through the microwave discharge. As is shown in trace (f) of Fig. 1, the absorptions of interest were approximately doubled in intensity, compared to those of trace (e). Subsequent experiments were conducted using the same sampling configuration and approximately the same concentrations in the sample mixture as had been used for the experiment of trace (f).

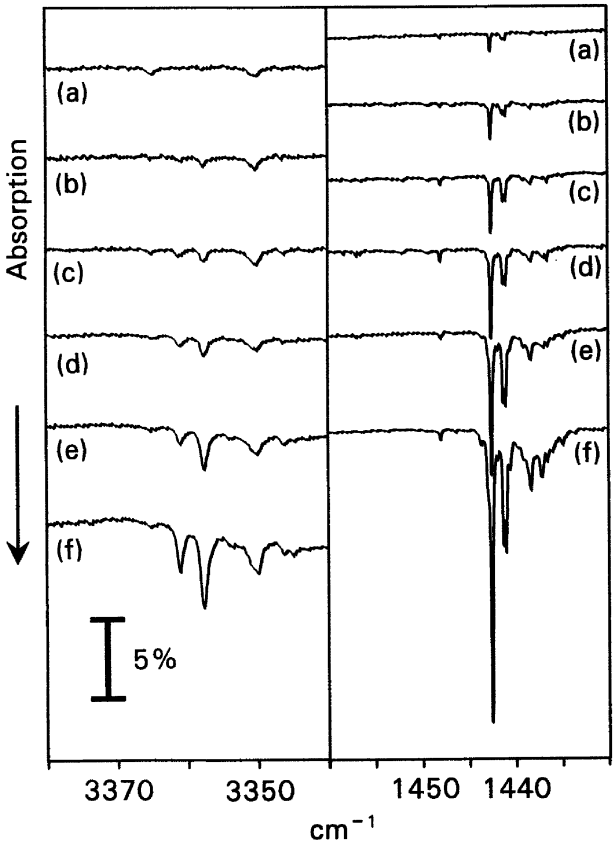

Fig. 1 (a) 10.7 mmol Ne : NH_3 = 400 : 1 that had been passed through a microwave discharge was codeposited at 4.3 K over a period of 205 min with 10.9 mmol undischarged Ne. (b) 9.04 mmol Ne : NH_3 = 200 : 1 that had been passed through a microwave discharge was codeposited at 4.3 K over a period of 180 min with 8.19 mmol undischarged Ne. (c) 9.17 mmol Ne : H_2 : NH_3 = 400 : 4 : 1 that had been passed through a microwave discharge was codeposited at 4.3 K over a period of 181 min with 9.23 mmol undischarged Ne. (d) 9.21 mmol Ne : H_2 : NH_3 = 400 : 10 : 1 that had been passed through a microwave discharge was codeposited at 4.3 K over a period of 180 min with 9.31 mmol undischarged Ne. (e) 7.20 mmol undischarged Ne : NH_3 = 400 : 1 was codeposited at 4.3 K over a period of 140 min with 6.68 mmol Ne : H_2 = 39 : 1 that had been passed through a microwave discharge. (f) 9.77 mmol undischarged Ne : H_2 : NH_3 = 400 : 6 : 1 was codeposited at 4.3 K over a period of 231 min with 9.96 mmol Ne that had been passed through a microwave discharge.

The assignment of the absorption at 1442.5 cm^{-1} to the ν_4 fundamental of NH_4^+ is supported not only by its proximity to the gas-phase band center of that species but also by the enhancement in its intensity as hydrogen is added to the system. The absorption at 3357.5 cm^{-1} and a less intense absorption at 3361.0 cm^{-1} that grow at a rate proportional

to that of the structured 1442.5 cm^{-1} absorption in the experiments summarized by Fig. 1 lie suitably close to the 3343.14 cm^{-1} gas-phase band center[1–4] of ν_3 of NH_4^+ for the corresponding assignment. A series of molecular beam studies by Dopfer, Maier and co-workers, recently reviewed by Bieske and Dopfer,[18] have shown that the H-stretching vibrational band centers of complexes of the rare gases with protonated molecules are often shifted to appreciably lower frequencies because of proton sharing with the rare gas atom. However, the proton affinity of NH_3 is relatively high, and the ν_3 band center of gas-phase NH_4^+ complexed to a single neon atom appears at 3344.0 cm^{-1},[19] very close to the band center for the uncomplexed cation.

When both NH_3 and H_2 are present in the sample deposit, the detailed structure of the infrared absorptions of the NH_3 differs from that characteristic of simple Ne : NH_3 deposits.[20,21] This phenomenon is attributed to complex formation between H_2 and NH_3, previously reported by Moroz and co-workers.[22] Further discussion of perturbations to the spectrum of NH_3 is beyond the scope of the present study.

In the experiment of Fig. 1(f), as well as in the other experiments here reported, the presence of H_2 or its isotopomers greatly inhibits the stabilization of NH_3^+ or its isotopomers.

All of the absorptions shown in Fig. 1 except that of NH_3 at 3350 cm^{-1} were somewhat diminished in intensity when the sample was exposed for a few minutes to mercury-arc radiation of wavelength longer than 490 nm and were destroyed when a 420 nm cutoff filter was instead used or the filter was removed during the irradiation. The absorptions of ammonia showed little or no change as a result of this irradiation.

B. Isotopic dependence of the NH_4^+ absorptions

Still further support for the assignment of the 1442.5 and 3357.5 cm^{-1} neon-matrix absorptions to the two infrared-active vibrational fundamentals of NH_4^+ has been obtained from experiments on isotopically substituted samples. In addition, these experiments have yielded the first infrared spectroscopic data for several isotopomers of NH_4^+.

As is shown in Table 1, the 1442.5 and 3357.5 cm^{-1} neon-matrix absorptions also agree well with the positions obtained for these two vibrational fundamentals of NH_4^+ in the CCSD(T)/cc-pVTZ calculations including anharmonic corrections by Martin and Lee.[9] Although these workers obtained vibrational fundamental frequencies for all of the $^{14}NH_4$-d_n^+ species, estimates of their relative intensities were not reported. Since these would also be helpful in the assignments and since some of the experiments were conducted using ammonia samples which were enriched in nitrogen-15, we performed calculations for the various isotopomers of the ammonium cation at the RMP2/6-311++G(3*df*,3*pd*) level using the Gaussian 98 program package.[23] The intensities estimated for the vibrational fundamentals of the $^{14}NH_4$-d_n^+ species by these calculations are included, in parentheses, in Table 1. Assignments of observed absorptions are also summarized. The observations leading to these assignments are described in the following discussion.

NH_3D^+ should have two relatively prominent deformation fundamentals, one only slightly shifted from the triply degenerate deformation fundamental of NH_4^+, the other near 1278.6 cm^{-1}. The latter spectral region is shown in Fig. 2. As is shown in trace (a), from the same experiment on a Ne : H_2 : NH_3 sample as that illustrated in Fig. 1(f), when the sample was not enriched with deuterium no absorption appeared between 1265 and 1280 cm^{-1}. In another experiment in which HD was substituted for H_2, shown in trace (b) of Fig. 2, a weak, photosensitive new absorption appeared at 1277.3 cm^{-1}. The absorption pattern near 1442.5 cm^{-1} was unchanged from that obtained using H_2. In the NH-stretching region, a photosensitive absorption with a high frequency shoulder appeared at 3353.7 cm^{-1}. In still another experiment using D_2 instead of H_2, shown in Fig. 2(c), the 1277.3 cm^{-1} absorption appeared with slightly lower intensity and was accompanied by several

Table 1 Calculated[a] vibrational fundamentals (cm^{-1}) of $^{14}NH_4^+$-d_n compared with absorptions observed[b] in neon-matrix experiments

	NH_4^+	NH_3D^+	$NH_2D_2^+$	NHD_3^+	ND_4^+
Calculated	3345.1(581)	3336.6(390)	3333.4(196)	3311.4(156)	2492.0(300)
Observed	3357.5	3354.2	3350.0		2502.1
Calculated			3297.9(110)	2479.2(200)	
Observed			3306.4		
Calculated		3279.7(58)	2461.8(100)		
Calculated	3236.6(0)	2430.8(65)	2393.5(38)	2370.5(17)	2325.9(0)
Calculated	1690.1(0)	1624.2(50)	1583.7(52)	1426.9(80)	1205.8(0)
Observed				1425.0	
Calculated			1469.2(0)		
Calculated	1447.2(417)	1442.4(136)	1363.5(114)	1140.6(84)	1094.9(153)
Observed	1442.5		1365.9	1139.9	1092.0
Calculated		1278.6(160)	1198.7(73)		
Observed		1277.3			
Calculated			1136.1(42)	1101.0(52)	
Observed				1103.4	

[a] Positions of fundamentals from CCSD(T)/cc-pVTZ calculations, with anharmonic correction, reported by Martin and Lee.[9] Intensities (km/mol), in parentheses, were estimated from RMP2/6-311++G(3df,3pd) calculations performed as a part of the present study. A blank space for a calculated fundamental indicates that it is degenerate with the fundamental above it. [b] Ne matrix, this work. Based on previous investigations, the standard uncertainty (Type B) in the frequency measurement is ±0.1 cm^{-1} (coverage factor, $k = 1$: *i.e.*, 1σ). Where the absorption is structured, the position of the most prominent peak is given.

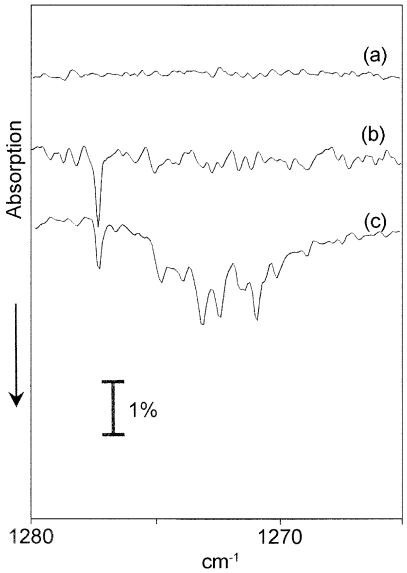

Fig. 2 (a) 9.77 mmol undischarged Ne : H_2 : NH_3 = 400 : 6 : 1 was codeposited at 4.3 K over a period of 231 min with 9.96 mmol Ne that had been passed through a microwave discharge. (b) 11.1 mmol undischarged Ne : HD : NH_3 = 400 : 6 : 1 was codeposited at 4.3 K over a period of 228 min with 11.4 mmol Ne that had been passed through a microwave discharge. (c) 9.74 mmol undischarged Ne : D_2 : NH_3 = 400 : 6 : 1 was codeposited at 4.3 K over a period of 184 min with 8.01 mmol Ne that had been passed through a microwave discharge.

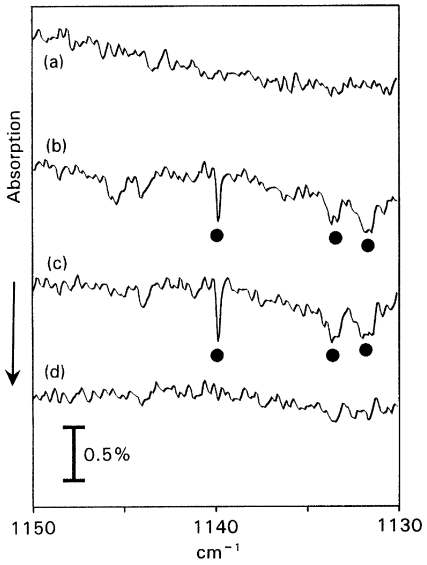

Fig. 4 (a) 9.77 mmol undischarged Ne : H_2 : NH_3 = 400 : 6 : 1 was codeposited at 4.3 K over a period of 231 min with 9.96 mmol Ne that had been passed through a microwave discharge. (b) 13.4 mmol undischarged Ne : H_2 : ND_3 : NH_3 = 400 : 5 : 0.7 : 0.3 was codeposited at 4.3 K over a period of 250 min with 11.1 mmol Ne that had been passed through a microwave discharge. (c) 11.8 mmol undischarged Ne : H_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 220 min with 9.63 mmol Ne that had been passed through a microwave discharge. (d) 11.4 mmol undischarged Ne : D_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 215 min with 9.30 mmol Ne that had been passed through a microwave discharge.

photosensitive lower frequency absorptions, the most prominent of them at 1274.8, 1273.1, 1272.4 and 1270.9 cm^{-1}.

Because of the facile isotopic exchange of ND_3 in the vacuum system, spectra obtained in experiments with more extensive deuterium enrichment are quite complicated. Various spectral regions in which most of the product absorptions appear are shown in Figs. 3–8. Each of these figures shows the results from the same set of four experiments, arranged in the order of increasing deuterium enrichment. The traces labeled (a) were obtained for the same sample as that used for Fig. 1(f) and for Fig. 2(a), with no deuterium enrichment. The traces labeled (b) were obtained in an experiment on a Ne : H_2 : ND_3 : NH_3 = 400 : 5 : 0.7 : 0.3 sample, those labeled (c) in a study of a Ne : H_2 : ND_3 = 400 : 5 : 1 sample, and those labeled (d) in a study of a Ne : D_2 : ND_3 sample. The latter

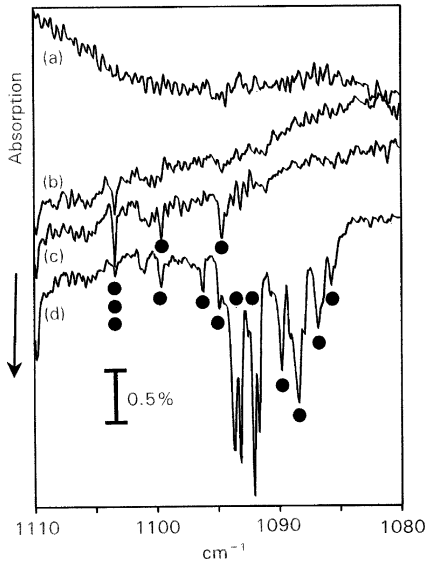

Fig. 3 (a) 9.77 mmol undischarged Ne : H_2 : NH_3 = 400 : 6 : 1 was codeposited at 4.3 K over a period of 231 min with 9.96 mmol Ne that had been passed through a microwave discharge. (b) 13.4 mmol undischarged Ne : H_2 : ND_3 : NH_3 = 400 : 5 : 0.7 : 0.3 was codeposited at 4.3 K over a period of 250 min with 11.1 mmol Ne that had been passed through a microwave discharge. (c) 11.8 mmol undischarged Ne : H_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 220 min with 9.63 mmol Ne that had been passed through a microwave discharge. (d) 11.4 mmol undischarged Ne : D_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 215 min with 9.30 mmol Ne that had been passed through a microwave discharge.

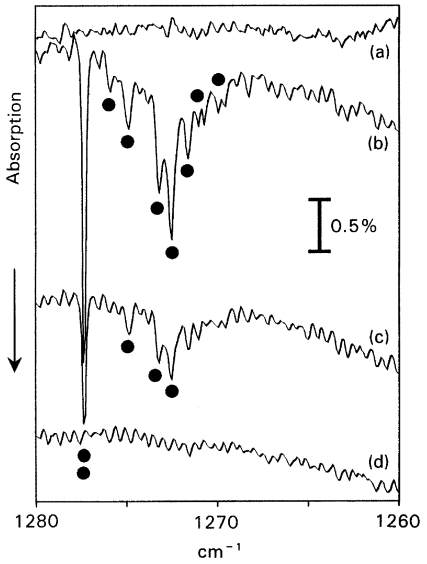

Fig. 5 (a) 9.77 mmol undischarged Ne : H_2 : NH_3 = 400 : 6 : 1 was codeposited at 4.3 K over a period of 231 min with 9.96 mmol Ne that had been passed through a microwave discharge. (b) 13.4 mmol undischarged Ne : H_2 : ND_3 : NH_3 = 400 : 5 : 0.7 : 0.3 was codeposited at 4.3 K over a period of 250 min with 11.1 mmol Ne that had been passed through a microwave discharge. (c) 11.8 mmol undischarged Ne : H_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 220 min with 9.63 mmol Ne that had been passed through a microwave discharge. (d) 11.4 mmol undischarged Ne : D_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 215 min with 9.30 mmol Ne that had been passed through a microwave discharge.

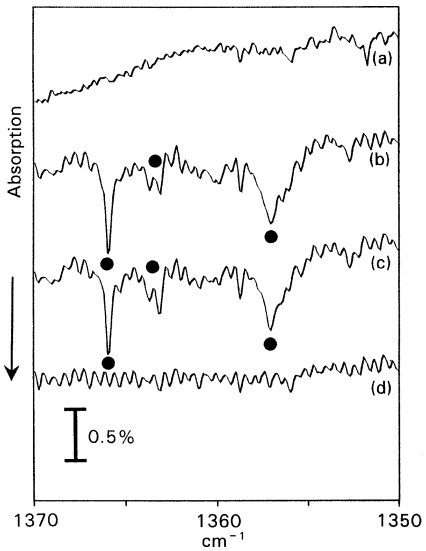

Fig. 6 (a) 9.77 mmol undischarged Ne : H_2 : NH_3 = 400 : 6 : 1 was codeposited at 4.3 K over a period of 231 min with 9.96 mmol Ne that had been passed through a microwave discharge. (b) 13.4 mmol undischarged Ne : H_2 : ND_3 : NH_3 = 400 : 5 : 0.7 : 0.3 was codeposited at 4.3 K over a period of 250 min with 11.1 mmol Ne that had been passed through a microwave discharge. (c) 11.8 mmol undischarged Ne : H_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 220 min with 9.63 mmol Ne that had been passed through a microwave discharge. (d) 11.4 mmol undischarged Ne : D_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 215 min with 9.30 mmol Ne that had been passed through a microwave discharge.

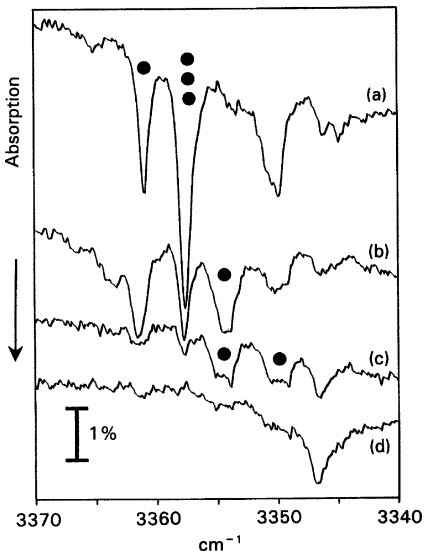

Fig. 8 (a) 9.77 mmol undischarged Ne : H_2 : NH_3 = 400 : 6 : 1 was codeposited at 4.3 K over a period of 231 min with 9.96 mmol Ne that had been passed through a microwave discharge. (b) 13.4 mmol undischarged Ne : H_2 : ND_3 : NH_3 = 400 : 5 : 0.7 : 0.3 was codeposited at 4.3 K over a period of 250 min with 11.1 mmol Ne that had been passed through a microwave discharge. (c) 11.8 mmol undischarged Ne : H_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 220 min with 9.63 mmol Ne that had been passed through a microwave discharge. (d) 11.4 mmol undischarged Ne : D_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 215 min with 9.30 mmol Ne that had been passed through a microwave discharge.

sample achieved the highest extent of deuterium enrichment attained in this series of experiments.

As is shown in Fig. 3(d), highly structured, photosensitive absorption appeared between 1085 and 1097 cm^{-1}. The strongest absorption maximum was at 1092.0 cm^{-1}, but absorptions at 1093.6 and 1093.1 cm^{-1} were only slightly weaker. Other relatively prominent absorptions appeared at 1091.6, 1089.7, 1088.3 and 1086.8 cm^{-1}. The 1092.0 cm^{-1} absorption and its satellites lie close to the 1094.9 cm^{-1} position calculated for the previously unreported ν_4 fundamental of ND_4^+. (Here and in the following discussion, all of the calculated positions for isotopomers of the ammonium cation – summarized in Table 1 – are those obtained in the study by Martin and Lee.[9]) The photosensitive absorption at 1103.4 cm^{-1}, most prominent in traces (b) and (c) of Fig. 3, also lies close to the absorption of NHD_3^+ which is calculated to appear at 1101.0 cm^{-1}. Photosensitive absorptions at 1099.6 and 1094.6 cm^{-1} may possibly be contributed by the same fundamental of NHD_3^+.

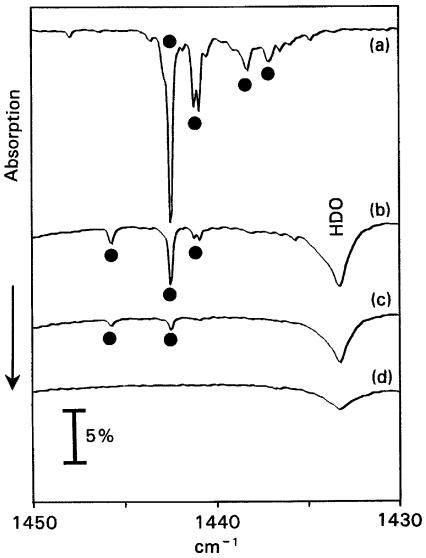

Fig. 7 (a) 9.77 mmol undischarged Ne : H_2 : NH_3 = 400 : 6 : 1 was codeposited at 4.3 K over a period of 231 min with 9.96 mmol Ne that had been passed through a microwave discharge. (b) 13.4 mmol undischarged Ne : H_2 : ND_3 : NH_3 = 400 : 5 : 0.7 : 0.3 was codeposited at 4.3 K over a period of 250 min with 11.1 mmol Ne that had been passed through a microwave discharge. (c) 11.8 mmol undischarged Ne : H_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 220 min with 9.63 mmol Ne that had been passed through a microwave discharge. (d) 11.4 mmol undischarged Ne : D_2 : ND_3 = 400 : 5 : 1 was codeposited at 4.3 K over a period of 215 min with 9.30 mmol Ne that had been passed through a microwave discharge.

In the 1130 to 1150 cm^{-1} spectral region, shown in Fig. 4, a sharp, photosensitive absorption appeared at 1139.9 cm^{-1} in the experiments with a moderate extent of deuterium enrichment. This peak was accompanied by less well defined, photosensitive peaks at 1133.5 and 1131.6 cm^{-1}. The correlation of the 1139.9 cm^{-1} peak with the 1140.6 cm^{-1} peak calculated for NHD_3^+ is evident.

The 1260 to 1280 cm^{-1} spectral region is shown for these four samples in Fig. 5, which may be compared to the related observations for samples prepared using HD or D_2 illustrated in Fig. 2. In the experiments of Fig. 5(b) and 5(c), as in those of Fig. 2(b) and 2(c), the most prominent photosensitive product absorption appears at 1277.3 cm^{-1}, very close to the 1278.6 cm^{-1} position calculated for one of the vibrational fundamentals of NH_3D^+. Within the experimental error, the most prominent satellite absorptions, at 1273.2 and 1272.5 cm^{-1}, correspond with relatively prominent peaks in the experiment of Fig. 2(c).

As is shown in Fig. 6, a sharp, photosensitive absorption appears at 1365.9 cm^{-1} in the spectrum of samples with an intermediate extent of deuterium substitution. This peak corresponds well with the most intense deformation fundamental of $NH_2D_2^+$, calculated to appear at 1363.5 cm^{-1}. Satellite absorptions also appear at 1363.4 and 1357.0 cm^{-1}.

The 1430 to 1450 cm^{-1} spectral region is shown for this set of samples in Fig. 7. The photosensitive absorption at 1442.5 cm^{-1} and its less intense companions at 1441.2 and 1440.9 cm^{-1} decrease rapidly in intensity as the extent of deuterium substitution of the sample grows. A weak, photosensitive

absorption appears at 1447.9 cm^{-1}. Possibly this absorption is contributed by a deformation vibration of NH_3D^+, detectable at the concentration of NH_3D^+ achieved in the experiments shown in Fig. 7(b) and 7(c) but not in the experiments of Fig. 2(b) and 2(c). However, this identification is tentative. In the experiments of Fig. 7(b) and 7(c), a weak, sharp, photosensitive absorption also appeared at 1425.0 cm^{-1}, close to the 1426.9 cm^{-1} position calculated for a deformation fundamental of NHD_3^+.

The 2500 cm^{-1} spectral region, characteristic of the ND-stretching vibrations of both uncharged deuterium-substituted ammonia and the fully and partially deuterium substituted ammonium cation, shows a very complicated absorption spectrum. The most prominent photosensitive peak in the highest deuterium enrichment study lies at 2502.1 cm^{-1}, in good agreement with the calculated position of 2492.0 cm^{-1} and the gas-phase band center[2] observed at 2495.0 cm^{-1} for ν_3 of ND_4^+.

The 3340 to 3370 cm^{-1} absorption region, shown in Fig. 8, includes several NH-stretching absorptions of NH_4^+ and its partially deuterium-substituted isotopomers. In trace (a), the most prominent absorption is the photosensitive peak at 3357.5 cm^{-1}, which has a less intense companion at 3361.0 cm^{-1}. The major peak acquires a lower frequency counterpart at 3354.2 cm^{-1} when some deuterium is introduced into the ammonia molecule, as in traces (b) and (c). The assignment of that absorption to NH_3D^+ is consistent with the calculations and with the identification[8] of the gas-phase band center of ν_4 of NH_3D^+ at 3341.08 cm^{-1}, 2.06 cm^{-1} below the position of the NH_4^+ stretching absorption. Although the peak at 3350.0 cm^{-1} did not decrease on mercury-arc irradiation of the deposits of traces (a) and (b), it did decrease in the experiment of trace (c), suggesting that in the latter experiment much or all of the absorption at that frequency arises from $NH_2D_2^+$. In the experiments of traces (b) and (c), a photosensitive absorption (not shown in Fig. 8) also appeared at 3306.4 cm^{-1}, a position appropriate for its assignment to the second NH-stretching fundamental of $NH_2D_2^+$.

Experiments were also conducted on samples prepared using $^{15}NH_3$ and $^{15}ND_3$. The results were analogous to those already described, except that each of the absorptions is shifted to a slightly lower frequency. In Table 2, the observed shifts are compared with those obtained from RMP2/6-311++G(3df,3pd) calculations. To correct for anharmonicity, each vibration calculated for the nitrogen-15 substituted cation was scaled by a factor derived from the ratio of the observed vibrational frequency for the nitrogen-14 substituted species to the corresponding calculated value. None of the observed isotopic shifts deviated from the calculated shift by more than 0.9 cm^{-1}, providing further support for the proposed assignments.

Table 2 Nitrogen-15 shifts (in cm^{-1}) for observed absorptions of NH_4-d_n^+

Species	ν_{obs} [a]	Δ_{obs}	Δ_{MP2} [b]
NH_4^+	3357.5	8.4	9.3
	1442.5	6.8	6.8
NH_3D^+	3354.2	8.6	8.1
	1277.3	6.6	6.7
$NH_2D_2^+$	3350.0	9.0	9.3
	1365.9	5.8	6.0
NHD_3^+	1139.9	5.5	5.1
	1103.4	8.4	8.5
ND_3^+	2502.1	12.6	13.4
	1092.0	7.5	7.6

[a] Nitrogen-14 species, Ne matrix, this work. Based on previous investigations, the standard uncertainty (Type B) in the frequency measurement is ±0.1 cm^{-1} (coverage factor, $k = 1$: *i.e.*, 1σ). [b] From RMP2/6-311++G(3df,3pd) calculations (this work), scaled to match MP2 frequency of $^{14}NH_4$-d_n^+ to observed value.

C. Processes which occur in the matrix

The results of all of the earlier studies in this laboratory using a beam of pure neon that had been passed through a microwave discharge are consistent with ion production by interaction of a suitable precursor with excited neon atoms and their resonance radiation, in the 16.6 to 16.85 eV energy range. Since those energies, for the first group of excited states of the neon atom, exceed the first ionization energy of both NH_3 (10.17 eV [11,24]) and H_2 (15.43 eV [25]), the two reactions

$$H_2^+ + NH_3 \rightarrow NH_4^+ + H \quad (1)$$

and

$$H_2 + NH_3^+ \rightarrow NH_4^+ + H \quad (2)$$

may both occur in the region between the pinhole in the discharge tube and the cryogenic surface, as well as on the surface itself. However, because of the large disparity between the values of the first ionization energies of H_2 and NH_3, collisional charge exchange between H_2^+ and NH_3 is likely to occur. Therefore, Reaction (2) would be likely to predominate.

Early gas phase studies[26,27] determined a relatively slow rate ($k = 5 \times 10^{-13}$ cm^3 s^{-1}) rate for Reaction (2) at room temperature. This rate increased as the temperature was raised, permitting estimation of an activation energy of 8.8 kJ mol^{-1} (2.1 kcal mol^{-1}). When the reaction mixture was cooled, it was found[28,29] that the rate levels off between 80 and 100 K. At lower temperatures, the rate increases again.[30,31] Studies of isotopically enriched samples determined[29,32] that the rate of the reaction between D_2 and NH_3^+ is only about 10% as great as that for H_2 and NH_3^+. Several laboratories[32–35] have also studied the comparative yields of NH_3D^+ and NH_2D^+ in the $D_2 + NH_3^+$ system for various NH_3^+ vibrational energies and center-of-mass collision energies. Although NH_3D^+ is always the predominant product, at higher collision energies some NH_2D^+ is also formed.

Herbst and co-workers[36] obtained good agreement between their calculated rate coefficients and the values derived from the experimental data for a mechanism that postulated the initial formation of a $NH_3^+\cdots H_2$ complex, bound by 5.9(1.3) kJ mol^{-1}, or 1.4(3) kcal mol^{-1}, which has a long lifetime at low temperatures and decomposes by tunneling. The exit channel complex, $NH_4^+\cdots H$, is bound by less than 3 kJ mol^{-1} and readily decomposes to form $NH_4^+ + H$. Their model is consistent with the observed reaction rates for the deuterium-substituted species. Herbst and co-workers also calculated the rates for the three-body reaction (which also involved a helium atom) and found that the results were compatible with other observations.[30] The three-body reaction differs by collisional stabilization of the $NH_3^+\cdots H_2$ complex, which is found still to be able to undergo tunneling to form the products on a time scale shorter than that of the observations. These conditions are likely to predominate during matrix depositions and in solid neon.

The structure observed for the vibrational fundamentals of the NH_4-d_n^+ species may arise in part from the trapping of the molecules in various types of site in the solid neon. Site splittings have been observed for NH_3[20,21] and for many other molecules trapped in the solid rare gases. However, other phenomena must be invoked to explain the disparity between the absorption patterns observed for ν_4 of NH_4^+ and ND_4^+.

The complicated vibrational absorption patterns observed in the present series of experiments might arise from molecular

Table 3 Comparison of calculated[a] absorptions (in cm^{-1}) for selected isotopomers of NH_4^+ and $NH_4^+\cdots H$

NH_4^+	$NH_4^+\cdots H$	$NH_4^+\cdots D$	ND_4^+	$ND_4^+\cdots H$	$ND_4^+\cdots D$
3538.1(580) f_2	3539.9(374) e	3539.9(376) e	2607.6(300) f_2	2608.7(192) e	2608.8(192) e
	3497.4(299) a_1	3497.4(299) a_1		2576.2(165) a_1	2576.2(165) a_1
3402.3(0) a_1	3384.7(36) a_1	3384.7(36) a_1	2406.7(0) a_1	2396.5(7) a_1	2396.5(7) a_1
1741.0(0) e	1742.5(0.6) e	1742.5(0.6) e	1231.5(0) e	1232.6(0.2) e	1232.6(0.2) e
1478.7(417) f_2	1482.7(244) e	1482.7(244) e	1110.3(153) f_2	1113.0(88) e	1113.0(88) e
	1474.3(132) a_1	1474.3(132) a_1		1106.8(46) a_1	1106.8(46) a_1
	260.7(13) a_1	189.2(14) a_1		259.4(11) a_1	187.4(11) a_1
	147.6(0.1) e	140.4(0.01) e		114.5(0.04) e	104.8(0.1) e

[a] MP2/6-311++G(3*df*,3*pd*) calculations, unrestricted for complexes. Infrared intensities (in km mol^{-1}) are given in parentheses. The symmetry of NH_4^+ and ND_4^+ is T_d, but that of the atom-cation complexes is C_{3v}.

rotation. Simple uncharged molecular hydrides usually can rotate in a neon matrix. The rotation of ammonia in solid neon has previously been studied.[20,21] High-resolution infrared observations[37] of a very dilute Ne : CH_4 sample suggested that although CH_4, which is geometrically similar to NH_4^+, can rotate in argon and the heavier rare-gas matrices, it cannot rotate in solid neon. Beginning with the high-resolution observations by Momose and co-workers,[38] the rotation of CH_4 in solid parahydrogen has been extensively studied. At 4.8 K, the most prominent absorption of each of the two infrared-active vibrational fundamentals of CH_4 is contributed by the R(0) transition. Other components of the rotational structure are symmetrically placed about it, with spacings of approximately 5 cm^{-1}. Although, with appropriately smaller spacings, a similar pattern of absorptions is observed for ND_4^+, the pattern for NH_4^+ is quite different. Whether NH_3^+ and other ions of the simple hydrides can rotate in a neon matrix is not known with certainty. However, there is abundant evidence that the rotation of uncharged hydride molecules is suppressed in the presence of an ion field.[11] Therefore, other explanations for the observed structure must also be considered.

A major contributor to the observed structure is likely to be complexation of NH_4^+ by other species present in the matrix. The interaction energy for the $NH_4^+\cdots NH_3$ pair[39] is relatively large, but in the present experiments the probability of collisional interaction between NH_3 and NH_4^+ is much smaller than that between H_2 and NH_4^+.

At the H_2 concentrations necessary to obtain an appreciable yield of NH_4^+, the stabilization of that species with one or more nearest neighbor H_2 molecules is highly probable. Calculations by Urban and co-workers[40] indicate that up to eight H_2 molecules can complex with NH_4^+. The first solvation shell is filled by four H_2 molecules, each oriented with its axis perpendicular to that of the NH bond with which it interacts. At the MP4 level, the solvation energy of each of these four H_2 molecules is approximately 10 kJ mol^{-1} (2.4 kcal mol^{-1}). When deuterium atoms are introduced into the system, interactions with HD and with D_2 will also occur, resulting in small changes in the infrared absorption pattern. Because of the several possible interactions, the absorption pattern in the deuterium-substitution experiments may become quite complex, as is observed.

The calculations by Herbst and co-workers[36] indicate that the transition state for the reaction between NH_3^+ and H_2 rearranges into a weakly bound $NH_4^+\cdots H$ complex, raising the possibility that this entrance channel complex may also contribute to the observed spectrum. Some of the H atoms are likely to be formed with sufficient kinetic energy to escape from the site of their production. However, the presence of an abundance of neon atoms will encourage collisional deactivation of the initially formed complex. The results of calculations of the positions of the vibrational fundamentals of NH_4^+ and ND_4^+ complexed with a single H or D atom, performed at the UMP2/6-311++G(3df,3pd) level using the Gaussian 03 program package,[41] are summarized in Table 3. The reduction in symmetry from T_d to C_{3v} because of complex formation leads to a splitting of approximately 40 cm^{-1} in the infrared-active NH-stretching vibration and 8 cm^{-1} in the infrared-active deformation vibration. The magnitudes of these splittings are independent of whether an H atom or a D atom participates in the complex. The calculated splitting of the deformation vibration could explain some of the observed structure. However, a lower frequency component of the NH-stretching fundamental was not identified. Such an absorption may have been obscured by one of the prominent absorptions of the photolytically stable $NH_3\cdots(H_2)_n$ species which appeared in these experiments at 3314, 3319 and 3333 cm^{-1}. Therefore, the contribution of infrared absorptions of the exit channel complex to the observed spectrum remains uncertain.

As in the earlier study of the infrared spectrum of NH_3^+,[11] the identity of the anion(s) which provide for the requisite overall charge neutrality of the sample deposit is not revealed by the present experiments, presumably because these species are weak infrared absorbers. A leading candidate would be NH_2^-, which is calculated[42] to have its bending vibration fundamental in the same spectral region as that of ν_4 of NH_4^+. However, the two stretching fundamentals of NH_2^- are calculated[42,43] to lie between 3100 and 3200 cm^{-1} and to be much more strongly infrared absorbing than the bending fundamental. The experimentally determined band centers of these stretching fundamentals lie at 3121.93 and 3190.29 cm^{-1}.[44,45] In the present experiments, no new absorptions were detected in that spectral region.

IV. Conclusions

A considerably higher yield of NH_4^+ is obtained in cryogenic sampling experiments when NH_3 and H_2 are introduced into the system downstream from neon atoms that are excited in a microwave discharge than when either molecule is introduced into the discharge region. Since extensive atomization occurs in discharges, the predominant source of NH_4^+ in these experiments is believed to be the reaction of NH_3^+ with H_2. The neon-matrix shifts in the infrared-active vibrational fundamentals of NH_4^+ are smaller than 0.5%. These experiments have yielded the first identifications of the ν_4 vibrational fundamental of ND_4^+ and of several of the vibrational fundamentals of each of the partially deuterated ammonium cations. Complexation of H atoms and of H_2 with the NH_4-d_n^+ is believed to be a major contributor to the satellite absorptions which appear close to each of the fundamental absorptions of the NH_4-d_n^+ species trapped in the neon matrix.

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