the signal-to-noise ratio. The curves are corrected for instrument response. A detailed description of the system has appeared.²³

The experimental rise or decay curves obtained from the streak camera are fitted to a convolution of the excitation pulse with the intrinsic fluorescence response. The convoluted function is given by

$$F'(t') = \int S(t) F(t'-t) dt$$
 (5)

where S(t) is a Gaussian function describing the excitation pulse and F(t) is the fluorescence response function, which is given by

$$F(t) = a \exp(-t/\tau_1) + (1-a) \exp(-t/\tau_2) - b \exp(-t/\tau_3) - (1-b) \exp(-t/\tau_4)$$
(6)

where τ_1 and τ_2 are lifetime values weighted according to the preexponential factor a, and τ_3 and τ_4 are risetime values weighted according to the preexponential factor b.

B. Chemicals. 2-Methyl-3-hydroxychromone (3-HC) was synthesized and purified at the Institute for Drug Research in Budapest Hungary, and used as received. The solvents cyclohexane (Fisher Co., spectral grade), benzene (Fisher Co., spectral grade), acetonitrile (Fisher Co., HPLC grade), and methanol (Fisher Co., spectral grade) were used as received. Benzene was kept over 4-Å molecular sieves to avoid water contamination. Dioxane (Fisher Co., reagent grade) was distilled and kept under argon to prevent peroxide formation. Methylcyclohexane (Fisher Co., spectral grade) was distilled over an alumina column. The dye rhodamine 640 was purchased from Exciton Chemical Co.

The solutions used in the transient absorption and streak camera experiments were degassed by flowing nitrogen through the solution and were circulated in order to avoid sample decomposition. The vacuum-degassed sample was deaerated by repeated freeze-pump-thaw cycles (six times, 10^{-5} Torr). The solutions used in the ASE experiments were degassed by bubbling Ar through for 30 min and were stirred during the experiment to avoid interference from secondary processes (triplet population, local heating, etc.).

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EPR-ENDOR Spectroscopy of Matrix-Isolated NH₃⁺ and CH₃ Radicals

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Electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) spectra of ${}^{14}NH_3^+$ and ${}^{15}NH_3^+$, generated by X-ray irradiation of NH₃ in argon and neon matrices, and of CH₃ and ${}^{13}CH_3$, generated in an argon matrix from CH₃I during codeposition with Cs atoms, have been recorded. Analysis of the ENDOR spectra shows that the EPR spectra are inhomogeneously broadened due to a distribution of coupling constants for the central atom.

Introduction

Rare gas matrices have been demonstrated^{1,2} to be excellent hosts in which to study small radicals, both charged and uncharged, by EPR spectroscopy. While the EPR spectra of matrix-isolated radicals generally exhibit narrow linewidths, often less than 0.5 G, extraction of all the hyperfine parameters is only possible if the spectrum is sufficiently resolved. Powder spectra, observed when the radical is not tumbling rapidly, can be very complicated and poorly resolved if a number of magnetic nuclei with anisotropic hyperfine interactions are present and may be very difficult to interpret. In such cases, ENDOR offers considerable advantages over EPR spectroscopy alone. Its increased resolution and accuracy allow the determination of parameters not resolved by EPR, and the interpretation of powder spectra may be simplified as the principal components of the hyperfine coupling tensor may be obtained directly. In addition, ENDOR spectroscopy and related techniques can provide additional information such as the relative signs of the hyperfine coupling constants, unequivocal identification of the nucleus associated with a particular hyperfine coupling constant, and determination of quadrupole coupling constants from measurements on disordered samples.3,4

ENDOR spectroscopy has been performed upon a few molecules and atoms isolated in rare gas matrices: C_2H_5 in xenon,⁵ CH_3 in argon,^{6,7} vanadium dibenzene in argon,⁶ SiH₃ in argon,⁸ and Mn and MnH in argon.⁹ However, spectra with good signal to noise were only obtained for molecules that could be obtained in high concentrations and/or were freely tumbling in the matrix so that isotropic EPR spectra were observed. For example, in the case of MnH and SiH₃ in argon and C_2H_5 in xenon, ENDOR spectra were only recorded from the more intense perpendicular lines of the EPR spectrum. To date, all the experiments reported have used continuous flow cryostats. In this case, long signal averaging can be prohibitively expensive due to the high cost of the liquid helium cryogen.

Here we report a new design of an ENDOR apparatus for matrix-isolated samples, which uses a closed-cycle helium refrigerator and permits work with lower radical concentrations. The apparatus has been tested by performing a complete ENDOR study of matrix-isolated NH_3^+ and CH_3 radicals. These radicals

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Figure 1. Design of a matrix-isolation EPR-ENDOR apparatus: A, HS-4 "Heliplex" refrigerator; B, mounting flange; C, compressed air inlet; D, welded stainless steel bellows; E, matrix gas inlet; F, sapphire rod; G, pumping port; H, port for quartz X-ray window or cesium oven; I, see detail on right; J, Bruker EN805 ENDOR cavity; K, ENDOR coil; L, 10-mm-o.d. quartz tube; M, 8-mm-o.d. quartz tube.

were chosen for this study even though their matrix EPR spectra, and in the case of CH_3 also the matrix ENDOR spectrum, are well-known, because their ENDOR spectra would be expected to exhibit all the features of more complicated systems and therefore demonstrate the feasibility and utility of ENDOR and TRIPLE resonance (electron-nuclear-nuclear) experiments on disordered matrix-isolated radical systems. Also, we were able to test X-ray irradiation as a method of producing small molecular cations trapped in rare gas matrices. X-ray irradiation of rare gas matrices has been used as a source of organic radical ions for UV-vis¹⁰ studies, but it has apparently not been used before to prepare small molecular cations trapped in rare gas matrices.

Experimental Section

Apparatus. The matrix-isolation EPR-ENDOR apparatus used in this work is shown in Figure 1. It was constructed from stainless steel alloy no. 304, except for parts between the magnet poles where the "nonmagnetic" alloy no. 310 was used to minimize any degradation of the magnetic field homogeneity. Individual sections of the apparatus were fabricated with argon-arc welds and sections joined by means of Viton O-rings. For noncorrosive matrix dopants the apparatus is pumped with a 100-mm turbomolecular pump (Alcatel) and for corrosive dopants with a 50-mm liquid nitrogen trapped diffusion pump (Varian), giving a base pressure lower than 10⁻⁷ and 10⁻⁶ Torr before cooldown, respectively. Matrices were deposited upon a 2.5-mm-diameter sapphire rod (INSACO) cooled by a HS-4 "Heliplex" closed-cycle helium refrigerator (APD Cryogenics). The base temperature of the Heliplex, measured by means of a GaAs diode (Scientific Instruments) at the bottom of the third stage, was 4 K. The refrigerator could be moved up and down a distance of 60 mm by pressurizing the space about a welded stainless steel bellows (Huntington) such that matrices were deposited in front of the 25-mm port and then lowered into an 8-mm-o.d., 7-mm-i.d. precision ground quartz tube (Wilmad) at the base of the vacuum system about which the cavity was placed. A pair of nylon bearings above the bellows guided the refrigerator to ensure the rod remained in the center of the quartz tube as it moved.

The cavity was positioned accurately with a Plexiglass jig referenced to the base of the vacuum system and mounted by bracing the waveguide against the magnet coils and wedging it between the magnet poles with Styrofoam strips. As the cavity was outside the vacuum system, it was possible to exchange the cavity without disturbing the matrix. A Bruker 4102ST rectangular cavity was used for high-sensitivity EPR measurements and a Bruker EN805 cylindrical cavity for ENDOR measurements. For ENDOR measurements the ENDOR RF coil was glued with cyanoacrylate cement to a precision-ground quartz tube (Wilmad) of 10-mm o.d. and 9.5-mm i.d., which was slipped up around the 8-mm tube into the cavity. The position of the coil was adjusted to optimize the cavity Q factor and the ENDOR baseline.

The "Heliplex" is a three-stage refrigerator. In the first two stages a pulsed expansion of compressed helium gas is used to cool a second helium gas stream which is expanded through a JT nozzle to cool the third stage. This type of refrigerator therefore produces an inherent low-frequency vibration. This vibration is transmitted to the sapphire rod and causes an oscillation in the resonant frequency of the cavity which increases the spectrometer noise level. The deeper the rod is inserted into the cavity, the larger this effect. In order to minimize the vibration the apparatus was bolted to a 50-mm-thick aluminum plate which replaced the standard top of the magnet (Bruker ER075) and lead weights were placed on top of the Heliplex. Extra braces from the magnet to the plate were added to make the apparatus as rigid as possible. These measures reduced the vibration to such an extent that a reasonable amount of the rod and therefore matrix could be inserted into the cavity and a good signal-to-noise ratio maintained.

Samples. Matrices containing NH_3^+ were prepared by depositing 15 mmol of a 1:2000 mixture of $^{15}NH_3$ (Aldrich) or $^{14}NH_3$ (Matheson High Purity) in argon (Spectra Gases Research Grade) or neon (Alphagaz Research Grade) upon the sapphire rod at 4 K. The mixtures were prepared by standard techniques using pressure ratios (MKS Baratron). After deposition the matrices were irradiated with unfiltered X-rays through a 1-mm quartz window (Phillips MCN101 tungsten target tube, MG161 generator, located about 150 mm from the rod). Typical irradiation lasted between 4 and 8 h with a tube voltage of 80 kV and current of 19 mA. Addition of electron traps such as CH_2Cl_2 , Cl_2 , and SF_6 did not increase the yield of ions.

Argon matrices containing ${}^{13}CH_3$ were prepared by the reaction of ${}^{13}CH_3I$ (MSD) with Cs (Aldrich) atoms during deposition of the matrix.¹¹ Two streams of argon (5 mmol/h), one doped with ${}^{13}CH_3I$ at 1:1000 and the other doped with Cs atoms from a Teflon-stoppered Pyrex cell at 170 °C, were directed at the cooled sapphire rod. The reaction time was minimized as the point of intersection of the two streams was at the center of the rod. ${}^{12}CH_3$ was formed as an impurity by this method both from the 10% residual ${}^{12}C$ in the isotopically labeled sample and from the normal background produced by the use of a diffusion pump.

Measurements. All spectra were recorded on a Bruker ESP300 EPR-ENDOR spectrometer. The microwave frequency was measured with a 7450 frequency counter (Hewlett-Packard). Field-frequency lock (ER033) was usually used during the acquisition of the ENDOR spectra. The ENDOR measurement employed either a A500 (ENI) or a 3200L (ENI) broad-band amplifier. For neon matrices the applied ENDOR power had to be less than 150 W to avoid heating and matrix evaporation. For argon matrices the full 500 W available from the A500 unit could be used. Typical conditions for the ENDOR spectra were as follows: ten 5-min scans per spectrum, 12.5-kHz modulation with 99-kHz modulation depth, resolution of 10 kHz per point, time constant of 0.25 of the acquisiton time per point, 120-W radiofrequency power, 0.2-mW microwave power, and a sample temperature of 4 K.

Calculations were performed on an Alliant FX/8 computer. The EPR simulations were produced using a program obtained from Prof. L. B. Knight.¹

Results

EPR. The EPR spectra of ${}^{14}NH_3^+$ and ${}^{15}NH_3^+$ generated by X-ray irradiation in both neon and argon matrices were consistent

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Figure 2. EPR spectrum of ${}^{14}NH_3^+$ trapped in argon at 4 K. Dots mark lines due to a ${}^{14}NH_2$ impurity. The ordering of the transitions assumes $A_H < 0$. The directions "perpendicular" and "parallel" do not correspond simply to the molecular axes. The inset shows an enlargement of the $|-3/2,1\rangle$ EPR lines with their simulation below.



Figure 3. EPR spectrum of ${}^{14}NH_3^+$ trapped in neon at 4 K. Dots mark lines due to a ${}^{14}NH_2$ impurity. The ordering of the transitions assumes $A_{\rm H} < 0$.

with those produced by photoionization and reported earlier.^{12,13} In the case of the argon matrices the X-ray method was apparently more specific than photoionization as fewer side products, nitrogen atoms and NH₂ radicals, were observed. Otherwise, the EPR spectra observed were identical. Their appearance approximated the expected powder pattern, with its parallel and perpendicular lines, but was clearly affected by partial rotational averaging (Figure 2). In the following, we place these descriptive terms in quotation marks to indicate the lack of simple correspondence to molecular axes, caused by the partial rotational averaging. For the neon matrices an isotropic spectrum was observed, but the relative intensities of the lines departed considerably from those expected, the $M_1^N \neq 0$ lines being broader than $M_1^N = 0$ lines (Figure 3). However, no evidence for preferential rotation of the NH_3^+ ion in the neon matrix was apparent. Annealing the matrix at 7 K had no effect upon the EPR spectrum.

The EPR spectra of ${}^{12}CH_3$ and ${}^{13}CH_3$ trapped in argon (Figure 4) were also in good accord with those observed previously.^{6,14-17}



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Figure 4. EPR spectrum of ¹²CH₃ and ¹³CH₃ trapped in argon at 4 K. The double arrow shows the range of field over which the ENDOR spectra in Figure 8 were recorded. The ordering of the transitions assumes $A_{\rm H} < 0$.



Figure 5. ENDOR spectra of ${}^{14}NH_3^+$ trapped in argon at 4 K as a function of the EPR line monitored.



Figure 6. ENDOR spectra of "perpendicular" and "parallel" EPR transitions: (A) the $|-3/2,-1\rangle$ "parallel" and "perpendicular" EPR transition of ¹⁴NH₃⁺ trapped in argon at 4 K; (B) the ENDOR of the "perpendicular" EPR transition at field b; (C) the ENDOR of the "parallel" EPR transition at field c.

 ${}^{12}CH_3$ in argon exhibited an essentially isotropic spectrum with slight intensity discrepancies from the expected 1:3:3:1 pattern. ${}^{13}CH_3$ in argon showed an analogous line width variation as observed for ${}^{14}NH_3^+$ trapped in neon. In this case, where the M_I value for the central atom cannot equal zero, all the ${}^{13}CH_3$ lines were broader than the ${}^{12}CH_3$ lines. If the matrix deposited at 4

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Figure 7. Dependence of the nitrogen ENDOR frequencies as a function of the field position within the EPR line monitored: (A) $|3/2,-1/2\rangle$ EPR line of ¹⁵NH₃⁺ trapped in neon at 4 K; (B) ENDOR at field b; (C) ENDOR at field c.



Figure 8. ENDOR spectra of ¹³CH₃ trapped in argon at 4 K as a function of the position of the EPR line pumped. See Figure 4.

K was annealed for 10 min at 35 K, the ¹³CH₃ lines were found to narrow from an initial value of 2.0 to 1.8 G after annealing. However, the ¹³CH₃ lines were still broader than those of ¹²CH₃.

ENDOR. ENDOR spectra were recorded for all EPR tran-sitions of ${}^{14}NH_3^+$ and ${}^{15}NH_3^+$ trapped in both argon and neon matrices and of ${}^{12}CH_3$ and ${}^{13}CH_3$ trapped in argon matrices. The ENDOR spectra observed depended on the particular EPR transition monitored as shown in Figure 5 for $^{14}NH_3^+$ trapped in argon and on whether a "perpendicular" or "parallel" EPR transition was monitored as shown in Figure 6 for ${}^{14}NH_3^+$ in argon. Also, the nitrogen ENDOR frequencies for ${}^{15}NH_3^+$ (Figure 7) and carbon ENDOR frequencies for ¹³CH₃ depended upon the position within the envelope of the EPR line pumped. The magnitude of this effect was proportional to the EPR line width and was much greater for the $|-3/2,1/2\rangle$ line of ¹³CH₃ trapped in an argon matrix (Figure 8).

The line width of the ¹H ENDOR lines was typically 0.14 MHz, and that of ¹⁴N, ¹⁵N, and ¹³C lines was 0.2 MHz. The proton ENDOR lines from the $\sum M_1^{H} = 1/2$ or -1/2 EPR transitions were split into a doublet with components of comparable intensities. The ¹⁴N ENDOR lines from the EPR transitions where $M_1^N =$ 0 were broader than those from $M_1^N \neq 0$. For ${}^{15}NH_3^+$ in neon, where there is an accidental degeneracy between the hydrogen and the nitrogen coupling constant, the ENDOR spectra observed were the sum of those expected from each overlapping EPR transition.

The splitting of the ENDOR transitions observed when the nominally degenerate $\sum M_1^{H} = 1/2$ or -1/2 EPR transitions were monitored is due to "second-order" effects, which cause the ΔM_1 = -1 and ΔM_1 = 1 transition to have slightly different energy. This effect has been observed previously for the CH₃ radical trapped in single crystals.¹⁸ However, the splitting was not





Figure 9. TRIPLE spectrum of ¹⁵NH₃⁺ trapped in neon at 4 K obtained by monitoring the $|-3/2,1/2\rangle$ line.

observed in another study of CH₃ in argon matrix.⁷ As the ENDOR field was scanned across the $|1/2,0\rangle$ EPR line of ¹⁴NH₃⁺ in neon, the proton ENDOR line width increased from a value of 0.14 MHz at the center to a value of 0.45 MHz at a field higher by 90 mG. The relative intensity of the doublet also changed slightly.

In all cases a weak absorption, the "matrix line", was present at the free proton frequency. The origin of this line has been discussed 19,20 and is attributed to electron-nuclear dipolar interactions of the radical under observation with adjacent protons in the matrix. As this line was always very weak and unstructured, we believe that the NH3⁺ and CH3 species were well isolated. The ENDOR spectra of CH_3 in argon showed no lines at the free nuclear frequency of cesium or iodine, again showing that the radicals were well isolated in the matrix.

In a dilute matrix, the frequency of the matrix line should be exactly equal to the proton Larmor frequency, a direct function of the magnetic field at the sample. Therefore, the frequency of this line was used to calculate the magnetic field at which the ENDOR spectrum was recorded. The error in the field determination using this method was estimated to be less than 100 ppm. This approach eliminated the need to measure the offset between the magnetic field external to the cavity and that actually present at the sample.

General TRIPLE Resonance. General TRIPLE spectra were recorded for the $|-3/2,-1\rangle$ EPR line of ¹⁴NH₃⁺ in argon and the $|-3/2,1/2\rangle$ line of ¹⁵NH₃⁺ in neon shown in Figure 9. In both cases pumping the low-frequency proton line leads to an increase of the low-frequency line of the other nucleus.

Analysis

The isotropic spin Hamiltonian for a system containing one unpaired electron may be written as the sum of three terms, the electron Zeeman, nuclear Zeeman, and hyperfine interaction:

$$H = g\beta B \cdot S_z - \sum g_n \beta_n B \cdot I + \sum h A S \cdot I$$

If quadrupole and intramolecular nuclear-nuclear couplings are ignored, this Hamiltonian is directly applicable to CH₃ and ¹³CH₃ trapped in argon, and ¹⁴NH₃⁺ and ¹⁵NH₃⁺ trapped in neon, where free tumbling of the radical was observed. In the case of ¹⁴NH₃⁺ and ¹⁵NH₃⁺ in argon, whose spectra exhibit apparent axial symmetry, it was assumed the g and A tensors were coaxial and that the "perpendicular" and "parallel" components could be treated separately with two independent isotropic spin Hamiltonians. The validity of this approach is justified in that an isotropic ENDOR line shape was observed when the monitoring field was positioned at any part of the envelope of either a "perpendicular" or "parallel" EPR transition.

To analyze the ENDOR spectra, a direct diagonalization of the full spin matrix was employed.²¹ A computer program was written to compute the spin matrix, the "matrix line" frequency being used directly as the hydrogen nuclear Zeeman frequency and the nuclear Zeeman frequency for ¹⁴N, ¹⁵N, and ¹³C, and the

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	AN	AN	A	AH	Á́́́́́́́́́́́A	AH	A ^{iso}
 ¹⁴ NH ₃ ⁺ (Ne, 4 K ^a)	54.6 (3)			-76.78 (3)			
$^{15}NH_3^+$ (Ne, 4 K ^a)	75.9 (3)			-76.78 (3)			
$^{14}NH_{3}^{+}$ (Ne. 4 K ^b)	54.9			76.8			
¹⁵ NH ₃ ⁺ (Ne, 4 K ^b)	77.1			77.1			
¹⁴ NH ₃ ⁺ (Ar. 4 K ^a)		55.3 (3)	49.2 (3)		-75.60 (3)	-74.89 (3)	
¹⁵ NH ₃ ⁺ (Ar. 4 K ^a)		76.6 (3)	67.9 (3)		-75.57 (3)	-74.85 (3)	
¹⁴ NH ₃ ⁺ (Ar. 14 K ^c)		52.8	47.9		75.0	74.2	
¹³ CH ₂ (Ar. 4 K ^a)				-64.81 (3)			106
$^{12}CH_3$ (Ar. 4 K ^d)				64.7			
¹² CH ₂ (Ar. 10 K ^e)				-64.39			
$^{12}CH_{2}$ (Ar. 4 K ⁴)				-64.38			
¹³ CH ₁ (Xe. 4 K ^g)				64.5			108

"This work. The perpendicular and parallel directions do not correspond simply to molecular axes (see text). bReference 12. CReference 13 (assignment reversed). ^dReference 17 (assuming g = 2.0022). ^eReference 6 (no second-order correction). ^fReference 7 (incorrect second-order correction). ^gReference 27 (g = 2.0026).

electron Zeeman frequency being obtained by multiplication by the appropriate ratio of the gyromagnetic ratios.²² This matrix was then diagonalized. The ENDOR selection rules $\Delta M_s = 0$ and $\Delta M_1 = \pm 1$ were applied to derive a set of all ENDOR transitions at constant field. From there, the appropriate transitions were selected for each EPR transition monitored. The hyperfine coupling constants were calculated by minimizing the differences between the calculated and observed ENDOR transition frequencies using the Levenberg-Marquardt algorithm.²³ The EPR transitions were assigned by using opposite relative signs for the hydrogen and nitrogen or carbon coupling constants as shown by the TRIPLE experiment and using the known¹⁸ negative absolute sign for the hydrogen coupling constant. Consideration of the magnitudes of the nuclear Zeeman interaction and the hyperfine coupling interaction for the ¹⁵N nucleus showed that the relative ordering of the energy levels is the same even though the nuclear magnetic moment has an opposite sign to that of the ¹⁴N nucleus. Consequently, the same intensity change is predicted for the TRIPLE experiment.

Application of this analysis to the hydrogen ENDOR transition frequencies was straightforward. The rms deviations between calculated and observed frequencies were typically less than 20 kHz, which compares favorably with the estimated error in the frequencies (± 10 kHz). The second-order splitting was also well modeled.

The nitrogen ENDOR transition frequencies were also analyzed by the method. However, the rms deviation between the observed and calculated frequencies was much higher, around 200 kHz. This was due to the monitoring field not being set to exactly the same position on the EPR lines for each ENDOR measurement. These deviations were not a function of M_1^N and occurred in all sets of the NH₃⁺ ENDOR spectra, including those in neon matrices, where isotropic spectra were observed, and the spectra of ¹⁵NH₃⁺. Quadrupole effects could therefore be discounted.

As the carbon ENDOR transition frequencies varied over such a wide range depending on the position within the EPR line monitored, the values used in calculating the carbon coupling constant were those corresponding to the peak of the Gaussian distribution of intensity versus monitoring field.

A summary of the coupling constants determined in this work, and those determined earlier, is given in Table I.

Discussion

Magnetic Parameters. The magnetic parameters determined by ENDOR for CH₃ trapped in argon and NH₃⁺ trapped in neon where isotropic EPR spectra are observed are essentially identical with those reported previously (Table I). For NH_3^+ trapped in argon, however, the values obtained by ENDOR are significantly more accurate than those found in earlier EPR work.¹³ This



Figure 10. EPR spectrum of ¹⁴NH₃⁺ trapped in neon; A, observed; B, simulated (see text for parameters).

demonstrates the advantage of ENDOR when interpreting an EPR powder spectrum. The TRIPLE experiment on NH₃⁺ shows that the hydrogen and nitrogen coupling constants have opposite signs.

Motional Effects of NH3⁺. In neon matrices there was no evidence for anisotropic rotation of NH_3^+ other than the deviation of the relative intensities of the $M_1^N = 0$ EPR lines from the expected 1:3:3:1 pattern. In argon matrices a powderlike EPR spectrum was observed, implying an anisotropy in the motion of the NH_3^+ ion. The dipolar components of the hyperfine coupling tensors for nonrotating NH₃⁺ are expected²⁴ to be $(\mathcal{A}_{ip}^{N})_{xx} = (\mathcal{A}_{ip}^{N})_{yy} = (-1/2)(\mathcal{A}_{ip}^{N})_{zz} = -\mathcal{A}_{dip}^{N}$ and $(\mathcal{A}_{dip}^{H})_{xx} = -(\mathcal{A}_{dip}^{H})_{yy}$ $(\mathcal{A}_{ip}^{H})_{zz} = 0$, where z is the 3-fold symmetry axis. Rapid rotation about z will not alter \mathcal{A}_{dip}^{N} and will average \mathcal{A}_{dip}^{H} to zero. For NH₃⁺ in argon, $\mathcal{A}_{dip}^{H} \simeq 0$ and $\mathcal{A}_{dip}^{N} = -2$ MHz. For a 2p_z electron on neutral ¹⁴N one expects² $\mathcal{A}_{dip}^{N} \simeq 56$ MHz, and for a charged ¹⁴N, an even higher positive number. Clearly the NH₂⁺ ions rotate ¹⁴N, an even higher positive number. Clearly, the NH₃⁺ ions rotate not only about the z axis but also about x and y, in a fashion that is not quite isotropic. This is also reflected in the shapes of the "perpendicular" lines which deviate from those expected for a powder spectrum of NH_3^+ rotating only about its z axis (inset in Figure 2).

Inhomogeneous Broadening. The dependence of the ENDOR frequencies on the field monitored within an EPR line for the central atom in NH₃⁺ and ¹³CH₃ shows that the EPR lines are inhomogeneously broadened due to a range of coupling constant values for the central atom. This is confirmed by the observation of much narrower EPR lines for ¹²CH₃ than ¹³CH₃ and of much narrower $M_1^N = 0$ lines of ¹⁴NH₃⁺ than $M_1^N \neq 0$ lines. The EPR spectra of ¹⁴NH₃⁺ in neon and ¹³CH₃ in argon were simulated by summing multiple spectra with a Gaussian distribution (1 and 15 MHz, respectively) of central atom coupling constants. The simulated spectrum of ${}^{14}NH_3^+$ in neon is shown together with the observed spectrum in Figure 10. A distribution of coupling constants and its effect on the observed ENDOR spectra has been postulated previously²⁵ for sodium atoms trapped in benzene, but

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^{1,} Ì.

we believe that the present results provide a particularly clear demonstration of the phenomenon.

This distribution of coupling constants is caused by interaction with the matrix, and for 13 CH₃ in argon annealing the matrix after deposition reduced its extent. Since the size of this effect is greater for CH₃ than for the charged species, NH₃⁺, it clearly does not reflect the overall strength of the solute-matrix interactions but is more specific. This observation also demonstrates that matrix effects on hindered molecular rotation, although probably present, are not the primary factor determining the inhomogeneous widths, since the rotation of the CH₃ radical is more nearly isotropic.

Ab initio calculations²⁶ of the coupling constants in CH₃ and NH₃⁺ predict them to be sensitive to the magnitude of out-of-plane distortions. This effect should be particularly strong for the coupling constant of the central atom. The frequencies of the out-of-plane vibrations are predicted to be 425 cm⁻¹ for CH₃ and 848 cm⁻¹ for NH₃⁺, so that out-of-plane deformation should be much easier for CH₃ than for NH₃⁺, accounting for the larger degree of inhomogeneous broadening observed for CH₃.

Second-Order Splitting. The magnitude of the observed second-order splitting agrees well with that predicted. However, the relative intensity of the split lines and their line width are a function of the ENDOR field. Their ratio, typically 1:1 at the EPR line center, is close to the predicted value¹⁸ of 4:5. This splitting was not observed in the earlier matrix-isolation ENDOR work on the methyl radical,⁷ possibly because the radical concentration was higher, at least judging by the intensity of the matrix line.

Radical Production Methods. X-ray irradiation has proven to be a successful method of generating a small molecular cation. We have not applied this method extensively; however, we have been able to produce SiH_2^+ trapped in neon from X-ray irradiation of a neon matrix doped with SiH_4 , the magnetic parameters derived being identical with those reported.²⁷ No preferential orientation was observed, presumably because we did not use a flat sapphire rod.

(28) Fessenden, R. W.; Schuler, R. H. J. Chem. Phys. 1965, 43, 2704.

Production of organic radicals from the corresponding iodide is shown to be a clean high-yield process. Cesium is a better alkali metal to use than lithium, sodium, or potassium, as cesium atoms and small oligomer clusters do not have EPR lines in the g = 2region. Cesium is also more reactive. It requires a lower temperature to vaporize than the lighter alkali metals and thus is more convenient.

Conclusion

The matrix-isolation EPR-ENDOR instrument design described in this work offers two main advantages: (i) as a closed-cycle refrigerator is used, it is cheap to operate and therefore signals may be averaged for several hours, thus allowing ENDOR spectra to be obtained from weak EPR signals; (ii) as the cavity is outside the vacuum system, it may be changed without destroying the matrix, and ENDOR and EPR experiments may be performed on the same sample using a higher sensitivity cavity for the latter. Using this apparatus has permitted a more accurate determination of the coupling constants of NH₃⁺ radicals trapped in an argon matrix, which exhibit a powderlike EPR spectrum. It has also provided an explanation of anomalous broadening of the EPR spectra of NH3⁺ radicals trapped in argon and neon matrices and of CH₃ radicals trapped in argon matrices, giving a clear demonstration of the dependence of hyperfine coupling constants on a range of matrix environments.

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Registry No. ${}^{14}NH_3^+$, 19496-55-0; ${}^{15}NH_3^+$, 130350-74-2; Ar, 7440-37-1; Ne, 7440-01-9; CH₃, 2229-07-4; ${}^{13}CH_3$, 13008-32-7; CH₃I, 74-88-4; C₅, 7440-46-2.

Infrared Spectra of Products Formed by the Photoinduced Reactions of $(P_2)_x (O_2)_y$ Clusters in Solid Argon

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Infrared spectra of the products of the photoinduced reaction of P₂ and molecular oxygen in solid argon at 12 K have been recorded. Concentration studies showed that the products were derived from the photolysis of phosphorus-oxygen clusters, $(P_2)_x(O_2)_y$, where x = 1, 2 and y = 2-5. In argon matrices with 1, 2, and 3% O₂, the major products of the reaction were oxo-bridged P₂O₃ and two isomers of oxo-bridged P₂O₄. With 5% O₂ the products included P₂O₅, and the P₄ oxides, P₄O₄, P₄O₆, P₄O₆, P₄O₈, and P₄O₁₀. The wavelength dependence of the photochemistry showed that reaction was initiated by one or more of the forbidden excited electronic states of P₂ accessed by absorption in the 220-380-nm region. Structural effects on the P-O-P bridge and the terminal -PO₂ and -PO group frequencies are discussed.

Introduction

The oxidation of phosphorus has been an important but mechanistically elusive chemical reaction since its investigation by Robert Boyle over 300 years ago. A large number of stable molecules can be produced by this reaction because of the strength of both bridging and terminal oxygen bonds and because of the multiple oxidation states available to phosphorus.¹ The reaction is extremely exothermic, but the matrix isolation technique permits the quenching of some of this energy, so that larger molecules do not all dissociate, and when they do the fragments that diffuse

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⁽²⁷⁾ Knight, L. B., Jr.; Winiski, M.; Kudelko, P.; Arrington, C. A. J. Chem. Phys. 1989, 91, 3368.

⁽¹⁾ Mellor, J. W. Inorganic and Theoretical Chemistry; Wiley-Interscience: New York, 1971; Vol. VIII, Suppl. III, Phosphorus. Chapters IV and V.