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13. ABSTRACT *(Maximum 200 words)*

The infrared spectra of a number of free radicals and molecular ions which are expected to be important in nitramine decomposition and combustion have been obtained in solid neon. The molecular ion studies resulted in the first infrared spectral detection of dimer ions in a non-interactive environment. The ions chosen for study are important in the lower ionosphere and in combustion and high energy processes involving carbon- and nitrogen-containing materials. Other studies used monomethylnitramine (MMN) as a model compound for elucidating the chemistry of nitramine decomposition. The infrared spectrum of MMN isolated in solid neon was obtained using a manifold designed for matrix isolation sampling of low vapor pressure materials. Supporting evidence was obtained for a mechanism recently proposed by Melius for water-catalyzed nitramine decomposition. The photodecomposition of matrix-isolated MMN was studied. Evidence was obtained supporting initial detachment of NO_2 and cage recombination to form the nitrite in a solid environment. Infrared and near infrared studies of other free radicals are briefly described.

14. SUBJECT TERMS
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SPECTROSCOPY OF REACTION INTERMEDIATES IN NITRAMINE DECOMPOSITION AND COMBUSTION

Final Report

Marilyn E. Jacox

20 June 1991

U. S. Army Research Office

Proposal 25664-CH

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Scientific Objectives

The research described in this report has as its ultimate objective the improvement of our understanding of the early stages of the decomposition and combustion of energetic materials, in order to promote efficient use of these materials and to aid in the design of systems which will minimize the hazards associated with handling them. Heretofore, little has been known about the properties of the molecular fragments which are produced in the early stages of energetic molecule decomposition. Many of these species are free radicals, which are highly reactive. This reactivity implies both that they are carriers of important chemical processes and that, except for the very short time interval after the initiation of the chemical process, their concentrations are small. Their detection in gas-phase reaction systems requires sophisticated observation techniques, often involving the use of lasers. Molecular ions, which are even more highly reactive, may be formed through solid-state interactions in the energetic material or through chemiionization processes during its combustion. The reactions of these transient molecules lead to the release of energy and to the formation of stable, readily detected final products.

Spectroscopy is an especially useful tool for studying molecular reaction intermediates. It is a sensitive, specific technique which provides a positive identification of molecular species. Analysis of the spectral data provides information on the structure and chemical bonding properties of the molecule. Once the molecular energy levels are known, it becomes possible to develop laser diagnostics which permit remote sensing of chemical reaction systems with both spatial and temporal resolution.

The studies described in this report apply the matrix isolation technique to obtain survey spectra, primarily in the infrared region, for free radicals and molecular ions which are expected to be important in the decomposition and combustion of energetic materials. A dilute solid solution of the species of interest is prepared using argon or neon as the solvent, or matrix, and a temperature sufficiently low that, although at least limited atomic diffusion is still possible, molecular diffusion does not occur. For covalently bonded species isolated in either of these two materials, the vibrational fundamentals and the band origins of electronic transitions involving the valence electrons typically are shifted by less than about 1% from the corresponding gas-phase values.[1-3] Free radicals are stabilized by ultraviolet or vacuum ultraviolet photolysis of a precursor molecule or are trapped among the products of the interaction of species such as H atoms or electronically excited argon atoms, produced in a low-power microwave discharge, with the molecule of interest. This report includes a summary of pioneering studies of the use of electronically excited neon atoms as an ionization source for study of the infrared spectra of small molecular cations which are potentially important in atmospheric and combustion systems. Molecular anions, formed by capture of the resulting electrons, are also detected and studied. In certain systems, photodecomposition products trapped in adjacent sites in the solid may undergo further reaction, yielding information on the early stages of reactions which may occur in solid energetic materials or in their reactions at relatively high pressures. Studies of the threshold and products of photodecomposition of the initially-formed free radicals and molecular ions provide further information on the range of stability of these species.

Scientific Accomplishments

A. Stabilization and Spectra of Molecular Ions

Photoionization and Penning ionization by excited argon atoms, which provide an 11.5-11.8 eV energy source, has for some time been used to obtain sufficient concentrations of molecular ions for infrared and ultraviolet detection in matrix isolation experiments.[4,5] However, this ionization source is most useful for molecules containing chlorine or the heavier halogens and for aromatic molecules, which have relatively low ionization potentials. Most simple molecules composed of the elements carbon, hydrogen, oxygen and nitrogen have their first ionization potentials above about 12 eV. In contrast, the first excited energy levels of neon lie between 16.6 and 16.8 eV, sufficiently high to ionize virtually any molecule. Photoionization and Penning ionization by excited neon atoms has been used together with matrix isolation sampling by Knight and co-workers[6] for the electron spin resonance detection of a variety of molecular ions. Because electron spin resonance is a much more sensitive detection technique than is infrared spectroscopy, when the present studies were begun it was uncertain whether a sufficient concentration of molecular ions could be stabilized for infrared detection.

Experiments using excited neon atoms require the use of a neon matrix at a temperature approaching 4 K. Although the technical difficulties associated with these experiments are somewhat greater than those for heavier matrix materials, the neon matrix offers several important advantages. Matrix shifts in neon are generally smaller than in any other material.[1] The exceptionally low polarizability of neon implies a relatively small interaction with ions. Moreover, the optical scattering of neon is much less than that of other commonly used matrix materials, with concomitant improvement in the optical quality of the matrix deposits.

1. Test of the Technique

Because CO_2 has a relatively high first ionization potential, 13.77 eV, and because the position of the band center of the ν_3 fundamental of ground-state CO_2^+ had been determined in the gas phase,[7] CO_2 was chosen for a test of the application of excited neon atoms for the infrared detection of matrix-isolated molecular ions. An infrared absorption appeared[8] only 1.4 cm^{-1} from the gas-phase CO_2^+ ν_3 absorption. The shift in this absorption on carbon-13 and on oxygen-18 substitution of the CO_2 agreed with the calculated shift in ν_3 of linear CO_2^+. Another absorption appeared in this experimental system at 1658.3 cm^{-1}. Isotopic substitution studies were consistent with its assignment to ν_3 of CO_2^-, which has a valence angle of approximately 135°. This absorption was substantially shifted from the absorption pattern near 1600 cm^{-1} which had previously been assigned[9-15] to ν_3 of CO_2^- in the $M^+CO_2^-$ complex, formed by the interaction of an alkali metal with CO_2 in an argon matrix.

2. Atmospheric Ions

With the demonstration that infrared absorptions of molecular ions could be detected using this discharge sampling configuration, it became necessary to determine the absorption pattern of other molecular ions which might be formed as a result of residual atmospheric gases in the sample or of small leaks in the system. These ions are important in a wide variety of systems, including not only the lower ionosphere but also high energy processes.

<u>O_4^+ and O_4^-</u>. The introduction of a small concentration of oxygen into the system led to the appearance of several prominent infrared absorptions which have been assigned[16] to O_4^+ and to O_4^-. These experiments provided important information regarding the characteristics of the discharge configuration. Dissociation of O_2 played only a minor role, and isotopic

randomization of the products in a study of a Ne:$^{16}O_2$:$^{18}O_2$ = 200:1:1 sample did not occur, indicating that the oxygen did not backstream into the discharge region. The study of this Ne:$^{16}O_2$:$^{18}O_2$ sample also required that the two principal products each contain two symmetrically equivalent O_2 units. Conway and co-workers[17,18] had first reported the mass spectra of these two dimer ions, which they and later workers[19] found to be bound by approximately 10 kcal/mol. Mass spectrometric studies have determined[20-22] that these two dimer ions play important roles in the chemistry of the lower ionosphere. Although $M^+O_4^-$ had previously been stabilized in an argon matrix,[23-26] there were no previous observations of the spectrum of uncomplexed O_4^-, nor had any discrete absorptions of O_4^+ been detected. Indeed, these observations represented the first infrared spectroscopic detection of a dimer ion in a non-interactive environment.

$\underline{CO_4^-}$. When both O_2 and CO_2 were present in the neon sample, three new infrared absorptions appeared which could be assigned[27] to vibrations of the CO_2 moiety in the CO_4^- molecular ion, known from mass spectrometric studies[28] to be bound by approximately 21 kcal/mol. The infrared spectrum demonstrated that this species possesses a planar $O_2C\cdot\cdot O_2^-$ structure, with the negative charge localized on the O_2 moiety.

$\underline{N_4^+}$. Because the ionization potential of N_2 is 15.58 eV,[29] this molecule provides a severe test of the ionization capability of the experimental configuration used for these experiments. Although Knight and co-workers[30] had detected the electron spin resonance spectrum of N_4^+, known from mass spectrometric studies[31] to be bound by approximately 23 kcal/mol, in neon matrix experiments, they were not able to stabilize it using this discharge configuration. Nevertheless, when a Ne:N_2 sample was subjected to infrared study[32] a weak, sharp absorption with isotopic substitution behavior appropriate for assignment to N_4^+ appeared at 2237.6 cm^{-1}.

3. Nitrogen Oxide Ions

The ions derived from the nitrogen oxides are of potential importance in high energy processes involving the nitramines. The work on these important molecules is not yet complete, but two papers have been published reporting the results of studies on Ne:NO and Ne:N_2O samples.

Ions Derived from NO. Although the ionization potential of NO is only 9.264 eV,[33] the detection of NO^+ has been difficult. In part, this is because of the ease of formation of the $(NO)_2^+$ dimer ion, known to be stable by about 13.8 kcal/mol.[34,35] Nevertheless, the ground-state energy levels of gas-phase NO^+ have been determined, and the infrared spectrum of this species has been observed in the hot air resulting from a high altitude nuclear detonation.[36] In the presently reported infrared studies of Ne:NO samples,[37] the NO^+ absorption was identified at 2345.2 cm^{-1}, very near the gas-phase value of 2343.9 cm^{-1} for $\Delta G(\frac{1}{2})$ of ground-state NO^+. The most prominent infrared absorption, at 1619.2 cm^{-1}, was assigned to *trans*-$ONNO^-$. The argon-matrix counterpart of this absorption has recently been identified[38] at 1593 cm^{-1}. The exceptionally large shift in this absorption in going from a neon to an argon matrix may be a consequence of the greater polarizability of argon. Other absorptions in this experimental system were attributed to *cis*-$ONNO^-$ and, tentatively, to $ONNO^+$.

Because there are no reports of the infrared spectra of dimer ions in the gas phase, the matrix shifts of these species, which possess anomalously weak bonds linking the two monomer units, cannot be assessed. However, several absorptions of the weakly bound neutral species *cis*-ONNO and N_2O_3, for which gas-phase spectral data are available, were also present. For these two species, all of the observed neon-matrix shifts were less than 0.6%, well within the guidelines for neon-matrix shifts of molecules which do not possess unusually weak bonds.

Ions Derived from N_2O. In experiments on Ne:N_2O samples,[39] the two stretching fundamentals of N_2O^+ were detected close to the gas-phase values determined in a study[40] of the emission spectrum of that species. The threshold for the detachment of O^- from N_2O^-, the initial product of capture of the photoelectrons by N_2O, amounts to only 0.43 ± 0.10 eV.[41] For many years, it had been presumed that O^- attacks N_2O at the end N atom, despite a partial positive charge on the central N atom. However, the recent photoelectron spectroscopy study of Posey and Johnson[42] indicated that three different $N_2O_2^-$ isomers exist. They suggested that O^- may also attack the central N atom, yielding a NNO_2^- intermediate. That intermediate may rearrange to the previously postulated $ONNO^-$ structure, which was detected in the argon- and neon-matrix studies discussed above. Subsequent mass spectrometric studies[43,44] of isotopically labelled N_2O support these conclusions. In an earlier matrix isolation study of the interaction of alkali metal atoms with an Ar:N_2O sample, Milligan and Jacox[45] assigned an infrared absorption near 1200 cm^{-1} to NNO_2^-, produced by the reaction of O^- with N_2O. That assignment was confirmed both in the argon-matrix study of Hacaloglu et al.,[38] who sampled Ar:N_2O mixtures that had been passed through a chemical ionization source, and in the present neon-matrix study.[39] Two new infrared absorptions of NNO_2^- were detected in the neon-matrix study, making possible a more complete vibrational analysis which indicated that the NN bond of this product has approximately single bond character. Consistent with the exclusion of N_2O from the discharge region, very little *trans*-$ONNO^-$ was stabilized in the neon-matrix experiments.

The observation of a product of the reaction of O^- with N_2O in the neon matrix opens the possibility of studying the products of the reaction of O^- with other molecules. Preliminary experiments have been conducted on the reaction of O^- with NO, with NO_2, and with O_2. Further studies of these and other systems are planned.

4. Ions Important in Combustion

Ions Derived from CO. In studies of the interaction of excited neon atoms and their resonance radiation with Ne:CO samples,[46] the ground-state vibrational fundamental of CO^+ was observed approximately 10 cm^{-1} from the gas-phase value.[47] As in the earlier electron spin resonance studies,[48-50] evidence was also obtained for the stabilization of *trans*-$OCCO^+$. In addition, two infrared absorptions of *trans*-$OCCO^-$ were identified.

Ions Derived from C_2H_2. Recently, studies have been conducted on the Ne:C_2H_2 system. In an earlier study[51] of the interaction of excited argon atoms with an Ar:C_2H_2 sample, prominent absorptions of the HCC free radical dominated the spectrum. However, an absorption near 3106 cm^{-1} behaved appropriately on carbon-13 isotopic substitution of the sample for assignment to a product with two equivalent carbon atoms. Since the ionization potential of C_2H_2 is 11.4 eV,[33] it would be energetically possible to form $C_2H_2^+$ in the argon-matrix system. In the corresponding Ne:C_2H_2 experiments, this peak shifted to 3137.6 cm^{-1}, very near the gas-phase band center recently determined in the laboratory of Oka[52] for the ν_3 fundamental of $C_2H_2^+$, 3135.98 cm^{-1}. Isotopic substitution studies have confirmed the assignment of the neon-matrix absorption to $C_2H_2^+$. The relatively large shift in the argon-matrix absorption, presumably a consequence of polarization interactions with the argon matrix, emphasizes the importance of using a neon matrix for studies of the infrared spectra of molecular ions. In the neon-matrix study, an absorption at 1773 cm^{-1} was tentatively attributed to the HCC^- anion. Although in the argon-matrix study a high yield of HCC had been obtained, very little HCC resulted from the 16.6-16.8 eV excitation of C_2H_2 in the present study.

B. Photodecomposition of Monomethylnitramine

In an important series of papers, Melius[53-55] conducted a theoretical study of the thermochemistry and kinetics of the decomposition and combustion of the nitramines, using monomethylnitramine (MMN) and species derived from it as model compounds. A second major objective of Proposal 25664-CH was the use of MMN as a model compound for spectroscopic studies. It was hoped that experimental conditions might be found under which photodecomposition of MMN would lead to the stabilization of $H_2C{=}N{-}NO_2$, the monomer unit from which HMX and RDX are derived. Very little is known regarding the stability of that species, for which no spectral data have been reported. Determination of its spectrum would constitute a first step in the ultimate development of laser-based diagnostics which might probe its role in nitramine decomposition.

Since MMN has a vapor pressure amounting to about 25 Pa (approximately 0.2 torr) at room temperature, it was necessary to develop a special system for matrix sampling of it. A diagram of the sampling manifold is shown in Figure 1. The solid MMN was placed in a sample tube, which was attached to the manifold and evacuated. During the sampling, a controlled pressure of the matrix gas (neon) was maintained over the solid sample. In these experiments, this pressure was between 5000 and 10000 Pa (about 40 to 80 torr). The capacitance manometer head M2 provided a control signal to a servo-controlled variable leak. As the mixture flowed through the manually controlled variable leak into the cryogenic cell, the

APPARATUS FOR SAMPLING LOW VAPOR PRESSURE MATERIALS

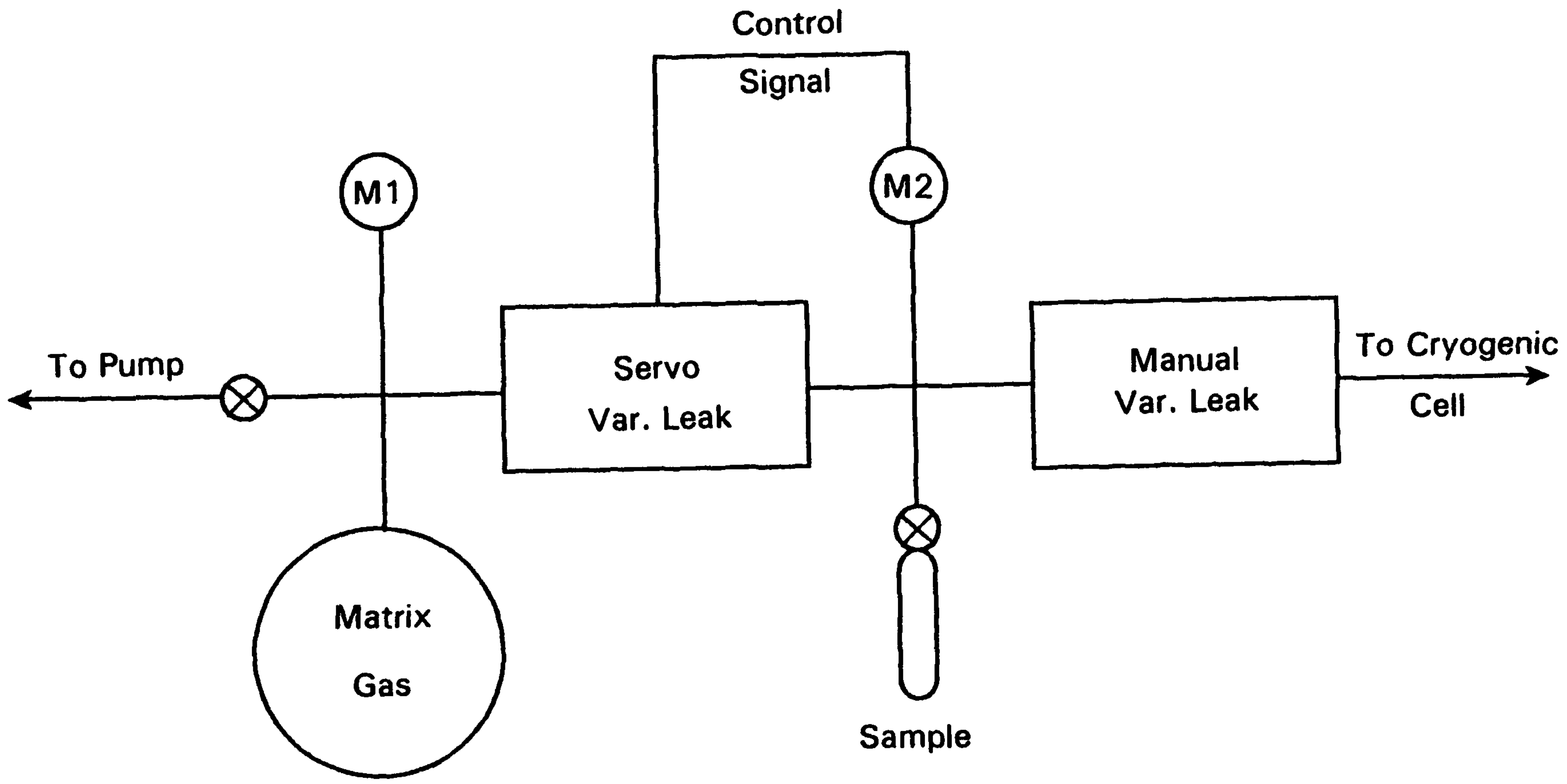
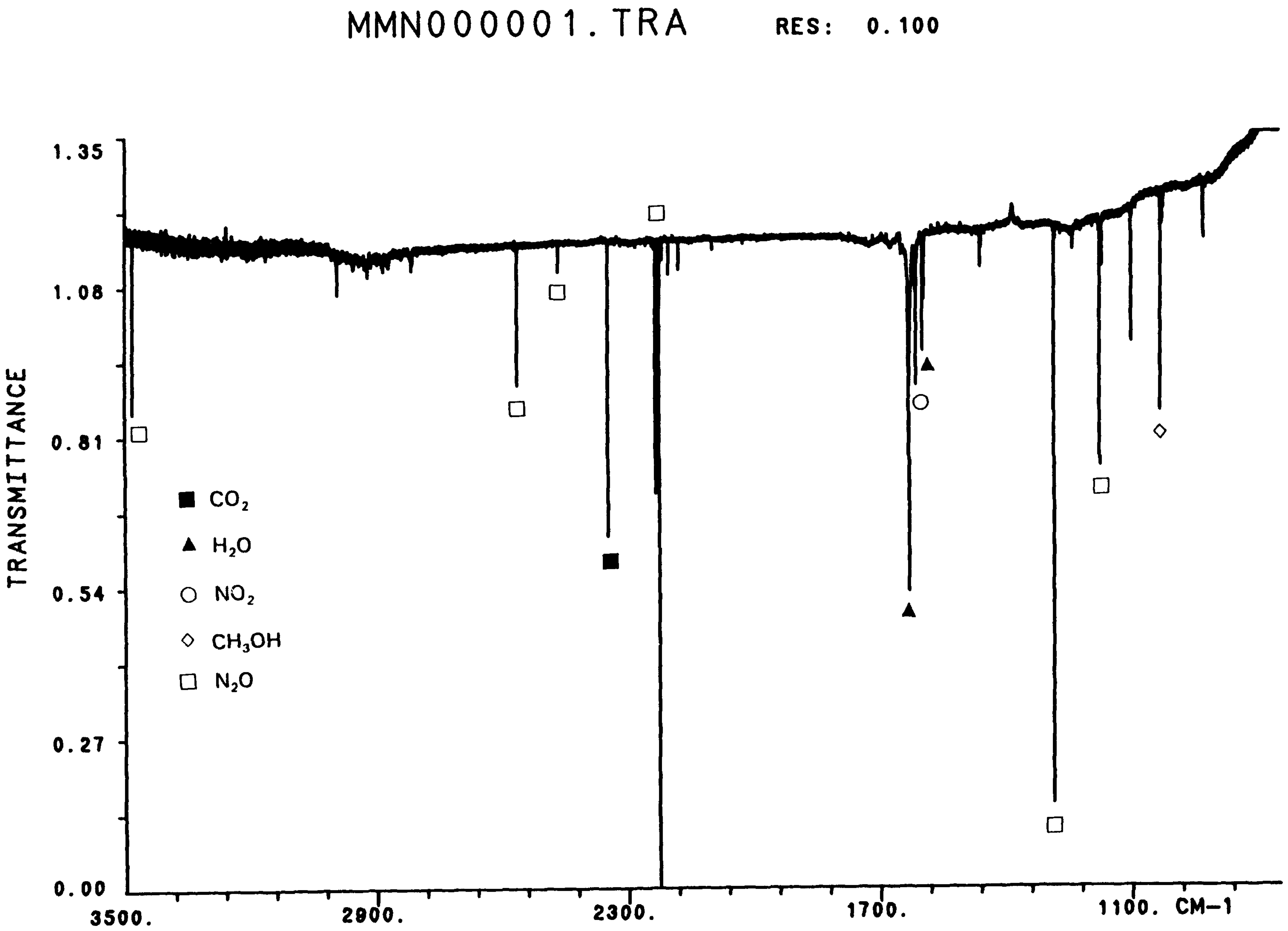


Figure 1

matrix gas was replenished from the matrix gas reservoir. The pressure drop in this reservoir, measured by capacitance manometer M1, indicated the amount of matrix material which had passed through the sampling manifold into the cryogenic cell, where the mixture is frozen onto the 4 K observation surface. If it is assumed that the equilibrium vapor pressure of MMN is maintained in the sample manifold, the Ne:MMN mole ratio of these experiments ranged from 300 to 500.

The absorption spectrum recorded between 750 and 3500 cm^{-1} for the first sample deposited using this manifold is shown in Figure 2. As is indicated in Figure 2, most of the infrared absorptions can be assigned to H_2O, N_2O, and CH_3OH. The prominent CO_2 peak near 2350 cm^{-1} is common to most matrix samples. Because the absorption coefficient of this CO_2 absorption is very large, it represents only a small amount of CO_2 in the deposit. The sharp peak near 1612 cm^{-1}, intermediate between two H_2O absorptions, represents a very small concentration of NO_2. This fundamental of NO_2 also has an exceptionally large absorption coefficient. There is very little evidence for the stabilization of MMN. Although an absorption near 930 cm^{-1} and that near 1612 cm^{-1} lie close to absorptions of gas-phase MMN reported by Dakhis and co-workers,[56] the very strong absorption of MMN near 1332 cm^{-1} did not appear. Unassigned absorptions appeared near 930, 1240, 1460, 2990, and 3590 cm^{-1}. The last three of these absorptions may possibly have been contributed by CH_3OH.

After the spectrum of Figure 2 had been obtained, approximately three times as much sample was added to the deposit, and the spectrum of Figure 3 was then recorded. As is evident from comparison of the intensities of relatively weak N_2O absorptions such as that near 2460 cm^{-1} and the absorptions of singly ^{15}N-substituted N_2O present in natural abundance, slightly



MMN000001.TRA RES: 0.100

Figure 2

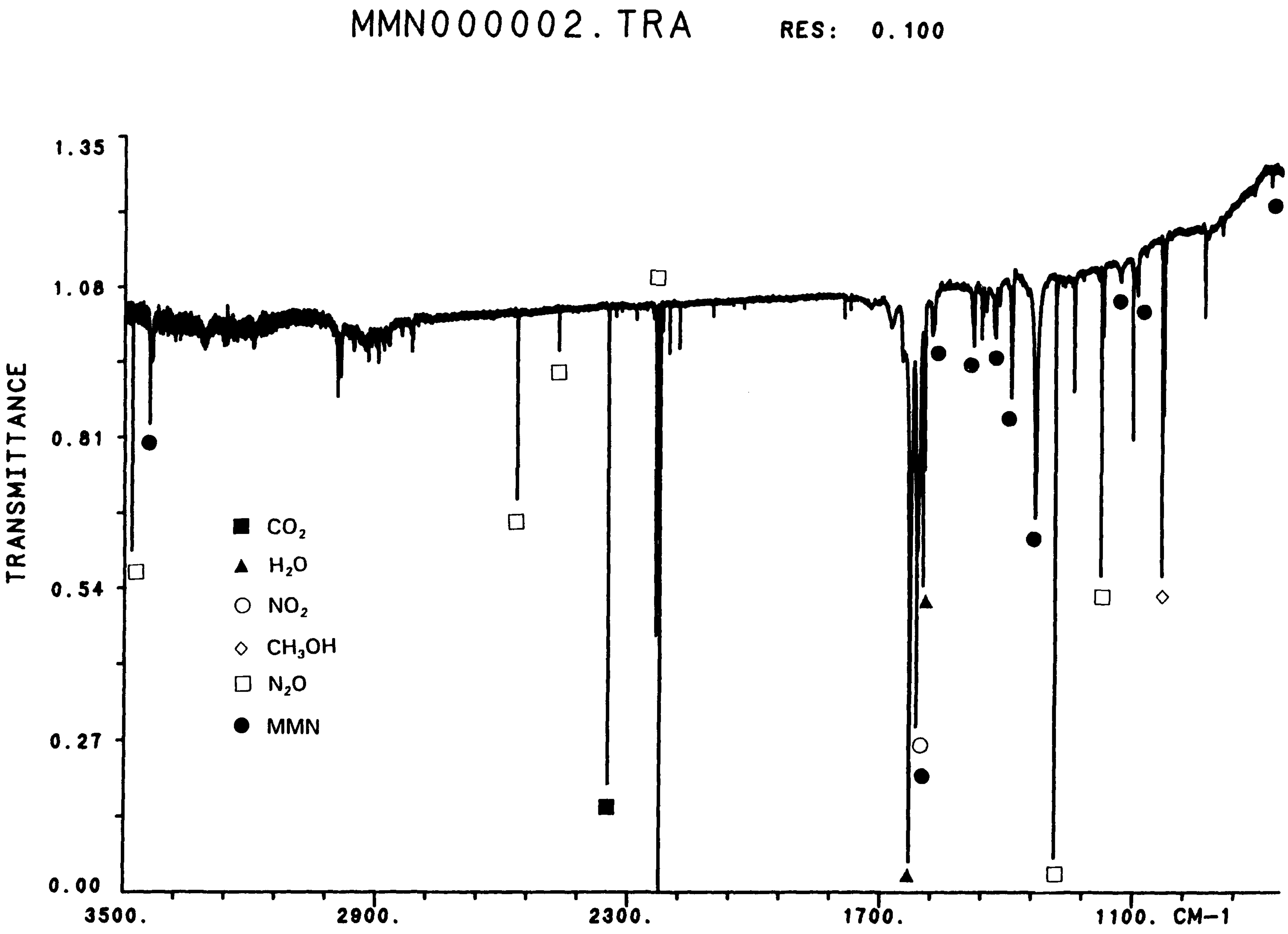

MMN000002.TRA
RES: 0.100
TRANSMITTANCE
1.35
1.08
0.81
0.54
0.27
0.00
3500.
2900.
2300.
1700.
1100. CM-1
■ CO_2
▲ H_2O
○ NO_2
◇ CH_3OH
□ N_2O
● MMN

Figure 3

below the very strong 2225 cm^{-1} N_2O peak, the amount of N_2O in the deposit approximately doubled. Moreover, ten new absorptions, marked in the spectrum of Figure 3 by filled circles, appeared. Among these is a relatively broad absorption at 1614 cm^{-1}, very near the sharp NO_2 absorption. In Table I, the positions of these absorptions are compared with the infrared absorptions of MMN reported by Dakhis and co-workers.[56] The agreement between the positions of the major neon-matrix absorptions and the gas-phase band centers of MMN is very close. As is common in the spectra of matrix-isolated species, there are some less prominent peaks within a few cm^{-1} of the principal absorptions; these peaks are attributed to the presence of multiple trapping sites in the rare gas solid. Several of the MMN fundamentals were previously observed only for the solid material at 77 K. Because of the occurrence of relatively strong molecular interactions in the solid, the positions of the absorptions of polycrystalline material may be substantially shifted both from the gas-phase band centers and from the absorptions observed in rare gas matrices.

The difference in the composition of these two deposits is attributed to the occurrence of water-catalyzed decomposition of the first portion of the sample. On introduction to the sample tube, crystalline MMN holds an appreciable amount of adsorbed water, accounting for the very prominent water absorptions in the spectrum of Figure 2. Very recently, Melius[54] has predicted that the water-catalyzed decomposition of nitramines should lead to the formation of N_2O and of partly degraded chain structures containing -CH_2OH units. For MMN, this unit would be simplified to CH_3OH, which is seen. According to this proposed mechanism, H_2CO results from further chain degradation. Because for MMN there is no residual chain, H_2CO would not be expected to appear--and is not observed. Once the concentration of water in the

Table I

Comparison of the Absorptions (cm^{-1}) of Monomethylnitramine Observed in the Gas Phase[a] and in a Neon Matrix

Gas	Ne Matrix
772	774.5wm
928	
1092	
1097[b]	1096.8wm
1177[b]	1132.0wm
1332	1332.6vs
1394	1390.2s
	1427.8wm
	1429.8m
1434[b]	1432.1sh
1454[b]	
1470[b]	1479.8m
	1483.0sh
	1575.0wm
	1578.0wm
1614	1611.4vs
	3434.7wm
	3436.4wm
	3438.6wm
3438	3441.9ms

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[a] Reference 56.

[b] Polycrystalline sample measured at 77 K.

sample is reduced through its deposition with the initial decomposition products, the probability of undecomposed MMN reaching the cryogenic deposit increases. In subsequent experiments using this same portion of crystalline MMN, the absorptions of the decomposition products became less prominent, and the MMN absorptions predominated.

In a neon matrix, the threshold for the photodecomposition of MMN was observed near 260 nm. It is possible that photodecomposition of gas-phase MMN may occur at longer wavelengths but that cage recombination suppresses this photodecomposition process in the matrix. The absorptions which result on photodestruction of MMN are summarized in Table II. Definite assignment of relatively prominent absorptions to CH_4 and to *cis*-$(NO)_2$ can be made, indicating that the fragmentation

$$\mathrm{MMN} + h\nu \rightarrow \mathrm{CH_4} + 2\mathrm{NO} \qquad (1)$$

is important. This overall process might result from an initial N-N cleavage

$$\mathrm{MMN} + h\nu \rightarrow \mathrm{CH_3NH} + \mathrm{NO_2} \qquad (1a).$$

In the matrix, the free radical products are likely to undergo cage recombination either to re-form MMN or to form the nitrite:

$$\mathrm{CH_3NH} + \mathrm{NO_2} \rightarrow \mathrm{CH_3NHONO} \qquad (1b).$$

Other possible photodecomposition processes include HONO elimination

$$\mathrm{MMN} + h\nu \rightarrow \mathrm{CH_3N}\ (\text{or } \mathrm{CH_2NH}) + \mathrm{HONO} \qquad (2),$$

H_2 elimination

$$\mathrm{MMN} + h\nu \rightarrow \mathrm{CH_2{=}N\text{-}NO_2} \qquad (3),$$

and (4) H atom elimination from either the C or the N atom. The H atoms produced in this last process could, in turn, attack other MMN molecules to give a variety of products.

Table II

Absorptions (cm^{-1}) Which Appear on 254 nm Irradiation of Monomethylnitramine Isolated in Solid Neon at 4 K

cm^{-1}	Assignment
700.8m	
869.1m	
873.2w	
874.3w	
912.0w	
934.4w	
949.3wm,-	
955.9wm,-	
974.1w	
1043.1w	
1067.6w	
1111.0wm	
1118.7sh	
1119.2wm	
1259.3vw	
1308.2m	CH_4
1415.6wm	
1446.9m,-	
1494.6wm	
1502.3w	
1646.9wm	
1777.1m	*cis*-$(NO)_2$
1777.9m	*cis*-$(NO)_2$
1779.1m	*cis*-$(NO)_2$
1834.5wm	*cis*-$(NO)_2$
1836.6wm	*cis*-$(NO)_2$

Table II--Continued

cm^{-1}	Assignment
1865.5wm	
1874.9wm,-	NO
2234.5m,-	
2234.9m,-	
2834.8m,-	

The identification of most of the absorptions in Table II is uncertain. The weak absorption at 1043 cm^{-1} may possibly be contributed by CH_3N.[57] Although there are several near coincidences with absorptions of CH_2NH,[58] the prominent 1348-cm^{-1} CH_2NH absorption is missing. There is no evidence for the lowest energy rotamer of HONO, *trans*-HONO, but the absorptions at 869 and 1646 cm^{-1} lie in the same spectral region as prominent absorptions of *cis*-HONO. There is no evidence for the formation of NO_2, HCN, H_2CO, N_2O, or CH_3OH on photolysis of the deposit.

In one experiment, a filter which excluded visible light from the sample but transmitted the very strong 254 nm mercury-arc radiation was used during photolysis of the sample. The product absorptions at 949.3, 955.9, 1446.9, 1874.9, 2234.5, 2234.9, and 2834.8 cm^{-1}, labelled with a minus sign in Table II, were relatively less intense in the resulting spectrum. The 1874.9 cm^{-1} peak is readily assigned to NO, but the other peaks have not been assigned. The variation in the intensity of these peaks suggests that the primary photolysis product (or one of the primary photolysis products) is subject to photodestruction by visible light, leading to the formation of NO and of one or more other products which have infrared absorptions at the positions of the other peaks marked with the minus sign. The identification of NO suggests that the species which photolyzes on irradiation with visible light may be a nitrite.

In one experiment, the Ne:MMN sample was exposed to the 185 nm radiation passed by an interference filter from a microwave-powered low-pressure mercury arc lamp which was affixed to the cryogenic cell by a nitrogen-purged spacer. Photodecomposition was minimal, and products were not detected.

In another experiment, the Ne:MMN sample was exposed to 122 nm H atom radiation during deposition. Complete degradation of the MMN resulted; only the infrared absorptions of H_2O, CO, and CO_2 were detected in the resulting sample. N_2 is expected also to have been present in the deposit, but it does not possess an infrared absorption.

In summary, the room temperature vapor over pure solid MMN can be sampled in a neon matrix without decomposition. In the presence of water, MMN decomposes into N_2O and CH_3OH, supporting the water-catalyzed nitramine decomposition mechanism recently proposed by Melius.[54] The absence of H_2CO is also consistent with that mechanism. The threshold for the photodecomposition of MMN in solid neon lies near 260 nm. Photofragmentation of MMN into $CH_4 + 2NO$ occurs. Infrared absorptions of one or more other products also contribute to the spectrum of the photolyzed sample. There is evidence for secondary photodecomposition by visible light, leading to the formation of NO. Since NO is produced on photolysis of nitrites, it is quite possible that the detachment of NO_2 and its cage recombination to form a nitrite is an important process. It is noteworthy that cage recombination should also play an important role in the early stages of decomposition of solid nitramines.

C. Other Studies

A number of other experiments designed to lead to the stabilization of free radicals which are expected to play an important role in nitramine decomposition and combustion have been conducted. Two of these, plus a major data evaluation and compilation activity (not supported by the Army Research Office) are worthy of note.

1. Reaction of H with N_2O

It has been proposed[59] that the HNNO intermediate is important in the high temperature reaction of H atoms with N_2O. In experiments in which a Ne:N_2O sample was codeposited with a Ne:H_2 or Ne:D_2 mixture that had been passed through a microwave discharge, one infrared absorption which may have been contributed by the NH-stretching fundamental of HNNO and two possible absorptions of DNNO have been detected. Further experiments using isotopically substituted N_2O are planned and may help to clarify this identification.

2. Spectrum of HCC

The HCC free radical is ubiquitous in combustion systems. Although it had long been known to have an electronic transition in the near infrared, the formation of electronically excited HCC led to the appearance of quasicontinuous emission from the green spectral region to the mid-infrared. Several infrared absorption bands of HCC, observed at high resolution, have been analyzed, providing abundant evidence for extensive perturbation of energy levels associated with the near infrared electronic state by high vibrational energy levels of the ground state. As a part of work associated with an earlier Army Research Office Proposal (#21495-CH), Jacox and Olson[51] reported a large number of bands in the first survey absorption spectrum of HCC over the 4000-8000-cm^{-1} spectral region. In this study, HCC was isolated in solid argon, resulting in complete deactivation to the zero-point vibrational energy level. Therefore, all transitions of HCC observed in this study must originate in $\tilde{X}(000)$. Subsequent gas-phase studies, recently summarized by Yan and co-workers,[60] have extended higher into the near-infrared spectral region and have yielded band positions in good agreement with the argon-matrix studies.

In order to clarify the origin of a number of unassigned infrared absorptions in the argon-matrix study of HCC and to refine and extend the near infrared spectral measurements, a study of the spectrum of HCC in a neon matrix has been initiated. Several overtones and combination bands of HCC in the infrared spectral region have been assigned in this study, and there is promise of a partial band assignment in the mid-infrared. Because neon matrix deposits are much more transparent than are argon matrix ones, uncertainties in band observations between 6500 and 8000 cm^{-1} have been removed. Moreover, measurements have been extended to 12000 cm^{-1}. Newly developed lasers may make possible the development of diagnostics for gas-phase HCC in the 7000-12000 cm^{-1} spectral region.

3. Vibrational and Electronic Energy Level Data

During the period of this proposal, two critically evaluated compilations of vibrational and electronic energy level data for small polyatomic transient molecules have appeared.[3,58] While the publication of these two compilations was not supported by the U. S. Army Research Office, the material in them may be of interest to research workers concerned with the decomposition and combustion of energetic materials. Each of these publications presents vibrational and electronic energy level data for approximately 500 molecules. A number of somewhat less reactive molecules which are important in the study of energetic materials, including *cis*- and *trans*-HONO, H_2O_2, HNCO, and HCNO, have been included in the more recent compilation.[3]

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"The Vibrational Spectra of Molecular Ions Isolated in Solid Neon. I. CO_2^+ and CO_2^-." M. E. Jacox and W. E. Thompson, J. Chem. Phys. 91, 1410-1416 (1989).

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Participants in ARO Research

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Dr. Warren E. Thompson, Guest Researcher (no salary charged to this project)

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