[Contribution from the Department of Chemistry, The Johns Hopkins University]

Imine and Imine-*d* Radicals Trapped in Argon, Krypton and Xenon Matrices at 4.2°K.[1]

By M. McCarty, Jr., and G. W. Robinson

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Imine and imine-*d* radicals have been trapped in argon, krypton and xenon matrices at liquid helium temperature. The radicals are identified by the isotopic shifts in the vibrational structure of the electronic spectrum. The concentration of the radicals in the solid phase is estimated to be a few tenths of a per cent. in xenon and krypton matrices and an order of magnitude smaller in the argon matrix presumably because of surface reactions in the latter during deposition. Fine structure lines in absorption and fluorescence can be correlated with rotational motions of imine in the solid phase suggesting that the radicals are trapped at normal lattice sites rather than in interstitial positions. A measurement of the 1-0 band position shows indirectly that $\Delta G_{1/2}$ in the ground electronic state of NH in argon is about 3074 cm.$^{-1}$. Other vibrational constants for NH and ND in argon have been determined, in particular $\Delta G_{1/2}$ for ND in its excited electronic state was found to be 2211 ± 10 cm.$^{-1}$. On several occasions an observable concentration of NH radicals in the metastable $^1\Delta$-electronic state has accumulated in the matrix. Shifts to the red of the electronic spectrum of imine in the various rare gas matrices are explained on the basis of van der Waals binding between imine and the rare gas atoms.

Introduction

In the past few years a number of papers[2] have been published concerning the possible trapping of the imine radical at low temperatures from decomposition products of hydrides of nitrogen. Most of these experiments have been concerned with the so-called blue deposit obtained by trapping out at 77°K. the products of electrically discharged or thermally decomposed hydrazoic acid, HN_3. Mador and Williams[3] postulate that the broad absorption bands in the blue solid at 3500 and 6500 Å. correspond to NH and NH_2, respectively. Other papers have appeared in the literature[4] giving evidence which suggested that if free radicals were present their concentration must be small.

Becker, Pimentel and Van Thiel,[5] using the matrix isolation technique, have given infrared evidence that imine radicals as well as NH_2 radicals are present in photodecomposed HN_3 in argon and molecular nitrogen matrices at 20°K. The vibrational fundamental of NH in the matrix was not definitely known at the time, and the lack of knowledge about the kinds of secondary reactions in the solid and the absence of data on the deuterated molecule caused the interpretation of their results to be not wholly conclusive. The presence of some sort of trapped reactive species was definitely demonstrated, however, and the infrared evidence did indirectly suggest NH and NH_2.

Mass spectrometric studies[4,6,7] of products from an HN_3 discharge have failed to reveal the presence of NH radicals, but recently Foner and Hudson[6] have shown that diimide, N_2H_2, can be formed in large quantities from such a discharge. In another paper[7] where a discharge in hydrazine or simply N_2 plus H_2 was placed near the sampling orifice, H, H_2, N, NH_2, NH_3, N_2, N_2H_2, N_2H_3, N_2H_4 and N_3H_3 could be detected. It is interesting that NH was not observed from any of these discharges. These results might be interpreted to indicate that NH is not present, but it should be remembered that NH may be lost in some way in the mass spectrometer.

The results of this paper as well as those of the past[8-12] show that NH is present in these discharges and therefore that the mass spectrometric technique as used in these experiments must not be sensitive to NH detection. This study of the imine-*d* electronic spectrum gives further strong evidence that the 3380 Å. absorption is indeed caused by trapped imine radicals. The cause of the matrix red shift is discussed and a number of new features concerning the molecular structure of the imine free radical are presented.

Experimental

The experimental technique is similar to that described previously.[12] Ammonia, hydrazine or nearly any mixture of hydrogen and nitrogen-containing molecules with about a 30-fold excess of rare gas is leaked into a discharge tube at the rate of 4 ml. S.T.P./min. A simple discharge tube which has been employed recently consists of a 1 mm. i.d. Pyrex capillary tube sealed by means of a ring seal through a larger tube which leads into the high vacuum system and is located so that it faces directly toward the liquid helium cooled surface 3.5 cm. away. Only a few millimeters of the capillary are allowed to protrude into the system, forming a 1 mm. diam. hole through which the decomposition products and matrix gas spray onto the cold finger. The enlarged space at the ring seal serves as a well defined region in which the discharge can be sustained by a 100 watt 2450 Mc. microwave oscillator and the discharge glow itself can be adjusted so that it extends through the hole into the high vacuum chamber. All the gas which enters the discharge tube leaks into the high vacuum part of the system. Two 60 l./sec. oil diffusion pumps remove most of the randomly directed molecules, and only a small fraction (about 1%) of the discharge products solidify in what appears to be a microcrystalline film on the cold finger. When gas is leaking into the system, an ionization gauge shows the pressure in the high vacuum side to be 1 × 10^{-4} mm. The discharge tube pressure is about 0.1 mm. In the high vacuum portion of the system, the mean-free-path is sufficiently long for the bulk of the radicals to travel from the pin-hole to the cold finger without suffering collisions. Radical–radical reactions may, however, take place on the cold finger in the cooling down process since kinetic energy corresponding to a room temperature distribution must be lost to the surface before the matrix can be considered rigid. The efficiency

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(1) Supported in part by Office of Ordnance Research and the National Science Foundation.

(2) F. O. Rice and C. Grelecki, This Journal, **79**, 1880 (1957), and earlier papers by Rice and Freamo.

(3) I. L. Mador and M. C. Williams, *J. Chem. Phys.*, **22**, 1627 (1954).

(4) See, for example, J. L. Franklin, J. T. Herron, P. Bradt and V. H. Dibeler, This Journal, **80**, 6188 (1958).

(5) E. D. Becker, G. C. Pimentel and M. Van Thiel, *J. Chem. Phys.*, **26**, 145 (1957).

(6) S. N. Foner and R. L. Hudson, *ibid.*, **28**, 719 (1958).

(7) S. N. Foner and R. L. Hudson, *ibid.*, **29**, 442 (1958).

(8) G. W. Robinson and M. McCarty, Jr., *ibid.*, **28**, 350 (1958).

(9) G. W. Robinson and M. McCarty, Jr., *Can. J. Phys.*, **36**, 1590 (1958).

(10) G. W. Robinson and M. McCarty, Jr., "Informal Discussion on Free Radical Stabilization," Sheffield, Sept. 4–5, 1958.

(11) G. W. Robinson and M. McCarty, Jr., *J. Chem. Phys.*, **28**, 349 (1958).

(12) G. W. Robinson and M. McCarty, Jr., *ibid.*, **30**, 999 (1959).

of this process depends upon the thermal conductivity of the deposit, which probably is poor, as well as the kind of matrix used.

That the latter consideration is important is borne out by experiments with neon, argon, krypton and xenon matrices. A good criterion for trapping efficiency at a given temperature might be the ratio of the Lennard-Jones intermolecular well depth, ϵ, of the rare gas to kT. Argon at 4.2°K. ($\epsilon/kT \approx 30$) has been found to be a suitable matrix while neon at 4.2°K. ($\epsilon/kT \approx 8$) has been found unsuitable, only rather unreactive species such as NO_2 and HNO having been trapped successfully in neon (the spectrum of NH in neon after 5 hr. depositing at 1.5°K. was weak and very broad). On the other hand, krypton at 4.2°K. ($\epsilon/kT \approx 48$) and xenon at 4.2°K. ($\epsilon/kT \approx 56$) are much superior to argon for trapping radicals in a deposition technique. Imine radicals are readily observed to be present after about a minute deposit time with the latter matrices, while in argon about 10 minutes of depositing usually is required before the radicals are detected. The maximum concentration of radicals obtained is estimated from deposit thickness and absorption intensity to be about 0.2% which corresponds to about a 5% conversion of ammonia molecules to trapped imine radicals. The effective deposit thickness can be estimated roughly by a comparison of absorption intensity of a stable molecule such as H_2CO or NO_2 in the matrix phase with that in the gas phase at a known pressure and path length. Such estimates yield about 1 mm. as the maximum effective path length attained in these deposits. The actual thickness because of the fact that light scatters through the deposit rather than travels straight through must be somewhat less than this value. The oscillator strength for the $^3\Pi \leftarrow {}^3\Sigma^-$ transition was taken to be 0.003[13] which may be in error by a factor of three. A big problem with a neon matrix arises because of the poor thermal conductivity of the cold finger and the deposit. Neon is very difficult to condense under our conditions at 4.2°K. or even at 1.5°K. as evidenced by extreme pressure instability during deposition. Molecular nitrogen at 20°K. ($\epsilon/kT \approx 4$) and argon at 20°K. ($\epsilon/kT \approx 6$) would also appear to be poor choices as matrices in a deposition technique such as ours. For radicals produced by photodecomposition of a parent molecule which previously has been deposited in a matrix the above conditions probably are less restrictive, and as a matter of fact a certain amount of tunneling is desirable if the dissociation fragments are to be able to separate successfully in the solid.

Photographs of the spectra were made in the first- and second-orders of a 15,000 line per inch grating in a 2-meter Czerny-Turner mounting. A tungsten filament bulb having a Pyrex envelope or a Hanovia high pressure xenon lamp can be used as source and exposure times were never more than thirty minutes with Eastman 103a-O plates. Matheson C.P. grade rare gases passed over powdered titanium metal at 900° to remove the oxygen and nitrogen impurities were used. The hydrazine was dried over barium oxide before use, but considerable oxygen-containing impurity remained as evidenced by the presence of strong HNO, OH and NO_2 absorption spectra.[9] Tank C.P. ammonia was found to introduce negligible impurity spectra due to the presence of oxygen or water and was used throughout most of these experiments.

The Electronic Spectrum.—The gas phase electronic emission[14] and absorption[15] spectra of imine have been known for some time. A fairly strong transition between the ground $^3\Sigma^-$ state and an excited $^3\Pi$ state occurs near 3360 Å. There are no other observed or predicted strong electronic transitions involving the ground state in the near ultraviolet, visible or infrared regions so that imine should be colorless. Weak predicted intercombinations $^1\Delta \leftarrow {}^3\Sigma^-$ and $^1\Sigma^+ \leftarrow {}^3\Sigma^-$ should occur at long wave lengths but have never been observed.

In the solid phase spectrum, the 3360 Å. transition is shifted to the red by a few hundred cm.$^{-1}$ depending upon the matrix used. This absorption corresponds to the 0–0 band of the electronic transition. Under favorable conditions sharp emission lines appear to the red of the absorption band. These were found to be induced by the light source and occur from low-lying rotational levels in the excited electronic state to rotational levels in the ground electronic state. This emission is not an afterglow since it appears only under the influence of the source either during deposition or many hours after deposition is discontinued. The presence of emission shows that the lifetime for radiationless transitions is longer than or of the same order of magnitude as the lifetime of the electronic transition, *i.e.*, ~ 10^{-6} sec. The intensity of emission is extremely weak in some deposits and in krypton and xenon matrices is not detectable, possibly because of broadening or short radiationless lifetimes due to lattice interactions.

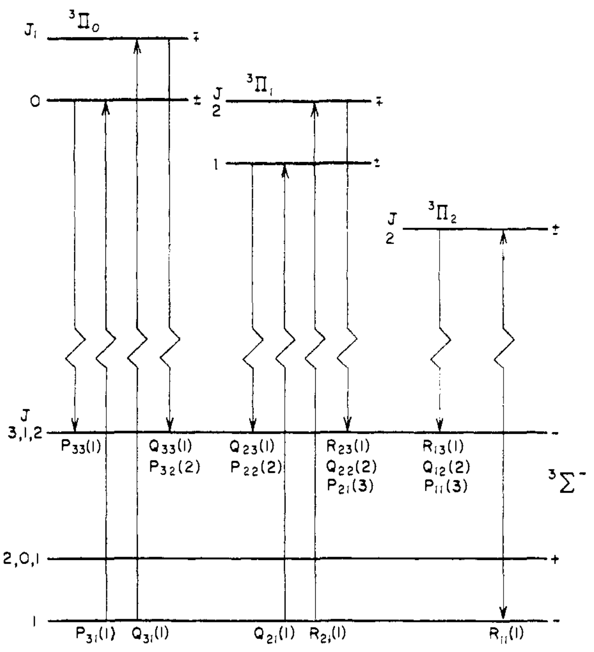

Fig. 1.—Energy level diagram of the $A^3\Pi \leftrightarrow X^3\Sigma^-$ transition in NH showing the first lines.

Figure 1 gives the energy level diagram for NH and shows which transitions are expected at 4.2°K. Table I lists observed emission and absorption lines of NH in an argon matrix and compares these with their most reasonable free molecule analogs. It is interesting to note that the + ↔ − selection rule is strictly obeyed and that there is no evidence

TABLE I

NH(IN ARGON) ROTATIONAL STRUCTURE

	Matrix, cm.$^{-1}$	Gas, cm.$^{-1}$	Transition	Matrix shift, cm.$^{-1}$
Abs.	29671	29868	$Q_{31}(1)$	−197
Abs.	29642	29836	$P_{31}(1)$, $R_{21}(1)$	−194
Abs.	29597	29806	$Q_{21}(1)$	−209
Abs.	29581	29773	$R_{11}(1)$	−192
Em.	29575	29773	$R_{11}(1)$, $Q_{33}(1)$, $P_{32}(2)$	−198
Em.	29523	29741	$R_{23}(1)$, $Q_{22}(2)$, $P_{21}(3)$, $P_{33}(1)$	−218
Em.	29500	29712	$Q_{23}(1)$, $P_{22}(2)$	−212
Em.	29477	29674	$R_{13}(1)$, $Q_{12}(2)$, $P_{11}(3)$	−197

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(13) G. Herzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 386.

(14) G. W. Funke, *Z. Physik*, **96**, 787 (1935).

(15) G. W. Funke, *ibid.*, **101**, 104 (1936).

Table II

Electronic Spectra of NH and ND in Rare Gas Matrices

	NH 0-0, cm.$^{-1}$	M-G, cm.$^{-1}$	NH 1-0, cm.$^{-1}$	ND 0-0, cm.$^{-1}$	ND 1-0, cm.$^{-1}$	$\Delta G'_{1/2}$ (ND), cm.$^{-1}$
Gas[14]	29773					
A	29581 ± 3	−192	32560 ± 3	29608 ± 6	31819 ± 6	2211
Kr	29509 ± 6	−264		29522 ± 6	31711 ± 6	2189
Xe	29403 ± 30	−370		29467 ± 50	31610 ± 60	2143

for rotational relaxation in the excited state during the electronic lifetime. Since the matrix perturbation is electronic in nature, it is not surprising that the correlation between gas and solid phase lines is poorer for states of different $\Omega = \Lambda + S$ where Λ and S are the electronic orbital and spin angular momenta components along the internuclear axis. The lines involving excited rotational levels in a state of given Ω correlate reasonably well (*i.e.*, have equal matrix shifts) with gas phase lines, showing that within experimental error NH radicals experience free rotation in the solid phase.

Because the NH internuclear distance is nearly identical in the ground and excited states (double prime and prime, respectively), the Franck-Condon principle limits strong transitions to the type $v' \leftrightarrow v''$. At 4.2°K. only the lowest rotational level of the $v'' = 0$ state is populated so the strongest features at this temperature are the first lines of the 0–0 band. The small change in bonding between ground and excited states causes almost a zero deuterium isotope shift in the 0–0 band since the shift arises solely from a difference in zero point energies in the two states. Transitions of the type $v' + 1 \leftarrow v''$ are so weak that they have not previously been reported in absorption, and in emission[16] they have been observed only if great care is taken to avoid spectral contamination by OH. The solid phase spectrum reveals rather strong $1 \leftarrow 0$ absorption after 1 to 5 hr. of depositing (depending on the matrix) illustrating the long effective absorbing paths obtainable in the solid. Table II lists the longest wave length absorption line of the 0–0 and 1–0 transitions of NH and ND in some of the rare gas matrices in addition to the position of the $R_{11}(1)$ lines of the free molecule to which the solid phase lines probably correspond. The lines become broader for imine in krypton and much broader for imine in xenon so that larger errors are present in these measurements. The deuterium isotope shift shows up very clearly in the 1–0 transition since $\Delta G_{1/2}(\mathrm{ND}) \approx 0.73\ \Delta G_{1/2}(\mathrm{NH})$. A more detailed discussion of the vibrational constants of imine and imine-*d* will be given in the next section.

In an argon matrix an extremely sharp (~1 cm.$^{-1}$ wide) absorption line at 30466 cm.$^{-1}$ can sometimes be found if the spectrum is photographed during the deposition. This absorption line disappears in a time short compared with the exposure time after the discharge is turned off suggesting that it arises from some metastable species. In NH there is a $^1\Delta$ state which is metastable with respect to the ground state by virtue of electron spin and orbital angular momentum selection rules. In the oxygen molecule the infrared electronic transition, $^1\Delta_g \leftarrow {}^3\Sigma_g^-$, has an estimated transition probability[17] of 0.007 sec.$^{-1}$ which might be expected to be of the same order as the transition probability for the decay of $^1\Delta$ imine to the ground $^3\Sigma^-$ state. If this is so and losses are not too great because of radiationless transitions, then it would be possible to build up an observable steady state concentration of metastable NH molecules in the matrix.

The gas phase $^1\Pi \rightarrow {}^1\Delta$ transition occurring at 3240 Å. has been studied in detail by Pearse.[18] In the matrix phase spectrum, because of the low concentration of metastable radicals, only one weak line was observed which corresponds presumably to the strongest line of the transition. If the solid phase spectrum arises from the $^1\Pi \leftarrow {}^1\Delta$ transition the line must be the P(2) line which is predicted to be the strongest of all possible transitions from the rotationless ground state. The gas phase line lies at 30685 cm.$^{-1}$ giving a matrix red shift of 219 cm.$^{-1}$. This value can be compared with the argon shift of 192 cm.$^{-1}$ observed for the $^3\Pi \leftarrow {}^3\Sigma^-$ transition of NH. The agreement between these values is quite good, which is expected considering the fact that the electronic structures in the initial and final states of the two transitions are similar. The slight observed difference is real and reflects the differences in intermolecular interaction between the various electronic states of NH and the rare gas atoms.

Vibrational Constants.—The only attempt to evaluate the vibrational constants of the imine radical which has appeared in the literature is the work of Pannetier and Gaydon[16] based upon a vibrational analysis of some NH bands from HN_3 explosion spectra. A rotational analysis, however, was not made.[18a]

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[16] G. Pannetier and A. G. Gaydon, *J. chim. phys.*, **48**, 221 (1951).

[17] L. Herzberg and G. Herzberg, *Astrophys. J.*, **105**, 353 (1947).

[18] R. W. B. Pearse, *Proc. Roy. Soc.* (*London*), **A143**, 112 (1934).

[18a] Note added in proof.—While this paper was in press a partial rotational analysis of the (1–0) and (0-1) bands of NH was published by G. Pannetier and H. Guenebaut (*Bull. Soc. Chim. France*, 1463 (1958). A very complete rotational analysis of the (0–0) and (1–0) bands of NH in absorption was also quite recently completed by R. N. Dixon (private communication) and it indicates that part of the analysis in refs. 14 and 15 is in error. The new gas phase rotational line measurements and numbering cause a revision of the rotational matrix shifts and assignments in Table I. The revised shifts and assignments are listed below in the order that the matrix lines appear in the table.

Absorption Transition	Matrix shift cm.$^{-1}$	Emission Transition	Matrix shift cm.$^{-1}$
$R_{21}(1)$	−195	$Q_{22}(2)$, $R_{23}(1)$, $P_{21}(3)$	−193
$P_{31}(1)$	−185	$P_{33}(1)$	−206
$Q_{21}(1)$	−210	$Q_{23}(1)$, $P_{22}(2)$	−210
$R_{11}(1)$	−190	$R_{13}(1)$, $Q_{12}(2)$, $P_{11}(3)$	−196

In view of the revision the 29575 cm.$^{-1}$ emission line need not be interpreted as $R_{11}(1)$ and thus our statements about the emission absorption shifts may not be correct in the case of NH. That such an effect can exist, however, is shown in the case of C_2 in xenon (ref. 25) where the shifts are about 50 cm.$^{-1}$. Another result of the revision is that the suggested Ω-dependency of the shifts is no longer

By using the relationships[19]

$$\Delta G_{1/2} = \omega_e - 2\omega_e x_e \quad (1)$$

$$\omega_e(\mathrm{NH}) = \left(\frac{\mu_{\mathrm{ND}}}{\mu_{\mathrm{NH}}}\right)^{1/2}\omega_e(\mathrm{ND}) \quad (2)$$

$$\omega_e x_e(\mathrm{NH}) = \left(\frac{\mu_{\mathrm{ND}}}{\mu_{\mathrm{NH}}}\right)\omega_e x_e(\mathrm{ND}) \quad (3)$$

and the observed $\Delta G_{1/2}'(\mathrm{NH})$ and $\Delta G_{1/2}'(\mathrm{ND})$ from the present work it is possible to calculate some of the vibrational constants of NH and ND in an argon matrix. These constants are listed in Table III together with those of Pannetier and Gaydon for comparison. Our experimental error is about ±3 cm.$^{-1}$, but errors may accumulate in the evaluation of ω_e and $\omega_e x_e$. The differences between our results and the gas phase results are no doubt caused partly by matrix perturbations.[20] In some of our previous work on NH_2,[11,12] the effect of the matrix on the vibrational levels was so slight that even at $v_2' = 18$ the perturbation amounted to only 25 cm.$^{-1}$ and was much smaller for the very low levels. Larger perturbations are expected for stretching vibrations because of larger changes in polarizability for this type of mode. The presence of such a matrix perturbation can be seen in the $\Delta G_{1/2}'(\mathrm{ND})$ results in Table II. Further work on the gas phase spectrum is needed to establish the vibrational constants for free imine and imine-*d* in order that they may be compared with the solid phase constants. In any case the differences between the existing gas-phase and solid-phase data are not very great and the agreement between the constants is sufficiently good that it serves as further verification that the imine radical in a nearly unperturbed form has been trapped in the rare gas matrix.

TABLE III[a]

VIBRATIONAL CONSTANTS OF NH AND ND IN ARGON

		Ground state			Excited state		
		$\Delta G_{1/2}$ cm.$^{-1}$	ω_e, cm.$^{-1}$	$\omega_e x_e$, cm.$^{-1}$	$\Delta G_{1/2}$ cm.$^{-1}$	ω_e, cm.$^{-1}$	$\omega_e x_e$, cm.$^{-1}$
NH	This work	3074[b]	...	...	2979	(3155)	(88)
	Ref. 15	3109	3266	78.5	3014	3188	87.5
ND	This work	...	...	...	2211	(2305)	(47)

[a] Values in parentheses are calculated from eq. 1–3. [b] Estimated from excited state matrix perturbation and ground state gas phase value.

Becker, Pimentel and Van Thiel[5] in their hydrazoic acid photolysis experiments have observed a reactive species absorbing in the infrared at 3080 cm.$^{-1}$. Our estimated value of $\Delta G_{1/2}''$ lends some support to their claim of having trapped the imine radical in these experiments. However, full confidence in this interpretation must await similar experiments with DN_3 which should produce a line at about 2275 cm.$^{-1}$. A study of the electronic spectra of photolyzed pure and mixed HN_3 and DN_3 in rare gases might be more informative, since the solid state spectra of NH, ND, NH_2[11,12], ND_2[21] and NHD[21] are now known.

Matrix Perturbations.—As we mentioned earlier matrix perturbations are not expected to affect vibrational transition energies to a great extent since the intermolecular forces depend upon the electronic structure of the trapped species and are not very much changed in the first excited vibrational state. The effect of the matrix on the electronic spectrum, however, reflects the relative magnitudes of the binding between the upper and lower electronic states of the trapped species and the matrix molecules, and this difference may be large.

Because of the large space requirements for van der Waals binding, the presence of nearly free rotation of the trapped species and the observation of sharp but shifted spectral lines, we assume trapping at lattice sites rather than in interstitial positions. A fairly good approximation to the intermolecular potential between non-polar spherical molecules in a face-centered cubic or hexagonal close-packed lattice is given by a Lennard-Jones potential of the form[22]

$$V = 4\epsilon\left[12.13\left(\frac{\sigma}{d_0}\right)^{12} - 14.45\left(\frac{\sigma}{d_0}\right)^{6}\right] \quad (4)$$

where d_0 is the nearest neighbor distance, ϵ is the well depth for the attractive potential between two molecules and σ is a parameter which is interpreted as an effective molecular size.

For unlike molecules denoted by subscripts 1 and 2 it is known that ϵ_{12} and σ_{12} may be estimated by the combining laws

$$\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2} \quad (5)$$

$$\sigma_{12} = {}^1/_2(\sigma_1 + \sigma_2) \quad (6)$$

The validity of eq. 5 might be questionable, especially for free radicals and excited states with which we are dealing, but for interactions of such species with rare gas atoms the approximation should be fairly good. Naturally any interaction parameters obtained from such a picture are valid only for dispersion interactions and not for NH–NH interactions, for example, which are expected to be of the valence type. Equation 6 is probably a good approximation for spherical molecules and hence is satisfactory for NH which may be only slightly aspherical. The value of σ_{NH} is probably not very different in the ground and excited states and will be considered constant. The matrix shift in the electronic transition under the above approximations is given by

$$\Delta V = 4(\sqrt{\epsilon'_{\mathrm{NH}}} - \sqrt{\epsilon''_{\mathrm{NH}}})(\sqrt{\epsilon_{\mathrm{matrix}}})\left[12.13\left(\frac{\sigma}{d_0}\right)^{12} - 14.45\left(\frac{\sigma}{d_0}\right)^{6}\right] \quad (7)$$

where $\sigma = {}^1/_2(\sigma_{\mathrm{NH}} + \sigma_{\mathrm{matrix}})$. A plot of experimental shift against

$$4\sqrt{\epsilon_{\mathrm{matrix}}}\left[12.13\left(\frac{\sigma}{d_0}\right)^{12} - 14.45\left(\frac{\sigma}{d_0}\right)^{6}\right] \quad (8)$$

yields a straight line through the origin if eq. 6 is assumed and σ_{NH} is taken as 4.11 Å. The intermolecular parameters for the rare gas atoms listed in Table

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apparent, the solid phase rotational lines now showing fewer divergencies from the gas phase lines than before. Thus the upper limit to the hindering effect on the rotational motions is even less than previously supposed. Dr. Dixon has also found that $\Delta G_{1/2}' = 3034.0$ cm.$^{-1}$ and $\Delta G_{1/2}' = 3125.6$ cm.$^{-1}$. The gas phase values in Table III accordingly should be revised. Thus the environmental perturbation caused by argon decreases $\Delta G_{1/2}'$ (NH) by 55 cm.$^{-1}$.

(19) Ref. 13, Chap. III.

(20) E. D. Becker and G. C. Pimentel, *J. Chem. Phys.*, **25**, 224 (1956).

(21) G. W. Robinson and M. McCarty, Jr., unpublished.

(22) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 1040, *et seq.*

IV are those obtained from crystal data.[23] The slope of the line yields 1.80 (cm.$^{-1}$)$^{1/2}$ for ($\sqrt{\epsilon'_{NH}} - \sqrt{\epsilon''_{NH}}$) showing as expected a stronger interaction between excited NH and the matrix atoms than between normal NH and the matrix atoms. It is not possible to obtain the interaction energies themselves, but since ϵ''_{NH} is probably close to 50 cm.$^{-1}$,[24] ϵ_{NH} must increase by about 20 cm.$^{-1}$ in the excited state. The value of σ_{NH} required to explain the matrix shifts seems at least 0.5 Å. too large, but it should be remembered that this is an effective parameter whose interpretation depends upon the validity of the individual assumptions made. A slight collapsing of the lattice about NH for example might be expected and the data then would be consistent with a smaller σ_{NH}.

Table IV

Lennard-Jones Parameters for Imine in Rare Gas Matrices

	A	Kr	Xe
ϵ_{matrix} (cm.$^{-1}$)[23]	82.7	114.7	159.2
$d_{0matrix}$ (Å.)[22]	3.83	3.95	4.34
σ_{matrix} (Å.)[23]	3.46	3.60	3.98

σ_{NH} = 4.11 Å.

$\Delta\sqrt{\epsilon_{NH}}$ = 1.80 (cm.$^{-1}$)$^{1/2}$

Since there are only two unknown parameters in this treatment, namely σ_{NH} and ($\sqrt{\epsilon'_{NH}} - \sqrt{\epsilon''_{NH}}$), it is possible to calculate from argon and krypton data a shift in xenon of −385 cm.$^{-1}$. This is in fair agreement with the observed value of −370 cm.$^{-1}$. The above interpretation of the matrix shifts requires considerable polish but even in its present simple form appears to be rather convincing, having already led to some interesting results concerning intermolecular interactions.[25]

It is interesting to note that the $R_{11}(1)$ absorption line is about 6 cm.$^{-1}$ to the blue of the corresponding fluorescence line. This can be interpreted as being caused by a slight difference in the equilibrium lattice geometry for the two electronic states of trapped NH. Because of the larger magnitude of ϵ_{NH}, the intermolecular distance between NH and the matrix atoms is expected to be smaller in the excited state. The Franck–Condon principle requires the change in lattice geometry to take place after the absorption of light, and emission then occurs from a state of lower lattice energy. That the emission lines are sharp and not shaded to the blue indicates that the lattice collapses about the excited imine molecule in a time short compared with the electronic lifetime.

Conclusions

It has been shown that imine radicals are present in moderately large concentrations in the products of discharges containing ammonia or hydrazine frozen out in rare gas matrices at 4.2°K. Imine is also formed in discharges containing nitrogen and hydrogen in many other forms. The vibrational constants obtained from the low temperature spectrum are in agreement with those of the free molecule. Although none of our experiments have dealt directly with HN_3, the accumulating evidence points to the fact that imine can be produced in discharge decomposition, photodecomposition and thermal decomposition of this molecule. There is therefore little doubt that imine radicals can be trapped from these sources at sufficiently low temperatures using a sufficiently inert matrix. Whether imine can be trapped at liquid nitrogen temperature in a reactive matrix (such as hydrazoic acid decomposition products) in sufficient quantity to produce the observed 3500 Å. absorption is still open to question. Certainly the blue material itself cannot be imine unless it is so strongly interacting with its environment that its electronic structure is greatly changed. Since NH_2 radicals also have been trapped by our technique, it is possible that the blue color is due to this radical. Further work must be done in order to bridge the gap between the study of slightly perturbed trapped radicals at low temperatures as presented in this paper and the study of trapped species at higher temperatures in very highly perturbing environments.

Baltimore, Maryland

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[23] R. D. Present, "Kinetic Theory of Gases," McGraw-Hill Book Co., New York, N. Y., 1958, p. 253.

[24] 1 cm.$^{-1}$ = 2.86 cal./mole.

[25] M. McCarty, Jr., and G. W. Robinson, paper presented at 9th Annual Meeting, Société de Chimie Physique, Paris, May 26–29, 1959.