THE INFRARED SPECTRUM OF THE HYDROXYLAMINE DIMER

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ABSTRACT

The infrared spectra of the hydroxylamine monomer and dimer, trapped in nitrogen and argon matrices at ca. 17 K, have been obtained. Assignments have been made, based on concentration and matrix diffusion experiments, and on the wavenumber shifts arising from deuteration. The proposed assignments have been checked by comparison with those of a spectrum predicted for the dimer by means of a series of ab initio calculations, reported recently. The spectra have been interpreted in terms of a cyclic, doubly hydrogen bonded dimer of $C_{\rm ob}$ symmetry, consistent with that predicted theoretically.

INTRODUCTION

The study of the matrix isolation infrared spectrum of hydroxylamine and its dimer forms part of a series of studies of the experimental and theoretical spectra of the monomers of water,² ammonia² and hydroxylamine,^{2,3} the water,¹ ammonia^{4,5} and hydroxylamine⁶ dimers, and the binary hydrogen bonded complexes formed from among them.¹ The hydrogen bonding properties of hydroxylamine would be intuitively expected to be similar to those of water and ammonia, with the OH group acting as proton donor and the nitrogen atom as electron donor. In our theoretical studies of this hydrogen bonded dimer, we considered two distinct structures as probable candidates for the species likely to be found trapped in cryogenic matrices, a five-membered cyclic dimer of C symmetry and a six-membered cyclic isomer belonging to the C_{2h} point group.⁶ We predicted the wavenumbers and infrared band intensities of each dimer at the SCF level of theory, using both the 4-31G and 6-31G ** basis sets and the Gaussian-76^{7,8} and Gaussian-80^{9,10} ab initio molecular orbital computer programs.

This paper represents our attempts to settle the question of which of the two structures considered is the more likely isomer to exist, by recording the infrared spectra of hydroxylamine isolated in nitrogen and argon matrices by deposition at about 17 K. Matrix annealing experiments have been carried out, and the spectra have been recorded of mixtures with a number of concentrations of hydroxylamine and of its various deuterated derivatives, in an attempt unambiguously to assign the bands observed in either matrix to

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the vibrations of one dimeric species or the other. The criteria used to make the assignments were that the bands attributed to monomer or dimer should exhibit the correct intensity behaviour on warm-up, that the wavenumbers and relative intensities should correlate consistently with those predicted by our ab initio calculations, 6 and that reasonable isotopic shifts should be observed on deuteration.

EXPERIMENTAL

The spectra were recorded using a Perkin-Elmer model 580B grating infrared spectrophotometer, interfaced with a model 3600 data station, at a resolution of 2 cm⁻¹ in the range 4000 to 180 cm⁻¹. Wavenumber calibration was effected by using standard indene-camphor-cyclohexanone mixtures and DC ℓ gas;¹¹ quoted wavenumbers are believed to be accurate to ± 1 cm⁻¹.

The cryogenic system consisted of an Air Products Displex model CS-202A two-stage closed cycle helium refrigerator linked with a model APD-B temperature controller. Temperatures were measured with a gold-doped iron (0.07%)/chromel thermocouple and were taken from the analogue read-out without further correction. The vacuum shroud and cold tip windows were caesium iodide.

Research grade nitrogen and argon (99.9995%) (Air Products) were used without further purification. Hydroxylamine phosphate was prepared from sodium phosphate (Merck) and hydroxylamine hydrochloride (BDH).¹² The precipitated salt was purified by recrystallization from hot water and dried over P_2O_5 in a vacuum desiccator. Deuterated hydroxylamine phosphate was prepared by refluxing hydroxylamine phosphate in D_2O for a few minutes. On cooling, the crystalline product obtained was filtered off and dried over P_2O_5 in a vacuum desiccator. The degree of deuteration could be increased by repeating the process on the deuterated salt.

Samples were prepared by standard manometric procedures on an all-glass vacuum line. The glass vessel in which the hydroxylamine/matrix gas mixtures were produced consisted of a 1 dm³ flask attached via a vacuum tap to a tube, containing a thermometer pocket, which was fitted at each end with a porous glass disc. The free end of the tube was also fitted with a vacuum tap, so that the whole assembly could be evacuated. The concentration of hydroxylamine in the matrix was varied by changing the temperature at which the free base was generated from its salt. The section of the tube between the glass discs was externally wound with heating cord. The rate of heating was adjusted by means of a variable transformer. Temperature measurement was achieved using a thermocouple attached to the outside surface of the glass tube and to an analogue controller. Temperatures were set so that a thermometer, placed inside the thermometer pocket and in direct contact with

the salt, registered the required temperatures, which were maintained constant within + $0.5^{\circ}C$.

In a typical experiment, 1 g of hydroxylamine phosphate (or its deuterated analogue) was placed in the glass tube and the whole vessel was evacuated. The matrix gas was then introduced into the 1 dm³ flask at a pressure of 60 kPa. Free hydroxylamine/matrix gas mixtures were prepared by heating the phosphate salt to a temperature between 25 and 60°C, while allowing the matrix gas to flow over the heated salt. For both nitrogen and argon, a constant flow rate of 5 mmol h^{-1} was used. Deposition of the matrix, at about 17 K, was continued until the resulting spectrum showed bands having acceptable intensities. This generally occurred after between 2 and 5 h deposition, depending on the temperature of the salt. Where necessary, weaker bands were enhanced by co-addition of a number of spectra. In warm-up experiments, the matrix was annealed by heating to 30 K, maintaining it at that temperature for 5 min, and re-cooling to 17 K.

RESULTS

Representative spectra of samples trapped in nitrogen, prepared by heating the phosphate salt at 55°C, both before and after annealing the matrices, are shown in Figures 1 to 3, in the regions 4000 - 3000,



Fig. 1. Infrared spectrum, from 4000 to 3000 cm^{-1} , of hydroxylamine, generated at 55°C, trapped in nitrogen at 17 K : (a) before, (b) after annealing.



Fig. 2. Infrared spectrum, from 1700 to 1050 cm^{-1} , of hydroxylamine, generated at 55°C, trapped in nitrogen at 17 K : (a) before, (b) after annealing.

1700 - 1050 and 1000 - 650 cm⁻¹ respectively. Table 1 lists the wavenumbers of the major bands observed in both nitrogen and argon matrices, with our assignments to the monomer modes and to those of both dimer species. Figure 4 illustrates the effect of successive deuterations on the spectrum recorded in nitrogen in the torsional region of the monomer, from 500 to 250 cm⁻¹. The positions of the observed bands of the deuterated monomers are presented in Table 2, with assignments to the fundamental modes of the various isotopomers.

DISCUSSION

Assignment of NH_OH Monomer Spectrum

In assigning the bands in the spectrum of the hydroxylamine monomer, we have been guided by the normal coordinate analysis of Withnall and Andrews (WA), based on their spectra of NH₂OH and thirteen of its deuterium, ¹⁵N and ¹⁸O analogues recorded in argon matrices.¹³ Our band positions in argon agree well within 1 cm⁻¹ with those reported by WA,¹³ with the exception of the OH-stretching band at 3634 cm⁻¹, which we find to be 1.2 cm⁻¹ lower. Our nitrogen matrix wavenumbers differ from WA's argon values by up to 16 cm⁻¹ in some cases, and by 47 cm⁻¹ for the torsional mode. The discrepancy is comparable with that found by Nonella et al¹⁴ in their study of nitramide in argon and nitrogen, where the NH₂-torsional mode was observed at 401.5



Wavenumber / cm⁻¹

Fig. 3. Infrared spectrum, from 1000 to 650 cm^{-1} , of hydroxylamine, generated at 55°C, trapped in nitrogen at 17 K : (a) before, (b) after annealing.

 $\rm cm^{-1}$ in argon and at 433.8 cm⁻¹ in nitrogen. This mode appears to be particularly sensitive to the environment. In addition to the eight fundamental bands of NH₂OH reported by WA,¹³ we have also observed the elusive NH₂-twisting mode at 1301 cm⁻¹ in nitrogen. Neither we nor they observed this band in argon, as a result of its negligible calculated intensity,³ and in nitrogen it appears as a very weak feature only in the spectrum obtained at the highest temperature at which we heated the phosphate salt. Its observed position, however, is close to the 1311.4 cm⁻¹ predicted by WA's normal coordinate treatment,¹³ and is consistent with the value of 1347 cm⁻¹ predicted by our ab initio calculations at the MP2/6-31G** level,³ and this encourages us to claim to have seen this band for the first time.

While our observed wavenumber values are in generally good accord with those of WA, 13 we do differ in our interpretation of the spectra in the

ASSIGNMENTS OF BANDS OF HYDROXYLAMINE OBSERVED IN NITROGEN AND ARGON MATRICES

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	WAVENUMB	ER/cm ⁻¹		ASSIGNM	1ENT ^a
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	NITROGEN	ARGON	MONOMER	FIVE-MEMBERED DIMER	SIX-MEMBERED DIMER
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3635	3634	ν		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3497	3521	- 1	¥16	να
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3472	3489	νī	- 10	5
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3444	3449		ν_{17}	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3425	3390		ν_3	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3359	3354	ν_2	-	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3346	3340	-	ν_1	ν_{18}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3302	3289		ν_2	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3290	3282		ν_4	ν_{19}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1623	1607		ν_5, ν_6	ν_{20}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1605	1599	ν_3		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1472	1470	-	ν_7, ν_8	ν_{21}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1367	1351	ν_4		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1301		ν_8		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1290	1289	•	ν_{18}, ν_{19}	ν_{10}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1165	1152		ν_{9}, ν_{10}	ν_{22}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1134	1118	ν_5		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	904	910	-	ν_{11}, ν_{12}	ν_{23}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	895	896	ν_6		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	813		$2\nu_9$		
$\begin{array}{cccc} & 727 & 2\nu_9 \\ 449 & 406 & & \nu_{21} \end{array}$	761	736		ν_{20}	ν_{11}
$449 406 \nu_{21}$		727	$2\nu_9$		
	449	406		ν_{21}	
421 374 ν ₉	421	374	ν_9		

^a See references 3 and 6 for descriptions of normal modes of monomer and dimers respectively.

 NH_2 -stretching region. These authors assign the bands at 3289.6 and 3353.7 cm⁻¹ to the symmetric and antisymmetric stretching modes of the monomer, respectively, and a feature at 3489.2 cm⁻¹ to either the OH-stretching mode of the cis isomer or to a thermal decomposition product. Their assignment is supported by the results of their normal coordinate calculations, by the similarity of their argon matrix band positions to those reported by Giguère and Liu for hydroxylamine vapour,¹⁵ and by the empirical relationships of Bellamy and Williams,¹⁶ $\tilde{v}_{s}(NH_2) = 345.53 + 0.876 \tilde{v}_{a}(NH_2)$ and Colthup et al,¹⁷

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Fig. 4. Effect of successive deuterations on the infrared spectrum, from 500 to 250 cm⁻¹, of hydroxylamine, generated at 55°C, trapped in nitrogen at 17 K : (a) first, (b) second, (c) third deuteration.

 $\bar{v}_{\rm NH_2} = 0.98 \bar{v}_{\rm NH_2}$

WA's assignment is shown in Table 3 along with our first alternative assignment (I), which agrees with theirs, and a second alternative (II), in which the band at 3489 cm⁻¹ in argon is assigned to the antisymmetric $\rm NH_2$ -stretching and that at 3354 cm⁻¹ to its symmetric counterpart. We agree with WA¹³ that the 3489 cm⁻¹ band diminishes in intensity on annealing and we therefore feel confident in assigning it to the monomer. The band at 3289 cm⁻¹ in argon, however, which WA assign to the monomer $v_{\rm g}(\rm NH_2)$ mode, was found to have a positive temperature dependence on annealing, and we prefer to assign it to the dimer (see later). Our assignment II finds confirmation in the spectra of several related molecules, where $v_{\rm g}(\rm NH_2)$ often lies above 3400 cm⁻¹ and $v_{\rm g}(\rm NH_2)$ in the region 3345 to 3365 cm⁻¹, ¹⁴, ¹⁸, ¹⁹ as shown in Table 4.

The most powerful argument in favour of our assignment II being the correct assignment, however, is based on a consideration of relative intensities. Discussing the hydroxylamine vapour spectrum, Giguère and Liu¹⁵

	ND ARGON MATRICES
	NITROGEN A.
	IN
	MONOMERS
	HYDROXYLAMINE
	DEUTERATED
	OF
TABLE 2	ASSIGNMENTS

	MODE ^a			WAVENU	MBER/cm ⁻¹		
MATRIX	(SYMMETRY)	NH ₂ OH	HOUN	ND20H	NH2OD	NHDOD	ND20D
nitrogen	ν ₁ (a′)	3635	3636	3636	2687	2687	2687
	$\nu_2(\mathbf{a'})$	3359	3323	i	3302	I	2513
	$ u_3(a')$	1605	1470	1155	1598	1457	1175
	$ u_4(\mathbf{a'}) $	1367	1331	1335	967	1025	1043
	₩5(a')	1134	952	847	1195	935	917
	$ u_6(\mathbf{a}') $	895	883	923	1	875	828
	$\nu_7(a^{"})$	3472	ł	I		I	2567
	$\nu_8(a^{"})$	1301	I	I	I	!	ł
	ν ₉ (a")	421	406	400	340	322	312
rgon	$ u_1(\mathbf{a}^{\prime})$	3634	3634	3634	2685	2685	2685
	$\nu_2(a')$	3354	ł	2412	3290	I	2506
	$\nu_3(a')$	1599	1464	1156	1595	1450	1173
	$ u_4(a') $	1351	1342	1369	954	1020	1035
	$\nu_5(a^{\prime})$	1118	948	837	1145	935	915
	$\nu_6(a')$	896	880	918	892	869	818
	$\nu_7(\mathbf{a}")$	3489	ł	2506	ł	1	2579
	$\nu_8(a")$	ł	I		I	ŀ	ł
	$\nu_9(a'')$	374	356	347	313	291	277

POSSIBLE ASSIGNMENTS OF HYDROXYLAMINE MONOMER BANDS IN NITROGEN AND ARGON MATRICES

MODE		NITR	OGEN				ARGO	N		
(SYMMETRY)	ASSIGN	NENT I	ASSIGN	IMENT II	ASSIGN	VMENT I	ASSIGN	IMENT II	LITERA	TURE ^a
	<u>~</u> /cm ⁻¹	ratio ^b	$\overline{\nu}/\text{cm}^{-1}$	ratio ^b	<u> </u>	ratio ^b	<u>v/cm-1</u>	ratio ^b	<u>v/cm⁻¹</u>	ratio ^b
$\nu_1(a')$	3635	1.07	3635	1.07	3634	1.07	3634	1.07	3635.2	1.07
$\nu_2(\mathbf{a'})$	3302	1.07	3359	1.05	3289	1.07	3354	1.05	3289.6	1.07
$\nu_3(a')$	1605	1.06	1605	1.06	1599	1.07	1599	1.07	1598.7	1.07
$ u_4(a') $	1367	1.05	1367	1.05	1351	1.06	1351	1.06	1351.4	1.06
$\nu_5(\mathbf{a'})$	1134	1.05	1134	1.05	1118	1.07	1118	1.07	1117.6	1.07
$\nu_6(a')$	895	1.06	895	1.06	896	1.06	89Ġ	1.06	896.2	1.06
$\nu_7(a'')$	3359	1.08	3472	1.05	3354	1.08	3489	1.04	3353.7	1.08
$\nu_8(a'')$	1301	1.04	1301	1.04	I	I	I	1	1311.4 ^c	1.03
ν9(a")	421	0.97	421	0.97	374	1.09	374	1.09	374.0	1.09
^a R. Withnall ar	nd L. And	lrews, J. P	hys. Chei	m., 92 (1988) 2155.					
$\mathbf{p} = \frac{1}{2}$	1		-	-		0100	**	;		•

*V*caic/*V*exp, where *V*calc are the wavenumbers calculated at the MP2/6-31G level (G.A. Yeo and T.A. Ford, J. Chem. Soc., Faraday Trans., submitted).

^c Calculated from empirical force field.

MOLECULE	STATE	WAVENU	REFERENCES	
		$\nu_{a}(\mathrm{NH}_{2})$	ν _s (NH ₂)	
NH2OH	Ar matrix	3353.3	3289.7	a
NH2NO2	N_2 matrix	3474	3361	b
	Ar matrix	3478.0	3359.3	Ъ
CH ₃ NH ₂	vapour	3424	3360	c
	N ₂ matrix	3411	3349	c
	Ar matrix	3415	3352	c
CH3ONH2	vapour	3414	3273	d

ASSIGNMENTS OF NH2-STRETCHING MODES OF HYDROXYLAMINE AND SOME RELATED MOLECULES

a. R. Withnall and L. Andrews, J. Phys. Chem., 92 (1988) 2155.

b. M. Nonella, R.P. Müller and J.R. Huber, J. Mol. Spectrosc., 112 (1985) 142.

- c. C.J. Purnell, A.J. Barnes, S. Suzuki, D.F. Ball and W.J. Orville-Thomas, Chem. Phys., 12 (1976) 77.
- d. M. Davies and N.A. Spiers, J. Chem. Soc., (1959) 3971.

state that "the two NH stretching vibrations show ... apparently reversed intensity relationship", while Davies and Spiers,¹⁸ in describing the spectrum of O-methylhydroxylamine, remark that "contrary to the usual order, but as is found in NH₂OH itself, the $v_{\rm s}(\rm NH_2)$ is more intense than $v_{\rm a}(\rm NH_2)$ in the vapour". Our ab initio calculations at the MP2/6-31G** level³ have determined the $v_{\rm s}(\rm NH_2)$ intensity to be 1.56 and that of $v_{\rm a}(\rm NH_2)$ to be 0.04 km mol⁻¹, consistent with the order of intensities found in both nitrogen and argon matrices for assignment II. The alternative assignment would have required the relative intensities to have been transposed.

The correct assignment of those bands of the monomer which were calculated³ to have the highest intensities is confirmed by plotting their areas relative to that of the torsional mode at 421 cm⁻¹ in nitrogen (which is indisputably due to the monomer) as a function of the temperature at which the free base was generated. Those bands belonging to the same species as the absorption at 421 cm⁻¹ should yield straight lines of zero slope. The

strong bands v_5 , v_1 , v_3 and v_6 actually show a monotonic decrease of their relative intensities with increasing temperature (see Figure 5). The negative slopes, which are more pronounced the more intense the band, are due to the monomer torsional mode at 421 cm⁻¹ being partly overlapped by a nearby dimer band, which itself naturally grows in at higher temperatures, thus artificially enhancing the monomer v_9 band intensity. The temperature behaviour of the v_2 and v_4 bands, of intermediate intensity, is erratic, illustrating the difficulty of making accurate band area measurements on relatively weak bands under these conditions. Moreover, the weak v_7 band only appeared at temperatures above 50°C, while the very weak twisting band, v_9 , was only observed in the spectrum generated at 60°C.



Temperature / °C

Fig. 5. Plots of the areas of the v_5 , v_1 , v_3 and v_6 bands of hydroxylamine, trapped in nitrogen, relative to that of the v_9 band at 421 cm⁻¹, as functions of the temperature of generation of the free hydroxylamine.

Assignment of Deuterated Hydroxylamine Spectra

In preparing the deuterated derivative of hydroxylamine, the phosphate salt was dissolved in and recrystallized from D_2O a total of three times. After each recrystallization a matrix isolated spectrum was recorded. Comparison of the three spectra obtained clearly shows the growth of the bands associated with the more highly deuterated species at the expense of the normal and partly deuterated species. This is particularly evident in the region of the monomer torsional vibration near 400 cm⁻¹ (see Figure 4).

It was hoped that the isotopic ratios determined from the data of Table 2 would have enabled us to discriminate between the two alternative assignments, since if one assignment led to a significantly more consistent set of ratios than the other we might have been able to come to a decision on that basis. However neither of our two proposed assignments, nor that of WA,¹³ allowed us to eliminate the ambiguity. On balance, however, we favour our assignment II, and our subsequent discussion is based on that choice.

Assignment of Five-membered Cyclic Hydroxylamine Dimer

WA, in their spectra of hydroxylamine in argon matrices, have assigned five bands to the hydroxylamine dimer, based on their positive temperature behaviour on annealing.¹³ These bands occur at 3339, 1469.0, 1155.7, 909.7 and 735.7 cm⁻¹. Without prejudice to the structure of the most probable dimer, these bands can be described as perturbed OH-stretching, NOH-bending, NH_o-wagging, NO-stretching and NOH-torsional modes of the dimer, although WA assign the 735.7 cm^{-1} band to the torsional overtone.¹³ These five bands were all among the most intense bands which we have calculated for both the five- and six-membered cyclic dimers.⁶ Table 1 shows our assignments of the observed dimer bands in nitrogen and argon to the calculated normal modes.⁶ These normal modes are mostly described as coupled motions of the corresponding groups of the two monomer units constituting the dimer.⁶ As a result, the calculated wavenumbers for the related pairs of vibrations, $\boldsymbol{\nu}_{r}$ and v_c , v_{τ} and v_o , etc. often do not differ by more than a few cm⁻¹, and it is difficult to assign an observed band preferentially to one member of the pair. The assignments of Table 1 therefore show a number of such pairs of bands listed together.

Our ab initio calculations⁶ indicate that the modes of the five-membered cyclic dimer labelled ν_1 and ν_2 in Table 1 are both hydrogen bonded OH-stretching modes, and ν_3 , ν_4 , ν_{16} and ν_{17} are relatively unperturbed NH₂-stretching vibrations. As a result of hydrogen bonding, the wavenumbers of the two OH-stretching absorptions are lowered to such an extent that they appear in the non-bonded NH₂-stretching region, and actually lie at lower

wavenumbers than ${}^{\nu}_{16}$, ${}^{\nu}_{17}$ and ${}^{\nu}_{3}$. The numbering of the modes has been retained, however, in order to preserve the correlation between the theoretically calculated and experimentally observed band positions.

The validity of these assignments may be estimated by determining the calculated:experimental wavenumber ratios; these ratios are shown in Table 5. The calculated wavenumbers reported in reference 6 were determined at the RHF/6-31G** level using the Gaussian-76^{7,8} and Gaussian-80^{9,10} computer programs. We subsequently acquired a copy of Gaussian-86,²⁰ which features a normal coordinate analysis package for calculating the vibrational force constants analytically, and we made use of this program to recalculate the wavenumbers of both dimeric species, at the same level. The calculated results shown in Table 5 were taken from this later series of computations. Table 5 indicates that reasonable assignments have been proposed for all the modes of the five-membered isomer, except the three lowest-lying modes in each symmetry species, which are predicted to lie outside our range of observation, after allowing for the 5 to 20% overestimation typical of calculated wavenumbers at the RHF/6-31G** level of theory. 21 Moreover, the intermolecular modes, v_{13}^{ν} to v_{15}^{ν} and v_{22}^{ν} to v_{24}^{ν} , are predicted to be very weak.^b Most calculated:experimental ratios lie within the 5 to 20% error bounds suggested by Amos et al, ²¹ with the exception of the OH-stretching modes, ν_1 and ν_2 , and the NO-stretching modes, ν_{11} and ν_{12} , which are overestimated, and the torsional mode, v_{20} , which is calculated to be far too low.

Assignment of Six-membered Cyclic Hydroxylamine Dimer

The interpretation of the spectrum of the six-membered cyclic hydroxylamine dimer is simplified since, owing to its centrosymmetric structure, only one band of each coupled pair is infrared active, that for the respective antisymmetric mode. Thus, as shown in Table 6, each observed band in a particular wavenumber region may be linked with only a single calculated mode. Again, the intermolecular modes, v_{12} , v_{13} and v_{24} , v_{13} are predicted by the RHF/6-31G** calculations, using Gaussian-86, to lie outside our range of observation, although their intensities are predicted to be larger than those of their counterparts in the five-membered dimer. 6 0f the remaining nine active modes, reasonably consistent calculated:experimental wavenumber ratios have been determined, as shown in Table 6. In the case of the six-membered dimer, v_{18} is the antisymmetric OHstretching combination, and v_{9} and v_{19} are the two infrared active NH2stretching modes.⁶ Here, v_{18} is lowered sufficiently by hydrogen bonding that it lies below v_{0} . Such dramatic hydrogen bonding wavenumber shifts are

SYMMETRY	MODE	w , /		NITROGEN	MAT	RIX	ARGON	MATRIX
SPECIES		cm ⁻¹ a	-	$\overline{\nu}_{obs}/cm^{-1}$	$\overline{\nu}_{calc}/$ $\overline{\nu}_{obs}$		$\overline{\nu}_{obs}/cm^{-1}$	$\overline{\nu}_{calc}/$ $\overline{\nu}_{obs}$
a'	ν_1	4142		3346	1.24		33 40	1.24
	ν_2	4126		3302	1.25		3289	1.25
	ν_3	3718		3425	1.09		33 90	1.10
	ν_4	3718		32 90	1.13		3282	1.13
	$ u_{S}$	18 2 8	ļ	1623	1.13	Ì	1607	1.14
	ν_6	1824	ſ		1.12	}		1.14
	ν_7	1614	ļ	1472	1.10	ļ	1 47 0	1.10
	ν_8	1533	J		1.04	ſ	•	1.04
	ν_9	1270	ļ	1165	1.09	ļ	1152	1.10
	ν_{10}	1267	ſ		1.09	ſ		1.10
	ν_{11}	1129	ļ	904	1.25	Ì	910	1.24
	ν_{12}	1126	1		1.25	J		1.24
	ν_{13}	248		-	-		-	-
	<i>v</i> 14	140		-	-		_	
	ν_{15}	80		-	-		-	_
a"	ν_{16}	3 810		3497	1.09		3521	1.08
	ν17	3 807		3444	1.11		3449	1.10
	V18	1467	ł	1900	1.14	l	} 1289	1.14
	ν ₁₉	1457	Ĵ	1250	1.13	Ì		1.13
	ν_{20}	668		761	0.88		736	0.91
	ν_{21}	467		449	1.04		406	1.15
	ν_{22}	233		-	-		-	-
	ν_{23}	159			-		-	
i.	ν_{24}	_b		<u> </u>	-		-	-

CALCULATED: EXPERIMENTAL WAVENUMBER RATIOS FOR THE PROPOSED FIVE-MEMBERED CYCLIC HYDROXYLAMINE DIMER

^a Calculated at the RHF/6-31G^{**} level.

^b Negative eigenvalue.

SYMMETRY	MODE		NITROGEN	MATRIX	ARGON	MATRIX
SPECIES		cm ⁻¹ a	$\overline{\nu}_{obs}/cm^{-1}$	$\overline{\nu}_{calc}/$ $\overline{\nu}_{obs}$	$\overline{\nu}_{obs}/cm^{-1}$	ν _{calc} / ν _{obs}
a _u	Vg	3803	3497	1.09	3521	1.08
	ν_{10}	1450	1290	1.12	1289	1.12
	ν_{11}	788	761	1.04	736	1.07
	ν_{12}	212	-	-	_	-
	ν_{13}	81			-	-
bu	ν_{18}	4045	3346	1.21	334 0	1.21
	ν_{19}	3716	3290	1.13	3282	1.1 3
	ν_{20}	1824	1623	1.12	1607	1.14
	ν_{21}	1618	1 472	1.10	1470	1.10
	ν_{22}	1289	1165	1.11	1152	1.1 2
	ν_{23}	1136	904	1.26	910	1.25
	V24	209	-	-	_	-

CALCULATED: EXPERIMENTAL WAVENUMBER RATIOS FOR THE PROPOSED SIX-MEMBERED CYCLIC HYDROXYLAMINE DIMER

^a Calculated at the $RHF/6-31G^{**}$ level.

not predicted by the ab initio calculations at these levels.⁶ Thus $v_{18}^{}$ and $v_{23}^{}$ (antisymmetric NO-stretching) again appear to be overestimated relative to the observed wavenumbers, compared with the other modes. Clearly, calculations at the RHF/6-31G** level tend to underestimate the effects of hydrogen bonding on the computed wavenumbers.

Rationalization of Spectrum with Structure

The principal changes to the monomer spectrum resulting from dimer formation are indicated in Table 7. These include the large red shifts of the OH-stretching bands and the blue shifts of smaller magnitude of the NOH-bending modes, both of which are characteristic of a hydrogen bonding interaction,²² as pointed out by WA.¹³ In addition, the torsional modes, v_{20} (five-membered) or v_{11} (six-membered), show large blue shifts, as a result of the formation of a cyclic hydrogen bonded species, thereby effectively

MATRIX	MO	NOMER		DIM	ER	$\Delta \overline{\nu} /$
	ASSIGNMEN	$T^{a} \overline{\nu}/cm^{-1}$	ASSIGNMENT ^a ,	^b ASSIGNMENT ^{a,c}	$\overline{\nu}/\text{cm}^{-1}$	cm ⁻¹ d
nitrogen	$\nu_1(\mathbf{a}^t)$	3635	$\nu_1(\mathbf{a}^i)$	$\nu_{18}(b_u)$	3346	-289
			$\nu_2(\mathbf{a}')$		3302	-333
	$\nu_2(\mathbf{a}')$	3359	$\nu_3(a')$	(1)	3425	66
			$\nu_4(\mathbf{a}^1)$	$\nu_{19}(b_u)$	3290	-69
	$\nu_3(\mathbf{a}')$	1605	$\nu_{5}, \nu_{6}(a')$	$\nu_{20}(b_u)$	1623	18
	$\nu_4(a^1)$	1367	$\nu_7, \nu_8(a')$	$\nu_{21}(b_u)$	1472	105
	$\nu_5(\mathbf{a}')$	1134	$\nu_{9}, \nu_{10}(a')$	$\nu_{22}(b_u)$	1165	31
	$\nu_6(\mathbf{a}')$	895	$\nu_{11}, \nu_{12}(a')$	$\nu_{23}(b_{y})$	904	9
	$\nu_7(\mathbf{a}^0)$	3472	$\nu_{16}(a'')$	$\nu_9(\mathbf{a}_u)$	3497	25
			$\nu_{17}(a'')$		3444	28
	$\nu_8(a^{\prime\prime})$	1301	$\nu_{18}, \nu_{19}(a'')$	$\nu_{10}(\mathbf{a}_u)$	1290	-11
	$\nu_{g}(\mathbf{a}^{"})$	421	$\nu_{20}(a^{"})$	$\nu_{11}(\mathbf{a}_{u})$	761	34 0
			$\nu_{21}(a'')$		449	28
argon	$\nu_1(\mathbf{a}^t)$	3634	$\nu_1(a^{\dagger})$	$\nu_{18}(b_u)$	334 0	-294
			$\nu_2(\mathbf{a}^i)$		3289	-345
	$\nu_2(\mathbf{a}^t)$	3354	$\nu_3(a')$		3390	36
			$\nu_4(\mathbf{a}^r)$	$\nu_{19}(b_u)$	3282	-72
	$\nu_3(a^1)$	1599	$\nu_5, \nu_6(\mathbf{a}')$	$\nu_{20}(b_u)$	1607	8
	$\nu_4(\mathbf{a}^{r})$	1351	$\nu_{7}, \nu_{8}(a')$	$\nu_{21}(b_u)$	1470	119
	$\nu_5(\mathbf{a}')$	1118	$\nu_{9}, \nu_{10}(a')$	$\nu_{22}(b_u)$	1152	34
	$\nu_6(a^{\dagger})$	896	$\nu_{11}, \nu_{12}(a')$	$\nu_{23}(b_u)$	910	14
	$\nu_7(\mathbf{a^{H}})$	3489	$\nu_{16}(a'')$	$\nu_{g(a_{u})}$	3521	32
			$\nu_{17}(a'')$		3449	-40
	$\nu_8(a^{\prime\prime})$	-	$\nu_{18}, \nu_{19}(a'')$	$\nu_{10}(a_u)$	1289	-
	ν ₉ (a")	374	$\nu_{20}(a^0)$	$\nu_{\rm H}({\rm a_u})$	736	362
			$\nu_{21}(a^{11})$		406	32

OBSERVED WAVENUMBER SHIFTS IN HYDROXYLAMINE SPECTRUM RESULTING FROM DIMERIZATION

^a See references 3 and 6 for descriptions of normal modes of monomer and dimers respectively.

- ^b Five-membered cyclic dimer.
- ^c Six-membered cyclic dimer.
- ^d $\Delta \overline{\nu} = \overline{\nu} (\text{dimer}) \overline{\nu} (\text{monomer}).$

constraining the torsional motion and forcing its frequency upwards.

The observed wavenumber shifts on dimerization may be accommodated equally well by the assumption of either the five-membered or the six-membered cyclic dimer. The choice of one or the other as the more likely dimer must therefore rest on the relative abilities of the observed spectra to reproduce the respective predicted spectra. Since only one dimer band was observed in some of the absorption regions of the perturbed monomer, as predicted for the six-membered species, and since the calculated: experimental wavenumber ratios of this species were found to be more consistent than those of the five-membered cyclic dimer (cf. Tables 5 and 6) we are inclined to propose the six-membered hydrogen bonded cyclic hydroxylamine dimer as that which would be more likely to exist in cryogenic nitrogen or argon matrices. This suggestion is consistent with our finding that the six-membered isomer has the higher dimerization energy and is therefore thermodynamically more stable.⁶

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