J. CHEM. SOC. FARADAY TRANS., 1995, 91(18), 3111-3116

Molecular Complexes of Nitric Acid with N_2, CO and NO studied by Matrix Isolation IR Spectroscopy

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The interaction of nitric acid with dinitrogen, carbon monoxide and nitric oxide has been investigated by IR spectroscopy in low-temperature argon matrices. The spectra show that under these conditions N_2 interacts strongly and specifically with HNO_3, forming several distinct 1 : 1 complexes. The probable structures of these complexes are discussed. CO behaves in a similar manner to N_2, forming complexes of the type $O{\equiv}C\cdots H{-}ONO_2$; weak bands due to a $C{\equiv}O\cdots H{-}ONO_2$ complex were generated by photolysis. For NO, complexes of HNO_3 were observed with both monomeric and dimeric NO. The strength of interaction with HNO_3 was found to increase in the order $N_2 < NO < CO$.

HNO_3 is an important atmospheric species, acting as a stratospheric reservoir for NO_x; its relative stability allows it to be transported down to the troposphere where it is eventually rained out of the atmosphere. It is a fundamental constituent of polar stratospheric clouds, which are composed of HNO_3 ice based on a core of sulfuric acid, and it can also be incorporated into aerosols by reaction with ammonia to form ammonium nitrate.

Lee and co-workers[1,2] reported spectra of HNO_3 in both argon and nitrogen matrices as part of a study of its photolytic behaviour in low-temperature matrices. They point to the large shifts between argon and nitrogen matrices of the O—H stretching and NOH in-plane bending modes as evidence of a strong interaction between HNO_3 and N_2, but apparently did not look for an HNO_3–N_2 complex in argon matrices.

As part of a wider study of the hydrogen-bonded molecular complexes of HNO_3 with a variety of molecules of atmospheric significance,[3] we examined the interaction of HNO_3 with N_2 in argon matrices and found evidence of a number of distinct 1 : 1 complexes. The present work reports a detailed investigation of the complexes of HNO_3 with N_2, and the related molecules CO and NO, in argon matrices.

Experimental

HNO_3 was prepared by vacuum distillation from a 1 : 1 mixture of concentrated sulfuric acid and potassium nitrate and collected at −40 °C. For N_2 or CO as bases, a mixture of base, HNO_3 and matrix gas (argon) was prepared using standard manometric techniques. For NO, separate mixtures of base–matrix gas and HNO_3–matrix gas were prepared. In a typical experiment, the mixture was sprayed onto a caesium iodide window maintained at a fixed temperature of 5 K, 15 K or 20 K by an Air Products HS-4 Heliplex refrigeration system so as to give an overall ratio of *ca.* 1 : 1 : 200. The window was pre-coated with a layer of pure matrix gas to inhibit reaction between HNO_3 and the window material. IR spectra were recorded, with the matrix normally maintained at *ca.* 5 K, at 1 cm^{-1} resolution using a Bruker IFS-88 Fourier transform IR spectrometer.

Results

N_2–HNO_3 Complexes

Spectra of N_2 : HNO_3 : Ar matrices at concentrations around 1 : 1 : 200, deposited at 15 K, showed a number of prominent new absorptions. The most intense new band in the OH stretching region was at 3488 cm^{-1}, a medium intensity band appeared at 3484 cm^{-1} and there were other weak absorptions on both the high and low wavenumber sides of these bands (monomer HNO_3 absorbs at 3522 cm^{-1}). Varying the ratio of N_2 : HNO_3 from 1 : 2 to 2 : 1, while keeping the HNO_3 : Ar ratio constant at 1 : 200, had little or no effect on the relative intensities of these absorptions. Annealing the matrix at *ca.* 30 K for a few minutes also had no effect on these absorptions, despite the formation of some HNO_3 dimer (characterised by absorptions around 3216 cm^{-1}). Deposition of a 1 : 1 : 200 mixture at 5 K led to very little complex being formed; annealing this matrix at 32 K for a few minutes led to the appearance of the 3488 and 3484 cm^{-1} bands but with little trace of the high- and low-wavenumber components. However, deposition of a similar mixture at 20 K had a dramatic effect on the spectrum: there was practically no trace of monomer HNO_3, the 3488 cm^{-1} band was very intense, and the 3484 cm^{-1} band had disappeared (Fig. 1). The high (3502, 3498 and 3496 cm^{-1}) and low (3486, 3482 and 3479 cm^{-1}) wavenumber absorptions had increased a little in intensity and the high wavenumber bands were considerably sharper. Deposition of a mixture containing excess N_2 (*ca.* 3 : 1 : 200) at 20 K resulted in a spectrum dominated by an absorption with a peak at 3479 cm^{-1} and a broader component at 3481 cm^{-1}; the 3486 cm^{-1} feature had also become more prominent.

Similar behaviour was evident (Fig. 1) in the NOH torsion region of the spectrum, where the monomer band is at 451 cm^{-1}. It is convenient to label the bands as type A, B, C or D according to their behaviour; type A bands are the most intense in 1 : 1 mixtures under all deposition conditions, type B bands are those that disappear in the spectra of matrices deposited at 20 K, type C bands are the weaker absorptions which become more prominent with increasing deposition temperature but do not display concentration dependence, while type D bands are those that become dominant in the spectrum of the 3 : 1 mixture deposited at 20 K. In this region the type A and B bands were found at 526 and 534 cm^{-1}, respectively. A number of weaker absorptions were apparent on either side of the main band, the most prominent being at 540 and 531 cm^{-1} on the high-wavenumber side and at 521 and 493 cm^{-1} on the low-wavenumber side. Although all these absorptions became more intense in the spectrum of a matrix deposited at 20 K, by far the largest increase in intensity was displayed by the band at 493 cm^{-1}. The 531 cm^{-1} band showed type D behaviour, while the other bands

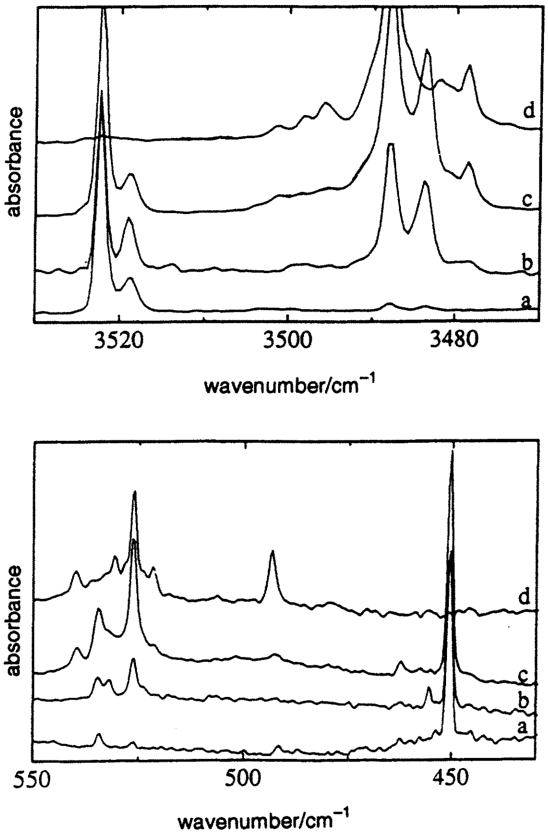

Fig. 1 OH stretching (upper) and NOH torsion (lower) regions of the spectrum, recorded at 5 K, from (a) HNO_3 : Ar (1 : 100) deposited at 15 K, (b) N_2 : HNO_3 : Ar (1 : 1 : 200) deposited at 5 K, then annealed at 32 K, (c) N_2 : HNO_3 : Ar (1 : 1 : 200) deposited at 15 K and (d) N_2 : HNO_3 : Ar (1 : 1 : 200) deposited at 20 K

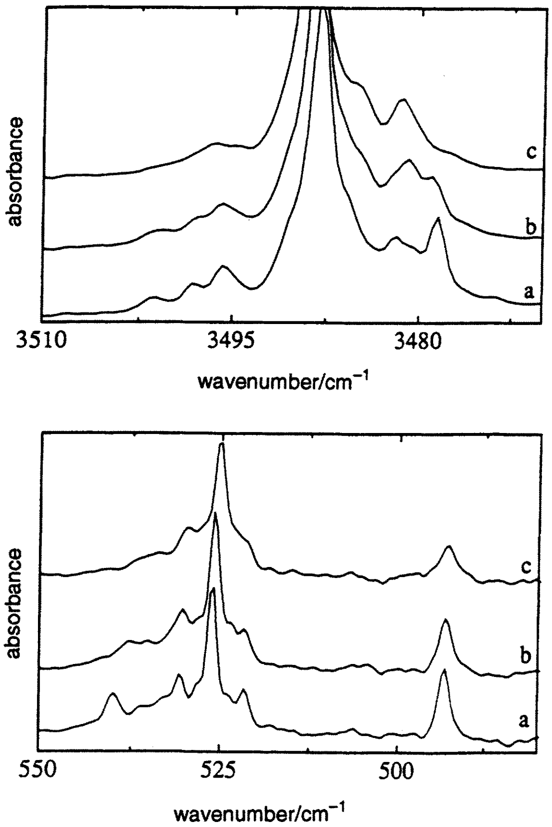

Fig. 2 OH stretching (upper) and NOH torsion (lower) regions of the spectrum of N_2 : HNO_3 : Ar (1 : 1 : 200), deposited at 20 K, and recorded at: (a) 5, (b) 20 and (c) 30 K

behaved as type C. Weaker type D absorptions were also observed at 536 and 480 cm^{-1} and as shoulders on either side of the 531 cm^{-1} band.

A remarkable feature of the type C/D bands is that they exhibit reversible temperature dependence (Fig. 2). As the temperature at which the spectrum was recorded was raised from 5 K to 30 K the bands broadened and, in many cases, virtually disappeared. Cooling the matrix back to 5 K restored the original spectrum.

New bands attributed to the NOH in-plane bending mode (monomer band at 1304 cm^{-1}) appeared in the region of *ca.* 1350–1340 cm^{-1} and showed similar characteristics, although with a much smaller spread of wavenumbers (Fig. 3). The type A band was at 1346 cm^{-1}, the type B band at 1350 cm^{-1} and type C/D bands were apparent at 1352 and 1342 cm^{-1}.

New absorptions were also observed in other regions of the spectrum, but the behaviour was not always as clear because of overlapping bands of HNO_3 monomer and dimer, as well as overlapping of bands of type A, B, C and D in many cases. The $-NO_2$ antisymmetric stretching mode (1699 cm^{-1}) shifted slightly to lower wavenumbers, the type A maximum apparently being at 1694 cm^{-1}, the type B maximum at 1691 cm^{-1} and the type D maximum at 1693 cm^{-1}. The persistence of an intense band at 1699 cm^{-1}, even in spectra where the other monomer HNO_3 bands were extremely weak, suggests that there is also a complex band at this position.

In the $-NO_2$ symmetric stretching region (monomer 1321 cm^{-1}), the type A band was prominent at 1308 cm^{-1} and the type B band appeared to be at 1299 cm^{-1} (in the spectrum of the matrix deposited at 5 K both the 1299 cm^{-1} band and that at 534 cm^{-1} split into doublets) with an almost coin-

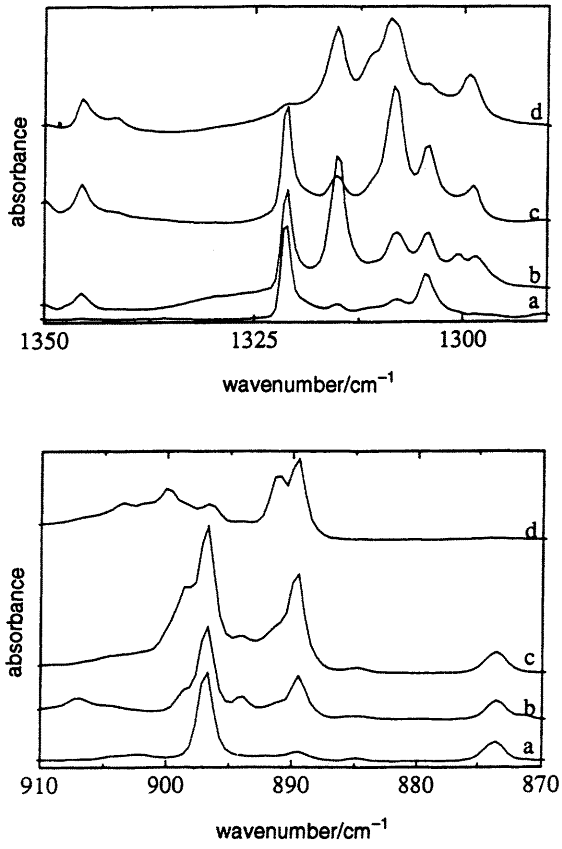

Fig. 3 NOH bending and NO_2 symmetric stretching (upper) and O—N stretching (lower) regions of the spectrum, recorded at 5 K, from samples (a)–(d) as in Fig. 1

cident type C band at 1300 cm^{-1}; the type D band occurred at 1311 cm^{-1} (Fig. 3).

Several new features were apparent (Fig. 3) in the O—N stretching region: the type A band was evident at 890 cm^{-1}, the shoulder at 899 cm^{-1} on the 897 cm^{-1} monomer band showed type B behaviour, a band at 900 cm^{-1} behaved as type C, while bands at 903 and 891 cm^{-1} appeared to be type D.

Weak new absorptions (most likely overlapping bands of the different types) were also observed at 766 and 594 cm^{-1} for the ONO_2 bending modes (out-of-plane 764 cm^{-1}, in-plane 588 cm^{-1}). There as no evidence of any absorption due to the N≡N stretching mode of perturbed N_2 molecules.

In two experiments (samples deposited at 15 K and 20 K) the matrix was subsequently exposed to the full light from a mercury lamp for 2 h. Although some photolysis had occurred, evidenced by loss of intensity of bands due to HNO_3, only very weak product absorptions were observed. These corresponded to bands of the HOONO isomer of HNO_3 observed by Cheng *et al.*[1] in the photolysis of HNO_3 in argon matrices. There was no trace of any absorption due to N_2O or HONO, which were the major products when HNO_3 was photolysed in a nitrogen matrix.[2]

CO–HNO$_3$ Complexes

Spectra of CO : HNO_3 : Ar matrices showed rather similar behaviour to that observed for N_2 : HNO_3 : Ar matrices. The new bands could be classified in the same way as type A, B, C or D, although there were some small differences: for example, the type B bands did not disappear completely in the spectrum of a matrix deposited at 20 K and the type C/D bands did not exhibit such strong temperature dependence. In the OH stretching region (Fig. 4), the type A band was located at 3399 cm^{-1} while two bands, at 3390 and 3369 cm^{-1}, were found to exhibit type B behaviour. A number of type C/D bands were observed, all on the low-wavenumber side of the main band, at 3386, 3383, 3373, 3366 and 3359 cm^{-1}; the last band became relatively prominent in the spectrum of the matrix deposited at 20 K and may thus be assigned as type D. In the NOH torsion region (Fig. 4), the type A and B bands were found at 589 and 600 cm^{-1}, respectively. A number of type C/D bands appeared on both the high (612 and 595 cm^{-1}) and low (581 and 526 cm^{-1}) wavenumber side of the main band. The bands observed in other regions of the HNO_3 spectrum were very similar to those observed for complexes of N_2 with HNO_3.

In the CO stretching region, a number of bands appeared on the high-wavenumber side of the isolated C≡O stretching mode at 2139 cm^{-1} (and also the aggregate band at 2143 cm^{-1}). Type A behaviour was manifested by a band at 2164 cm^{-1}, a band at 2167 cm^{-1} appeared to behave as type B, and the remaining absorptions (2168, 2161 and 2149 cm^{-1}) have to be assigned to type C/D.

Photolysis of the matrix deposited at 20 K, with the full light of a mercury lamp for 2 h, led to the appearance of prominent new absorptions due to carbon dioxide (2346 cm^{-1}) and the *trans* isomer of nitrous acid (at 3516, 1695 and 1305 cm^{-1}); there was no trace of any absorptions due to the *cis* isomer of nitrous acid. Very weak bands also appeared at 2128, 1335, 887, 737 and 498 cm^{-1}.

NO–HNO$_3$ Complexes

Spectra of NO : HNO_3 : Ar matrices at concentrations around 1 : 1 : 200, deposited at 15 K, showed a number of prominent new absorptions. In the OH stretching region (Fig. 5), the most intense new bands were at 3404 and 3376

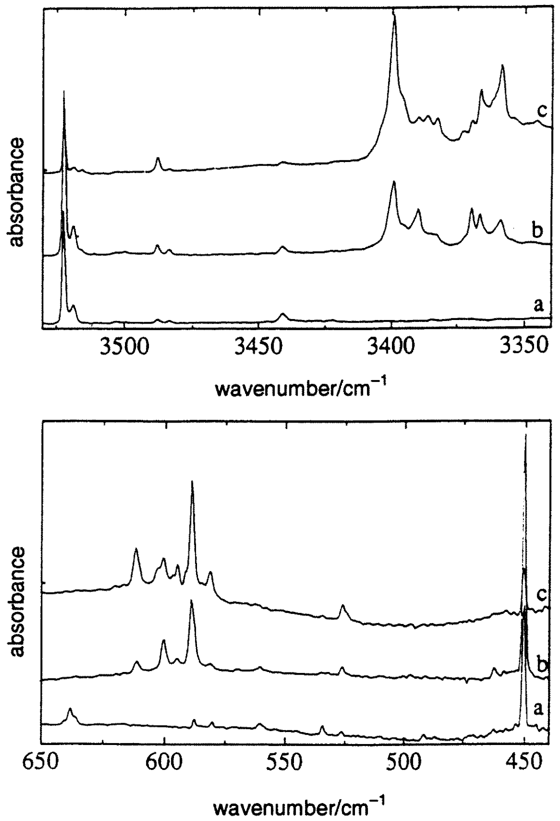

Fig. 4 OH stretching (upper) and NOH torsion (lower) regions of the spectrum, recorded at 5 K, from (a) HNO_3 : Ar (1 : 100) deposited at 15 K, (b) CO : HNO_3 : Ar (1 : 1 : 200) deposited at 15 K and (c) CO : HNO_3 : Ar (1 : 1 : 200) deposited at 20 K

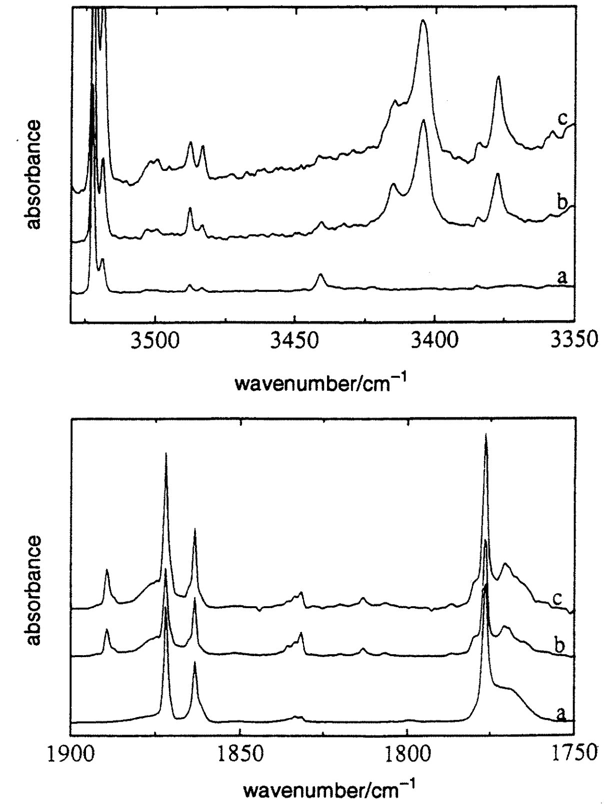

Fig. 5 OH stretching (upper) and NO stretching (lower) regions of the spectrum of NO : HNO_3 : Ar (1 : 1 : 200), recorded at 5 K, from (a) HNO_3 : Ar (1 : 100) deposited at 15 K or NO : Ar (1 : 100) deposited at 5 K, (b) NO : HNO_3 : Ar (1 : 1 : 200) deposited at 15 K and (c) NO : HNO_3 : Ar (2 : 1 : 200) deposited at 15 K

cm^{-1}, with weaker bands at 3414 and 3385 cm^{-1}, and a broad absorption at *ca.* 3350 cm^{-1}. New bands were evident in the NOH torsion region at 560 and 570 cm^{-1}, and in the NOH in-plane bending region at 1360 cm^{-1}. New bands, similar to those observed for the N_2 and CO complexes, were also found in other regions of the HNO_3 spectrum.

In the NO stretching region, a new band was observed at 1889 cm^{-1}, on the high-wavenumber side of the isolated NO stretching mode at 1872 cm^{-1}. A weak band at 1813 cm^{-1} was also observed, on the high-wavenumber side of the absorption due to the *cis* dimer of NO (1776 cm^{-1}).

Increasing the ratio of NO : HNO_3 from 1 : 1 to 2 : 1, while keeping the HNO_3 : Ar ratio at 1 : 200, increased the relative intensity of the band at 3376 cm^{-1}. Photolysis of the 2 : 1 : 200 NO : HNO_3 : Ar sample, deposited at 15 K, did not reveal any significant product bands.

Discussion

The bands observed for the various complexes of HNO_3 with N_2, CO and NO are summarised in Table 1.

N_2–HNO_3 Complexes

In low-temperature noble gas matrices, N_2 interacts strongly with a variety of molecules. The interaction is invariably a specific one with an X—H group in the molecule, for example the OH group of an alcohol.[4] Fig. 6 depicts some possible structures for an $N_2\cdots HNO_3$ complex. By analogy with complexes previously reported, a structure of the type shown in Fig. 6(a) would be expected. However, Chen *et al.*,[2] on the basis of the comparatively large shift in the HNO_3 fundamentals between argon and nitrogen matrices, suggested that a complex with structure (b) might be formed.

The behaviour manifested by the type A and B bands, observed in the present work, demonstrates that they must arise from specific 1 : 1 complexes between N_2 and HNO_3. The shifts observed for these complexes are considerably greater than those between argon and nitrogen matrices, thus the interaction in the nitrogen matrix must be general rather than specific. Since the shifts observed for the OH vibrations of the type A complex are consistently large (-34 cm^{-1} for the OH stretch, $+42$ cm^{-1} for the NOH in-plane bend and $+75$ cm^{-1} for the NOH torsion) the interaction has to be a pseudo-hydrogen bond with the O—H group, *i.e.* a structure similar to that depicted in Fig. 6(a). The shifts observed for the vibrational modes of the ONO_2 group are all small, but this provides no clear evidence about the site of interaction since these modes also show only small shifts in the HNO_3 dimer. The difference between the type B complex and the type A complex is small for all the vibrational modes, thus the difference between the structures must also be small. Plausibly, the type B complex, which has the lower O—H stretching wavenumber, has a linear arrangement of the O—H···N≡N hydrogen bond, whereas the type A complex has a non-linear arrangement of the hydrogen bond so as to give the most favourable overall configuration in the matrix cage (which can be more readily achieved at the higher deposition temperature). Since the dipole moment of HNO_3 is inclined at an angle of nearly 40° to the O—H bond,[5] the dipole–quadrupole interaction with an N_2 molecule will be

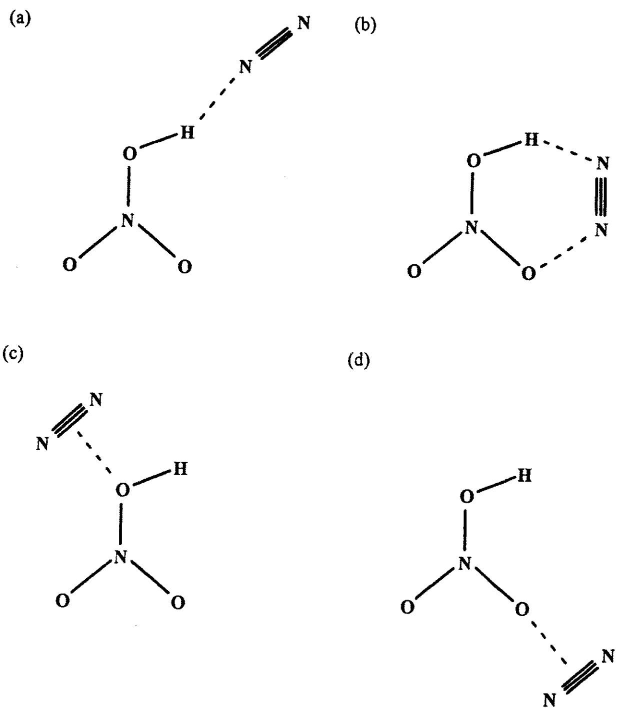

Fig. 6 Possible structures for an N_2–HNO_3 complex

Table 1 Summary of bands observed (cm^{-1}) in the O—H stretching, NOH torsion and base molecule stretching regions for the various HNO_3 complexes

complex	type	OH stretch	NOH torsion	CO/NO stretch
monomer		3522	451	2139/1872
N≡N···H—ONO_2	A	3488	526	
	B	3484	534	
	C	3502		
		3498		
		3496	493	
		3486	521	
		3482	540	
	D	3479	531	
O≡C···H—ONO_2	A	3399	589	2164
	B	3390	600	2167
		3369		
	C	3386	526	2168
		3383	581	2161
		3373	595	
		3366	612	
	D	3359		2149
C≡O···H—ONO_2			498	2128
O=N···H—ONO_2		3404	560	1889

most favourable for a complex in which the O—H···N≡N arrangement is non-linear.

The assignment of the type C/D bands to specific complexes is more difficult. It is difficult even to correlate the bands in the O—H stretching region with those in the NOH torsion region because of the number of overlapping absorptions. The behaviour of the type D bands shows that they are due to 2 : 1 or *n* : 1 $N_2 : HNO_3$ complexes; those bands which are present in the spectra of 1 : 1 mixtures must be due to 2 : 1 complexes while the absorptions appearing only in the spectra of mixtures with excess N_2 are likely to be higher-order complexes. Thus the 3479 and 531 cm^{-1} bands may be assigned to a 2 : 1 complex. The strong, reversible, temperature dependence observed for the type C (and D) bands suggest that the interaction is less well defined than for the type A and type B complexes, so that the distinction between different structures becomes blurred as the temperature of the matrix is increased. Among the type C bands, those at 3496 and 493 cm^{-1} exhibit the strongest growth between the spectra deposited at 15 K and 20 K and are probably due to the same (1 : 1) complex. The relatively small shift of the NOH torsion suggests a complex with a smaller interaction between the N_2 molecule and the O—H group of the HNO_3, for example a structure of the type shown in Fig. 6(c).

CO–HNO_3 Complexes

The behaviour exhibited by CO–HNO_3 mixtures in argon matrices is sufficiently similar to that found for N_2–HNO_3 mixtures for the spectra to be assigned in an analogous manner. As would be expected, the interaction is stronger than for N_2, giving shifts of the OH vibrations of the type A complex of -123 cm^{-1} for the O—H stretch, $+75$ cm^{-1} for the NOH in-plane bend and $+138$ cm^{-1} for the NOH torsion. Since the C≡O stretching mode is shifted to higher wavenumbers, the structure of the complex must be of the type O≡C···H—ONO_2 as found for other CO complexes, for example with the hydrogen halides in matrices[6–9] and in the gas phase[10] or with methanol in the gas phase.[11]

Photolysis of the CO–HNO_3 matrix gave intense product bands due to CO_2 and *trans*-HONO. The nitrous acid bands, particularly the O—H stretch, are appreciably shifted from those of the isolated molecule[12] suggesting that the products (which will be generated in the same matrix cage) are linked by a weak hydrogen bond. The weak product band at 2128 cm^{-1}, in the CO stretching region but on the low-wavenumber side of the band due to the isolated CO molecule, suggests that a small amount of the less stable complex C≡O···H—ONO_2 is generated by the photolysis (*cf.* the C≡O···H—F complex whose CO stretch was observed by Schatte *et al.*[9] at 2129 cm^{-1}, compared with 2139 cm^{-1} for monomer CO and 2162 cm^{-1} for the O≡C···H—F complex). The 1335, 887 and 498 cm^{-1} bands can then be assigned to the NOH in-plane bending, O—N stretching and NOH torsion modes of this weaker complex.

NO–HNO_3 Complexes

Although interpretation of the spectra of the NO : HNO_3 : Ar matrices is complicated by the presence of NO dimer, the regions in which the perturbed HNO_3 modes occur are much simpler than for the N_2- or CO-containing matrices. The bands observed are readily assigned by analogy with those observed by Davis *et al.*[13] in NO : HF : Ar matrices. Thus the 3404 cm^{-1} band, with a high-wavenumber component at 3414 cm^{-1}, is due to the complex between HNO_3 and monomer NO, while the band at 3376 cm^{-1}, with a high-wavenumber component at 3385 cm^{-1}, is due to a complex between HNO_3 and NO dimer. The perturbed NO stretching mode of the NO monomer–HNO_3 complex (1889 cm^{-1}) is observed at a very similar wavenumber to that for the NO–HF complex (1887 cm^{-1}). The NO absorption of the NO dimer–HNO_3 complex (1813 cm^{-1}) is also very close to the corresponding band for HF (1811 cm^{-1}). The strength of interaction of NO with HNO_3 lies between that of N_2 and CO, the shifts of the OH vibrational modes being -118 cm^{-1} for the O—H stretch, $+56$ cm^{-1} for the NOH in-plane bend, and $+109$ cm^{-1} for the NOH torsion.

These results provide no immediate pointer as to whether the HNO_3 forms a hydrogen bond to the nitrogen or the oxygen atom of NO, although by analogy with CO the blue shift of the NO stretching mode could suggest bonding to the nitrogen atom. Estimation of the proton affinity of the nitrogen and oxygen sites of the NO molecule, from thermochemical data[14] for HNO^+ and NOH^+, gave 549 and 474 kJ mol^{-1}, respectively, strongly suggesting the nitrogen atom as the proton acceptor site for a hydrogen bond. The shift of the HX stretching frequency in base–hydrogen halide complexes correlates reasonably well with the proton affinity of the base.[15] Assuming that a similar correlation holds for HNO_3 complexes, the higher value for the proton affinity of NO fits well with the value expected from comparison of the shift in the OH stretching frequency with those in the complexes with N_2 ($E_{pa} = 495$ kJ mol^{-1}) and CO ($E_{pa} = 594$ kJ mol^{-1}). Davis *et al.*[13] suggested that the HF complex has the structure NO···HF, on the basis of *ab initio* calculations and comparison with other complexes. However, de Saxce *et al.*[16] have recently studied the complexes of NO with HCl and HBr in argon matrices and carried out *ab initio* calculations which predicted that a linear ON···HCl complex is the most stable structure. The formation of ClNO on photolysis of the complex also suggested that the HCl interacts with the nitrogen atom rather than with the oxygen atom.

Conclusion

In a low-temperature inert matrix environment N_2, CO and NO all interact strongly and specifically with HNO_3 to form various 1 : 1 and higher-order complexes, the strength of interaction in the 1 : 1 complexes increasing in the order $N_2 < NO < CO$ (the strength of interaction in complexes of HF with these molecules increases in the same sequence).

Financial support from the Norwegian Research Council is acknowledged, and A.J.B. thanks the Norwegian Research Council for a Visiting Fellowship at the University of Oslo.

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Paper 5/02845K; *Received* 3rd *May*, 1995