The Dimeric Nitrogen Oxides. Part I. Electronic Absorption of the Nitrogen Oxide Dimer, and Comparison of Observed and Calculated Spectra for Dinitrogen Dioxide, Trioxide, and Tetraoxide

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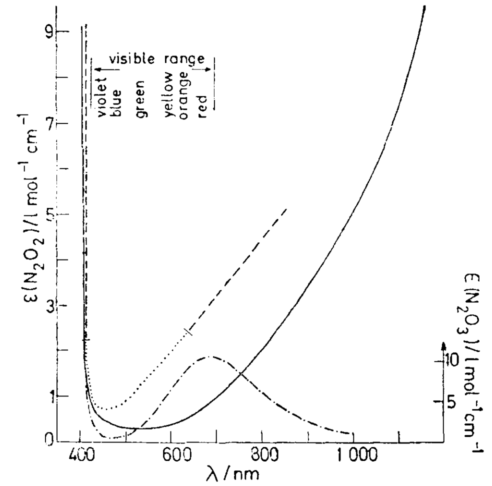
The spectrum of liquid nitrogen oxide, NO, in the visible and near-i.r. region is reported. Nitrogen oxide in condensed phases is colourless, and the colours commonly reported are due to contamination, notably with dinitrogen trioxide. Reasonable agreement has been found between the electronic absorption measured for dinitrogen dioxide, N_2O_2, trioxide, N_2O_3, and tetraoxide, N_2O_4, and the transitions predicted by the CNDO/S method of Del Bene and Jaffe. For N_2O_2 this describes the near-i.r. band as $(\sigma,n_O,n^*)\rightarrow\pi^*$ and the strong u.v. absorption as $(\sigma,n_O,n^*)\rightarrow\sigma_{NN}^*$. The low energy of the magnetically active transition probably accounts for the feeble paramagnetism of the dimer molecule. For N_2O_3 the visible-absorption band is given as $(n_O,n^*,\sigma_{NN})\rightarrow\pi^*$ and the strong u.v. absorption as $\pi_O\rightarrow\pi^*$. For N_2O_4 the two fairly weak u.v. bands are calculated as $n^*\rightarrow\pi^*$ and $\pi^*\rightarrow\sigma^*$ respectively, and the strong u.v. band as a mixture of $n^*\rightarrow\sigma^*$ and $\pi_O\rightarrow\pi^*$.

GASEOUS nitrogen oxide, NO, is monomeric at normal pressures, but the liquid and solid contain the *cis*-dimer O:N·N:O as shown by i.r.,[1] Raman,[1a] and *X*-ray crystallographic[2] measurements, supported by the magnetic[3] and thermodynamic[4] properties. When purified as in the Experimental section, solid nitrogen oxide is white and the liquid colourless, as reported by many workers[5] beginning with an early cryogenist in 1885. Many other workers, however, found condensed nitrogen oxide to be blue, and it is so described in most of the reference literature of 1974,[6] following the standard work[4a] on the tensimetric and thermodynamic properties by Johnston and Giauque, who were emphatic that their liquid and solid nitrogen oxide was highly pure and deeply blue, and the electronic spectra of Vodar[7] and Bernstein and Herzberg,[8] recorded on blue liquids. Other workers have described liquid nitrogen oxide as slate-blue, straw-green, light blue-green, *etc.*

Nitrogen oxide gas is transparent down to 230 nm under normal conditions.[8] The Figure contains a plot of Vodar's spectrum[7] of liquid nitrogen oxide at —150 °C as extended by his co-worker Mayence,[9] and 'confirmed' by Bernstein and Herzberg[8] who reported short and long wavelength cut-offs at 400 and 560 nm respectively for 3 cm of the liquid. Also drawn in the Figure is the absorption spectrum of liquid nitrogen oxide measured as described below: 1 cm of the liquid is opaque from 410 to 200 nm, and from 1 200 to 2 000 nm. The spectrum of N_2O_3 is given on a reduced scale: the visible band is blue shifted in polar media,[10] but it is likely that the position found[11] for liquid N_2O_3 mixed with N_2O_4, which is transparent above 400 nm, is reasonably close to that for N_2O_3 in liquid N_2O_2. The Figure shows that a small concentration (less than 0·002 mol fraction) of N_2O_3 in N_2O_2 could in principle account for the long-wavelength cut-off which was previously reported in the visible[7-9] and is now shifted well into the near-i.r. region. Dinitrogen trioxide is very deep blue and is difficult to exclude completely. Nitrogen oxide gives NO_2 with oxygen adsorbed on vessels or solids that have not been flamed out *in vacuo*; NO and NO_2 give N_2O_3.



The visible and near-i.r. spectrum of liquid N_2O_2 (——) compared with earlier determinations [(· · · ·), ref. 7; (— — —), ref. 9] and with the spectrum of liquid N_2O_3 (— · — · —). The molar absorption coefficients are based on N_2O_2 and N_2O_3; note the reduced scale for N_2O_3 (given on the right-hand side)

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[2] (*a*) W. J. Dulmage, E. A. Meyers, and W. N. Lipscomb, *Acta Cryst.*, 1953, **6**, 760; (*b*) W. N. Lipscomb, F. E. Wang, W. R. May, and E. L. Lippert, *ibid.*, 1961, **14**, 1101.

[3] (*a*) A. L. Smith and H. L. Johnston, *J. Amer. Chem. Soc.*, 1952, **74**, 4696; (*b*) E. Lips, *Helv. Phys. Acta*, 1935, **8**, 247; H. Bizette and B. Tsai, *Compt. rend.*, 1938, **206**, 1288; 1937, **204**, 1638.

[4] (*a*) H. L. Johnston and W. F. Giauque, *J. Amer. Chem. Soc.*, 1929, **51**, 3194; (*b*) O. K. Rice, *J. Chem. Phys.*, 1936, **4**, 367; E. A. Guggenheim, *Mol. Phys.*, 1966, **10**, 401; **11**, 403.

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[6] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, 1972, p. 357; 'Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, H. J. Emeléus, R. S. Nyholm, and A. F. Trotman-Dickenson, Pergamon, 1973, vol. 2, p. 325; 'Handbook of Chemistry and Physics,' Chemical Rubber Company, Cleveland, Ohio, 1973—1974, B-115; W. L. Jolly, 'Inorganic Chemistry of Nitrogen,' Benjamin, 1964, p. 73; but see J. R. Partington, 'General and Inorganic Chemistry,' Macmillan, 1967, p. 570.

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[8] H. J. Bernstein and G. Herzberg, *J. Chem. Phys.*, 1947, **15**, 77.

[9] L. Mayence, *Ann. Physique*, 1952, **7**, 453.

[10] J. Mason, *J. Chem. Soc.*, 1959, 1288.

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Compressed or liquid nitrogen oxide also slowly disproportionates at room temperature to N_2O and N_2O_3.[12] The Figure shows that pure liquid nitrogen oxide is transparent across the region to which the eye is sensitive.

In the u.v. region, Bernstein and Herzberg [8] reported a continuum below 260 mm for 1 m of nitrogen oxide gas at 30 atm and normal temperatures and ascribed this absorption to HNO_2 impurity or perhaps to N_2O_2.* With 1 m of pure nitrogen oxide gas near the b.p. (−152 °C) D'Or *et al.*[13] observed diffuse bands at 232—236 nm and continuous absorption below 230 nm which disappeared on warm-up. The band system suggested a wavenumber interval of *ca.* 140 cm^{-1} which they compared with a Raman fundamental at 167 cm^{-1} for the liquid.[1a] Recently the u.v. spectrum of N_2O_2 has been measured by Billingsley and Callear [14] using flash spectroscopy. They found that the continuum has oscillator strength (*f* value) 0·26 and sets in at 245 nm at −173 °C (250 nm at room temperature) reaching a maximum at 205 nm; the diffuse bands at 232—236 nm are prominent at the lowest temperatures.

EXPERIMENTAL

Nitrogen oxide was made by reduction of aqueous nitrous acid by iodine.[4a] The gas was shaken with the aqueous solution, passed through KOH pellets, and distilled to give a pale yellow-green product. The liquid was colourless only after slow fractional evaporation at low temperatures, a few degrees above liquid-nitrogen temperature, the last fractions which contained N_2O and N_2O_3 being removed. The liquid interval of nitrogen oxide at atmospheric pressure is fairly short, −152 to −164 °C. The electronic spectrum was measured at −160 °C with melting i-pentane as refrigerant in an all-quartz Dewar-jacketed cell with 1 cm path length.

RESULTS AND DISCUSSION

The Electronic Absorption.—We can compare the N_2O_2 spectrum with those of the analogous molecules $ON{\cdot}NO_2$ and $O_2N{\cdot}NO_2$ with the help of Del Bene and Jaffe's CNDO/S program.[15] This predicts valence-shell transitions using CNDO wave functions refined by configuration interaction (CI) over the 30 lowest singly excited states, with the inclusion of *s–p* overlap in the calculation of transition moments so that these do not vanish for $n \rightarrow \pi^*$ transitions allowed by local symmetry.[16]

The molecular geometry used for the N_2O_2 calculations was obtained by *X*-ray crystallographic measurement of the solid at −175 °C.[2b] This showed the solid to consist of the *cis*-dimer, as also does the liquid, according to the i.r. and Raman spectra, in which no sign of the *trans*-form could be detected.[1a] Unstable forms of N_2O_2 (as of N_2O_3 and N_2O_4) can be detected by matrix-isolation studies,[1b,c] but these show the *cis* to be the stable form, as does the i.r. spectrum of gaseous N_2O_2.[1d] The molecular dimensions in fluid phases may not differ very greatly from those in the solid since the i.r. frequencies are similar: ν_{sym} and ν_{asym} are found at 1 862—1 870 and 1 776 for the solid, at 1 863 and 1 770 for the liquid, and at 1 860 and 1 788 cm^{-1} for the gas.[1] For N_2O_3 the molecular geometry has been found by microwave spectroscopy [17] at −80 °C, and for N_2O_4 electron-diffraction [18] measurements at −20 °C were used. In each molecule the *x* axis lies along the N·N bond and the *y* axis is perpendicular to the molecular plane.

The Table compares the electronic absorption observed for N_2O_2, N_2O_3, and N_2O_4 with the bands calculated to fall above 200 nm. For N_2O_2 the transitions are all from the highest-occupied orbital (A_1) which is of (σ, n_O, n^*) type: it contains p_σ electrons in the weak N·N bond, and in the much weaker O·O bond formed by overlap of the $2p$ lone-pair orbitals on oxygen, n_O. It contains also $\pi_{NO}'^*$ electrons in the antibonding in-plane π (*i.e.* π') orbital formed by overlap of the n_N and n_O lone-pair orbitals. We refer to these π'^* electrons as n^*, and to the corresponding π' bonding electrons as n, in the NO groups of N_2O_2 and N_2O_3.

The partly allowed transition at 1 286 nm is consistent with the rising absorption in the near-i.r. region, the transition at 976 nm is symmetry forbidden, and the fully allowed u.v. transition accords with the observations of Billingsley and Callear [14] and D'Or *et al.*[13] It seems that the continuum and the banded absorption belong to the same system, since the next calculated bands are some way away (two triplets near 190 nm and singlets beyond 180 nm). The upper orbital (B_1) of the u.v. transition is N·N antibonding (and still n^*) so the transition has $\sigma_{NN} \rightarrow \sigma_{NN}^*$ character and excitation of the N·N stretching frequency is not unexpected (*cf.* ground-state frequencies [1a] at 167 and 196 cm^{-1}). The N·N stretching frequencies for N_2O_3 and N_2O_4 are at 260 and 265 cm^{-1} respectively. In the CNDO approximation the singlet and triplet are degenerate in bands of n or $\sigma \rightarrow \pi^*$ type. There is the possibility in these dimeric oxides near their b.p.s of triplet enhancement by the paramagnetic monomer(s), but none of the observed bands seem to be triplets. There remains the possibility of overtones of vibrational frequencies being observed in the near-i.r. region with 1 cm path lengths of the neat liquid. The first overtones of the NO stretching frequencies (at 1 863 and 1 770 cm^{-1}) were observed at 3 708 and 3 515 cm^{-1}, and possibly a second overtone at *ca.* 5 200 cm^{-1}.[1a] Very faint structure on the ascending curve of the N_2O_2 electronic spectrum at

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* 1 atm = 101 325 Pa.

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[13] L. D'Or, A. de Lattre, and P. Tarte, *J. Chem. Phys.*, 1951, **19**, 1064.

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[15] J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, 1968, **48**, 1807, 4050; **49**, 1221; 1969, **50**, 1126; J. T. D'Agostino and H. H. Jaffe, *J. Amer. Chem. Soc.*, 1970, **92**, 5160; R. L. Ellis, R. Squire, and H. H. Jaffe, *J. Chem. Phys.*, 1971, **55**, 3499.

[16] R. L. Ellis, G. Kuehnlenz, and H. H. Jaffe, *Theor. Chim. Acta*, 1972, **26**, 131.

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longer wavelengths might possibly represent the fifth or sixth overtones, but it is barely outside experimental uncertainty.

For N_2O_3 the highest-occupied orbital (A') is again of (σ,n) type. It contains n_O electrons (a bonding combination) in the NO_2 group, n^* electrons in the NO group, and also σ_{NN} (and to a smaller extent σ_{NO}) bonding electrons. The highest-occupied π orbitals are non-bonding, mainly on NO_2-oxygen (π_O) for N_2O_3 and for N_2O_4. The π_1^* orbital is mainly on the NO group and the π_2^* mainly on the NO_2 group. The visible band is well predicted as $(n_O,n^*,\sigma) \rightarrow \pi_1^*$; the blue shifts in polar solvents[10,19] are often diagnostic of transitions of n electrons. The next three predicted bands are only weakly allowed, by a small $s \rightarrow p$ component in the $p \rightarrow p$ excitations, and at shorter wavelengths may be masked by the strong u.v. absorption. For this the calculation gives a strong band at 227 nm due to excitations of π_O and n_O^* electrons, and a weaker one at 249 nm which involves charge transfer (c.t.) from the NO_2 to the NO group. This is matched by the u.v. spectrum of N_2O_3 which consists of a strong band at 225 nm for the gas which is red-shifted in solution, but which shows a blue shift of 1 350 cm^{-1} from n-hexane to aqueous solution.[19]

Electronic absorption of the dimeric nitrogen oxides above 200 nm (sh = shoulder)

	Calc. (CNDO/S)						Obs.		
	λ [a]/nm	f	Symmetry	Polarisation [b]	Transition orbitals (CI composition)	Type [c]	$\lambda_{max.}$/nm	f	Ref.
N_2O_2, C_{2v}	1 286	0·0002	B_2	o.p.	$11 \rightarrow 13$ (0·99)	$(\sigma,n_O,n^*) \rightarrow \pi_1^*$	$>$1 160	$>10^{-6}$	
	976	0·0000	A_2		$11 \rightarrow 14$ (0·99)	$(\sigma,n_O,n^*) \rightarrow \pi_2^*$	Absent	$<10^{-8}$	
	250	I	B_1	i.p(x)	$11 \rightarrow 12$ (0·96)	$(\sigma,n_O,n^*) \rightarrow \sigma^*$	Bands at	Strong	13, 14
	(10 834)						232—236		
					$6 \rightarrow 12$ (0·02)	$(\sigma,n_O,n) \rightarrow \sigma^*$	2 050	0·26	14
N_2O_3, C_s	644	0·0003	A''	o.p.	$14 \rightarrow 15$ (0·88)	$(n_O,n^*,\sigma) \rightarrow \pi_1^*$	684	0·0002	10, 11, 19
					$11 \rightarrow 15$ (0·09)	$(n,n_O) \rightarrow \pi_1^*$			
	440	0·0000	A''	o.p.	$14 \rightarrow 16$ (0·96)	$(n_O,n^*,\sigma) \rightarrow \pi_2^*$			
	352	0·0000	A''		$12 \rightarrow 16$ (0·83)	$n_O^* \rightarrow \pi_2^*$			
					$12 \rightarrow 15$ (0·16)	$n_O^* \rightarrow \pi_1^*$			
						(c.t.)			
	251	0·0000	A''		$13 \rightarrow 17$ (1·0)	$\pi_O \rightarrow \sigma_{NN}^*$			
	249	0·030	A'	i.p.(z)	$13 \rightarrow 15$ (0·94)	$\pi_O \rightarrow \pi_1^*$			
	(581)					(c.t.)			
	227	0·106	A'	i.p.(z)	$13 \rightarrow 16$ (0·52)	$\pi_O \rightarrow \pi_2^*$	225	0·27	19
	(369)				$12 \rightarrow 17$ (0·42)	$n_O^* \rightarrow \sigma_{NN}^*$			
	201	0·0002	A''	o.p.	$11 \rightarrow 15$ (0·46)	$(n,n_O) \rightarrow \pi_1^*$			
					$12 \rightarrow 15$ (0·35)	$n_O^* \rightarrow \pi_1^*$			
						(c.t.)			
N_2O_4, D_{2h}	463	0·0001	B_{2u}	o.p.	$17 \rightarrow 18$ (0·96)	$(n,\sigma) \rightarrow \pi_1^*$	Absent	$<10^{-5}$	20
	380	0·0000	B_{1g}		$17 \rightarrow 19$ (0·93)	$(n,\sigma) \rightarrow \pi_2^*$			
	348	0·0000	A_u		$14 \rightarrow 18$ (0·68)				
					$13 \rightarrow 19$ (0·32)	$n^* \rightarrow \pi_{1,2}^*$	340	0·003	20
	335	0·0000	B_{3g}		$14 \rightarrow 19$ (0·5)				
					$13 \rightarrow 18$ (0·49)				
	237	0·0000	B_{3g}		$16 \rightarrow 20$ (1·0)	$\pi_O \rightarrow \sigma^*$	268 (sh)	0·003	20
	234	0·0000	A_u		$15 \rightarrow 20$ (1·0)				
	232	0·196	B_{1u}	i.p.(z)	$14 \rightarrow 20$ (0·53)	$n^* \rightarrow \sigma^*$	$<$240	Strong	20
	(546)				$15 \rightarrow 18$ (0·35)	$\pi_O \rightarrow \pi_1^*$			
	225	0·0000	B_{2g}		$16 \rightarrow 18$ (0·62)	$\pi_O \rightarrow \pi_1^*$			
	(548)				$15 \rightarrow 20$ (0·28)	$n^* \rightarrow \sigma^*$			
	201	0·0002	B_{1u}		$16 \rightarrow 19$ (0·58)	$\pi_O \rightarrow \pi_2^*$			
	(201)				$15 \rightarrow 18$ (0·39)	$\pi_O \rightarrow \pi_1^*$			

(No other triplets above 200 nm)

[a] Wavelengths given in parentheses are those of the corresponding triplet. Where no triplet wavelength is given, the singlet and triplet are degenerate (in this approximation). [b] o.p. = Out-of-plane (y polarised); i.p. = in-plane polarised. [c] π_O Orbitals are located mainly on oxygen; π^* orbitals are numbered π_1^*, *etc.* in order of increasing energy.

For N_2O_4 there is no longer a NO group and low-energy absorption is absent.[20] The highest-occupied orbital (A_g) contains the bonding combination n of all the oxygen p-type lone-pair orbitals and is also N·N σ-bonding. An $(n,\sigma_{NN}) \rightarrow \pi_1^*$ transition is expected to have an oscillator strength of 10^{-4} at 463 nm but was not observed, *i.e.* $f < 10^{-5}$. Between 380 and 225 nm the calculation gives six transitions forbidden by molecular symmetry, though weakly overlap allowed by some s contribution to one or other transition orbital. The weak band and shoulder that are observed[20] at 340 and 268 nm can be ascribed to $n^* \rightarrow \pi_{1,2}^*$ and $\pi_O \rightarrow \sigma^*$ excitations respectively, gaining intensity from vibronic interactions. The 340 nm band also shows blue shifts in polar solvents.[21] The absorption below 240 nm can be ascribed to the mixed band at 232 nm.

Thus the known bands in the spectra of the three oxides are predicted reasonably well, and measurement of the remaining bands can provide a further test of the CNDO/S method, which was developed for organic molecules.

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Magnetic Properties of N_2O_2.—The $(n,\sigma) \rightarrow \pi^*$ band in N_2O_2 has a very low energy, which can be traced to the very low binding energy, less than 10 kJ mol^{-1}, of the dimer compared to the monomer.[4,14] The band at *ca.* 1 300 nm compares with those around 700 nm for N_2O_3 and the *C*-nitroso-compounds. This low energy may explain the unusual magnetic properties of N_2O_2, which has no unpaired spins but seems to have an intrinsic feeble paramagnetism. The contribution of the dimer to the susceptibility of a solution of nitrogen oxide in krypton at −155 °C has been estimated [3a] as $2{\cdot}6 \times 10^{-5}$ mol^{-1}; and at −210 °C, which is nearly 50° below the m.p. so that dissociation seems unlikely, the value $1{\cdot}98 \times 10^{-5}$ mol^{-1} was obtained.[3b]

This 'temperature-independent' paramagnetism is found in even molecules or ions if the positive or high-frequency term in Van Vleck's expression [22] for the susceptibility outweighs the negative term. Usually these are compounds of transition metals (*e.g.* $[MnO_4]^-$) with low-lying *d* orbitals. In N_2O_2 the diamagnetic term is small because the molecule is small, and the paramagnetic term is large because of the low energy of the $(n,\sigma) \rightarrow \pi^*$ state which involves a circulation of charge (p_x, some p_z) $\rightarrow p_y$. This is a very unusual combination. Both N_2O_3 and N_2O_4 are diamagnetic as liquid and solid, N_2O_3 from −10 to −95 °C,[23] and N_2O_4 at room temperature and below.[24] Similarly diamagnetic are *C*-nitroso-compounds [25] and nitrosyls, including nitrosyl halides, with all spins paired.

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