ABSORPTION SPECTRA OF NONH$_2$ ISOMERS AND NO IN LIQUID AMMONIA SOLUTION: POSSIBLE IMPLICATIONS FOR JUPITER

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Summary

Molar absorption coefficients of NONH$_2$ have been measured for bands at 285 nm, 365 nm and 550 nm, and the bands assigned to the tautomeric species HNNOH, NH$_2$NO and HNNHO respectively. Solutions of NO in liquid ammonia have an absorption band at 425 nm which is assigned to a charge transfer complex of NO with NH$_3$. It is suggested that coloured solutions of NONH$_2$ and NO in liquid ammonia may contribute to the colours observed in the atmosphere of Jupiter.

1. Introduction

The molecule nitrosamide (NONH$_2$) and its isomers are of great interest at present because of the part they are thought to play as transient intermediates in the fast reaction [1 - 4]

$$NO + NH_2 \longrightarrow N_2 + H_2O \tag{1}$$

Both vibrational and electronic spectra of these species are needed, the former to supply frequencies for use in RRKM calculations and the latter as a basis for future photochemical and thermochemical studies. The present paper describes some measurements of electronic absorption spectra between 250 and 750 nm for NONH$_2$, and also for NO, in liquid ammonia solutions. During the course of this work it was realised that these solutions, whose colours can be quite striking, have ingredients which could well be present under non-equilibrium conditions in the atmosphere of a planet such as Jupiter, and so might contribute to the visible colouration of the planet. This possibility is discussed in Section 5.

Unlike the related species nitramide (NO$_2$NH$_2$) [5], NONH$_2$ is not obtainable in the pure state or in the gas phase. Schwarz and Giese [6] prepared red, orange—red or purple solutions by a number of reactions of liquid or solid NH$_3$ and described how the presence of a trace of N$_2$O$_3$ in a sample of NO caused the normal yellow colour of NO in liquid ammonia to be replaced by an intense red colour, which they attributed to NONH$_2$. They pointed out that their experiments did not allow them to

distinguish between $NONH_2$ and its isomer HNNOH (hydroxydiimide), and suggested that the two species were probably both present in tautomeric equilibrium. Despite considerable effort they were unable to obtain $NONH_2$ other than in liquid NH_3 solution, all attempts to isolate or extract it resulting in the formation of white clouds of NH_4NO_2 and evolution of N_2:

$$NH_2NO \longrightarrow N_2 + H_2O \tag{2}$$

$$NH_2NO + H_2O \longrightarrow NH_4NO_2 \tag{3}$$

Ditchfield *et al.* [7] have reported the results of minimal basis set self-consistent field–configuration interaction calculations of the energy of the lowest $n \rightarrow \pi^*$ transition for a number of compounds, including NH_2NO (2.90 eV $\equiv$ 430 nm), *trans*-HNNOH (4.37 eV $\equiv$ 285 nm) and *cis*-HNNOH (5.54 eV $\equiv$ 224 nm). The calculated values were usually slightly lower than the experimental values, where available, but agreement with experiment tended to be better for the nitrogen-containing compounds than for the others (*trans*-HNNH, observed 3.55 eV, calculated 3.37 eV; CH_3NNH, observed 3.57 eV, calculated 3.58 eV; HNO, observed 1.61 - 2.35 eV, calculated 1.69 eV). Thus their calculations should provide a fairly reliable basis for distinguishing between NH_2NO isomers via the electronic spectra.

2. Experimental details

The absorption cell was a length of 1 cm $\times$ 1 cm square-cross-section quartz tubing, sealed at one end and suspended by its filling tube in an open quartz dewar. The dewar was mounted in the sample compartment of a Varian–Techtron Superscan 3 spectrophotometer. Spectra were run in double-beam mode with a 2 nm bandwidth, but true double-beam measurements could not be performed and measured spectra were compared numerically with the spectrum of pure liquid NH_3 measured in the same cell. In most of the experiments a known pressure of N_2O_3, ONCl or NO in a 500 ml volume was condensed in the cell with liquid nitrogen and excess solid NH_3 deposited on top. Slow addition of ethanol to the dewar then resulted in the formation of an alcohol slush bath, whose level was adjusted to just below the spectrometer probe beam. After the cell contents had thawed, the depth of liquid in the cell, and hence the volume, was measured with a ruler. Solutions of $NONH_2$ so produced ranged from pink to colourless depending on concentration. $NONH_2$ concentrations were calculated on the assumption that no decomposition occurred during the preparation of the most dilute solutions; thus the molar absorption coefficients reported here for $NONH_2$ are lower limits.

Nitric oxide solutions prepared as above were initially bright yellow and supersaturated, and their light absorption diminished with time, usually reaching a steady value after about 30 min at -30 °C. Equilibrium

concentrations of NO were estimated by a method due to Hildebrand [8], the listed vapour pressure formula for temperatures below the critical temperature being extrapolated to $-30\,°C$ and the mole fraction of NO in solution calculated assuming Raoult's law. In a typical experiment, for NO at a partial pressure of 120 Torr the calculated concentration in the liquid phase at 239 K was $6.2 \times 10^{-3}\,mol\,l^{-1}$.

The cell temperature was monitored with a copper–constantan thermocouple; spectra were run at between -25 and $-35\,°C$. The cell was not thermostatted, but the cell temperature always remained constant to within $1\,°C$ during a scan, and small quantities of liquid nitrogen were added to the dewar at intervals to keep the temperature below $-25\,°C$. Gas pressures were measured with a Texas Instruments quartz spiral gauge. Commercial NH_3 was purified by distillation from KOH pellets. Matheson NO was purified by repeated pumping at liquid nitrogen temperature and evaporation at $-80\,°C$. Matheson ONCl was purified in a LeRoy still immediately before use, Cl_2 being taken off first at -118 to $-110\,°C$, then ONCl at -100 to $-76\,°C$. N_2O_3 was prepared immediately before use by trapping the blue liquid from a mixture of NO_2 with excess NO.

Between measurements the cell was rinsed several times with distilled water and pumped to dryness with a trapped oil diffusion pump.

3. Observed spectra

The spectrum of a dilute solution of $NONH_2$, prepared from N_2O_3, is given in Fig. 1. The form of the band at 250 nm is not well established because of the onset of strong absorption by NH_3 at 235 nm. There is a
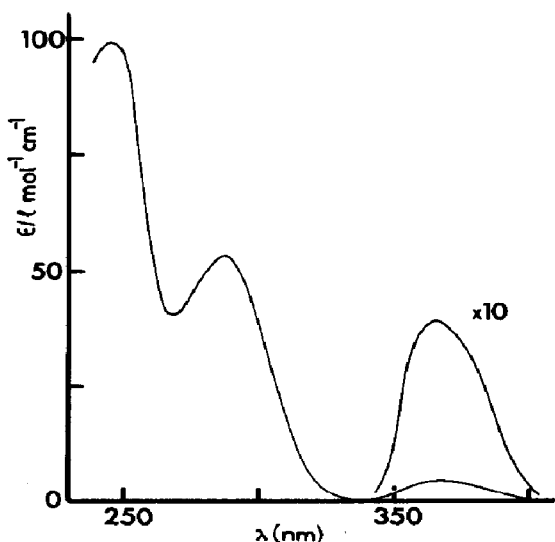

Fig. 1. Spectrum of a dilute solution of NH_2NO, prepared from N_2O_3, in liquid NH_3 at $T = -32\,°C$ (spectrometer bandwidth, 2 nm).

second clearly defined band at 285 nm and a less intense band at 365 nm. The dilute solution of Fig. 1 was not perceptibly coloured.

The band responsible for the pink colour of stronger solutions of $NONH_2$ is shown in Fig. 2. The 365 nm band and the 550 nm band could be measured simultaneously in strong solutions, and absorption coefficients of the 550 nm band were calculated from the ratio of the intensities of the two bands. Peak values of molar absorption coefficients were measured as 53 at 285 nm, 3.9 at 365 nm and 0.027 at 550 nm, with an uncertainty of about ±15% (one standard deviation) and without any allowance for decomposition of the $NONH_2$.

The spectrum of a solution of NO in NH_3 at −30 °C is given in Fig. 3. This spectrum was obtained at an NO partial pressure of 120 Torr, as described in Section 2, and in view of the possibility of some supersaturation remaining the peak molar absorption coefficient (7.3 ± 1.0) is best regarded as an upper limit.
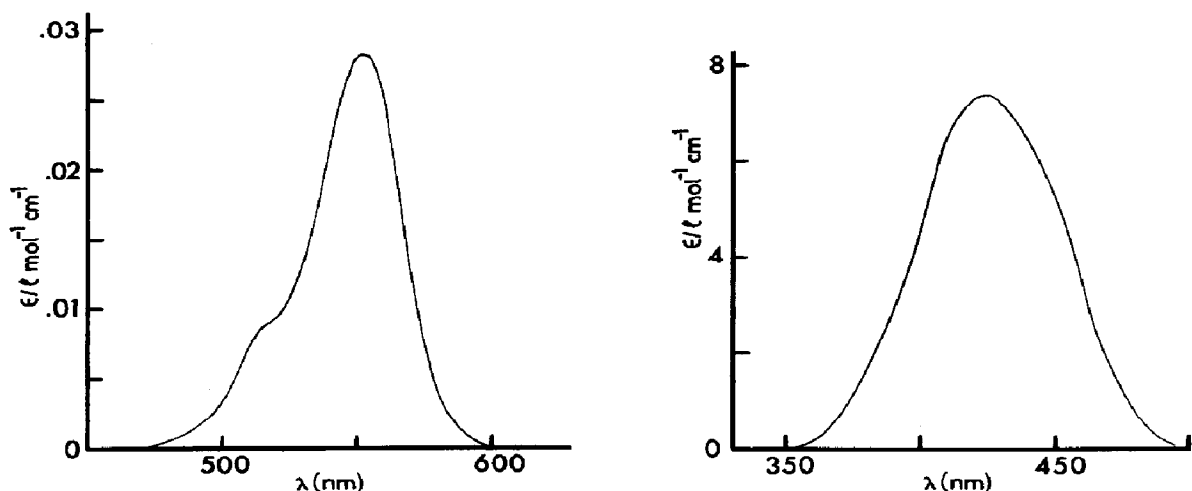

Fig. 2. Visible spectrum of a pink solution of NH_2NO, prepared from ONCl, $T = -25$ °C (bandwidth, 2 nm).

Fig. 3. Spectrum of NO in liquid NH_3. NO partial pressure, 120 Torr; $T = -34$ °C; bandwidth, 2 nm.

4. Assignment of the bands

The band at 365 nm is readily assigned to $NONH_2$, and that at 285 nm to *trans*-HNNOH, on the basis of the calculated n−π* energy differences. Thus the present results support the suggestion of Schwarz and Giese that both species are present. The relative intensity of the bands tends to support the relative energies determined by Casewit and Goddard [3] (HNNOH more stable by 12.6 kJ mol^{-1}) rather than those of Abou-Rachid *et al.* [4] (NH_2NO more stable by 6.7 kJ mol^{-1}), the observed factor of 14 in intensity corresponding to an energy difference of 5 kJ mol^{-1} in favour of HNNOH, assuming identical oscillator strengths.

The very intense band at 250 nm is tentatively assigned to the next higher $\pi \to \pi^*$ transition of one or more of the $NONH_2$ isomers present, on the grounds that a similar intense transition occurs for NO_2NH_2 in this region and that it does not fit any of the predictions for the lowest $n \to \pi^*$ band. However, the very weak band at 550 nm cannot be explained in this way, and it is necessary to look for another absorber. According to Casewit and Goddard, the next lowest bound H_2N_2O species is HNNHO at a level 55 kJ mol^{-1} above NH_2NO. The observed factor of 140 in relative intensity, 365 nm $vs.$ 550 nm, corresponds to an energy difference of only 10 kJ mol^{-1} but, in view of the uncertainty of the ab $initio$ calculations and the unknown effects of solvation and variations in oscillator strength, assignment of the 550 nm band to HNNHO appears very plausible. The only alternative seems to be a charge transfer spectrum of one of the more stable isomers plus NH_3, analogous to the NO spectrum considered next.

The NO band at 425 nm is interesting because of its similarity to the 365 nm band in form, wavelength and intensity. However, the lowest electronic transition of gaseous NO occurs at around 250 nm, so the origin of the NO band must be very different from that postulated for the 365 nm band. The most obvious assignment is to a charge transfer band of the species $NO \cdot NH_3$, having an excited state much more strongly bound (to the extent of about 240 kJ mol^{-1}) than the ground state, which raises the possibility that the $NONH_2$ bands observed here are also strongly affected by charge transfer interactions with the solvent. This possibility cannot be ruled out at present, the only evidence against a major shift of the relative energy levels being the excellent agreement between the observed and calculated positions of the 365 and 285 nm bands. Ab $initio$ calculations aimed at predicting the $n \to \pi^*$ energy difference for HNNHO are in progress [9].

5. Possible implications for Jupiter

According to the model of Weidenschilling and Lewis [10], Jupiter's clouds comprise an outer layer of solid NH_3 at about 150 K, a layer of NH_4SH at 200 K and a layer of water ice at 250 - 280 K. The model assumes uniform solar abundance of the elements and the existence of both thermodynamic and hydrostatic equilibrium, and the authors stress that it takes no account of supercooling, supersaturation or local departures from equilibrium such as are evident in Jupiter's complex atmospheric structure of belts, zones and great red spot. Following the observation of PH_3 as a minor constituent of Jupiter's atmosphere, Prinn and Lewis [11] proposed, on the basis of model calculations and the known laboratory photochemistry of PH_3, that the colour of the red spot is due to a haze of solid red phosphorus, present as the final stage of photodecomposition of PH_3. The model required that the red spot be a region of considerable upwelling of material from the interior (according to the equilibrium model, PH_3 should not be present

above the 850 K level) and it was necessary to postulate photodecomposition occurring in a relatively ammonia-free region because otherwise all the light near 200 nm would be absorbed by NH_3 instead of PH_3. Bosco *et al.* [12] showed that an alternative mode of PH_3 decomposition, the reaction of PH_3 with NH_2, is too slow at $T \approx 150$ K to give the required decomposition rate. We now raise an alternative possibility, namely that large local departures from equilibrium associated with lightning flashes in a region containing H_2O and NH_3 could give rise to a mist of coloured solutions in liquid NH_3.

The possible chemical role of thunderstorms on Jupiter has been discussed by Bar-Nun [13] and experimental data on the incidence of lightning on Jupiter have been presented by Bonicki *et al.* [14]. They conclude that lightning discharges occur on Jupiter, probably mainly at the 280 K ice-cloud level, with a frequency of strikes per square kilometre comparable with that on earth. Bar-Nun [13] suggests that lightning discharges should be more frequent in the red spot itself, which is reasonable in view of terrestrial experience with tornadoes and hurricanes.

A lightning flash can be expected to convert water to H, O and OH, and ammonia to NH_2, NH and N, with local concentrations great enough to produce transient populations of species such as O_2, NO (from the reaction of N with OH), HO_2, NO_2 (from the reaction of HO_2 with NO) and N_2O_3 (from the reaction of NO with NO_2). Thus, if liquid NH_3 is present at any level, it is liable to contain dissolved NO and/or NH_2NO. Weidenschilling and Lewis point out that precipitation of NH_3 or NH_4SH snow is likely to occur, although outside the scope of their model. The present suggestion requires this snow to reach a deep enough level for melting to occur rather than sublimation. The presence of water at such levels is not a major obstacle, since it was noticed in the course of the present work that, during the final evaporation of the pink solutions, the colour was retained and actually intensified as long as liquid was present, despite the presence of NH_4NO_2 and H_2O from material already decomposed; thus reaction (3) is slow provided excess liquid NH_3 is present. The spectra of Figs. 2 and 3 should be sufficiently distinctive to be observable, if present, in the spectrum of the red spot.

Acknowledgments

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