

DEGRADATION STUDIES ON NICKEL NITRATE HEXAHYDRATE. PART 3. RAMAN AND INFRARED ANALYSIS

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ABSTRACT

The deaquation of nickel nitrate hexahydrate has been studied using infrared and laser Raman techniques. The latter was carried out dynamically, under a linear rising temperature regime. When combined with work described in Parts 1 and 2 the data have enabled a detailed postulate of the degradation mechanisms involved during deaquation and denitration of this compound to be made. Laser Raman thermal analysis is also shown to be a valuable complementary aid in the elucidation of internal structural changes as a material is heated.

INTRODUCTION

Previous studies of the thermal degradation of nickel nitrate hexahydrate have [1] given frequently conflicting accounts of the intermediates formed during this process. In Part 1 [1] we showed that indeed several stoichiometric hydrates can be formed, and in addition an intermediate corresponding to anhydrous nickel nitrate. The deaquation process was found to be dominated by three factors: the coordination chemistry of nickel and ligand availability, the ease of liberated water removal from the sample, and the reactivity of water vapor.

In Part 2 [2] the degradation process was examined using evolved gas analysis (EGA). This enabled individual steps to be more clearly delineated and, through comparison with thermogravimetric (TG) and differential thermal analyses (DTA) mechanisms were postulated for some of these. EGA is frequently used to complement TG studies and is of great value in separating overlapping reactions involving loss of mass. It is of importance

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when used with DTA but clearly it cannot provide information on overlapping steps involving no mass loss, or phase changes. It is clear from the two earlier sections of this work [1,2] that there remains much unexplained information in the DTA traces. The aim of this study is to elucidate the many physical/chemical changes occurring within nickel nitrate hexahydrate which have been indicated by DTA. To this end two spectroscopic methods: infrared (IR) and laser Raman, have been used. The latter has been employed during programmed linear heating of the sample (RTA).

Two approaches to the use of infrared spectroscopy in thermal analysis studies have been made. Firstly IR investigations can be made on a sample of reactant previously heated to a known extent of reaction (α) and studied in the form of a mull or in a halide disc. An alternative approach is to incorporate the sample into a compact halide disc which is either placed in a heated holder in the IR beam path or withdrawn from an oven at intervals for IR measurement.

The first technique is very widespread and in keeping with the trend to gather as much information about a system as possible. Examples of the use of IR spectroscopy in this way are the study of cellulose degradation by Dollimore and Hoath [3] and pharmaceutical-transition metal complex solid state reactions by Allan and Gavin [4]. Also the decomposition and dehydration of inorganic complexes has been studied using IR by Nissen [5] who observed changes in anion absorption bands and Langfelderova et al. [6] who observed structural changes during the decomposition of copper sulfate pentahydrate. In addition Brown and Richardson [7] used IR spectroscopy to identify intermediates formed during the decomposition of chromium halide complexes.

The second approach has been used by Wydeven and Leban [8] and Tanaka et al. [9]. The disadvantage of heating a sample while it is present in a halide disc is that gaseous products will disrupt the disc. In addition care must be taken to ensure that reactions between the sample and disc material do not occur [10]. However, the advantage of this method is that the kinetics of a process occurring within a sample can be followed [11].

There are few reports of the use of Raman spectroscopy in thermal analysis in the literature. This is probably due to the lack of availability of such instruments rather than a comment on the technique's usefulness. In theory it is capable of being used in similar ways to IR spectroscopy. However, the technique generally utilizes a laser as the excitation source and so care must be taken to ensure that this does not degrade the sample during measurement. Indeed Taki et al. [12] utilized this property of lasers to study the decompositions of a series of copper salts. They irradiated the samples using a pulsed Ruby laser and followed the decomposition by analyzing the product gases using a gas chromatograph.

Cram and Davies [13] studied a series of basic lead nitrate compounds and their thermal decomposition products using Raman spectroscopy. By

also studying intermediate compounds that were formed they were able to speculate on the degree of involvement of the NO_3^- species in the complexes and their total structure.

Finally, in one of few examples of temperature related studies, Chan et al. [14] have obtained Raman spectra of supported oxide phases at different temperatures.

EXPERIMENTAL

A Perkin-Elmer Model 521 spectrophotometer was used to measure the IR spectra required. Samples were dispersed in Nujol and studied using KBr discs. In certain cases the hexahydrate was partially decomposed, prior to spectroscopic measurements, using the vacuum TG unit previously described [1]. For this work a heating rate of 1 K min^{-1} under vacuum, with single crystals of 8.5 mg were used. All sample handling was performed in a dry box.

For the Raman studies a Spex Ramalog 5M, double monochromator instrument with an argon ion tube, incorporating a spatial filter was utilized. The 514.5 nm laser line was used with a power of 500 mW at the sample. For sample presentation a glass tube (external diameter 8 mm) was wound with a length of flat heating wire. The windings were approximately 1 mm apart and the last wind at each end of the tube as secured with thermal cement. A sample tube of external diameter 5 mm proved to be a good fit

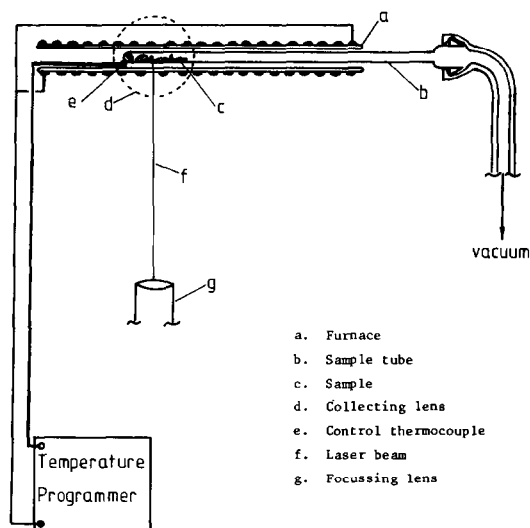


Fig. 1. The sample system-furnace assembly used for the laser Raman thermal analysis studies.

within the glass furnace and thus the whole assembly (Fig. 1) allowed the laser to reach the sample. The furnace was controlled by the temperature programmer used in the TG work [1]. Temperature control was via a thermocouple wedged between the top of the sample tube and the furnace. The end of the sample tube was connected via flexible tubing to a rotary vacuum pump, the latter being that used in the DTA studies [1].

Alignment of the sample in the beam was a lengthy procedure. Care had to be taken to ensure that scattering from the furnace windings was kept to a minimum. It proved to be necessary to use a sample size of approximately 30 mg, this consisting of several small crystals. It was thus possible to change the section of sample exposed to the beam during a run, if required.

Prior to heating, the portion of the scattered spectrum of interest was measured. This was repeated after approximately 20 min to ensure that the compound was not degraded by the laser. The heating program was then started and the spectrum measured at intervals. There proved to be two regions of interest and so a number of runs were made for each of these. Each scan of a region of interest took approximately 8 min and, using the TG derived α - T plot [1], was started at temperatures corresponding to the formation of reasonably stable intermediates.

The sample used was AnalaR grade nickel nitrate hexahydrate.

RESULTS

Infrared studies

The IR spectra for the partially decomposed nickel nitrate, ranging from the hexahydrate through to the sample after 50% mass loss are shown in Fig. 2. Sections of interest of these spectra are shown in Figs. 3 and 4. Pure nickel nitrate hexahydrate shows a strong absorption band at 3800–3000 cm^{-1} , this corresponding to antisymmetric and symmetric OH stretching, and a large peak at 1630 cm^{-1} , corresponding to HOH bending. The final band at 645 cm^{-1} may be due to the rocking mode of water ligands, although this is a tentative explanation made in the absence of information of the spectrum below 600 cm^{-1} .

As is evident by reference to the review of the structural aspects of coordinated nitrate groups by Addison et al. [15], the use of vibrational spectra to distinguish between different types of nitrate coordination is not straightforward. Nakamoto [16] notes that the use of such spectra for these purposes is difficult since the symmetry of the nitrate group differs very little between the nine basic geometries.

Lever et al. [17] proposed using the combination band in the 1800–1700 cm^{-1} region for structural diagnosis. After completing a comprehensive survey of the published data for nitrate complexes, they concluded that the

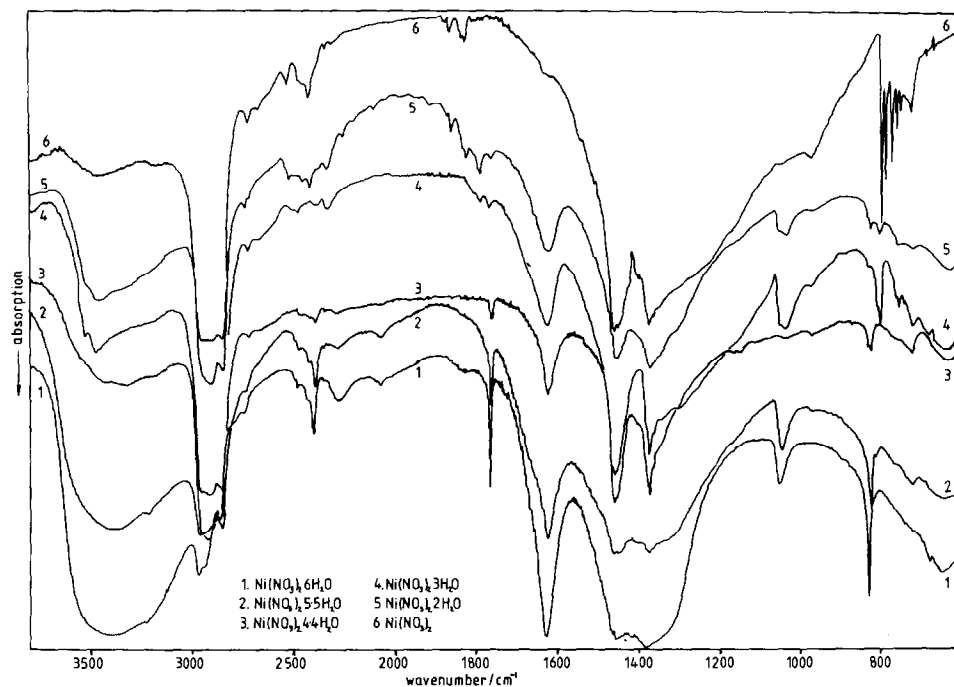


Fig. 2. The infrared spectra of partially decomposed samples of nickel nitrate hexahydrate.

separation of a split coordination band could be used for structural diagnosis. Upon coordination a nitrate fundamental near 700 cm^{-1} splits into two bands, and the magnitude of this splitting is expected to be larger for bidentate than for unidentate ligands. Lever et al. [17] found that this was reflected in the separation of the resultant combination band in the $1800\text{--}1700\text{ cm}^{-1}$ region. If the nitrate species is bidentate the separation is $66\text{--}20\text{ cm}^{-1}$ and if unidentate it is $26\text{--}5\text{ cm}^{-1}$.

Spectrum 1, for $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Figs. 2–4) shows bands due to the nitrate ion fundamentals which are very similar to those found by Rebane et al. [18] for free nitrate ions in a potassium chloride matrix at 300 K . They found four nitrate fundamental bands at 1370 , 1055 , 825 and 690 cm^{-1} . The band in the $1400\text{--}1300\text{ cm}^{-1}$ region would not be observed here due to the use of Nujol. In addition the combination band at 1765 cm^{-1} is sharp, indicating that the nitrate species present are uncoordinated and so it appears that $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ contains free nitrate ions only. A very small concentration of the nitrosonium ion (NO^+) may be present as shown by the peak at 2270 cm^{-1} which may have been induced by the presence of free water.

Spectrum 2, corresponding to $\text{Ni}(\text{NO}_3)_2 \cdot 5.5\text{H}_2\text{O}$ is essentially the same as the previous one and so the sample still contains free nitrate ions at this point. Small differences between the spectra indicate that the concentration

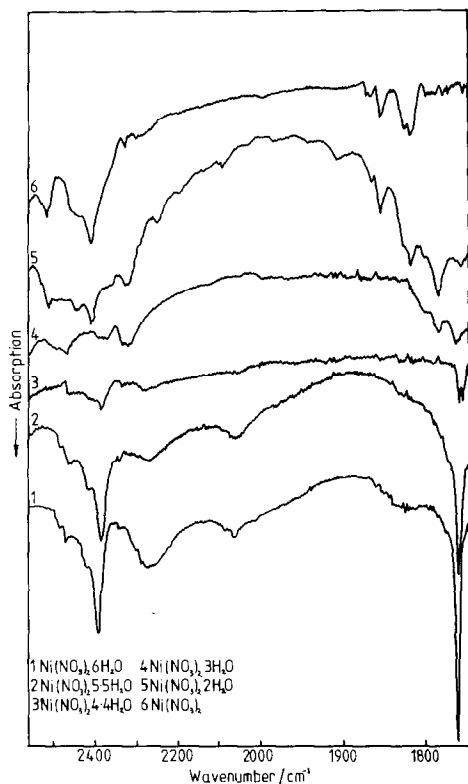


Fig. 3. The 2300–1750 cm^{-1} region of the IR spectra of partially decomposed samples of nickel nitrate hexahydrate.

of nitronium ions has been reduced and the amount of water present, as expected, is slightly lower.

Spectrum 3, due to $\text{Ni}(\text{NO}_3)_2 \cdot 4.4\text{H}_2\text{O}$, is different from the previous two in many ways. Firstly, the peaks due to water are considerably reduced. Secondly, the peak due to the nitronium ion has completely disappeared. The peak, previously at $\sim 1050 \text{ cm}^{-1}$, has disappeared and that at $\sim 830 \text{ cm}^{-1}$ has split. Finally the combination peak at 1760 cm^{-1} has split, giving a difference of 6 cm^{-1} . On its own, the latter would indicate the presence of unidentate nitrate ligands. However, the peak in the $1100\text{--}1000 \text{ cm}^{-1}$ region corresponding to $\nu_s(\text{NO})$ is absent from the spectra. This indicates that either the nitrate has been converted to nitrite, or it is completely symmetrical. However, then the combination peak would not be split. It would appear that the spectrum cannot be explained using simple point group analysis. More complex forms of analysis are available. For example Schutte [19] used unit-cell analysis to explain the IR spectra of barium and strontium nitrate. However, this method of analysis is time consuming and requires exact knowledge of the crystalline structure of the sample.

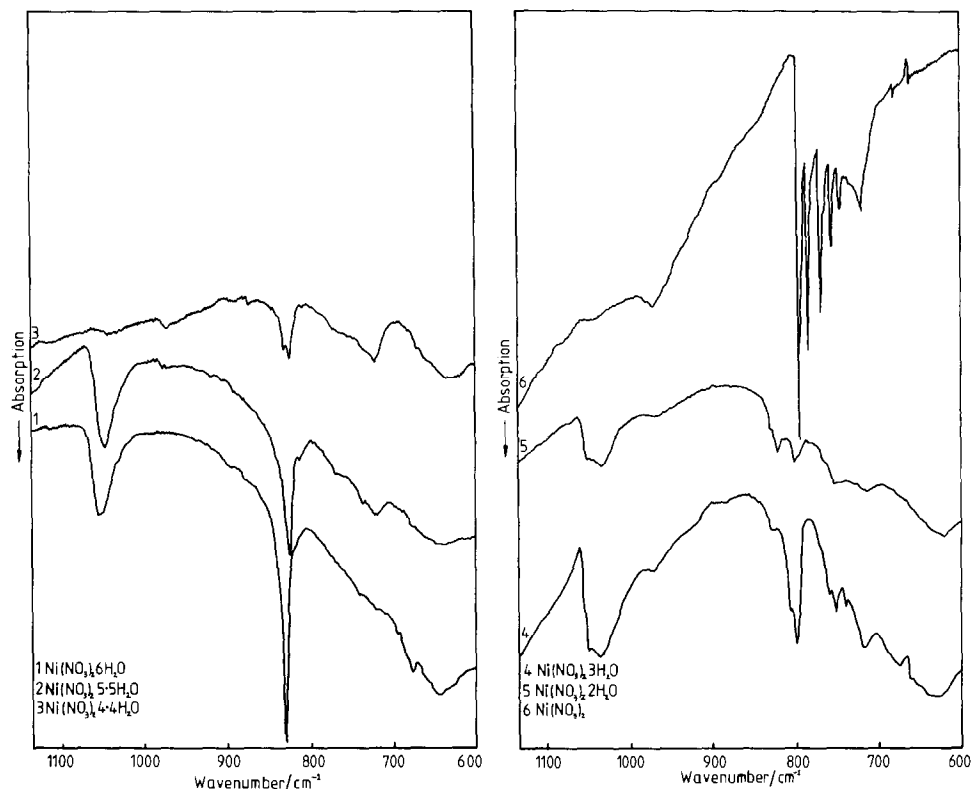


Fig. 4. The $1100\text{--}600\text{ cm}^{-1}$ region of the IR spectra of partially decomposed nickel nitrate hexahydrate samples.

Spectrum 4 shows that the bottom of the broad band at $3700\text{--}3100\text{ cm}^{-1}$ ($\nu_{\text{a,s}}(\text{OH})$) is better resolved than in the previous spectra and has a number of distinct maxima. This is probably due to the still smaller amount of water present; this spectrum corresponding to $\text{Ni}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The combination band in the 1760 cm^{-1} region has further separated giving a difference of 20 cm^{-1} . Close examination of the 1770 cm^{-1} peak shows that it may be split, with a shoulder at 1765 cm^{-1} . This could be due to traces of species present in the previous spectrum or the sample may contain both uni- and bidentate nitrate species. This is confirmed by the presence of two overlapping peaks in the $1050\text{--}1000\text{ cm}^{-1}$ region, indicating that two $\nu(\text{NO})$ modes are present. The spectrum in the region $850\text{--}600\text{ cm}^{-1}$ is more complex than for any of the previous samples. Again this may be due to the superposition of two spectra due to two types of nitrate species. However, the assignment of vibrations to the bands observed in this region is complicated by the fact that symmetrical metal–oxygen stretching may lead to absorptions at frequencies as high as 800 cm^{-1} due to interactions within a small M–O ring [20].

Spectrum 5, corresponding to $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, shows bands due to

water, in the 3400 and 1620 cm^{-1} regions which are smaller than previously observed. The rest of the spectrum is more complex than those already described. The appearance of a number of bands in the combination region was taken by Lever et al. [17] to indicate the presence of both unidentate and bidentate nitrate species. However, the bands now appear at least as high as 1870 cm^{-1} which is very unusual. It is very apparent from this spectrum that there is a great need to calculate the effects of other forms of nitrate symmetry than those discussed by Addison et al. [15] on the observed spectra.

Finally Spectrum 6, corresponding to $\text{Ni}(\text{NO}_3)_2$, exhibits traces of water in the 3400 cm^{-1} region although this may be due to contamination from the atmosphere. The combination bands in the 1800 cm^{-1} region are simpler than previously although they are not in any readily recognizable form. In the 1100–1000 cm^{-1} region the $\nu_s(\text{NO})$ band is absent. This, as with Spectrum 4, indicates that the nitrate species are present in a D_{3h} symmetry. All examples of nitro groups show $\delta(\text{ONO})$ at frequencies significantly above 800 cm^{-1} as do chelating nitro groups [16].

In addition to the absorption bands described above, all the spectra had a weak band in the 2730 cm^{-1} region and a series of peaks across the range 2700–2100 cm^{-1} . The latter are combination bands but an analysis of these requires a thorough understanding of the crystalline structure of each sample [19].

Laser Raman spectrometry

Several runs were performed in order to obtain an overall picture of the changes occurring during heating of the sample. The technique proved to be very time consuming, many samples moved in the laser beam at some time during an experiment, so necessitating realignment of the system. In addition a few samples decomposed, albeit in a controlled way, in the laser beam. It was thought that these samples may have been mechanically damaged during handling so enabling laser-induced decomposition to begin on damaged crystal faces and edges. However, these samples did allow larger areas of the spectra to be scanned, by virtue of their relatively low rate of decomposition. It was found that such results complemented those obtained under a rising temperature regime quite well.

The peak areas, calculated by multiplying peak height by width at half height, were plotted against the temperature programmer readings. Comparison of peak ratios for the 1042 and 1056 cm^{-1} peaks, since these were large and more accurately measured and in the same region, showed that three traces could be superimposed. This was essential as complementary regions of the spectra were obtained from these runs. A further run was found to be 15 K in advance by comparing the peak ratios and so an adjustment was made in temperature prior to superimposing the spectrum onto the other three. Figure 5 thus shows the resulting composite of four

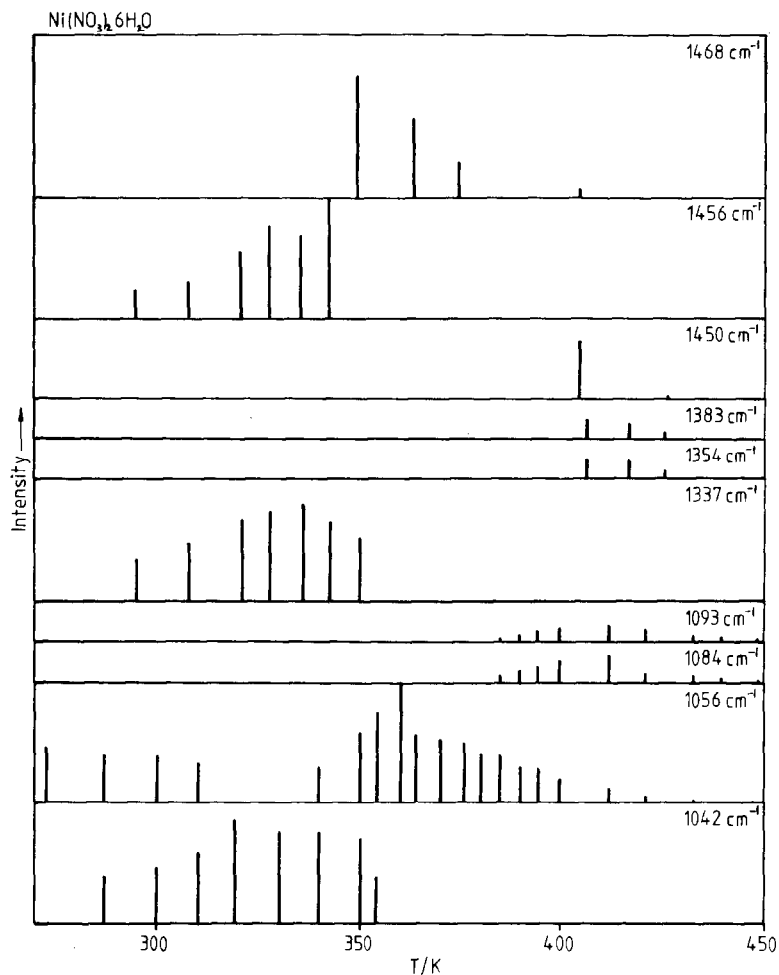


Fig. 5. The peak areas, plotted as intensity versus temperature, for the laser Raman thermal analysis studies of nickel nitrate hexahydrate for the wavenumbers indicated.

experiments. In this way the behavior of peaks at 1042, 1056, 1084, 1093, 1337, 1354, 1383, 1450, 1456 and 1468 cm^{-1} has been observed.

As can be seen the hexahydrate has two absorption bands in the range studied. Rebane et al. [18] found that free nitrate ions in a potassium chloride matrix at 300 K exhibit four Raman-active fundamental bands at 1370, 1055, 825 and 690 cm^{-1} . This suggests that the spectra of the hexahydrate are those of free nitrate ions, having peaks at 1337 and 1056 cm^{-1} . On heating, new bands appear, replacing those existing previously. Taking the scan traces in total there are points when two species exist, indicated by bands both growing and diminishing, and points when bands have reached a maximum or minimum. Assuming the latter situation to indicate the existence of a single species then the absorption bands for each

separate species can be noted. In addition there is one instance (at ~ 295 K) where two species may be present in a relatively stable intermediate. This supposition is based on the two equally sized 1056 cm^{-1} bands at 287 and 300 K. Thus the second intermediate exhibits four bands, two of which were present for the hexahydrate and three in the next intermediate.

Gatehouse et al. [21] found that $\text{Ni(en)}_2(\text{NO}_3)_2$, known to be unidentate with respect to the nitrate ions, exhibits three bands; 1420, 1305 and 1008 cm^{-1} , with the difference between the two highest bands being 115 cm^{-1} . A number of workers have proposed the use of the relative intensities of each band and the use of the frequency difference between the two highest frequency bands as a guide to the type of nitrate-metal ion interaction. The difference found here for the second intermediate is 119 cm^{-1} , this being very similar to that found by Gatehouse et al. [21] for a unidentate complex. However, the relative intensities of the bands do not readily concur with those given by Addison et al. [15]. In general though, the middle frequency is fairly strong for unidentate nitrate complexes, and weak and the least intense band for bidentate nitrate complexes. Thus the second intermediate is taken to be a unidentate complex with band assignments (cm^{-1}): $1456(\text{m})$, $\nu_a(\text{NO}_2)$; $1337(\text{m})$, $\nu_s(\text{NO}_2)$; $1042(\text{vs})$, $\nu(\text{NO})$.

Turning to the third intermediate, occurring at 360 K, it can be seen that there are only two absorption bands present: at 1468 and 1056 cm^{-1} . This indicates that the sample at this point does not contain nitrate groups of "conventional" geometry. Neither unidentate, bidentate or bridging nitrate groups give rise to two such peaks, at such a distance apart. Such bands are, however, characteristic of nitrito complexes (MONO), in which case the band assignments would be (cm^{-1}): $1468(\text{m})$, $\nu(\text{N}=\text{O})$; $1056(\text{s})$, $\nu(\text{NO})$.

The fourth intermediate, occurring after 410 K, has a number of peaks. The sample began to decompose rapidly in the beam at this point and it proved difficult to measure the spectrum in the regions studied. The existence of the 1450 cm^{-1} band has been inferred from two samples which decomposed without heating, simply by the laser alone. The spectrum is unusual in that the lower bands are at a higher frequency than any reported in the literature although nitrito complexes do have $\nu(\text{N}-\text{O})$ bands at frequencies as high as 1206 cm^{-1} [16]. In addition the two lowest bands are split although lattice forces may be the cause of this. Thus, given the presence of three bands, the species are probably nitrate groups, of unknown bonding geometries. Tentative band assignments are (cm^{-1}): 1450 , $\nu_a(\text{NO}_2)$; 1383 , 1354 , $\nu_s(\text{NO}_2)$; 1093 , 1083 , $\nu(\text{NO})$.

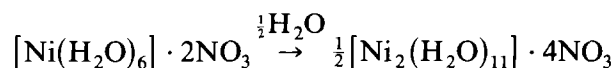
DISCUSSION

Of the two techniques used for this work the IR studies were much more straightforward. The method enabled samples of known degrees of decom-

position to be studied without any further degradation. Neither technique allows unambiguous structural determinations to be made but, together with the earlier DTA/TG [1] and MS-EGA [2] studies, they give considerable insight into the deaquation processes. The IR data will be discussed first.

IR studies

The IR spectra, for the samples corresponding to $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 5.5\text{H}_2\text{O}$, show that the nitrate species are present as free ions in both compounds. In view of the previous discussions [1,2] of thermal analysis studies of the hexahydrate in relation to the coordination chemistry of nickel, the first stage in the vacuum decomposition at 1 K min^{-1} can be written as



This is in accordance with the preferred six-coordination of the nickel and the ability of water to act as a bridging ligand.

The third spectrum, corresponding to $\text{Ni}(\text{NO}_3)_2 \cdot 4.4\text{H}_2\text{O}$, is much more difficult to explain. As described the bands obtained do not match those obtained for any known nitrate species. If the nickel was present in an octahedral ligand field then a mixture of unidentate and free nitrate species would be expected. However, the spectra clearly do not show the presence of free nitrate ions. This suggests that all the water may not be coordinated.

Gallezot et al. [22] produced the tetrahydrate by TG and studied it using IR. They found bands at 1460, 1310, 1035, 802 and 745 cm^{-1} . They were able to explain the spectra in terms of unidentate nitrate species. However, their spectra are very different from those obtained here for the 4.4 hydrate in one key detail: the presence of the 1035 cm^{-1} band. This ought to be very evident for any coordinated nitrate species.

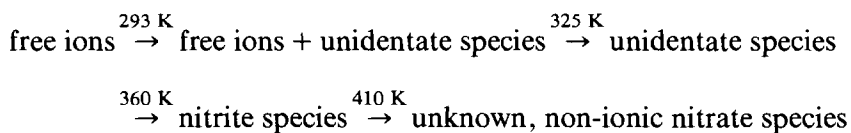
The fourth spectrum, for the 3 hydrate points to the existence of two types of covalently bonded nitrate species in the sample. This suggests that the nickel is still surrounded by an octahedral ligand field consisting of three water ligands and both a unidentate and a bidentate nitrate species. However, this does not account for the relative stability of the triamine complex over other potential intermediates [2]. Gallezot et al. [22] showed that each nickel ion in the tetrahydrate was associated with a free and a unidentate nickel species. If a structure of that type lost one water molecule then the resultant structure may involve two sterically different unidentate species, giving two types of IR spectra.

The fifth spectrum, corresponding to the 2 hydrate, cannot be interpreted readily. Hathaway et al. [23] found bands at 1560–1540, 1310, 1061, 810 and 760 cm^{-1} in an IR study of $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ prepared by non-thermal means. As with the spectrum obtained here this indicates that all the nitrate species present were non-ionic in nature although the two spectra are very different.

The sixth spectrum, corresponding to the anhydrous nickel nitrate, again could not be readily interpreted. However, as discussed earlier, for the nickel ions to be octahedrally coordinated the nitrate species would have to be in a terdentate configuration. Since there appear to be no examples of such binding in the literature then the spectrum cannot be analyzed accordingly. Interestingly, Addison et al. [24] prepared nickel nitrite as a pale green dust from nickel carbonyl and dinitrogen tetroxide and found that it had IR bands at 1388, 1333, 1240 and 830 cm^{-1} . In addition there were strong bands at 1575 and 1080 cm^{-1} . The former is indicative of $\text{M}-\text{NO}_2$ bonding while the latter is indicative of nitrito metal bonding ($\text{M}-\text{O}-\text{N}=\text{O}$). However, on exposure to the atmosphere both bands disappeared. The spectrum obtained here did not have bands in either region although a weak band was present at 970 cm^{-1} .

Laser Raman studies

The laser Raman results are best considered initially in terms of the sequence of changes observed. These can be written as follows, starting with the nitrate species present in the hexahydrate:



The first intermediate, in view of the earlier studies [1,2] probably corresponds to the 4.4 hydrate, this being the only one which can possess an octahedrally coordinated nickel ion and both free and unidentate nitrate species. However, the temperature is approximately 43 K lower than required. This could arise from the use of the laser, which may provide additional heating of the sample.

The next intermediate, containing unidentate nitrate species, would thus occur at 368 K. From the TG data [1] this corresponds exactly to the trihydrate. For the trihydrate to possess solely unidentate nitrate species the nickel must be penta-coordinated, thus lending support to the IR results.

The next intermediate corresponds exactly with the formation of the dihydrate at 403 K. It is unusual in that it clearly indicates the presence of nitrite species. Addison and Logan [25] have reviewed the effect of radiation on anhydrous metal nitrates. Many workers have found that the following, reversible reaction can occur:



This may have occurred in these studies, given the intense excitation source used. The subsequent intermediate may have stabilized the nitrate species although the structure is not known.

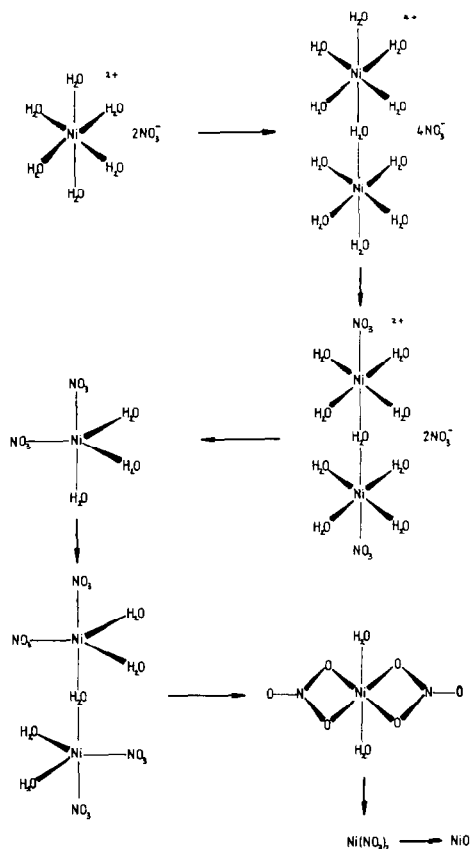


Fig. 6. The postulated reaction mechanism for the vacuum decomposition of nickel nitrate hexahydrate at 1 K min^{-1} .

Thus, using all the evidence discussed, the reaction mechanism for the vacuum decomposition of nickel nitrate hexahydrate at 1 K min^{-1} is thought to be that shown in Fig. 6.

CONCLUSIONS

The mechanisms of the deaquation processes on heating in vacuum are essentially determined by the chemistry of nickel and the stability of the hexa-coordinated species. This is also the case in various atmospheres, as discussed in Part 1 [1] although other factors, such as the removal and reactivity of loose water, are then involved. Clearly the use of Raman spectroscopy under a rising temperature regime is an excellent complementary technique. In the same way that EGA can provide a detailed mass

balance of weight loss shown on TG so the Raman technique used here provides detailed structural information about overall changes indicated by DTA.

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