Infrared Spectroscopy of Ammonia on Iron: Adsorption, Synthesis and the Influence of Oxygen

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We report on reflection absorption infrared spectroscopy (RAIRS) investigations into the influence of oxygen on the surface chemistry of NH_3 on Fe{111}. Pre-adsorption of oxygen is found to strengthen the interaction between ammonia and the surface, albeit at the lowest oxygen coverage examined the effect is only notable when the ammonia coverage becomes high. At higher oxygen coverage, the same effect is observed even with very low ammonia coverage. In cases where the oxygen overlayer is ordered, the effects are seen quite clearly, but for disordered overlayers the surface heterogeneity makes assignment of absorption features more difficult; nevertheless, comparison with the ordered examples allows us to identify the same underlying behaviour. When potassium is coadsorbed with oxygen, the effect on ammonia adsorption is threefold, including potassium-dominated and oxygen-dominated features, alongside features that suggest either cancelling or absent influences from the atomic adsorbates. Synthesis of ammonia from nitrogen adatoms in 0.6 mbar H_2 shows clear evidence of very similar surface interactions.

I. INTRODUCTION

Ammonia synthesis via the Haber-Bosch process is one of the most significant chemical processes underpinning global economic and population stability. Essential for the production of artificial fertilisers and a vital nexus in the nitrogen value chain of the chemical industry, ammonia is responsible both for feeding the world and for providing many of its most sought after commercial material products. The synthesis reaction proceeds over an iron catalyst, which dissociatively adsorbs both nitrogen and hydrogen, allowing the resulting adatoms to react and hence form ammonia, which then desorbs[1].

Considerable effort has been devoted to understanding the details of ammonia synthesis over iron, initially via experiments conducted with high-area catalysts[2–7] and latterly with single-crystal samples[8–13]. The consensus that emerges from this body of work is that the initial dissociative adsorption of nitrogen is generally the rate-limiting step, although self-poisoning can be dominant when the partial pressure of ammonia is high and the product blocks sites at which dissociation can occur. Potassium is commonly used as a promoter, acting both directly to facilitate nitrogen dissociative chemisorption and indirectly to enhance the rate of ammonia desorption. This latter effect was seen very clearly in our previous reflection absorption infrared spectroscopy (RAIRS) experiments, which demonstrate a measurable redshift in the ammonia umbrella mode frequency, indicative of a weakening in the ammonia–iron bond, due to coadsorption with potassium[14]. Furthermore, we have also shown that potassium promotes the intermediate hydrogenation steps that sequentially convert N to NH to NH_2 to NH_3 on the surface, so the alkali metal is found to be beneficial at every stage in the ammonia synthesis mechanism[15].

In commercial reactors, however, the potassium promoter is not the only species added to the iron surface.

In particular, the alkali metal is stabilised on the surface by the presence of oxygen, so that the working promoter is could arguably be considered more akin to a potassium oxide or sub-oxide than an array of separate adatoms. On the other hand, oxygen is generally considered to be a poison for the Haber-Bosch process[16] so its presence on the surface is potentially double-edged – stabilising the alkali metal promoter, but poisoning sites itself.

Accordingly, we here investigate, via RAIRS, the role of oxygen in modifying the behaviour of ammonia on the Fe{111} surface, initially on its own and subsequently upon coadsorption with potassium.

II. EXPERIMENTAL METHOD

A. RAIRS Apparatus

The experiments described below were carried out under ultra-high-vacuum (uhv) conditions, using apparatus described in detail elsewhere[17,18]. The main chamber is equipped for cleaning and characterisation of the sample, boasting an ion gun, Auger spectrometer, mass spectrometer, and low-energy electron diffraction facilities. A side chamber capable of operation up to atmospheric pressure is arranged so as to allow an infrared beam to strike the sample at grazing incidence for RAIRS experiments. The sample may be shuttled between the side and main chambers as necessary, by means of a magnetic transfer rod. Spectra presented below are shown as a ratio against a reference spectrum obtained from the clean surface immediately before each set of experiments. The spectrometer is purged with dry nitrogen, to keep the beam path free of atmospheric molecules, but variations in the quality of the purge subsequent to obtaining the reference spectrum give rise to spurious spikes in the range 1400-1800 cm^{-1}, corresponding predominantly to

water vapour. This region of the spectrum must, therefore, be interpreted with particular care. As discussed in an earlier paper, values quoted for ammonia exposure (99.999% purity) should be considered nominal (but proportional to the true exposure) because dosing occurred in the side chamber while pressures were monitored in the main chamber[14]. We believe the true exposure of ammonia at the sample position to be two or three orders of magnitude higher than those reported here, but it is not possible to be precise so we prefer to present the raw values. Oxygen, in contrast, was dosed in the main chamber, and exposures for this species should be considered to be accurate.

B. Preparation of the Clean Fe{111} Surface

Experiments were performed on an Fe{111} single-crystal surface of orientational accuracy better than $1°$, supplied by Metals, Crystals and Oxides Ltd. As described elsewhere[14], extensive cleaning was necessary to achieve a reproducibly pristine surface. In fact, the present sample had been used some years previously by Escott *et al*[19,20], and as part of *their* preparation protocol had been annealed at 900 K in a hydrogen atmosphere to remove bulk impurities, particularly sulphur. Subsequent *in situ* cleaning through sputtering and annealing was then capable of generating an acceptable surface for experiments. Despite deliberate passivation by nitrogen and storage in a desiccator between that work and the commencement of the studies described here, it was found that substantial impurities had built up on the surface, necessitating significant further *in situ* cycles of Ar^+ sputtering (680 K) and annealing (875-950 K) to remove accumulated carbon, nitrogen, oxygen and sulphur. Final removal of residual carbon was achieved through titration with oxygen at 320 K and annealing at 875 K, with any excess oxgyen removed by a further sputter/anneal cycle. Before each day's experiments, a routine sputter/anneal cycle was performed, to remove any build-up of carbon due to background adsorption of residual carbon monoxide from the chamber.

C. Preparation of Oxgyen Pre-Covered Surfaces

Oxgyen (99.998% purity) was dosed onto the clean Fe{111} surface at room temperature, and characterised by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). Relative coverages were gauged with reference to the ratio of AES peak-to-peak heights corresponding to the oxygen-related feature at 510 eV and the iron-related feature at 702 eV. At an O_{510}/Fe_{702} ratio of 0.28, annealing at 800 K produced a (4×4) LEED pattern after cooling to room temperature, while at a ratio of 0.55 the same procedure generated a $(2\sqrt{3} \times 2\sqrt{3})$-R30° LEED pattern (see Fig. 1 and Fig. 2). Both LEED patterns have been reported previ-
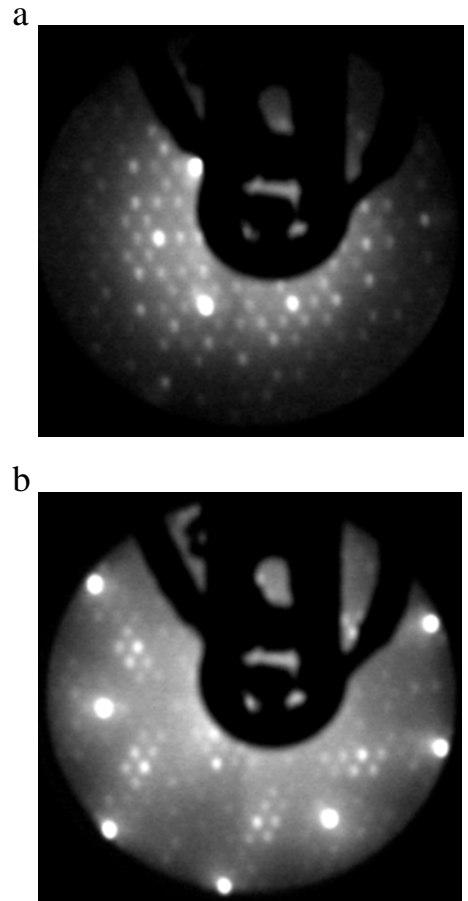

FIG. 1. (4×4) LEED patterns obtained after dosing with oxygen, to an O_{510}/Fe_{702} ratio of 0.28, at electron energies of (a) 130 eV, and (b) 175 eV.

ously by Arabczyk and Mussig[21] – the former upon annealing at 523 K after relatively low exposure to oxygen, and the latter upon annealing at the same temperature after rather higher exposures. We did not, however, observe the (5×5) and (3×3) LEED patterns found in that earlier work upon heating the (4×4) phase to between 573 and 623 K. It is possible that these phases may have been related to segregation of sulphur from the bulk in the earlier work, the onset of which appears to have coincided with an annealing temperatue of 573 K[21]; in the present work, the *ex situ* roasting in hydrogen and extensive *in situ* sputter/anneal cycles (described above) successfully rendered the selvedge essentially sulphur-free and precluded any such concerns.

We note in passing that Kelber and co-workers[22] have also reported a $(2\sqrt{3} \times 2\sqrt{3})$-R30° LEED pattern resulting from surface oxygen, although in that case impurity oxygen segregated to the surface from the bulk upon annealing, rather than being deliberately deposited from the gas phase. Indeed, the structure of the nominally "clean" surface used in those studies was highly dependent upon details of the precise annealing process em-

ployed in the preparation, with a diffuse (1×1) LEED pattern evident immediately after sputtering, a complex LEED pattern with ring-like features emerging after annealing had brought a relatively small quantity of oxygen to the surface, and the $(2\sqrt{3} \times 2\sqrt{3})$-R30° LEED pattern finally being established after further oxygen segregation. The lowest AES O_{510}/Fe_{702} ratio reported by the same group in a subsequent paper, corresponding to the nominally clean surface, was approximately 0.3[23], and although this figure is not directly comparable with our present results (because the precise experimental geometry used can alter the relative intensities of different AES features) it is nevertheless clear that a considerable quantity of oxygen was always present on their surfaces. In fact, the O_{510}/Fe_{702} ratio for their nominally clean surface was approximately one eighth of the corresponding value found at room-temperature saturation coverage, and changes in the lineshape of the 47 eV Fe AES peak indicate that this latter coverage is substantial – enough to provide evidence of well-developed Fe_2O_3 and Fe_3O_4 islands across most, if not all, of the surface. In contrast, the O_{510}/Fe_{702} ratio for our clean surface was essentially below the detection limit, perhaps 1–2% of the value achieved at room-temperature saturation, at most. We too observe characteristic changes in the lineshape of the Fe_{47} AES peak after high exposures of oxygen at room temperature (see Fig. 3) but our (4×4) and $(2\sqrt{3} \times 2\sqrt{3})$-R30° phases are prepared well below the threshold exposure where such changes begin to become apparent.

Most recently, Bowker and co-workers[24] have described the oxidation of Fe{111} at relatively high oxygen exposures in some detail. Particularly relevant to the present work are their experiments involving annealing to 773 K after room-temperature saturation with oxygen. Although the initial AES O_{510}/Fe_{702} ratio in that case is much higher than in our (4×4) or $(2\sqrt{3} \times 2\sqrt{3})$-R30° phases, it drops to around 0.7 upon annealing. Subject to the caveat that AES ratios should only be *approximately* transferable between different experimental geometries, it nevertheless seems reasonable to infer that the coverage ultimately achieved is in the same ballpark as that of our structures. Alternatively, a relatively similar AES O_{510}/Fe_{702} ratio of 0.4 was achieved by saturating the surface with oxygen whilst holding the temperature at 773 K during dosing. Intriguingly, the authors report the emergence of a (6×6) LEED pattern following *either* of these procedures, which may conceivably correspond to another LEED pattern of the same periodicity reported previously by Ertl and co-workers[25] (although the earlier work referred to the pattern as "complex" whereas the pattern shown in the later work might reasonably be described as relatively "simple"). We have not observed the (6×6) LEED pattern in our own experiments, but equally we have neither dosed oxygen at high temperature nor annealed a heavily oxidised surface.

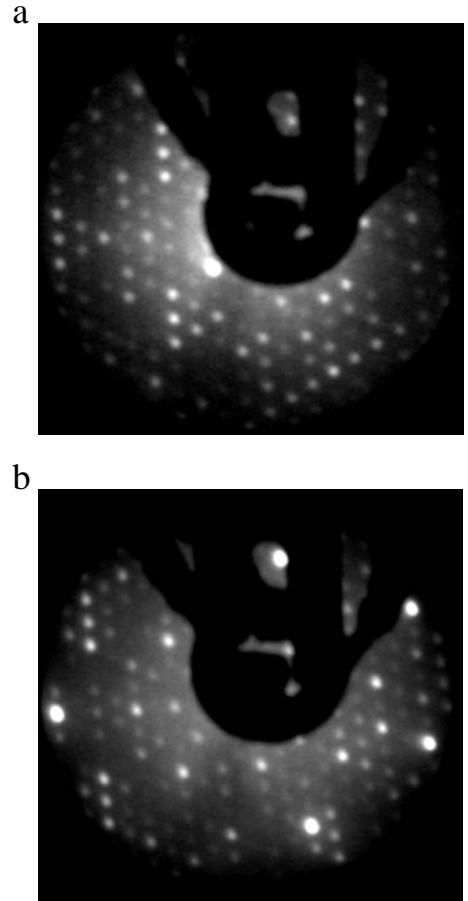The precise nature of the (4×4) and $(2\sqrt{3} \times 2\sqrt{3})$-R30° phases remains unresolved at the present time, but it

FIG. 2. $(2\sqrt{3} \times 2\sqrt{3})$ LEED patterns obtained after dosing with oxygen, to an O_{510}/Fe_{702} ratio of 0.55, at electron energies of (a) 130 eV, and (b) 175 eV.

seems certain that the coverage of the latter is close to twice that of the former, based on the AES O_{510}/Fe_{702} ratio. Furthermore, both phases are considerably below the coverage at which well-developed islands of Fe_2O_3 or Fe_3O_4 might be expected to form, although this does not preclude the possibility that some type of sub-oxide may exist as a thin surface layer. Accordingly, we can reasonably speculate that the coverage of the (4×4) phase probably lies within the range 0.25–1.00 ML, while that of the $(2\sqrt{3} \times 2\sqrt{3})$-R30° phase is bracketted within 0.50–2.00 ML; much lower coverage for the (4×4) phase would strain credulity for such a large unit cell, while much higher coverage for the $(2\sqrt{3} \times 2\sqrt{3})$-R30° phase would appear to be inconsistent with the absence of any spectroscopic evidence for oxide formation. These, then, are the likely coverage ranges employed in the ammonia adsorption experiments that follow below.
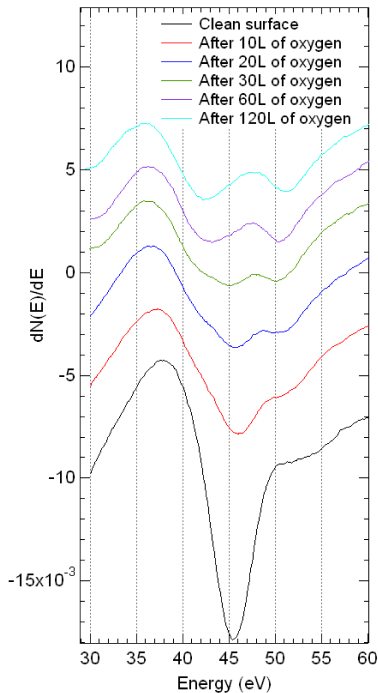
D. Preparation of Oxygen/Potassium

FIG. 3. Lineshape changes of the Fe 47 eV Auger peak with increasing oxygen exposure at 300 K

FIG. 4. RAIR spectra in the range 900-2000 cm^{-1} with increasing exposure of ammonia at 130 K on clean Fe{111}.

Pre-Covered Surfaces

As described in more detail previously[14] we deposited potassium on our sample in the main chamber by means of an alkali metal dispenser (SAES Getters) and monitored uptake by means of AES. The ratio of AES peak-to-peak heights corresponding to the potassium-related feature at 250 eV and the iron-related feature at 650 eV was taken to be the most reliable indicator of potassium coverage, and calibration against a potassium-induced (3×3) LEED pattern enabled us to associate a K_{250}/Fe_{650} ratio of 0.34 with a coverage of 0.11 ML. We hence infer a saturation coverage of 0.81 ML. Similarly, a coverage of 0.1 ML would correspond to an AES ratio of 0.31, and this we take as our standard potassium dose in the present experiments. Note that the Fe_{650} AES feature is hardly affected by deposition of oxygen, so the K_{250}/Fe_{650} ratio is expected to remain diagnostic of the potassium coverage irrespective of whether oxygen has been pre-dosed. In contrast, the Fe_{702} feature used in estimating oxygen coverage is somewhat attenuated upon deposition of potassium, and so would no longer provide a reliable benchmark. Accordingly, we prepare our surface by first depositing oxygen, and then depositing potassium, confident that the corresponding AES ratios can be used to quantify coverage of both species in that sequence. We have thus deposited 0.1 ML potassium either onto the $(2\sqrt{3} \times 2\sqrt{3})$-R30° oxygen phase, prepared as described above, or onto a disordered sur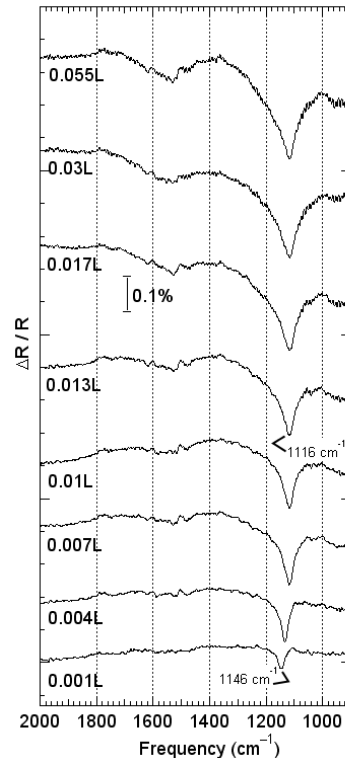face prepared without annealing but with oxygen coverage similar to that of the $(2\sqrt{3} \times 2\sqrt{3})$-R30° phase ($O_{510}/Fe_{702}$ ratio of 0.58, dosed at room temperature). At these sub-monolayer coverages, we anticipate that oxygen and potassium adatoms will both adsorb strongly into hollow sites of the iron surface, rather than forming a separate potassium oxide phase as might occur at higher coverage.

III. RESULTS

A. Adsorption of Ammonia on Clean Fe{111}

In a previous paper[14] we have reported on RAIR spectra obtained after adsorption of ammonia on our clean Fe{111} sample at a surface temperature of 112 K, so we will not dwell unduly upon repeating the details here. Since the present experiments involving an oxygen pre-covered surface were performed at a slightly higher surface temperature of 130 K, however, we have repeated our clean surface adsorption sequence under these slightly hotter conditions for ease of comparison. Figure 4 shows a set of spectra for exposures up to 0.055 L, each obtained as an average over 200 scans at a resolution of 8 cm^{-1} (as per the experiments reported below). It is likely that the lowest exposure at this temperature results in a slightly lower surface coverage than the same exposure at 112 K, and accordingly we find a slightly higher blueshift in the

NH$_3$ umbrella mode frequency than that noted in the earlier work (1146 cm^{-1} at 130 K, versus 1140 cm^{-1} at 112 K; *cf.* 968 cm^{-1} in the gas phase). Nonetheless, we see the same trend of decreasing frequency, increasing width and increasing intensity for this band as the exposure increases, with saturation occuring no higher than an exposure of 0.02 L at a frequency of 1116 cm^{-1}. As in our previous work, we interpret the blueshift in the umbrella mode frequency as indicative of the strength of the ammonia–iron bond, which progressively weakens due to through-surface intermolecular interactions as the coverage increases. The net donation of electrons from the molecule's lone pair to the surface is expected to render its hydrogen atoms more positively charged than in the gas phase, resulting in greater mutual electrostatic repulsion and a stiffening of the deformation potential, hence the increase in frequency at low coverages. Depolarisation of the adsorbate–substrate complex at higher coverages accounts for a reversal of this effect and a consequent decrease in the frequency towards the gas-phase value.

B. Adsorption of Ammonia on Oxygen Pre-Covered Fe{111}

Consider first the relatively low-coverage (4×4) phase of the oxygen pre-covered surface, prepared as described above. Adsorption of ammonia onto this structure results, as for the clean surface, in a distinct band associated with the umbrella mode of the molecule (see Fig. 5). Indeed, at low exposures of ammonia, the frequency of this band is hardly changed from that obtained on the clean surface, at 1147 cm^{-1}, indicating very little influence of oxygen on the adsorbed species. As the coverage increases with increasing exposure, however, the broadening of the umbrella mode band is similar to that observed on the clean surface, but the redshift is rather less, leading to a frequency of 1137 cm^{-1} at saturation. Since we have previously interpreted this redshift as diagnostic of a weakening in the ammonia–iron bond, we may conclude here that the presence of oxygen actually mitigates the effective repulsive interactions between ammonia molecules at higher surface coverages. Our assumption, here and throughout the following discussion, is that ammonia continues to bind directly to the iron surface, rather than attaching to an adsorbed oxygen atom. This supposition is based upon the rarity of azane oxide (-ONH$_3$) ligands in coordination chemistry; although we cannot entirely rule such a possibility out, we believe that direct interaction with adsorbed oxygen would more likely result in the formation of hydroxylamine.

Turning to the higher-coverage $(2\sqrt{3} \times 2\sqrt{3})$-R30° phase of the oxygen pre-covered surface, we find that adsorption of ammonia on this structure again results in a clear umbrella mode band, but this time the spectral feature is much sharper than before – suggesting that ammonia adsorption may be more ordered – and cen-
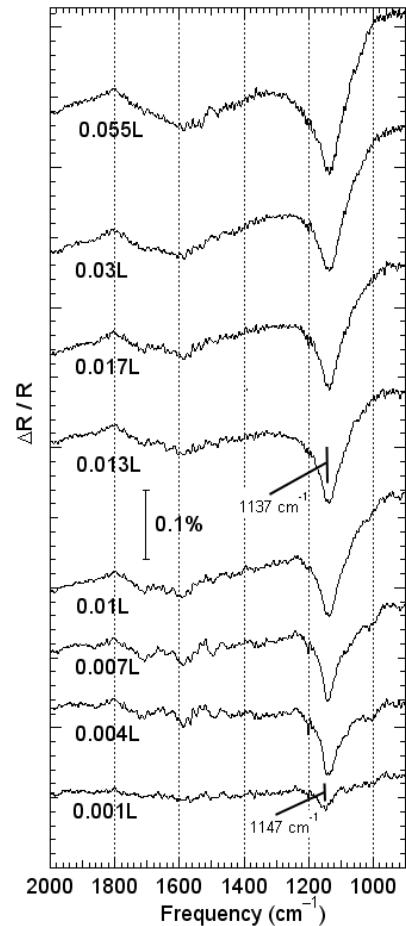

FIG. 5. RAIR spectra obtained with increasing exposure of ammonia at 130 K on Fe{111}–O(4×4).

tred on a frequency of 1172 cm^{-1} (see Fig. 6). This represents a substantial blueshift over and above that found at low ammonia coverage on either the clean surface or the surface with low oxygen pre-coverage. The most reasonable interpretation is that the pre-adsorbed oxygen here enhances the bonding of ammonia to the surface, presumably due to electrostatic effects. That is, the presence of an electron-withdrawing surface species promotes the donation of electrons from the lone pair of ammonia, strengthening the ammonia–iron bond and increasing the umbrella mode frequency. The effect is partially reversed, however, as the coverage of ammonia increases, until the umbrella mode frequency settles at 1165 cm^{-1} for exposures above 0.01 L. Interestingly, at all but the lowest exposures, a further peak is apparent at 1096 cm^{-1}, which may relate to ammonia adsorbed on less favourable sites, leading to a substantially weaker ammonia–iron bond and hence lesser blueshift relative to the gas-phase frequency. In this connection, it is notable that the higher-frequency band is virtually saturated before the lower-frequency band appears. We should stress,
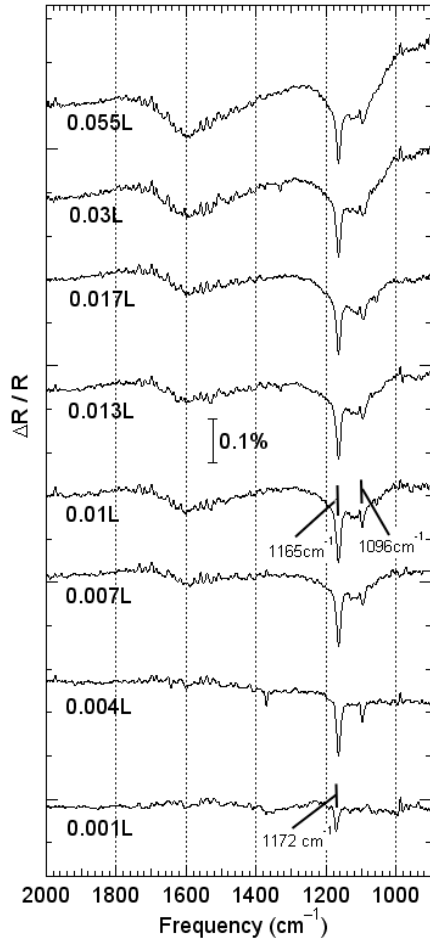
FIG. 6. RAIR spectra obtained with increasing exposure of ammonia at 130 K on Fe{111}–O($2\sqrt{3} \times 2\sqrt{3}$).
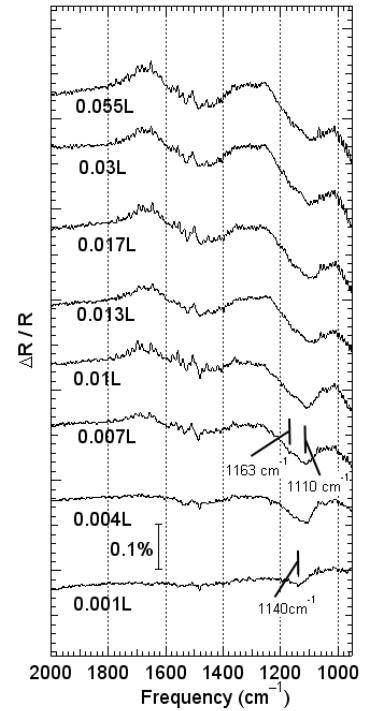

FIG. 7. RAIR spectra obtained with increasing exposure of ammonia at 130 K on Fe{111} pre-dosed with disordered oxygen to an AES O_{510}/Fe_{702} ratio of 0.58.

however, that we cannot determine the nature of these supposed less favourable sites, deducing their existence only because they possess a distinct spectroscopic signature and are not present at the lowest coverages.

Adsorption of ammonia onto a disorded oxygen pre-covered surface, formed by dosing oxygen at room temperature (up to an AES O_{510}/Fe_{702} ratio of 0.58) *without* subsequent annealing, results in a much broader and somewhat asymmetrically shaped umbrella mode band, peaking (at low coverage) at a frequency of 1140 cm^{-1} (see Fig. 7). As the ammonia coverage is increased, the frequency of the band maximum drops to about 1110 cm^{-1} at an exposure of 0.007 L, remaining roughly constant at all higher exposures. The frequency at which the umbrella mode band peaks is thus very little altered from that observed on the clean surface, but its broadness and asymmetry are rather marked. In particular, the broadness suggests significant surface heterogeneity, consistent with disorder, and the asymmetry in the lineshape reveals a high-frequency tail extending into the region of 1200 cm^{-1} or more

(albeit a strongly curving background makes it difficult to be precise about this). It appears likely that the majority of ammonia molecules adsorb at surface sites having rather low local oxygen coverage (frequencies centred around 1140 cm^{-1} or below) but a significant minority adsorb at sites with much higher local oxygen coverage (frequencies extending towards 1200 cm^{-1}).

C. Adsorption of Ammonia on Oxygen/Potassium Pre-Covered Fe{111}

To probe the effect of coadsorbed potassium and oxygen upon ammonia adsorption, we dosed oxygen to an O_{510}/Fe_{702} ratio of 0.55 and annealed at 800 K to obtain the ($2\sqrt{3} \times 2\sqrt{3}$)-R30° phase, then dosed potassium up to a K_{250}/Fe_{650} ratio indicating an approximate coverage of 0.1 ML, and finally obtained a sequence of RAIR spectra as a function of increasing ammonia exposure to the O/K co-adsorbed surface (see Fig. 8). As we do not anneal after potassium deposition, the surface is somewhat disordered when the RAIRS experiments are performed, although it is possible that the original order of the ($2\sqrt{3} \times 2\sqrt{3}$)-R30° phase may remain at a local level, to some degree, even if not observable in LEED. At any rate, we believe that surface oxygen likely remains
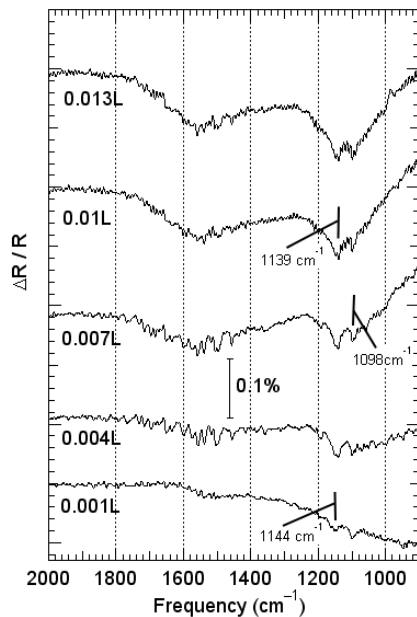
FIG. 8. RAIR spectra obtained with increasing exposure of ammonia at 130 K on Fe{111}–O($2\sqrt{3} \times 2\sqrt{3}$) pre-dosed with potassium to 0.1 ML.

FIG. 9. RAIR spectra obtained with increasing exposure of ammonia at 130 K on Fe{111} pre-dosed with disordered oxygen to an AES O_{510}/Fe_{702} ratio of 0.58 and potassium to 0.1 ML.

fairly uniformly distributed after potassium deposition, although this is not a view that we can confirm directly through experiment.

At the lowest exposure, two peaks relating to the ammonia umbrella mode are clearly visible at 1144 and 1098 cm^{-1}, and a shoulder around 1190 cm^{-1} emerges as a third distinct peak at intermediate exposures. This highest-frequency peak is a little blueshifted relative to the umbrella mode band observed on the ($2\sqrt{3} \times 2\sqrt{3}$)-R30° phase in the absence of potassium, but nevertheless we believe that the most straightforward interpretation is that it is associated with ammonia adsorbing at sites dominated by the influence of oxygen. The peak around 1144 cm^{-1}, which redshifts only very slightly to around 1139 cm^{-1} at higher exposures, is consistent with adsorption of ammonia either at sites with low local oxygen coverage, or possibly where the influences of oxygen and potassium are approximately equal and opposite.

The remaining 1098 cm^{-1} peak is at a very similar frequency to the spectral feature attributed to less favourable adsorption sites on the potassium-free ($2\sqrt{3} \times 2\sqrt{3}$)-R30° phase, but in contrast to that case is rather broader and becomes substantially populated even when the higher-frequency modes have not yet saturated. It is therefore possible that this feature may be related to the presence of potassium on the surface, and we note that we have previously reported a band at 1093 cm^{-1} at low exposures of ammonia on a surface pre-dosed with 0.1 ML potassium in the absence of oxygen[14].

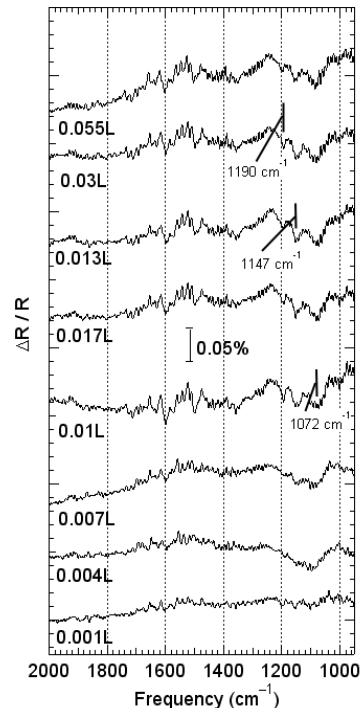To investigate further, we have also prepared the sur-

face by first dosing oxgyen (up to an O_{510}/Fe_{702} ratio of 0.58) without annealing, and then dosing potassium (up to a K_{250}/Fe_{650} ratio indicating an approximate coverage of 0.1 ML). The surface thus generated is expected to be much more thoroughly disordered than the one described immediately above, even at the shortest of length scales. A sequence of RAIR spectra obtained upon adsorption of ammonia onto this surface is shown in Fig. 9.

At the lowest ammonia exposures there is only a rather broad and asymmetric absorption band in the region associated with the umbrella mode, but as the exposure increases further this begins to resolve into three distinct peaks. The maximum of the broad asymmetric band observed at low coverages occurs at around 1093 cm^{-1} and evolves seemingly smoothly into the lowest frequency of the three peaks seen at higher coverage, ultimately settling at around 1072 cm^{-1}. Although we again note the existence of a band at 1096 cm^{-1} in data obtained on the ($2\sqrt{3} \times 2\sqrt{3}$)-R30° phase of the oxygen pre-covered surface (i.e. in the absence of potassium) the feature found here is once more substantially broader, and is arguably rather more reminiscent of the peak found previously between 1093 and 1077 cm^{-1} on the oxygen-free surface in the presence of 0.1 ML potassium[14]. The highest-frequency peak occurs at 1190 cm^{-1}, and may sensibly be related to the features at frequencies higher than 1165 cm^{-1} described above for sites with a high lo-

cal coverage of oxygen. The intermediate peak, found at 1147 cm^{-1} would again be consistent with ammonia adsorbed on regions of the surface that are locally bare, or at sites where the local coverages of potassium and oxygen exert roughly equal and opposite influences on the molecular vibrations.

D. Synthesis of Ammonia from N and H$_2$

Armed with an understanding of RAIR spectra obtained under uhv conditions for *adsorbed* ammonia, it became feasible to attempt an interpretation of similar spectra obtained during *synthesis* of ammonia at high pressures of hydrogen. In the first instance, we deposited 0.61 ML of nitrogen adatoms onto the clean surface, by dosing molecular nitrogen through the ion gun; this dosing procedure generates a combination of various nitrogen ions and excited neutral species, and greatly enhances dissociative sticking on the surface. The protocol for nitrogen deposition, and rationale for characterisation of the nitrogen coverage, is described in detail in our earlier work[15]. The sample was then exposed at 300 K to 0.6 mbar H$_2$ in the high-pressure side chamber, with RAIR spectra obtained at intervals, the lack of infra-red absorption bands in gas-phase hydrogen allowing us to collect spectra at this pressure without introducing additional complications.

Examining the resulting RAIR spectra (see Fig. 10) we find clear evidence of an ammonia umbrella mode band, with the strongest peak found at around 1115 cm^{-1}. This would be entirely consistent with the frequency reported above for ammonia adsorbed at relatively high coverage, although in this case it is likely that unreacted nitrogen adatoms block a significant fraction of the surface and that it is probably only the *local* ammonia coverage that is high. Note that our previous experiments on ammonia synthesis under identical conditions revealed that no more than 10% of the adsorbed nitrogen is susceptible to conversion into ammonia at this temperature[14]. It is arguable that a peak at around 1500 cm^{-1} may be discerned in the spectra, although spikes due to variations in the water content of the spectrometer purge gas make it difficult to be certain about this. If truly present, such a band would likely correspond to the scissor mode of NH$_2$.

We have also repeated our hydrogenation experiments on a surface pre-dosed with 0.1 ML potassium before adsorption of 0.61 ML nitrogen, and here observe three distinct peaks in the umbrella mode region (see Fig. 11) remarkably similar in appearance to those reported above for ammonia adsorption onto a surface pre-dosed with both potassium *and* oxygen. The peak at around 1190 cm^{-1} can once again be ascribed to ammonia in the vicinity of impurity oxygen, and that around 1141 cm^{-1} to ammonia located far from either oxygen or potassium, or where the effects of potassium and oxygen somehow cancel. The peak at 1070 cm^{-1} is most
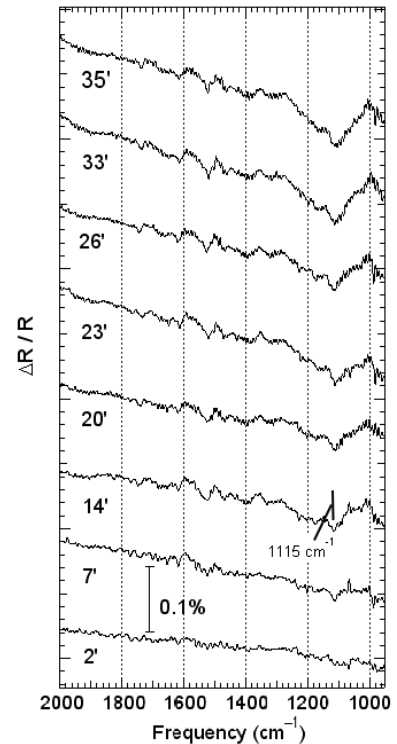

FIG. 10. Evolution in time, from 2-35 minutes, of RAIR spectra recorded during hydrogenation of 0.61 ML N adatoms on Fe{111} by 0.6 mbar H$_2$ at 300 K.

consistent with ammonia located in a site that is close to a potassium adatom. Once again, it is possible that the NH$_2$ scissor mode may account for a weak band at around 1500 cm^{-1}.

IV. DISCUSSION

The results described above suggest that ammonia is stabilised on the surface by the presence of pre-adsorbed oxygen. In the case of the lowest oxygen coverage studied here, corresponding to the (4×4) phase with O$_{510}$/Fe$_{702}$ ratio of 0.28, the frequency of the umbrella mode is hardly altered at low exposures, but undergoes a much smaller redshift upon increasing exposure than in the absence of oxygen. This may conceivably suggest initial adsorption of many ammonia molecules in sites that are relatively distant from oxygen adatoms, with the low surface temperature of 130 K hampering diffusion towards potentially more stable sites elsewhere; as the coverage increases, all viable sites must become occupied, including those lying close to the adatoms, leading to a progressively more pronounced oxygen-induced effect on the ammonia–iron bond.

With a higher oxygen pre-coverage, corresponding to the $(2\sqrt{3} \times 2\sqrt{3})$-R30° phase with O$_{510}$/Fe$_{702}$ ratio of 0.55, the umbrella mode frequency is increased relative
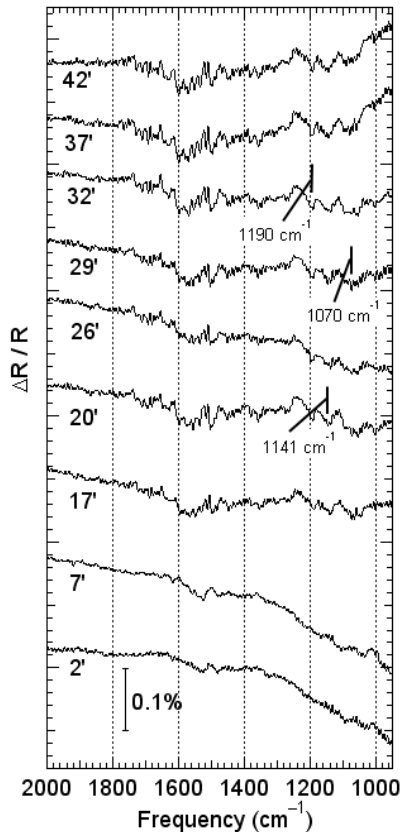
FIG. 11. Evolution in time, from 2-42 minutes, of RAIR spectra recorded during hydrogenation of 0.61 ML N adatoms on 0.1 ML potassium pre-dosed Fe{111} by 0.6 mbar H_2 at 300 K.

roughly cancel due to their joint proximity, and of other regions where ammonia adsorbs on patches of essentially bare iron revealed by the migration of oxygen adatoms to surround the potassium adatoms. Either possibility may explain the central peak, whose frequency is close to that found at low exposures on the clean surface.

Disorder in the higher-coverage oxygen overlayer leads, unsurprisingly, to a significant heterogeneous broadening of the umbrella mode absorption band. Although shifts in the frequency of the band maximum are most reminiscent of those seen for the low-coverage (4×4) phase, the peak is somewhat asymmetric and features a substantial high-frequency tail extending into a range consistent with the high-coverage $(2\sqrt{3} \times 2\sqrt{3})$-R30° phase. Presumably this behaviour reflects ammonia adsorbing onto sites having differing local oxygen coverage. On a similarly disordered surface dosed with potassium after deposition of oxygen, up to three peaks are observed, corresponding, in decreasing order of frequency, to adsorption of ammonia (i) near oxygen, (ii) either near both oxygen and potassium, or near neither, and (iii) near potassium.

V. CONCLUSIONS

The present infra-red experiments have confirmed our expectation that coadsorbed oxygen strengthens the ammonia–iron bond on the single-crystal surface thought to be most relevant to industrial ammonia synthesis. At the lowest oxygen coverage, the effect is mainly apparent only when the coverage of ammonia is high, while at higher oxygen coverage the effect is measurable even for the lowest ammonia coverage. These findings are most clear in data obtained using ordered overlayers of oxygen, but nevertheless also hold true for a disordered overlayer, albeit they are then reflected in the heterogeneity of absorption features rather than in distinct shifts.

When potassium is coadsorbed with oxygen, evidence emerges to suggest sites on the surface in which modulation of the ammonia–iron bond is dominated by potassium, sites in which it is dominated by oxygen, and still other sites where neither of the two atomic coadsorbates is dominant, either because they exert equal and opposite influences or because both are relatively distant from such sites. These results indicate considerable complexity in the interactions between ammonia, potassium and oxygen when all three are present at the surface. Certainly, they suggest that studies concentrating solely on the promotion effects of potassium in ammonia synthesis must necessarily be somewhat incomplete unless coadsorbed oxygen is included to more properly mimic the nature of the working catalyst. Indeed, our experiments involving the hydrogenation of nitrogen adatoms to form ammonia also reveal evidence of interactions between the product molecule and surface oxygen, as well as surface potassium.

to the clean surface even at low ammonia exposure, and again undergoes only a very small redshift at higher exposure. This would be consistent with the view that there are no sites within the unit cell that are relatively distant from the adatoms at this oxygen coverage. A small spectral feature at rather lower frequency than the main peak may indicate the existence of a second, less stable, type of adsorption site for ammonia, which becomes populated only once all sites of the favoured type are saturated. When potassium is also present, three separate umbrella mode absorption peaks are found, with the highest and lowest frequency bands most likely being due to adsorption of ammonia close to oxygen and close to potassium respectively. The expected attraction between electropositive potassium and electronegative oxygen, however, may possibly lead to the formation of some kind of disordered potassium oxide phase on the surface, implying the existence both of regions in which the influences of the two species on the ammonia–iron bond

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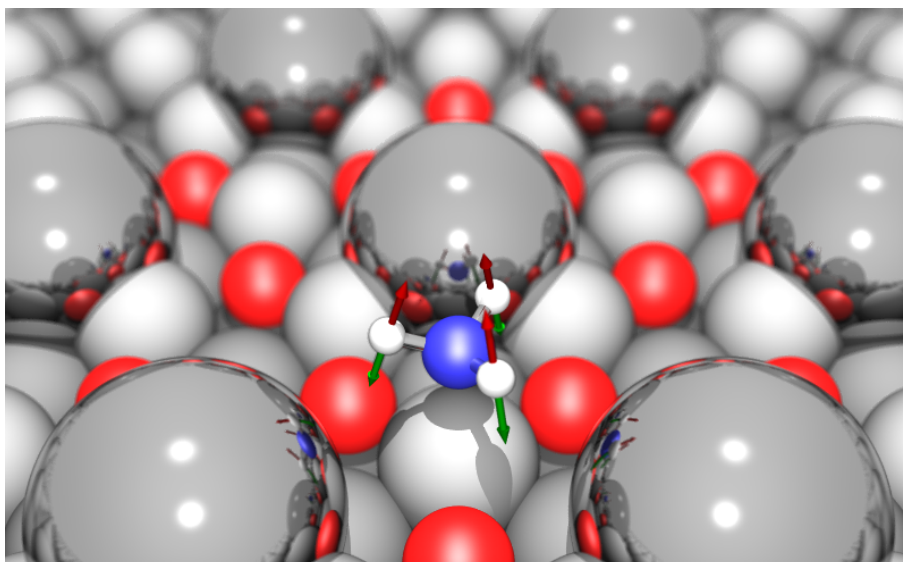
FIG. 12. **Table of Contents Graphic** - Conjectural image of ammonia adsorbed amongst oxygen and potassium adatoms.