Electronic spectroscopy of jet-cooled YbNH_3

Nicola M. Tonge, Cassandra A. Rusher, Nitika Bhalla, Luigi Varriale, and Andrew M. Ellis^{a)}
Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, United Kingdom

(Received 25 November 2011; accepted 19 January 2012; published online 13 February 2012)

We report the first spectroscopic study of a complex consisting of a rare earth atom in combination with ammonia. Using two-color resonance-enhanced multiphoton ionization (REMPI) spectroscopy, the lowest energy electronic transition of YbNH_3 has been found in the near-infrared. The spectrum arises from a spin-forbidden transition between the 1A_1 ground electronic state and the lowest 3E excited electronic state. The transition is metal centered and approximately correlates with the Yb $6s6p\ ^3P \leftarrow 6s^2\ ^1S$ transition. The observation of clear spin-orbit structure in the spectrum confirms the C_{3v} symmetry of YbNH_3 . Vibrational structure is also observed in the REMPI spectrum, which is dominated by excitation of the Yb–N stretching vibration. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3683220>]

I. INTRODUCTION

The physical and chemical properties of the rare earth element ytterbium (Yb) show many parallels to those of the alkaline earth elements. For example, Yb is a soft and malleable metal with a relatively low first ionization energy. Furthermore, while its prime oxidation state is +3, Yb also has a stable +2 oxidation state in many chemical compounds.¹ This similarity with the alkaline earth metals derives from the filled and compact $4f$ sub-shell of Yb, which leaves it with a residual valence configuration of $6s^2$. Also like the alkaline earths, as well as the alkali metals, Yb dissolves in liquid ammonia.^{2,3} When alkali metals dissolve in liquid ammonia, solvated electrons form.⁴ However, when alkaline earth and rare earth metals dissolve in liquid ammonia they do not appear to produce solvated electrons, an observation that can be attributed to their higher ionization energies when compared to the alkali metals. Thus, it is energetically more demanding to persuade an electron to depart from the metal and enter the solvent medium. Nevertheless, such metals could yield solvated electrons if they were transferred into an electronic excited state.

One way of extracting information on the microscopic behaviour of metal atoms in solvents such as ammonia is through the study of metal-solvent complexes in the gas phase. In the case of the alkali metals their complexes with NH_3 have received considerable interest in the past two decades. The earliest experimental work focused on photoionization, which was used (among other things) to extract indirect information on solvent shell closings.^{5,6} A more recent and state-of-the-art photoionization study has seen the photoionization data extrapolated to exceptionally large complexes with as many as 1500 NH_3 molecules attached to a single Na atom.⁷ Spectroscopic work appeared subsequent to the early photoionization studies, with NaNH_3 being characterized by resonance-enhanced multiphoton ionization (REMPI)

spectroscopy.^{8,9} REMPI is unsuitable for larger $\text{Na}(\text{NH}_3)_n$ complexes because of rapid excited state decay and so spectra of these complexes, with up to $n = 22$, were obtained in the near-infrared region using a photodepletion technique.¹⁰ The spectra obtained were attributed to perturbed $3p \leftarrow 3s$ transitions on the Na atoms and these shift strongly to the red in moving from $n = 1$ to $n = 4$, with very little change thereafter.

In our own laboratory we have exploited the photodepletion technique to obtain the first mid-IR spectra of $\text{Li}(\text{NH}_3)_n$ and $\text{Na}(\text{NH}_3)_n$ in the N–H stretching regions.^{11,12} These spectra have allowed a definitive identification of the first solvent shell closings. More recently, we have turned our attention to electronic spectra of alkali-ammonia complexes with the recording of the first electronic spectra of LiNH_3 and $\text{Li}(\text{NH}_3)_4$.^{13,14} For the latter we found a spectrum in the near-infrared which has much in common with the spectrum of an electron in liquid ammonia. Very recently, we have extended this work to include the alkaline earth metals and will report on this elsewhere.

Here, we present the findings from our first attempt to record gas phase spectra of a rare earth metal-ammonia complex, where the metal is Yb. We focus on the simplest species, YbNH_3 and its deuterated analogue, YbND_3 . While there have been many spectroscopic studies of Yb-containing diatomics, most notably YbF and YbO ,^{15,16} there has been only one previous study of a polyatomic Yb-containing molecule, YbOH .¹⁷ In the current work we have successfully recorded the electronic spectrum of YbNH_3 using two-color, two-photon resonance-enhanced multiphoton ionization spectroscopy. As will be described, the spectrum obtained is assigned to a spin-forbidden metal-centered transition on the Yb atom.

II. EXPERIMENTAL

The experimental procedure and apparatus employed was similar to that described in previous studies.^{11–14} Briefly, $\text{Yb}(\text{NH}_3)_n$ clusters were produced by laser ablation of a solid ytterbium target in the presence of gaseous NH_3 and the

^{a)} Author to whom correspondence should be addressed. Electronic mail: andrew.ellis@le.ac.uk. Tel.: +44 (0)116 252 2138. Fax: +44 (0)116 252 3789.

resulting mixture was expanded into vacuum to form a supersonic jet. The central portion of the jet was extracted by a skimmer (2 mm aperture diameter) and the resulting molecular beam passed into the source region of a time-of-flight mass spectrometer, where it was photoionized by the output from a frequency-doubled pulsed dye laser pumped by a Nd:YAG laser and operating using Rhodamine 6G dye. A range of $\text{Yb}(\text{NH}_3)_n^+$ cluster ions, produced by non-resonant two-photon ionization, could be observed at sufficiently high laser fluence, but the focus here is on the $n = 1$ cluster.

To record optical spectra, which was achieved using two-color REMPI spectroscopy, a second laser beam was added to electronically excite the neutral YbNH_3 complex. A LaserVision optical parametric oscillator/amplifier (OPO/A) was employed for this purpose. This system was pumped by the output from an injection-seeded Nd:YAG laser (Surelite II-10), although the injection seeder was not essential for the experiments described here since it did not affect the observable resolution. Since all of the spectra were recorded in the near-infrared, only the OPO part of the OPO/A system was used. This gave a wavelength tunable output with a pulse energy of up to 15 mJ, although only a small fraction of this available energy was used in the current study. The linewidth of the OPO output with the injection seeder switched off is expected to be $\sim 3 \text{ cm}^{-1}$. The OPO and photoionization laser beams were aligned into the source region of the mass spectrometer in a counter-propagating manner in order to achieve maximum spatial overlap between the two beams. The photoionization laser intensity was then reduced to minimize background YbNH_3^+ produced by non-resonant two-photon ionization. The temporal delay between the firing of the two laser pulses was controlled using a delay generator to optimize the observed REMPI signal when the OPO wavelength was tuned to an electronic transition of YbNH_3 . The wavelength of the OPO was calibrated using a Burleigh wavemeter.

Ammonia was sourced from a standard liquid ammonia cylinder and was used with no further purification. To assist with spectra assignments some experiments were also carried out using ND_3 (Sigma Aldrich, 99% D-atom substitution).

III. COMPUTATIONAL DETAILS

Ab initio geometry optimization and harmonic vibrational frequency calculations were carried out on YbNH_3 to assist with the spectroscopic analysis. These calculations employed complete active space self-consistent field (CASSCF) or MP2 methodology (see below) and were run using the GAUSSIAN 03 suite of programs.¹⁸ For N and H atoms, the standard Dunning cc-pVDZ basis sets were used.¹⁹ However, Yb is not included in the Dunning basis sets, and furthermore the large number of core electrons in this atom requires the use of a pseudopotential. Consequently, a Yb basis set and pseudopotential were downloaded from the EMSL basis set exchange website.²⁰ This basis set was of double-zeta quality and was designed for use with a pseudopotential: in this case the Stuttgart ECP28MWB pseudopotential was employed and the combined basis set/pseudopotential package is known as Stuttgart RSC 1997 ECP.

Calculations were begun at the MP2 level with separate calculations on the singlet and triplet manifolds. The expectation was that the ground states in both the singlet and triplet manifolds would correspond to the two electronic states assigned in the spectroscopic work (see later). However, although the triplet state MP2 calculations resulted in optimized geometries with no imaginary vibrational frequencies, the Yb virtual orbitals continually switched order (despite a number of attempts to force the orbitals into the correct order) giving a physically unrealistic situation in which the Yb 7s orbital was below the 6p orbitals, and thus giving a triplet state of the wrong spatial symmetry. Fortunately, the CASSCF calculations successfully bypassed this problem. The active space comprised two electrons and eight molecular orbitals. The specific orbitals in the active space were derived from the combination of the Yb 6s and 6p orbitals with what essentially amounts to the N 2s and 2p valence orbitals. This gives two a_1 orbitals and one e bonding orbital and their antibonding counterparts. The CASSCF calculations were performed to investigate the lowest energy singlet and triplet electronic states, in addition to the first singlet excited electronic state.

IV. RESULTS AND DISCUSSION

A. Photoionization mass spectrometry

Figure 1(a) shows the photoionization mass spectrum derived from the Yb/NH_3 system with the OPO laser beam off-resonance with any spectral transitions of YbNH_3 . Many peaks can be seen, all of which can be assigned to Yb^+ and various $[\text{Yb}(\text{NH}_3)_n]^+$ complexes extending up to $n = 16$. At the photoionization wavelength used in the present work, 282 nm, there are signal maxima corresponding to $n = 7$ and $n = 13$ but we are cautious in attaching any significance to these observations because the ion cluster distribution was found to depend on several factors, including the UV laser wavelength, the laser fluence, and the supersonic expansion conditions. We are planning to explore this photoionization behaviour in detail, including the determination of ion appearance energies as a function of cluster size, and will report on this elsewhere.

The focus of this work is on YbNH_3 , and in particular the dramatic enhancement in the YbNH_3^+ signal when the OPO output was tuned to an appropriate wavelength. The mass spectrum shown in Figure 1(b) shows the effects of resonant absorption of the IR OPO beam. A large increase in the YbNH_3^+ signal occurs, such that the YbNH_3^+ signal is now far larger than the Yb^+ signal, and this is attributed to REMPI excitation of YbNH_3 . By measuring the YbNH_3^+ ion signal as a function of OPO wavelength a two-color REMPI spectrum of YbNH_3 was obtained.

The observation of resonance-enhanced increases in ion signal in the YbNH_3^+ ion channel does not rule out any contribution to the REMPI spectrum from larger $\text{Yb}(\text{NH}_3)_n$ clusters, but we think contributions from optical excitation of $n \geq 2$ clusters are highly unlikely for several reasons. First, we observe no ion signal enhancements in any higher mass channels in the wavelength range investigated, which means that if $n \geq 2$ clusters did contribute, then 100% of the resulting ions must fragment rapidly to yield YbNH_3^+ . Second,

FIG. 1. Photoionization mass spectra taken at a UV wavelength of 282 nm and with (a) the OPO laser off-resonance ($13\,901\text{ cm}^{-1}$) and (b) with the OPO laser on-resonance and exciting the electronic band origin in YbNH_3 ($13\,795\text{ cm}^{-1}$). The inset to (b) shows the region between m/z 165 and 202, highlighting the resolution obtained in the mass spectrometer; Yb has several observable isotopes and each is clearly observed. Note that plots (a) and (b) do not have the same y-axis scale; in both plots the signal intensity of Yb^+ is identical.

as will be explained in Secs. IV B and IV C, the structure observed in the REMPI spectra is consistent with our expectations for YbNH_3 , and in particular a species with high point group symmetry. Finally, we draw an analogy with $\text{Li}(\text{NH}_3)_n$ and $\text{Na}(\text{NH}_3)_n$ clusters, where the optical spectra for the lowest lying electronic transitions for $n \geq 2$ are strongly redshifted from the $n = 1$ species.^{10,13} Furthermore, $\text{Li}(\text{NH}_3)_n$ and $\text{Na}(\text{NH}_3)_n$ clusters undergo rapid non-radiative relaxation in the excited electronic state, rendering them all unobservable by REMPI except for $n = 1$.^{8,9,14} Although there is no precise correlation between the electronic states of $\text{Li}(\text{NH}_3)_n/\text{Na}(\text{NH}_3)_n$ and $\text{Yb}(\text{NH}_3)_n$, as detailed below the strongly metal-centered nature of their low-lying electronic transitions would lead us to expect broadly similar behaviour. For all of these reasons we can confidently assign the spectrum in Figure 2 to YbNH_3 .

B. Electronic structure

Figure 2 compares the REMPI spectra of YbNH_3 and YbND_3 . These spectra were recorded by summing the mass spectral signals over all possible Yb isotopes, since no dif-

FIG. 2. REMPI spectra of YbNH_3 and YbND_3 . These spectra have not been corrected for variations in OPO pulse energy with wavelength. Both spectra were recorded as two overlapping scans, which gives rise to the increased noise level at the high wavenumber ends of the spectra. Increased ion signals in these spectra correspond to negative-going (downward) peaks. Also shown are the band assignments above each spectrum.

ferences in the optical spectra were found to be resolvable when choosing isotopologues arising from different Yb isotopes. The lowest energy band in the spectrum of YbNH_3 is observed at $13\,795\text{ cm}^{-1}$. After substitution of all H-atoms with D, the equivalent band is redshifted to $13\,770\text{ cm}^{-1}$. There are no bands to the red of this feature, and it therefore seems reasonable to infer that this band represents an electronic band origin.

There are several bands to higher energy in the spectra of both YbNH_3 and YbND_3 . Some of these bands derive from vibrational structure. Indeed, at first sight there looks to be a very obvious low frequency vibrational progression in the REMPI spectra. However, the situation is more complex. Considering the third lowest energy feature in the spectra of both YbNH_3 and YbND_3 for illustration, close inspection shows that there are at least two bands here, with a shoulder appearing on the low energy side of a stronger band. For reasons that will become clear as the discussion progresses, we assign the stronger feature to another electronic origin transition, rather than to vibrational structure. We defer discussion of any vibrational structure to Sec. IV C.

As shown in Table I, bands in the spectrum of YbNH_3 at $13\,795$, $14\,282$, and $14\,755$ are assigned to spin-orbit sub-states in the excited electronic state, specifically to the

TABLE I. Band positions and assignments for the YbNH₃ REMPI spectrum (in cm⁻¹) and quoted relative to the YbNH₃ and YbND₃ band origins at 13 795 and 13 770 cm⁻¹, respectively.

YbNH ₃	YbND ₃	Assignment ^a
0	0	0 ₀ ⁰ (³ E ₀)
232	217	3 ₀ ¹ (³ E ₀)
447	416	3 ₀ ² (³ E ₀)
487	443	0 ₀ ⁰ (³ E ₁)
663	617	3 ₀ ³ (³ E ₀)
722	663	3 ₀ ¹ (³ E ₁)
888	787	3 ₀ ⁴ (³ E ₀)
931	830	3 ₀ ² (³ E ₁)
960	877	0 ₀ ⁰ (³ E ₂)
	1009	3 ₀ ³ (³ E ₁)
	1087	3 ₀ ¹ (³ E ₂)

^aThe excited state spin-orbit component is identified in parentheses.

³E₀, ³E₁, and ³E₂ components, respectively. The justification for this is as follows. First, we refer to the *ab initio* calculations which reveal that in the ground electronic state the YbNH₃ molecule adopts C_{3v} point group symmetry. The Yb atom binds to the N atom and the resulting electronic state has ¹A₁ symmetry. Given the availability of low-lying excited states of atomic Yb, which by contrast are not available for NH₃, we expect the lowest energy electronic transitions of YbNH₃ to be largely metal centered. The same behaviour is seen for LiNH₃ and NaNH₃ for exactly the same reasons.^{8,9,14} We can therefore draw upon the known electronic energy levels of Yb to construct a simple electronic structure model for YbNH₃.

The lowest energy electronic transition in atomic Yb involves excitation of one of the 6s electrons to a 6p orbital.²¹ This excitation can occur as both spin conserved (singlet-singlet) and spin-forbidden (singlet-triplet) and, because of its relatively high nuclear charge, spin-forbidden transitions are significant for Yb. In a metal-centered picture of YbNH₃, the 6s6p ¹P excited state of Yb will correlate with ¹E and ¹A₁ states of YbNH₃. Likewise, the ³P excited state of Yb will correlate with ³E and ³A₁ states of YbNH₃. However, only the ³E state of YbNH₃ can show any spin-orbit structure, and thus we provisionally assign the spectra in Figure 2 to three spin-orbit components of the lowest lying ³E electronic states of YbNH₃ (upper panel) and YbND₃ (lower panel), i.e., to the $\tilde{a}^3E - \tilde{X}^1A_1$ electronic system.

The lowest energy electronic transitions identified for LiNH₃ and NaNH₃, which are largely 2p ← 2s and 3p ← 3s in character, respectively, show redshifts of ~3500 and 4700 cm⁻¹ relative to the corresponding bare atom transitions.^{8,14} By analogy with these complexes we expect a significant redshift for the YbNH₃ 6p ← 6s transitions relative to the bare atomic Yb transitions. In atomic Yb the lowest energy spectroscopic transition from the ground electronic state is spin-forbidden. This 6s6p ³P₀-6s² ¹S atomic transition is observed at 17 288 cm⁻¹ and thus, with the expected redshift taken into account, the observed spectral features for YbNH₃ and YbND₃ are located in a region where it is plausible to assign the bands to the $\tilde{a}^3E - \tilde{X}^1A_1$ electronic transition. By comparison the lowest lying spin-allowed transi-

tion of atomic Yb, the 6s6p ¹P-6s² ¹S transition, occurs at 25 026 cm⁻¹.²¹ An exceptionally large redshift would be required if the transition responsible for the spectra in Figure 2 were to correlate with the ¹P-¹S transition. Such a large shift would require very strong perturbation of the unpaired electron density by the NH₃ group and there is no evidence for such an effect. In any case, we can rule out such a transition through the observation of excited state spin-orbit structure.

We can also use the *ab initio* calculations to extract information on the various electronic states of YbNH₃, although our primary aim in performing these calculations was to obtain information on geometries and vibrational frequencies, since electronic transition frequencies are difficult to predict without a good quality treatment of the dynamic electron correlation. The CASSCF calculations predict that the $\tilde{a}^3E - \tilde{X}^1A_1$ and $\tilde{A}^1E - \tilde{X}^1A_1$ transitions will occur at 22 519 and 29 409 cm⁻¹, respectively, which puts them well above the experimental region explored in this paper. Nevertheless, the $\tilde{a}^3E - \tilde{X}^1A_1$ transition is predicted to lie well below the $\tilde{A}^1E - \tilde{X}^1A_1$ transition. We can benchmark our calculations by performing corresponding CASSCF calculations on atomic Yb. These predict 6s6p ³P-6s² ¹S and 6s6p ¹P-6s² ¹S transitions at 28 122 and 32 866 cm⁻¹, respectively, which again are considerably above the experimental values. Consequently, while the CASSCF calculations do a poor job at predicting the absolute transition wavenumbers for the lowest singlet-singlet and singlet-triplet transitions of both YbNH₃ and atomic Yb, they do predict a redshift on addition of NH₃ and they also predict that the singlet-triplet transition will lie well below the singlet-singlet transition.

We now turn to the magnitude of the excited state spin-orbit splitting. For a linear molecule in the Russell-Saunders limit, each spin-orbit component should be located at position $T_0 + A\Lambda\Sigma$, where T_0 represents the unperturbed electronic transition frequency (i.e., in the absence of spin-orbit coupling), Λ is the projection of the electronic orbital angular momentum on the C₃ symmetry axis in the excited state, Σ is the corresponding value for the spin angular momentum, and A is the spin-orbit coupling constant. Russell-Saunders coupling will only approximately apply to YbNH₃ because of the heavy Yb atom, and of course it is a nonlinear molecule and so Λ in particular is no longer a good quantum number. The ³P state of atomic Yb splits into three spin-orbit components, ³P₀, ³P₁, and ³P₂, which are observed at 17 288, 17 992, and 19 710 cm⁻¹, respectively, relative to the ¹S ground electronic state.²⁰ This implies a spin-orbit coupling constant, ζ_{6p} , of 704 cm⁻¹ for atomic Yb. In order to gain an estimate of A in the excited state of YbNH₃, a simple calculation based on the *ab initio* molecular orbital simulations was performed, i.e.,

$$A = \sum_i c_i^2 \zeta_i, \quad (1)$$

where c_i are the coefficients for those atomic orbitals making a substantial contribution to the excited state MO containing the unpaired electron and ζ_i is the spin-orbit coupling constant for atomic orbital i .²² According to our *ab initio* calculations, the unpaired electron in the $\tilde{a}^3E$ state of YbNH₃ is in an orbital strongly dominated by the Yb 6p_{x,y} orbitals, with

TABLE II. *Ab initio* vibrational frequencies of YbNH₃ and YbND₃ (in cm⁻¹) calculated at the CASSCF/cc-pVDZ level of theory.

Vibration	Description ^a	$\tilde{X}^1A_1$		$\tilde{A}^1E$		$\tilde{a}^3E$	
		YbNH ₃	YbND ₃	YbNH ₃	YbND ₃	YbNH ₃	YbND ₃
ν_1 (a_1)	Symm. N–H stretch	3634	2765	3637	2607	3614	2591
ν_2 (a_1)	NH ₃ Umbrella	1316	999	1355	1025	1390	1052
ν_3 (a_1)	Yb–N stretch	178	165	186	173	240	223
ν_4 (e)	Antisymm. N–H stretch	3758	2765	3740	2749	3716	2731
ν_5 (e)	N–H scissor	1788	1295	1790	1296	1784	1291
ν_6 (e)	Yb–N–H bend	425	313	447	330	493	364

^aThese descriptions describe the approximate character of the vibrational modes.

a much smaller contribution from the N $2p_{x,y}$ orbitals. The respective normalized coefficients were 0.954 and 0.300, and thus inserting these into Eq. (1) with the appropriate atomic orbital spin-orbit coupling coefficients leads to a predicted spin-orbit coupling constant, A_{YbNH_3} , of ~ 644 cm⁻¹. However, the off-axis H atoms in the YbNH₃ complex are expected to partially quench the electronic orbital-angular momentum and, therefore, reduce the effective spin-orbit coupling. Consequently, 644 cm⁻¹ should be an upper limit to the true spin-orbit coupling constant of the $\tilde{a}^3E$ state.

The 3E_1 - 3E_0 and 3E_2 - 3E_1 separations observed from the YbNH₃ spectra are 487 and 473 cm⁻¹, which are consistent with the theoretically derived value when the partial quenching of the electronic orbital angular momentum is taken into account. It is noteworthy that $A_{\text{YbNH}_3} \neq A_{\text{YbND}_3}$ with the latter reduced to ~ 440 cm⁻¹. This difference is not huge, but it is significant given that the spin-orbit coupling would normally be expected to be isotope invariant. The fact that this is not, suggests that substantial perturbations are in action, as noted recently for the $\tilde{A}^2\Pi$ states of BaOH and BaOD.²³ The most likely candidate for the perturbing state is the lowest 3A_1 state, which like the $\tilde{a}^3E$ state correlates with the $6s6p^3P$ excited state. We have not located the 3A_1 state but it is likely to be reasonably close to the $\tilde{a}^3E$ state and must have a differential perturbing effect on the two isotopologues, YbNH₃ and YbND₃, in order to generate different effective spin-orbit coupling constants.

C. Vibrational structure

We now turn to the remaining features in the REMPI spectra of YbNH₃ and YbND₃, which are attributed to vibrational structure. YbNH₃ will have six vibrational normal modes, with approximate descriptions and symmetries as follows: the Yb–N stretch (a_1), the Yb–N–H bend (e), the NH₃ umbrella vibration (a_1), the H–N–H bending mode (e), the symmetric N–H stretch (a_1), and the antisymmetric N–H stretch (e). To gain some idea of the frequencies of these vibrations, we show the *ab initio* predictions for YbNH₃ and YbND₃ in several electronic states in Table II.

Most of the vibrational structure seen in the YbNH₃ spectrum can be accounted for by excitation of the Yb–N stretching vibration, ν_3 . The first band to the blue of the $\tilde{a}^3E_0 - \tilde{X}^1A_1 0_0^0$ band is a strong band located at +232 cm relative to the origin band. This interval is very close to the

ab initio prediction for the Yb–N stretching vibrational frequency in the $\tilde{a}^3E$ state. Other members of the ν_3 progression associated with this spin-orbit component, as well as the other spin-orbit components, can be readily found, as shown in both Figure 2 and as summarized in Table I. These assignments are supported by the small shifts in the measured vibrational intervals on deuteration, which would be inconsistent with all vibrations except the Li–N stretch. For example, we measure a 3^1-3^0 interval of 217 cm⁻¹ for YbND₃, which is 15 cm⁻¹ smaller than that determined for YbNH₃. This compares very well with the redshift of 17 cm⁻¹ for the $\tilde{a}^3E$ state predicted from the *ab initio* calculations (see Table II). Furthermore, we note that a substantial reduction in the Yb–N equilibrium bond length, from 2.72 to 2.59 Å, is predicted by the CASSCF calculations for excitation from the $\tilde{X}^1A_1$ state to the $\tilde{a}^3E$ state. This is consistent with the observation of a significant progression in this vibrational mode.

The combination of excited state spin-orbit coupling and vibrational structure in mode ν_3 accounts for all of the bands with significant signal-to-noise ratios in Figure 2. There is no evidence for excitation of the Yb–N–H bend (ν_6), whose predicted frequency is sufficiently low to be observable in the scan range covered in Figure 2. Structure in this non-totally symmetric vibration would require vibronic coupling to gain significant intensity, but such coupling has been seen previously in spectra of LiNH₃ and NaNH₃.^{8,9,11,12} However, this vibration would be characterized by relatively large isotope shifts on deuteration, which would be inconsistent with the YbNH₃ and YbND₃ spectra in Figure 2. Equally, there is no evidence for excitation of the umbrella mode, although in the case of YbNH₃ this is likely to fall outside of the scan range reported here. The scan range in the current study is constrained by the OPO, whose output pulse energy declines dramatically beyond 15 000 cm⁻¹. It would, therefore, be interesting to extend this work using dye laser excitation to try and access higher lying vibrational levels in the $\tilde{a}^3E$ state, as well as for finding the 3A_1 state and the singlet electronic excited states.

V. CONCLUSIONS

The first spectroscopic observation of a rare earth metal-ammonia complex in the gas phase has been reported. The spectrum of YbNH₃ was obtained using two-color REMPI spectroscopy and the features observed have all been assigned

to the spin-forbidden $\tilde{a}^3E - \tilde{X}^1A_1$ electronic band system, which correlates with the lowest $6s6p\ ^3P \leftarrow 6s^2\ ^1S$ transition of atomic Yb. The measured spin-orbit coupling constant is close to that expected for the $\tilde{a}^3E$ state on the basis of the calculated molecular orbital composition, although it is reduced by off-axis quenching of the orbital angular momentum by the H atoms. Vibrational structure is seen which can be accounted for by excitation of the Yb–N stretching vibration.

ACKNOWLEDGMENTS

The authors would like to thank the UK Engineering and Physical Sciences Research Council (EPSRC) for a grant in support of this work. Computational aspects were supported through the University of Leicester Mathematical Modelling Centre.

¹F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed. (Wiley-Interscience, New York, 1999).

²R. L. Schroeder, J. C. Thompson, and P. L. Oertel, *Phys. Rev.* **178**, 298 (1969).

³R. Hagedorn and J. P. Lelleur, *J. Phys. Chem.* **85**, 275 (1981).

⁴J. C. Thompson, *Electrons in Liquid Ammonia* (Clarendon, Oxford, 1976).

⁵I. V. Hertel, C. Hueglin, C. Nitsch, and C. P. Schulz, *Phys. Rev. Lett.* **67**, 1767 (1991).

⁶C. P. Schulz, A. Gerber, C. Nitsch, and I. V. Hertel, *Z. Phys. D: At., Mol. Clusters* **20**, 65 (1991).

⁷C. Steinbach and U. Buck, *J. Chem. Phys.* **122**, 134301 (2005).

⁸C. P. Schulz and C. Nitsch, *J. Chem. Phys.* **107**, 9794 (1997).

⁹D. A. Rodham and G. A. Blake, *Chem. Phys. Lett.* **264**, 522 (1997).

¹⁰P. Brockhaus, I. V. Hertel, and C. P. Schulz, *J. Chem. Phys.* **110**, 393 (1999).

¹¹T. E. Salter, V. A. Mikhailov, C. J. Evans, and A. M. Ellis, *J. Chem. Phys.* **125**, 034302 (2006).

¹²T. E. Salter, V. Mikhailov, and A. M. Ellis, *J. Phys. Chem. A* **111**, 8344 (2007).

¹³L. Varriale, N. M. Tonge, N. Bhalla, and A. M. Ellis, *J. Chem. Phys.* **132**, 161101 (2010).

¹⁴L. Varriale, N. M. Tonge, N. Bhalla, A. M. Ellis, and T. G. Wright, *J. Chem. Phys.* **134**, 124303 (2011).

¹⁵C. Linton, S. McDonald, S. Rice, M. Dulick, Y. C. Liu, and R. W. Field, *J. Mol. Spectrosc.* **101**, 332 (1983).

¹⁶T. Ma, C. Butler, J. M. Brown, C. Linton, and T. C. Steimle, *J. Phys. Chem. A* **113**, 8038 (2009).

¹⁷T. C. Melville and J. A. Coxon, *J. Chem. Phys.* **115**, 6974 (2001).

¹⁸M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

¹⁹T. H. Dunning, *J. Chem. Phys.* **55**, 716 (1971).

²⁰K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, and T. L. Windus, *J. Chem. Inf. Model* **47**, 1045 (2007); see <http://bse.pnl.gov/bse/portal>.

²¹See <http://www.nist.gov/pml/data/asd.cfm> for NIST atomic spectra database.

²²R. N. Dixon and H. W. Kroto, *Trans. Faraday Soc.* **59**, 1484 (1963).

²³J. D. Tandy, J.-G. Wang, and P. F. Bernath, *J. Mol. Spectrosc.* **255**, 63 (2009).