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Fourier transform emission spectroscopy of YbO in the near-infrared region[☆]

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Abstract

The emission spectrum of gas-phase YbO has been investigated using a Fourier transform spectrometer. Chemiluminescence was observed from excited YbO molecules produced in a Broida-type oven by the reaction of ytterbium metal vapor with N_2O. A total of eight red-degraded bands in the range $9800-11\,300\,cm^{-1}$ were recorded at a resolution of $0.04\,cm^{-1}$. Because of the multiple isotopomers present in the spectra, only three bands were rotationally analyzed. Perturbations were identified in two of these bands and all three transitions were found to terminate at the $X\,^1\Sigma^+$ ground electronic state. The electronic configurations that give rise to the observed states are discussed and molecular parameters for all of the analyzed bands are reported.
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1. Introduction

A considerable interest in lanthanide-containing molecules has arisen during past two decades [1]. For diatomic molecules, the lanthanide monoxides were studied most extensively both theoretically and experimentally. The spectra are difficult to interpret because of the huge number of electronic states arising from open $4f$ configurations. Moreover, large spin–orbit coupling effects split and mix the various spin components that arise from the numerous $^{2S+1}\Lambda$ terms. The only remaining good quantum numbers are thus J and Ω, in the absence of nuclear spin. Ab initio calculations thus need to include relativistic effects before any meaningful comparison with experiment can be made.

The first experimental work on YbO, apart from bandhead positions found in the Vatican plates [2], was by

Linton et al. [3]. They recorded a number of visible bands by laser excitation spectroscopy and examined some of the low-lying states by dispersing the laser-induced fluorescence. The ground state of YbO was found to be $X\,^1\Sigma^+$ arising from the $4f^{14}$ Yb^{2+} configuration, as predicted from a ligand-field calculation [3,4] on $Yb^{2+}O^{2-}$. Such a closed-shell ground state was unusual because all lanthanide oxides except EuO and YbO have ground states that arise from $M^{2+}4f^n6s^1$ configurations rather than $4f^{n+1}$ configurations [4,5]. The extra stability of the half-filled $4f^7$ Eu^{2+} and the filled $4f^{14}$ Yb^{2+} leads to $X\,^8\Sigma^-$ and $X\,^1\Sigma^+$ ground states, respectively, for EuO and YbO.

The combination of ligand-field theory [4,5] and laser spectroscopy [3,6] has led to a rather satisfactory picture of the first few low-lying electronic states of YbO. In spite of a large number of papers [7–13], ab initio calculations do not predict a $X\,^1\Sigma^+$ ground state but rather a 0^- ground state that correlates with the $4f^{13}6s^1$ configuration of Yb^{2+}. Experimentally, this 0^- state is found at just $910\,cm^{-1}$ above the $X\,^1\Sigma^+$ state [6] so it is not surprising that calculations have difficulty obtaining the correct energy ordering. There is also substantial

configuration mixing between the $4f^{13} 1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$ and $4f^{14} 1\sigma^2 2\sigma^2 1\pi^4$ configurations (i.e., $4f^{13}6s^1$ and $4f^{14}$ on Yb^{2+}) in the ground state as deduced from the dipole moment of 5.89 D [14]. The most recent experimental work is the detection of the infrared vibrational fundamentals of both YbO and YbO^+ in an argon matrix [15]. The exited states of YbO seen in the visible bands are ascribed to states correlating with the $4f^{13}5d^1$ and $4f^{13}6p^1$ configurations of Yb^{2+} as well as charge transfer states associated with Yb^+O^- [6]. The details are uncertain, however, and it would be helpful to locate additional transitions in the near infrared region, where the density of states is lower. We, therefore, report on eight new bands near 1 μm. A rotational analysis was possible for three of these bands.

2. Experimental arrangement

Gas-phase YbO was generated in a Broida-type oven [16] by the reaction of ytterbium metal vapor with N_2O. About 10 g of ytterbium metal was resistively heated in an alumina crucible with a current of about 45 A. A flow of argon gas carried the Yb metal vapor from the crucible to the reaction region where it was mixed with the oxidant gas. The partial pressures of the argon and nitrous oxide were adjusted to optimize the reddish chemiluminescent flame. Total pressures in the oven were approximately 6–8 Torr, with the oxidant gas making up a small fraction of this total.

The chemiluminescence from the flame was imaged onto the entrance aperture of a Bruker IFS 120 HR Fourier transform spectrometer. The YbO emission spectrum was recorded in the range 9000–12 000 cm^{-1} using a silicon photodiode detector. An 800-nm red pass filter was used to eliminate the signal from the He–Ne laser of the spectrometer. To obtain a good signal-to-noise ratio (S/N), a total of 50 scans were co-added at a resolution of 0.04 cm^{-1}. Line positions were measured using a Windows-based program called WSpectra, written by Dr. Michel Carleer (Laboratoire Chimie Physique Moléculaire, Université Libre de Bruxelles, Belgium). A zero filling factor of 4 was used to generate enough points for good data reduction and Voigt lineshape functions were fitted to the observed rotational lines. For calibration, argon atomic lines were recorded from an argon pen lamp immediately after the experiment and compared to the list of Norlén [17]. The accuracy of measurements in similar previous work of this nature is typically 0.005 cm^{-1} (or better) for strong, unblended lines.

3. Results and discussion

The observed YbO chemiluminescence spectrum of the strongest band obtained in the present work is dis-

played in Fig. 1. A total of eight red-degraded bands were identified in the region 9800–11 300 cm^{-1}. However due to the presence of several isotopomers, as well as perturbations in some of the bands, only three were rotationally analyzed. The bandhead positions of all the observed bands are listed in Table 1, along with the band origins for the three analyzed systems.

Once the spectrum was recorded and measured, preliminary assignments of the rotational numbering for the principal isotopomer (^{174}YbO) were achieved by using graphical methods [18]. In addition, for systems 1 and 2 it was possible to observe the "first lines" of the bands, which confirmed our initial rotational assignments. System 1 has a simple *P–Q–R* branch structure, which is typical for a $^1\Pi$–$^1\Sigma$ transition, while systems 2 and 3 possess only *P*- and *R*-branches, indicative of a $^1\Sigma$–$^1\Sigma$ transition. The data for system 3 and the combined data for the systems 1 and 2 were then employed in least-squares fits that contained the usual analytical expressions for $^1\Sigma^+$ and $^1\Pi$ states. For the lower states the fitted parameters were the rotational parameters B and D, and for upper states: the band origin, v_0, rotational parameters B, D, and H, and the Λ-doubling parameters, q and q_D for system 1.
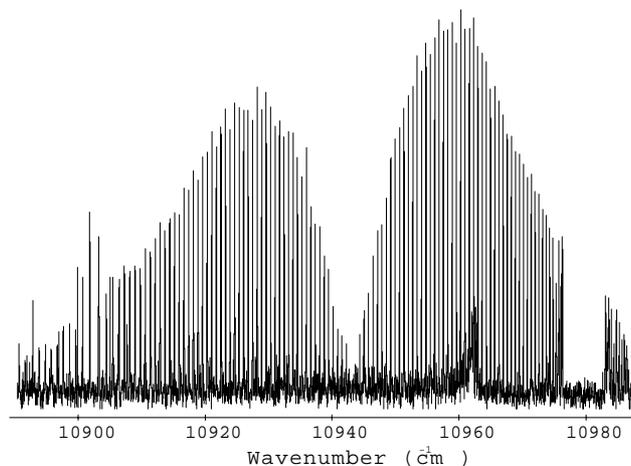

Fig. 1. The observed YbO chemiluminescence spectrum of the strongest band with a perturbation clearly visible in the *R*-branch near 10 980 cm^{-1}.

Table 1
Observed YbO bandhead positions (cm^{-1})

Bandhead	Type	Band origin	Note
9888.40	*R*-head	–	–
10200.28	*R*-head?	–	–
10256.08	*Q*-head	10256.11	System 1
10537.02	*R*-head	–	–
10862.66	*R*-head	–	–
10963.13	*R*-head	–	Perturbed
10992.03	*R*-head	10943.04	System 2
11200.26	*R*-head	11196.90	System 3

3.1. System 1: $v_0 = 10256\,cm^{-1}$

As mentioned above, this band has a simple *P–Q–R* branch structure, and no perturbations were identified in the observed *J*-range ($1 \leqslant J \leqslant 50$). In total, more than 100 lines were assigned for this band. By comparing combination differences for the lower state to those from the work of Linton et al. [3], it was determined that this band connects to the $X^1\Sigma^+$ $v = 0$ level.

3.2. System 2: $v_0 = 10943\,cm^{-1}$

System 2 has the best *S/N* of all of the observed bands, and the first lines of this system were easily identified. Furthermore, a strong perturbation was immediately obvious in the spectrum at high-*J* (see Fig. 1). The perturbation appears to be a classic level crossing, though attempts to assign the more severely perturbed lines were met with frustration. The shifts in the line positions indicate that the perturber's origin lies at higher energy, but the identity of the perturbing state is unknown. Assignments were made for both branches up to $J' = 55$ and it is believed the perturbation occurs at $J' \geqslant 56$.

Because we were unable to completely assign the perturbation, the perturbed lines were omitted from the data set in order to obtain a satisfactory fit. The lower state of this band was found to be the $X^1\Sigma^+$ $v = 0$ level.

3.3. System 3: $v_0 = 11197\,cm^{-1}$

Of the three analyzed bands, system 3 had the poorest *S/N*, and we were only able to assign about 60 lines to ^{174}YbO. Least-squares fitting of the data revealed a perturbation at high-*J*, occurring at $J' \geqslant 44$. As with system 2, the more severely perturbed lines were omitted from the final least-squares fits. It should be noted that the perturbation found in this band is not due to system 1, that is, they are not the same perturbation. The lower state of this band was determined to be the $X^1\Sigma^+$ $v = 1$ level located at $683.107\,cm^{-1}$ above $v = 0$ [3].

The molecular parameters for all three of the bands analyzed in the present work are summarized in Table 2. A complete list of the line positions used in the fits, as well as residuals between the measured lines and those calculated using the parameters in Table 2, is available as supplementary data. Our ground state rotational constants are in agreement with those of Linton et al. [3].

The standard deviations of the fits were on the order of $0.005\,cm^{-1}$, indicating that the deviations between the calculated and measured line positions were consistent, on average, with the estimated measurement precision.

The results from the study of YbO by McDonald et al. [6], which includes laser-induced fluorescence results and ligand-field predictions, can shed some light on the transitions observed in the present study. In their work, McDonald et al. showed the ground state of YbO arises primarily from the $Yb^{2+}(4f^{14})O^{2-}$ electronic configuration. In addition, they investigated the manifold of electronic states arising from the $Yb^{2+}(4f^{13}6s)O^{2-}$ configuration. Based on the magnitude of the rotational constant, *B*, for the upper state of system 3 from the present work, it seems unlikely that it arises from the $f^{13}s$ configuration, since all of the observed $f^{13}s$ states in the work of McDonald et al. have $B \approx 0.35\,cm^{-1}$. Also noted by those authors is the fact that all states with $f^{13}s$ electronic configurations have a vibrational spacing of about $830\,cm^{-1}$. In the present work, unfortunately, we have observed only one vibrational level and therefore could not determine a vibrational spacing for any of the observed states. At this point it is unclear what type of electronic configuration would give rise to a rotational parameter with a value similar to that observed for the upper state of system 3 ($B' \approx 0.31$ cm^{-1}, $r \sim 1.92\,\text{Å}$). Unlike system 3, both systems 1 and 2 have $B' \approx 0.35\,cm^{-1}$ ($r \sim 1.81\,\text{Å}$), so it is plausible that these upper states could arise primarily from the $Yb^{2+}(f^{13}s)O^{2-}$ electronic configuration. Interestingly, the ligand-field fit of the low-lying states in YbO by McDonald et al. [6] predict an electronic state with $\Omega = 0^+$ at $11981\,cm^{-1}$ and $\Omega = 1$ at $11675\,cm^{-1}$. These calculated states are close to the observed states in the present work in which we have system 2 ($\Omega = 0^+$) at about $11000\,cm^{-1}$ and system 1 ($\Omega = 1$) at about $10250\,cm^{-1}$.

After our work was completed we learned of an unpublished ligand-field calculation for YbO that uses relativistic atomic wavefunctions [19]. The use of relativistic

Table 2
Molecular parameters (cm^{-1}) for the observed ^{174}YbO bands

Parameter	System 1	System 2	System 3
v_0	10256.1246(19)	10943.0413(20)	11196.9197(30)
B'	0.346383(30)	0.350130(30)	0.310778(47)
$10^7 D'$	4.99(12)	4.27(15)	2.31(27)
$10^{11} H'$	$-1.53(17)$	$-6.71(36)$	$-22.84(81)$
$10^4 q'$	$-9.516\,(4)$	–	–
$10^8 q_{D'}$	4.59(21)	–	–
B''		0.350326(27)	0.346116(48)
$10^7 D''$		3.91(9)	4.45(23)
Lower state		$X^1\Sigma^+$ $v = 0$	$X^1\Sigma^+$ $v = 1$

wavefunctions rather than the usual non-relativistic electronic wavefunctions cause small shifts in the YbO energy levels. For example the $\Omega = 0^+$ and 1 states from the $Yb^{2+}(f^{13}s)O^{2-}$ configuration predicted by McDonald et al. [6] shift from $11\,981\,cm^{-1}$ and $11\,675\,cm^{-1}$ to $11\,884\,cm^{-1}$ and $11\,708\,cm^{-1}$, respectively.

Kaledin et al.'s calculations [19] show that the states arising from the $Yb^{2+}(f^{13}p)O^{2-}$ and $Yb^{2+}(f^{13}d)O^{2-}$ configurations lie too high in energy to be responsible for any of our new states, although the integer charge model may not be very reliable for these configurations. However, the singly charged configurations $Yb^{1+}(f^{14}s)O^{1-}(p^5)$ and $Yb^{1+}(f^{13}s^2)O^{1-}(p^5)$ give rise to a number of electronic states in the $10\,000$–$13\,000\,cm^{-1}$ region. In particular, the $Yb^{1+}(f^{14}s)O^{1-}(p^5)$ configuration has a [12.3]1 $(A'^1\Pi_1)$ state at $12\,283\,cm^{-1}$, [12.0]0^+ $(a^3\Pi_0)$ at $12\,026\,cm^{-1}$, and [11.9]1 $(a^3\Pi_1)$ at $11\,950\,cm^{-1}$, while the $Yb^{1+}(f^{13}s^2)O^{1-}(p^5)$ configuration has states with $\Omega = 2, 1, 1, 0, 0$ (probably $^3\Pi$ and $^1\Pi$ states) around $12\,565\,cm^{-1}$. The square bracket notation corresponds to $[T_0]\Omega$ and the A' and a notation is based on a comparison with CaO [19]. The upper state of system 3 probably originates from one of the singly charged Yb^+ configurations and the $A'^1\Pi$ state at $12\,283\,cm^{-1}$ is a plausible match. Note however that the $A^1\Sigma^+$ state of YbO with $r = 2.062\,Å$ is attributed to the same $Yb^{1+}(f^{14}s)O^{1-}(p^5)$ configuration as the $A'^1\Pi$ state (and should have the same bond length), while the observed r value for the upper state of system 3 is only $1.92\,Å$.

In conclusion, we have made the first observation of several electronic transitions in the near-infrared spectrum of YbO using Fourier transform emission spectroscopy. A rotational analysis of three transitions identified the lower states as the ground electronic state of YbO. While two of the upper states involved in the transitions appear to arise primarily from the $f^{13}s$ electronic configuration, it is unclear which configuration gives rise to the third observed state. Additional calculations, both ligand field and ab initio, are required to provide more information about low-lying states. Experimental work for transitions in infrared region will be very helpful as well.

References

[1] M. Dolg, H. Stoll, in: K.A. Gschneider, L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 22, Elsevier, Amsterdam, 1996, p. 6071.
[2] A. Gatterer, J. Junkes, E.W. Salpeter, B. Rosen, Molecular Spectra of Metallic Oxides, Specola Vaticana, Vatican City, 1957.
[3] C. Linton, S. McDonald, S. Rice, M. Dulick, Y.C. Liu, R.W. Field, J. Mol. Spectrosc. 101 (1983) 332–343.
[4] M. Dulick, E. Murad, R.F. Barrow, J. Chem. Phys. 85 (1986) 385–390.
[5] P. Carette, A. Hocquet, J. Mol. Spectrosc. 131 (1988) 301–324.
[6] S.A. McDonald, S.F. Rice, R.W. Field, C. Linton, J. Chem. Phys. 93 (1990) 7676–7686.
[7] M. Dolg, H. Stoll, Theor. Chim. Acta 75 (1989) 369–387.
[8] M. Dolg, H. Stoll, H.-J. Flad, H. Preuss, J. Chem. Phys. 97 (1992) 1162–1173.
[9] M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta 85 (1993) 441–450.
[10] S.G. Wang, W.H.E. Schwarz, J. Phys. Chem. 99 (1995) 11687–11695.
[11] S.G. Wang, D.K. Pan, W.H.E. Schwarz, J. Chem. Phys. 102 (1995) 9296–9308.
[12] W. Liu, G. Hong, D. Dai, L. Li, M. Dolg, Theor. Chem. Acc. 96 (1997) 75–83.
[13] W. Liu, M. Dolg, L. Li, J. Chem. Phys. 108 (1998) 2886–2895.
[14] T.C. Steimle, D.M. Goodridge, C. Linton, J. Chem. Phys. 107 (1997) 3723–3725.
[15] S.P. Willson, L. Andrews, J. Phys. Chem. A 103 (1999) 6972–6983.
[16] J.B. West, R.S. Bradford Jr., J.D. Eversole, C.R. Jones, Rev. Sci. Instrum. 46 (1975) 165–168.
[17] G. Norlén, Phys. Scr. 8 (1973) 249–268.
[18] G. Herzberg, in: Molecular Spectra and Molecular Structure, Spectra of Diatomic Molecules, vol. 1, Van Nostrand Reinhold, New York, 1989, pp. 177–178.
[19] L.A. Kaledin, private communication; L.A. Kaledin, M.C. Heaven, R.W. Field, unpublished manuscript.