LASER SPECTROSCOPY OF SAMARIUM MONOXIDE

C. Linton, Guo Bujin, R. Rana, J. Gray

To cite this version:

C. Linton, Guo Bujin, R. Rana, J. Gray. LASER SPECTROSCOPY OF SAMARIUM MONOXIDE. Journal de Physique Colloques, 1987, 48 (C7), pp.C7-663-C7-666. <10.1051/jphyscol:19877160>. <jpa-00226983>

HAL Id: jpa-00226983
https://hal.archives-ouvertes.fr/jpa-00226983
Submitted on 1 Jan 1987

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
LASER SPECTROSCOPY OF SAMARIUM MONOXIDE

C. LINTON, GUO BUJIN, R.S. RANA* and J.A. GRAY**

University of New Brunswick, Physics Department, PO Box 4400, Fredericton, Canada, NB E3B 5A3
*Holy Cross College, Physics Department, Worcester, MA 01610, U.S.A.
**Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.

ABSTRACT

By combining various laser spectroscopic techniques it has been possible to assign eleven low lying electronic states of SmO. The experimental results are compared with predictions of detailed Ligand Field Theory calculations.

INTRODUCTION

In another paper in these proceedings, the application of a Ligand Field Theory (LFT) model to the electronic structure of rare earth oxides has been outlined. This paper will present some details of the results of recent resolved fluorescence and excitation spectroscopy experiments on Samarium monoxide and their correlation with LFT predictions.

The spectrum of SmO is very complex and there was nothing previously known about its electronic and rotational structure. The complexity arises from the very large number of low lying electronic states and the fact that samarium has seven stable isotopes, nearly all of which will be observable in the spectrum.

The expected ground state can easily be predicted using a simple ligand field argument. The SmO molecule is represented by the ionically bonded Sm$^{2+}$O$^{2-}$ configuration. The ground state will result from the 4f$^5$6s configuration of Sm$^{2+}$. The lowest state from the f$^5$ "core" will be $^6H_{25}$. The core will thus have an angular momentum quantum number, $J_a = 2.5$ which will couple with the s electron spin ($\frac{1}{2}$) to give two states with $J_a = 2$ and 3, where $J_a$ is the total atomic angular momentum. The exchange interaction will split these states such that the $J_a = 2$ state will lie lower. The field of the O$^{2-}$ ligand will split each $J_a$ state such that its projection, $\Omega$, on the internuclear axis will be $\Omega = 0, 1 \ldots J_a$, with the $\Omega = 0$ states lying lowest. Thus the ground state of SmO will be an $\Omega = 0$ state with $J_c = 2.5$ and $J_a = 2$. Ab initio calculations (1) predict that this will be a 0$^-$ state.

ASSIGNMENT OF ELECTRONIC STATES

Extensive resolved fluorescence spectra were observed when the laser excited a transition in the 5910 Å region. The two spectra displayed in Figure 1 show that the fluorescence in the laser region was either a single Q line (the laser line) when the Q branch was excited or an RP doublet when the R or P branch was excited. This is unique to an $\Omega = 1-0$ transition in which all the rotational levels of the 0 state have the same e/f symmetry (e for 0$^+$, f for 0$^-$) and the allowed branches depend on whether the e or f component of the $\Omega$-doublet in the 1 state is excited. A fluorescence transition at ~6100 Å showed similar features but with Q vs. RP branch patterns reversed (the weak lines in this region come from an $\Omega = 2$ state which is nearby). A Q line in the laser transition was always accompanied by a PR doublet in the other transition and
vice versa. The two states are thus both 0 states but with opposite +/- symmetry. This effect is clearly seen in Figure 1. The system used for labelling the states is described elsewhere (3).

The Ω=1 and 2 states labelled in Figure 1 were assigned on the basis of the characteristic separations (730 cm⁻¹ between (1)l and (2)l and 1035 cm⁻¹ between (1)2 and (2)2) which had been obtained from spectra excited directly from the (1)1 and (1)2 states. The Ω assignments of the XO⁻, (1)l and (1)2 states were confirmed from first line measurements in the excitation spectra (3).

The excitation spectrum of the [16.91]-XO⁻ transition, shown in Figure 2, was obtained by setting the monochromator to make maximum use of the unique nature of 1-0 transitions. The monochromator was set to detect only lines in the Q branch of the [16.9]-(2)O⁻ fluorescence. As these are all f-e transitions, only transitions which excite the f levels of the Ω=1 state can be detected. As the 0⁻ state only has f levels, only the P and R branches of the 1-0⁻ transition will satisfy this condition and the Q branch lines will not appear in this selectively detected excitation spectrum. This enables us to detect the first R and P lines.

The isotope structure is clearly seen in figure 2. All 7 isotopes are distinguishable in the P branch. Only the two most abundant are labelled. A very localized perturbation in J'=-5 of the 154 isotope can be clearly identified in R(4) and P(6). Only one J and one isotope are affected. A sub-Doppler scan of R(4) (inset) clearly shows the perturbation and the broadening of the odd mass isotope lines by unresolved hyperfine structure (I=3.5).

In Figure 3, the observed electronic states are compared with the predictions of (a) Hocquet (2) and (b) Dulick (1). The overall agreement with Hocquet's predictions is excellent and confirms the assignment of the states to the f⁸S configuration of Sm²⁺.

**ZEPWAN EFFECT**

In order to confirm assignments and test the calculated eigenfunctions by determining g values, sub-Doppler Zeeman effect experiments were performed. The source was placed between the poles of a large magnet and the intermodulated fluorescence technique was used. A spectrum of the [16.9]1-XO⁻R(2) transition is shown in Figure 4 for the 154 and 152 isotopes. As the Ω=0 state does not split in a magnetic field, we expect to observe only the splitting of the upper J=3 state into 7 components. The observed spectra are consistent with this and confirm the assignment. Zeeman patterns have been observed for transitions to the (1)1 and (1)2 states (3) but the analysis is incomplete.
Figure 5 shows resolved fluorescence of the [17.02-(1)1] and (2)1 transitions. The asymmetry in the RQP spacings indicates a large \( \Omega \)-doubling in the \( \Omega=1 \) states. The reversal of the asymmetry indicates that the e/f parity ordering in the \( \Omega \)-doublets is reversed in the two states. In the bottom spectra, the laser is tuned to the opposite parity component, reversing the RQP asymmetries in both states. This can be understood in terms of the observed energy levels. Each \( \Omega=1 \) state is perturbed by the \( \Omega=0 \) state directly below it. As the 0 states are of opposite symmetry, the perturbed levels of the 1 states, which are pushed up by the interaction, will be of opposite e/f parity, thus accounting for the opposite asymmetries in the spectra.

The doubling can be examined in a more quantitative fashion in order to test the calculated eigenfunctions. Using the unique perturber approximation and assuming that the doubling in each 1 state is caused entirely by the 0 state directly below it, we can show that the splitting, \( \Delta T \), is given by \( \Delta T = qJ(J+1) \) where

\[
q = \frac{2\hbar}{\Delta \omega_{sf}} |<J_a^- | 0 >|^2 / \Delta \omega
\]

is the separation of the 0 and 1 states.

Experimentally we found that

\[
q_{(1)} = 0.0072 \text{ cm}^{-1} \quad \text{(from high resolution analysis)}
\]

and

\[
q_{(2)} = 0.0058 \text{ cm}^{-1} \quad \text{(from resolved fluorescence)}
\]

Hocquet's calculated eigenfunctions are

\[
|\text{XO}^+ > = 0.98|2.5,2,0 > + 0.18|3.5,4,0 > - 0.12|4.5,4,0 >
\]

\[
|[(1)1] > = 0.79|2.5,2,1 > - 0.46|2.5,3,1 > + 0.39|3.5,3,1 >
\]

The only terms in the above eigenfunctions that are connected by the \( J_a^- \) operator are the leading terms. Thus,

\[
< (1) | J_a^- | \text{XO}^+ > = 0.79 \times 0.98 < 2.5,2,1 | J_a^- | 2.5,2,0 > = 0.79 \times 0.98 [ J_a^- (J_a^- +1)]^{0.5}
\]

\[
= 1.896 \text{ cm}^{-1} \quad (\text{as } J_a = 2) \quad \text{ and } q_{(1)} = 0.0077 \text{ cm}^{-1}
\]
A similar calculation for the $(2)\ell_1$ and $(2)\ell_0^*$ states gives $q[(2)\ell_1] = 0.0051 \text{ cm}^{-1}$. The agreement with experiment is excellent and attests to the quality of the eigenfunctions.

Thus, we have observed and assigned 11 low lying states of SmO and have shown that the LFT calculations reproduce the observations to remarkable accuracy. We have also demonstrated the value of $\Omega$-doubling as a diagnostic tool for testing the eigenfunctions of $\Omega=0$ and 1 states.

REFERENCES