

## Spectra of the Monoxides of Cerium and Praseodymium

WILLIAM W. WATSON

*Sloane Physics Laboratory, Yale University, New Haven, Connecticut*

(Received February 21, 1938)

Vibrational quantum assignments are presented for five sparsely developed emission band systems of CeO and one of PrO. Comparison is made with two known GdO systems (Piccardi) and one LuO system (Watson and Meggers). Nd has no evident oxide spectrum in the flame of the arc, and Meggers and Scribner report none for Yb and Tm. Reasons for the general poor development or complete lack of oxide band systems for a number of the rare earths are discussed. Fairly intense band systems seem to exist only for those rare earths having a *d* electron in their normal configuration.

LITTLE is known about the band spectra of the group of elements from cerium to lutecium, although evidence for the existence of spectra associated with oxide molecules of some of these rare earths has existed for years. Piccardi<sup>1</sup> has given a vibrational quantum analysis of two GdO systems in the blue region of the visible spectrum plus a few isolated band sequences in the orange and red regions. Some of the latter are surely due to impurities such as CaCl. Recently W. F. Meggers and the writer<sup>2</sup> have made an analysis, based on the data of Meggers and Scribner,<sup>3</sup> of a LuO band system. No other analyses of band spectra from rare earth molecules have as yet been reported.

This paucity of data on rare earth molecular spectra is of course in part due to the same difficulties which hinder the analyses of their atomic spectra; impurity of materials, complexity of the term schemes, high multiplicities, etc. In addition there is the probable prevalence of predissociation and the operation of the Franck-Condon principle, both tending to severely delimit the extent of existing band systems. Furthermore, the existence of fairly intense band systems seems to be correlated with the presence of a *d* electron in the normal configuration of the rare earth atom. The rare earths fulfilling this condition are to be found at the beginning, middle (Gd) and end (Lu) of the group.<sup>4</sup> We return to these points below after a brief de-

scription of a few regularities in the spectra of CeO and PrO.

Oxide spectra of cerium, praseodymium and neodymium were produced by using as the source a 220-volt d.c. arc between pure silver electrodes on to which appropriate salts were fused. Chlorides of all these elements were used, together with anhydrous CeO<sub>2</sub>. Light was taken mostly from the flame of the arc, with constant renewal of the rare earth material during the exposure. Spectrograms covering the range 3500A–8700A were obtained in the first and second orders of a 21-foot grating. The spectrum of the cerium arc contains a large number of bands in the near infra-red from 6600A to 8700A, some of which are quite intense, sharp, single-headed bands degraded to the red. There are in addition some band groups in the blue for which CeO is the indicated emitter. In the praseodymium spectrum there are several fairly prominent band sequences in the interval from 5000A to 6000A, similar in arrangement to the blue CeO systems, but of a doublet character.<sup>5</sup> Both of these, the short wave-length CeO systems and the PrO systems, in turn resemble the GdO band systems described by Piccardi. All of these may represent corresponding transitions in the respective molecules.

The spectrum of the neodymium arc contains no conspicuous bands not assignable to impurities. A background of faint lines, probably molecular in origin, exists in some regions, but a quantum description of these bands is impossible.

<sup>5</sup> G. Piccardi, *Accad. Lincei Atti* **23**, 358 (1936) has reported praseodymium oxide bands in the flame spectrum in this same wave-length range. His dispersion was low, however, and no quantum analysis was presented.

<sup>1</sup> G. Piccardi, *Gazz. chim. ital.* **63**, 887 (1933).

<sup>2</sup> W. W. Watson and W. F. Meggers, *Nat. Bur. Stand. J. Research* **20**, 125 (1938).

<sup>3</sup> W. F. Meggers and B. F. Scribner, *Nat. Bur. Stand. J. Research* **19**, 31 (1937).

<sup>4</sup> W. Albertson, *Phys. Rev.* **47**, 370 (1935).

TABLE I. *A system of CeO emission bands. cm<sup>-1</sup> units.*

$v' \backslash v''$	0	1	2	3	4	5	6
0	12764.9	11906.9					
1	13546.0	12687.9	11830.0				
2	14320.6	13464.6	12611.7	11768.1			
3		14243.1	13388.2	12536.3			
4				13312.7	12463.7	11626.5	
5					13229.2	12393.3	
6							12321.1

TABLE II. *B and C systems of CeO bands.*

$v' \backslash v''$	0	1	2	3	$v' \backslash v''$	0	1	2
0	13816.4 13805.1	12957.0			0	13700.1		
1	14601.8	13741.0 13736.5			1	14467.8	13607.5	
2		14522.0	13668.5 13664.6		2		14368.0	13514.0
3			14447.3	13600.4	3			

CaCl bands in the red are present on all spectrograms when chloride compounds are used in the source, and LaO bands occur in the Pr and Nd spectra. The cerous chloride and ceric oxide (Eimer and Amend) proved to be practically free of the usual lanthanum impurity.

### CeO SPECTRUM

Clearly visible among the large number of bands in the near infra-red spectrum of the cerium arc are two sequences, one composed of intense single-headed bands degrading to the red from 7832A, the other a short group of prominent double-headed bands beginning at 7236A and also degrading to the red. At about the proper interval for a monoxide vibrational frequency on both sides of the first sequence there are similar but less intense sequences. This stronger sequence must therefore represent  $\Delta v=0$  transitions, and the resulting frequency assignments of all the observed band heads in this *A* system are given in Table I. The restriction of vibrational transitions to two or three sequences about an intense  $\Delta v=0$  sequence holds for all the rare earth oxide band systems so far investigated. It is associated with the small percentage change in the vibrational frequency in the two electronic states involved, and indicates an approximate equality of the stability of the various electronic energy levels of any one of these molecules.

Since odd multiplicities are demanded for CeO, the two heads in each of the bands starting at 7236A might be, say, *R* and *Q* heads of a  $^1\Pi \rightarrow ^3\Sigma$  transition. There are no very evident  $+1$  or  $-1$  sequences accompanying this group of bands which we designate system *B*. The best possible assignments are listed in Table II, together with the frequencies of another fragmentary system of single-headed bands starting at 7297A (13700.1  $\text{cm}^{-1}$ ). From the  $\Delta G_v''$  intervals the lower state of this *C* system apparently is the same as that of the *B* system, but the intervals are too few in number to justify giving the usual vibrational energy equation.

Some rather prominent red-degrading band groups also occur in the blue region of the Ce arc spectrum. They are produced when either cerium chloride or oxide is placed in the arc but are not found in the praseodymium or neodymium spectra. Some of these heads occur at almost the same frequencies as given by Piccardi for GdO, but the spacing of bands in the sequences is only about half that for GdO. We therefore conclude that these bands are really due to CeO. The vibrational quantum assignments of two principal systems are given in Table III. Each system consists of but two sequences, the  $\Delta v=0$  sequence being the more intense in each case. There is probably a third system some 300  $\text{cm}^{-1}$  to the red of the *D* system but since only a single

TABLE III. *D and E systems of CeO bands. cm<sup>-1</sup> units.*

<i>E</i>						<i>D</i>					
$v' \backslash v''$	0	1	2	3	4	$v' \backslash v''$	0	1	2	3	4
0	20863.6					0	20556.9				
1	21667.5	20830.6				1	21344.9	20511.6			
2		21632.3	20798.5			2		21295.9	20469.8		
3			21590.8	20763.3		3			21253.4	20432.4	
4				21555.3	20732.0	4				21209.2	20392.6

sequence is evident we do not enumerate its frequencies. The constants of the usual vibrational energy equations for all these CeO systems are displayed in Table V.

#### PrO SPECTRUM

Bands apparently characteristic of PrO occur in the range 5000–6000Å. CeO, NdO, LaO and GdO have definitely been eliminated as their source, they have good intensity in the arc fed with Pr compounds, and some of them show the doublet structure expected for PrO whose atoms have normal terms  $^4K$  and  $^3P$ , respectively. In Table IV is displayed the one system that can be organized for these bands. Again there are principally just the two main sequences. There are also two rather prominent sequences 17614.9, 17566.9, 17523.7, 17479.1 and 17390.7, 17346.0, 17305.4, 17262.6 which are probably associated with others some 800  $\text{cm}^{-1}$  to the violet in a region so replete with diffuse bands that accurate assignments are impossible. It is conceivable that the two sequences enumerated together form a system with vibrational intervals of plausible values for a PrCl molecule, but the evidence is rather in favor of the monoxide molecule as the emitter. The constants of the usual vibrational energy equation fitting this one PrO system are given in Table V.

#### DISCUSSION

Although the oxide spectra of only a minority of the rare earths have been examined, it is already evident that well-developed systems of sharp bands are practically nonexistent for this group of elements. The band systems that do occur are usually abbreviated, the bands are often diffuse, and a background of uneven continua or large numbers of low intensity molecular lines with no apparent heads is frequently present. Admittedly this is not a

TABLE IV. PrO system of emission bands.  $\text{cm}^{-1}$  units.

$v'$ \ $v''$	0	1	2	3	4	5
0	18679.4	17863.0				
1		18628.2	17813.8			
2		19387.0	18574.6	17762.9		
3					17710.6	
4					18464.5	17657.9

TABLE V. Molecular constants for CeO and PrO bands.  $\text{cm}^{-1}$  units.

SYSTEM	$\nu_e$	$\omega_e'$	$\chi_e'\omega_e'$	$\omega_e''$	$\chi_e''\omega_e''$
CeO A	12803.9	785.3	2.13	863.4	2.68
B	13855.2	788.3	1.76	866.7	3.30
D	20580.3	791.7	1.72	838.9	2.92
E	20880.3	807.9	2.04	841.4	2.24
PrO	18704.5	769.0	1.92	818.9	1.20

particularly attractive field for band spectra research! These characteristic features of rare earth band spectra are undoubtedly due to a combination of circumstances. There is a rather large density of energy levels for most of these atoms, the multiplicities are high and the ionization potentials are low. Under such conditions the vast majority of possible molecular states are probably repulsion states, with resulting great prevalence of predissociation. These radiationless transitions must either eliminate completely or severely limit the extent of most of the possible band systems, and transitions to repulsion states could account for some of the continuous spectrum often present. Also the fact that the percentage difference between the vibrational frequencies of the two states of all the rare earth oxide band systems analyzed is always quite small leads to a Franck-Condon parabola so narrow as to have both its branches fall close to the main diagonal of the  $v'v''$  array. One may then too predict from the Mecke rule that for many transitions the rotational  $B$  constants should be nearly identical in the two states concerned so that the resulting bands are practically headless.

The vibrational frequencies listed in Table V, together with those found for GdO<sup>1</sup> and LuO,<sup>2</sup> indicate but a small variation in the vibrational frequencies of the lower states of corresponding molecules of all the rare earths. As pointed out in

TABLE VI. Wave-lengths of most intense band heads. Angstrom units. All bands degrade to the red.

CeO	PrO	GdO	LuO
7926.96	5763.42	4892.2	4708.00
7879.34	5690.95	4615.6	4695.46
7831.78	5596.63		4684.16
7297.18	5352.00		4672.31
7275.51			4661.75
7235.78			
4863.20			
4791.70			

reference 2, only a 1 percent decrease in vibrational frequency is to be expected in going from CeO to LuO due to change in reduced mass, while approximate equality of the force constants governing the vibrations should exist because of the similarity in the outer electron configurations of these fourteen elements.

For qualitative chemical analysis the most intense bands for each of these molecules should prove more convenient than atomic lines for identifying the rare earths present in a mixture. This is especially true if the available spectrograph has not large dispersion. The wave-lengths of the heads of the most intense bands are listed in Table VI for all of the rare earth monoxide spectra so far analyzed. All bands degrade to the red.

Some of the rare earth elements apparently do not have any conspicuous band systems in the spectrum of the arc in air. In addition to the

present search of the Nd spectrum, Meggers and Scribner report no characteristic bands for Yb<sup>6</sup> or from Tm<sup>7</sup> such as those found for Lu under identical conditions. Observations on the spectra of a number of the rare earths are lacking, of course, but it is apparent that for some of the atoms in this group oxide band systems of good intensity are missing. We venture to suggest that for such band systems to exist, a *d* electron must be present in the normal configuration of the rare earth atom. Lanthanum with its *ds*<sup>2</sup> configuration, together with a simple term scheme, has some seven well-developed monoxide band systems. Ce, Pr, Gd and Lu also have that same configuration in addition to 1, 2, 7 and 14 4*f* electrons, respectively. Sm, Eu, Tm and Yb, on the other hand, have 4*f*<sup>*n*</sup>6*s*<sup>2</sup> normal configurations.

<sup>6</sup> W. F. Meggers and B. F. Scribner, Nat. Bur. Stand. J. Research **19**, 651 (1937).

<sup>7</sup> W. F. Meggers, private communication.

## Electrostatic Generator Operating Under High Air Pressure—Operational Experience and Accessory Apparatus

D. B. PARKINSON, R. G. HERB, E. J. BERNET AND J. L. MCKIBBEN  
*Department of Physics, University of Wisconsin, Madison, Wisconsin*

(Received February 11, 1938)

A description is given of experience gained in operation of the Wisconsin electrostatic generator with particular reference to the use of CCl<sub>4</sub> and CCl<sub>2</sub>F<sub>2</sub> and to the problem of the fire hazard. Improvements in the charging belt system and the accelerating tube are discussed; and generator equipment, including the generating voltmeter, the voltage stabilizer and the ion source, is described.

### INTRODUCTION

**I**N general design the Wisconsin electrostatic generator (Fig. 1) has not been changed since described in the first publication.<sup>1</sup> Although the generator has been in operation for almost two years all the original Textolite supports and the aluminum hoops are still in good condition. Corona points for the distribution of potential along the hoop system and accelerating tube are still satisfactory, although the points appear to

be very dull. Additional operational experience has been acquired, however, and improvements have been made in the charging belts and in the accelerating tube. With (CCl<sub>4</sub> air and CCl<sub>2</sub>F<sub>2</sub> air mixtures) the generator has been operated at 2.4 Mv for data on proton-proton scattering. Trouble has been experienced due to fires, and alterations have been made to reduce the fire hazard. These experiences and improvements are described in the present paper, and in addition a description is given of certain accessory apparatus, including the generating voltmeter, the voltage stabilizer, and the ion source.

<sup>1</sup> R. G. Herb, D. B. Parkinson, D. W. Kerst, Phys. Rev. **51**, 75 (1937).