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SPECTRUM OF LUTECIUM MONOXIDE

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ABSTRACT

A vibrational quantum analysis is given for the most conspicuous band system of the LuO spectrum. The wave numbers of band heads in this system are represented by the equation:

$$\nu = 21471.8 + 791.60(v' + \frac{1}{2}) - 3.12(v' + \frac{1}{2})^2 - 841.66(v'' + \frac{1}{2}) + 4.07(v'' + \frac{1}{2})^2 - 2.07v'v''.$$

The unexpected singlet character of the spectrum and the value of the vibrational frequency are discussed.

Spectra of the monoxides of a large number of the elements are known, and for many of these, quantum analyses, at least for the measurements of the band heads, have been made. For the rare-earth group, however, but one analysis has so far been reported, that of two apparently unrelated band systems of GdO observed in the oxyhydrogen flame by Piccardi,² who states that many of the bands appear very bright at flame temperature but disappear completely at arc temperature. Instability at arc temperature may account for the general lack of data on the band spectra of the rare earths, although it may be attributed in part to the same difficulties hindering the analysis of their atomic spectra (scarcity of pure materials, complexity of spectra, high multiplicities, low ionization potentials, etc.). Because of their probable low multiplicity, the molecular spectra of the first (cerium) and the last (lutecium) of the rare-earth group might be expected to be more amenable to vibrational quantum analysis than the others. Particularly is this true for lutecium, the ground-state configuration of which is similar to that of lanthanum but with the addition of the completed shell of 14 *f*-type electrons. Lutecium is, indeed, outstanding among the rare earths in showing a sequence of intense bands in the conventional arc spectrum.

A new description of the conventional arc and spark spectra of lutecium was recently published by Meggers and Scribner.³ Using a 220-volt d-c arc carrying 5 amperes between pure-silver electrodes on to which some lutecium oxide was fused, it was found that in the entire range from 2000 to 11 000 Å the only bands attributable to lutecium com-

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² G. Piccardi. *Gazz. chim. ital.* **63**, 887 (1933). Although Piccardi displays 10 systems of bands only 2, in our opinion, can be ascribed to GdO molecules. Two systems with 0,0 bands at 17597.3 and 16931.8 cm⁻¹ and vibrational frequencies of 276.1 and 303.1, respectively, for the lower states are suggestive of a fairly heavy monochloride; they may be due to GdCl. The remaining systems are isolated sequences, two of which, with 0,0 heads at 16169.1 and 16093.1 cm⁻¹, are most probably identified as CaCl, while the rest may be fragmentary chloride systems of Gd or of impurities.

³ W. F. Meggers and B. F. Scribner. *J. Research NBS* **19**, 31 (1937) RP1008.

pounds occur in the blue portion of the spectrum. These bands degrade to the red, are apparently single-headed, and fall principally into two groups or sequences, one quite intense with principal head at 4662 Å, the other much weaker and beginning with a band at 4509 Å. That this spectrum is emitted by the LuO molecule is indicated by structural resemblance with other monoxide spectra. Although the observed bands, about 35 in number, may not constitute the entire spectrum of LuO, it seems probable that no other band sequences of comparable intensity or length exist. And since further experimental study of the LuO spectrum is at present impossible because of the scarcity of material, we feel that the analysis of these bands should be presented as a contribution to the limited knowledge of the spectra of rare-earth molecules. A reproduction of the principal bands of this spectrum is shown in figure 1.

The more intense group of bands starting at 4662 Å forms the $\Delta v=0$ sequence of the system, while the less intense group on the shorter wave length side of this is the $\Delta v=-1$ sequence. Placing these band head frequencies in a $v'v''$ array in such a fashion as to give plausible values for $\Delta G''(1/2)$, the frequencies of a possible $\Delta v=+1$ sequence were computed. These were found to agree quite closely with "hazy" lines of low intensity in the wave-length tables of Meggers and Scribner, who assumed them to be characteristic of neutral Lu atoms. However, none of these lines have been found essential in the Lu I analysis, and inspection of the spectrograms shows that they are weak band heads.

Two additional weak band heads needed to complete the -1 sequence were found on the most intense spectrogram. The $v'v''$ array of LuO bands in table 1 shows the wave numbers corresponding to band heads, whose wave lengths and estimated intensities appear in table 2.

The wave numbers of these heads are given by the equation:

$$\nu = 21471.8 + 791.60(v' + 1/2) - 3.12(v' + 1/2)^2 - 841.66(v'' + 1/2) + 4.07(v'' + 1/2)^2 - 2.07 v'v''$$

Allowance for the variation in the interval $\nu_{\text{head}} - \nu_0$ with v is made with the final $v'v''$ term. The coefficient 2.07 for this term is unusually large, indicating that there is but a very small change in the moment of inertia of the molecule in its transition from one electronic state to the other. One would also expect this from the relatively small change (6 percent) in the vibrational frequency, which apparently causes the Condon parabola for the distribution of the most intense bands to be so narrow as to give only the $\Delta v=0$ sequence good intensity. There is some indication of the necessity of a cubic term in v' , but random fluctuations in the course of the few $\Delta G(v' + 1/2)$ intervals make its evaluation uncertain. The magnitude of the $\nu_{\text{obs}} - \nu_{\text{calc}}$ differences, as well as the low intensities for the bands involving the $v'=5$ level, indicate a perturbation of this level.

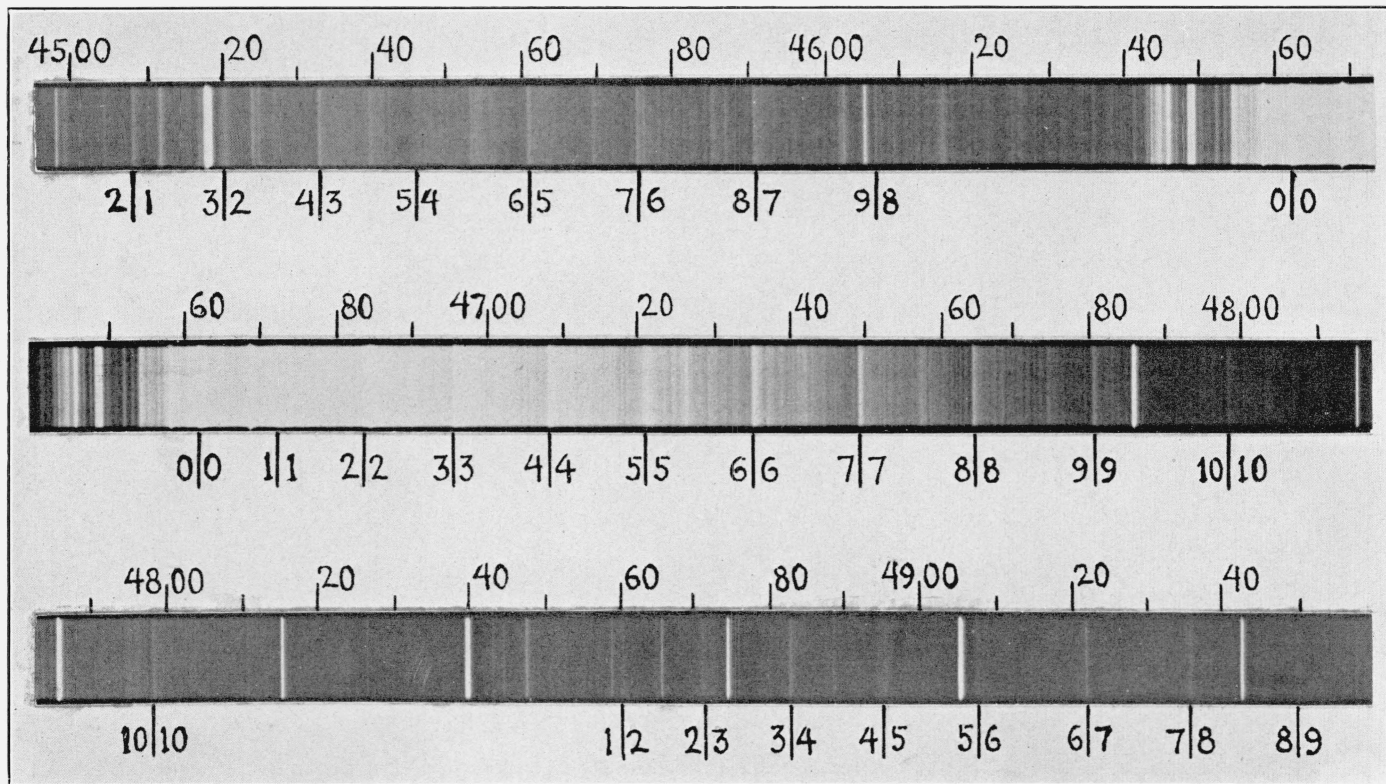


FIGURE 1.—*Spectrum of lutecium monoxide (LuO).*

Wavelengths marked above, band heads below.

TABLE 1.—Wave numbers and differences between progressions of LuO bands

ν' \ ν''	0	1	2	3	4	5	6	7	8	9	10	
0	21445.2											
1		21396.7 775.4	827.0 772.9	20569.7 772.9								
2		22172.1	829.5	21342.6 769.8	817.7 766.3	20524.9 766.3						
3			22112.4	821.2	21291.2 761.2	815.2	20476.0 758.5					
4				22052.4	817.9	21234.5 755.7	811.2	20423.3 753.4				
5					21990.2	813.5	21176.7 742.4	804.0	20372.7 740.7			
6						21919.1	805.7	21113.4 756.9	800.9	20312.5 738.2		
7							21850.3	799.6	21050.7 726.5	795.1	20255.6 728.4	
8								21777.2	793.2	20984.0 717.0	786.8	20197.2 717.0
9									21701.0	786.8	20914.2	
10											20836.2	

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TABLE 2.—Band heads in the spectrum of lutecium monoxide (LuO)

v', v''	$\lambda_{\text{air}} \text{ \AA}$	Intensity	$\nu_{\text{vac. cm}^{-1}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
2, 1	4508.91	5	22172.1	-1.7
3, 2	4521.08	2	22112.4	-0.5
4, 3	4533.39	5	22052.4	+2.4
5, 4	4546.2	1	21990.2	+5.4
6, 5	4560.95	8	21919.1	+1.8
7, 6	4575.31	5	21850.3	+2.8
8, 7	4590.68	3	21777.2	+1.7
9, 8	4606.8	1	21701.0	-0.3
0, 0	4661.75	150	21445.2	-1.8
1, 1	4672.31	120	21396.7	-0.1
2, 2	4684.16	100	21342.6	-1.7
3, 3	4695.46	80	21291.2	+1.6
4, 4	4708.00	60	21234.5	+1.0
5, 5	4720.86	5	21176.7	+3.3
6, 6	4735.00	25	21113.4	+1.4
7, 7	4749.11	10	21050.7	+2.3
8, 8	4764.22	7	20984.0	+1.6
9, 9	4780.11	5	20914.2	-0.1
10, 10	4798.00	3	20836.2	-7.7
1, 2	4860.15	1	20569.7	+0.4
2, 3	4870.78	1	20524.9	+2.0
3, 4	4882.40	3	20476.0	+1.7
4, 5	4895.00	1	20423.3	-0.1
5, 6	4907.16	1	20372.7	+2.4
6, 7	4921.70	3 (+Lu n)	20312.5	-2.4
7, 8	4935.53	2 (+Yb n)	20255.6	-1.7
8, 9	4949.8	1	20197.2	-0.3

One would expect a multiplicity of two for the terms of the neutral LuO molecule, with considerable resemblance between the spectra of LuO and LaO molecules because of the similarity in their electron configurations. Seven or more band systems due to LaO have been described⁴ and the doublet character of the LaO levels has been reported for at least five of these systems. The LuO bands, although more or less diffuse, are apparently single-headed. The most plausible explanation of the appearance of just this singlet band spectrum would seem to be that it constitutes say a ${}^2\Delta_{2\frac{1}{2}} \rightarrow {}^2\Delta_{2\frac{1}{2}}$ or a ${}^2\phi_{3\frac{1}{2}} \rightarrow {}^2\phi_{3\frac{1}{2}}$ transition (possible types for LuO), with the other multiplet component, ${}^2\Delta_{\frac{3}{2}} \rightarrow {}^2\Delta_{\frac{3}{2}}$ or ${}^2\phi_{2\frac{1}{2}} \rightarrow {}^2\phi_{2\frac{1}{2}}$, respectively, practically eliminated by predissociation in the upper state. Such registration of just one component of the complete multiplet transition has been noted in other cases (NiH,⁵ CoH).⁶ Some of the unassigned bands (4094, 4096, 4239, 4242, 4569, 4654, 5161, 5170 Å) may represent a trace of the missing transition (or of other systems).

The vibrational frequency $\omega'' = 841.66$ differs but little from the value 841.00 for one of the GdO systems analyzed by Piccardi. This is not surprising, for in view of the nearly identical chemical behavior of all the rare earths the force constants for the vibrations of homologous molecules for all of these elements should be nearly the same. There should be but a 1 percent change in the vibration frequency due to the change in the *reduced mass* of the molecule in passing from CeO to LuO. It would seem then that all of the rare-earth monoxides should have one lower state vibrational frequency in the range 840 to 850 cm^{-1} .

WASHINGTON, November 15, 1937.

⁴ W. Jevons. Proc. Phys. Soc. (London) **41**, 520 (1929). W. F. Meggers and J. A. Wheeler. BS J. Research **6**, 239 (1931) RP273.

⁵ A. G. Gaydon and R. W. B. Pearse. Proc. Roy. Soc. (London) [A] **148**, 312 (1935). A. Heimer, Z. Phys. **105**, 56 (1937). (${}^2\Delta_{3\frac{1}{2}} \rightarrow {}^2\Delta_{2\frac{1}{2}}$ transition.)

⁶ A. Heimer, Z. Phys. **104**, 448 (1937). (${}^3\phi_4 \rightarrow {}^3\phi_4$ transition.)