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The Band Spectrum of HgIn

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An examination of the band spectrum of the HgIn molecule has been carried out using the second order of the Wisconsin 21-foot reflection grating. Band systems were obtained with intensity maxima at 4102, 4511, 4994, 5226, 5544, and 5760 angstrom units. The systems at 4102A and 4511A appear to be continuous, but the others have been resolved into bands. Vibrational analyses were made of the 4994A, 5226A, and 5544A systems; but the 5760A bands have not yet been successfully worked into a single square array.

I. INTRODUCTION

WHILE working with the sensitized fluorescence of indium in mercury vapor, Winans, Leitzke, and Davis[1] found that a Tesla discharge through the mercury-indium mixture gave rise to several band systems of the HgIn molecule. The system at 5227A was resolved into bands with heads on the long wavelength side. These early measurements showed the 5227A system, extending from 5270A to 4880A with a second maxima at 4998A, to be made up of bands spaced 11 to 15 angstroms apart. Another system at 5800A was observed to extend from 6390A to 5400A with minima in intensity at four places in this range. Continuous bands at 4132A and 4574A were also found.

The purpose of the present investigation was to make a more detailed examination of the HgIn bands using the second order of the Wisconsin 21-foot reflection grating. The spectra obtained show several new band systems most probably due to HgIn. Two of these new systems at 5760A and 5544A have been resolved into bands, while those at 4350A, 4740A, and 4825A appear to be continuous. A very weak system in the red was also observed, but it has not yet been possible to obtain it with sufficient intensity for detailed examination.

II. APPARATUS AND PROCEDURE

An electrodeless quartz discharge tube with a Tesla coil providing the excitation energy was found to be the most convenient source. After baking at 1000°C for a few days at a pressure of less than 10^{-7} mm of mercury, indium was first distilled into the tube, then mercury, and the tube was sealed off the vacuum system.

The purity of the indium was tested spectroscopically by placing a small sample of it in the lower of two carbon electrodes in an arc. The spectrum of the arc showed lines other than those of indium. These were identified as due to cadmium by comparison of the indium spectrum with a cadmium spectrum obtained in the same way.

In addition to the Tesla coil for producing excitation, a high frequency (60 Mc) oscillator was tried. The oscillator was of the push-pull type and employed two 250TH Eimac tubes. This produced bands of approximately the same intensity as the Tesla coil. Since the Tesla coil is more portable and less liable to require adjustment, it was used for most of the spectra obtained.

It was necessary to heat the discharge tube with an external source to obtain a sufficient pressure of indium vapor in the tube atmosphere to give the HgIn bands. For the first experiments a gas-air flame was used. As the discharge tube became older, the intensity of the mercury hybride bands in its spectrum increased. This was attributed to the diffusion of hydrogen from the flame through the hot quartz. When a furnace was used, this did not occur. The furnace was made with nichrome wire windings and was usually operated at 400 watts. An air space surrounding the nichrome wire prevented excessive local heating and gave long life, as described by Winans and Cram.[2] Small side arms were added to reduce the temperature gradient between the center of the furnace and the outside. Tesla coil leads were introduced through the side arms.

Five different spectrographs were used. Small Hilger quartz and glass spectrographs were used to determine best conditions for excitation. A Bausch and Lomb medium quartz spectrograph was used to obtain all bands on one plate and to determine the purity of the indium. Reflection grating spectrographs of 10- and 21-foot radius were used for greater dispersion. Most of the band head measurements were made on plates taken with the 21-foot grating. The dispersion of the 21-foot instrument is 1.31A per millimeter. The grating is one of 90,000 lines ruled on aluminum by R. W.

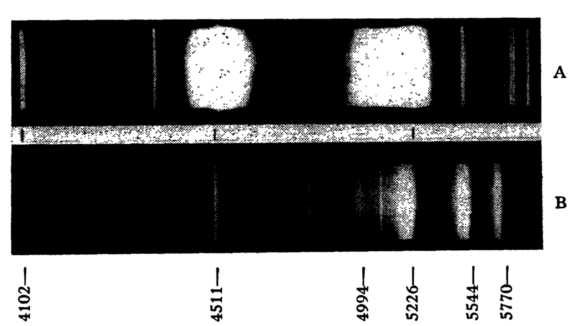

FIG. 1. Glass prism spectrograms of (A) the absorption in yellow region at high mercury pressure and (B) the band systems of HgIn.

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[1] Winans, Davis, and Leitzke, Phys. Rev. **57**, 70 (1940).
[2] J. G. Winans and S. W. Cram, Rev. Sci. Instr. **10**, 272 (1939).

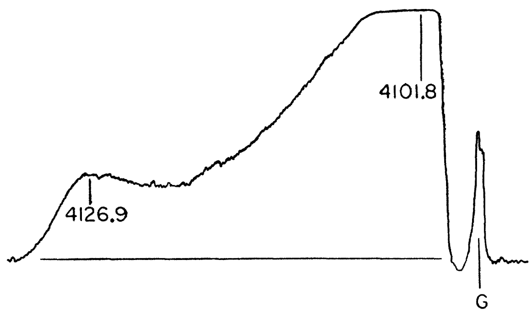

FIG. 2. Microphotometer trace of the 4102A band. A grating ghost of the indium 4102A atomic line appears at (*G*).

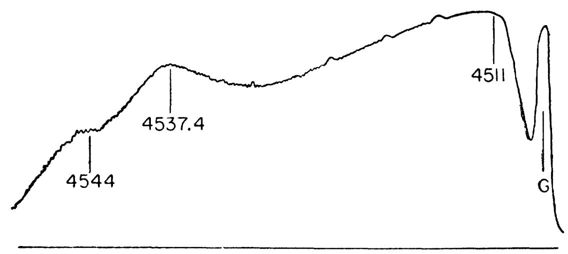

FIG. 3. Microphotometer trace of the 4511A band. A 4511A ghost line occurs at (*G*).

Wood to concentrate energy at wavelength 5500A in the second order.

III. THE BAND SYSTEM

Figure 1 shows two spectrograms of the HgIn band systems made with a small Hilger glass spectrograph. The long wavelength limit or the location of the most intense band of the system has been used to identify each group, with the exception of the two bands attached to the indium resonance lines at 4102A and 4511A. These are identified by the adjacent indium line.

The intensity of any given band system relative to that of the other band systems was found to depend upon the temperature and the mercury pressure in the discharge tube. High temperature and the resulting increase in indium atoms in the tube atmosphere favor the 4511A band, while lower temperature and higher mercury pressure increase the intensity of the 5226A and 4994A systems. In Fig. 1A it was necessary to overexpose the 4511A, 5226A, and 4994A bands to reveal the intensity variations in the region between the mercury yellow lines at 5770A and 5790A and the mercury green line at 5461A. A microphotometer trace

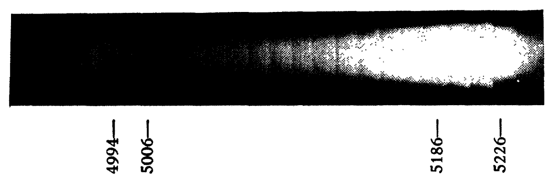

FIG. 4. Grating spectrogram of the 5226A and 4994A systems. Iron comparison lines were superimposed on all grating spectra.

of the negative from which this print was made showed that each of the intensity maxima is in turn made up of several intensity variations. Using a longer discharge tube made it possible to lower the mercury pressure

TABLE I. Square array of the bands of the 5226A system. Estimated relative intensities on a 1 to 10 scale are in brackets after the wave numbers of the band heads.

v' \ v''	0	1	2	3	4	5
0	19,128.3 (10) 19,130.1 (10)	19,076.8 (5)	19,034.7 (1)			
1	19,176.4 (9) 19,177.8 (9)					
2	19.226.2 (8)					
3	19,275.8 (7)		19,179.3 (6)			
4	19,326.8 (7) 19,328.4 (7)	19,275.2 (7)	19,233.2 (7)			
5	19,374.5 (7) 19,376.0 (7)			19,248.8 (6)		
6	19,424.2 (7)			19,297.1 (4)	19,269.5 (2)	
7	19,475.6 (6)					19,308.2 (4)
8	19,522.4 (5)					
9	19,572.8 (4)					
10	19,620.5 (4)		19,528.1 (2)			
11	19,671.4 (4)			19,543.0 (2)		
12	19,722.2 (4)				19,563.3 (2)	
13	19,769.2 (3)					19,605.5 (1)
14	19,819.2 (2)					

TABLE II. Square array of the 4994A bands.

v' \ v''	0		1		2		3
0	20,018.1 (5)	59.6	19,958.5 (4)				
	40.1		41.1				
1	20,058.2 (2)	58.6	19,999.6 (3)				
			40.5				
2			20,040.1 (2)	54.5	19,985.6 (3)	51.8	19,933.8 (1)
					39.3		
3					20,024.9 (1)		

and obtain the spectrogram of Fig. 1B which reveals the 5760A and 5544A systems.

If a pool of mercury and indium is placed at the center of the furnace in the discharge tube, at first the mercury vapor pressure is too great for a discharge. However, when most of the mercury has been boiled off, the discharge spectrum is produced. After the first nine minutes of operation, the band systems at 5760A and 5544A decrease in intensity until after 20 minutes they have almost disappeared. However, the bands at 5226A, 4994A, and 4511A increase slightly in intensity with time. The rapidity with which the 5760A and 5544A systems die out is determined by the temperature. If the temperature is high, they are intense but last for only a short period. If the temperature is lower, the bands are weaker but remain for a much longer time.

The band systems at 4102A, 4511A, 4994A, 5226A, 5544A, and 5760A have been investigated with the 21-foot spectrograph. Exposure times varied from one to fifteen hours. Figure 2 is a microphotometer trace of the 4102A band. It is continuous with an intensity maximum at 4126.9A. It extends to approximately 4133A. The microphotometer trace of the 4511A band in Fig. 3 shows it to be continuous with maxima at 4544A and 4537.4A. The long wavelength limit is at about 4551A.

Spectrograms of the 5226A and 4994A systems are shown in Fig. 4. Tables I and II list the wave numbers and relative intensities of these bands. Figure 5 is a spectrogram of the bands at 5544A. Table III gives their wave numbers. The system at 5760A is shown in Fig. 6; wave numbers are listed in Table IV. This system differs from those at 4994A, 5226A, and 5544A, since it contains bands shaded toward the violet and red, whereas those of the other systems are all shaded toward the violet.

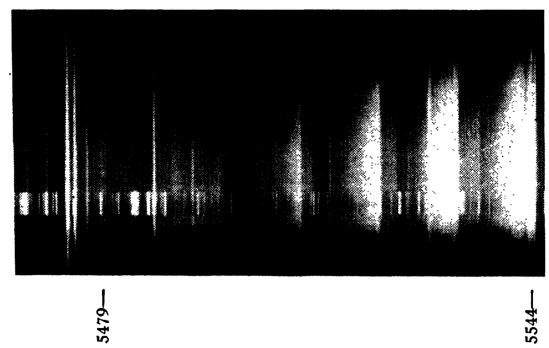

FIG. 5. Grating spectrogram of the more intense bands of the 5544A system. Higher order atomic lines also appear.

The bands at 4350A, 4740A, 4825A, and 6104A were too weak to be investigated with the grating spectrograph. They appear and disappear with the 5760A and 5544A systems. None of the bands attributed to HgIn have been found in absorption.

TABLE III. Square array of the 5544A system.

v' \ v''	0	1	2	3	4	5
0	18,031.2 (10) 18,033.5 (10) (18,038.0) (8)	17,970.6 (1)				
1		18.077.2 (9) 18,078.8 (9) (18,081.4) (3)	18,017.2 (3)	17,958.3 (3)		
2	18,242.8 (3) 18,247.1 (3)		18,123.4 (8)	18,064.4 (4)	18,007.5 (2)	17,951.9 (2)
3		18,288.8 (3)		18,170.8 (6)	18,113.5 (4)	
4			18,334.4 (3)		18,220.1 (4)	18,163.9 (4)
5				18,381.6 (2)		
6					18,430.1 (1)	

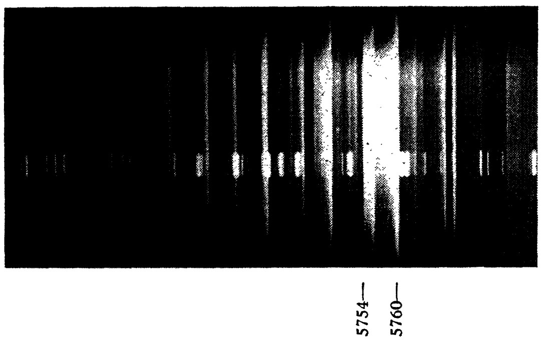

FIG. 6. Grating spectrogram of the 5760A system.

IV. DISCUSSION

A. The 4102A and 4511A Bands

Guernsey[3] and later Watson and Shambon[4] found continuous bands in the arc spectrum of indium which extend to the short wavelength side of the indium resonance lines at 4102A and 4511A. These bands were attributed to semistable molecules of In_2. Thus, it is reasonable to assume that the continuous bands on the long wavelength side of these same indium lines in a mercury-indium discharge spectrum are due to a semistable molecule of HgIn.

Potential curves which account for these bands are shown in Fig. 7. The upper electronic state, formed from excited indium and unexcited mercury, has a slight minimum, while the lower states, formed from unexcited indium and unexcited mercury, have no minima. This explains the maxima on the long wavelength side of the atomic lines and also the absence of an absorption spectrum.

TABLE IV. The wave numbers of the band heads of the 5760A system. (*) denotes bands shaded to the red.

Wave-number cm⁻¹	Intensity	Wave-number cm⁻¹	Intensity
17,275.6	1	17,453.6	1
17,290.5	3	17,457.6	1
17,296.8*	4	17,460.9	7
17,305.8	1	17,481.0	6
17,311.2	2	17,492.0	4
17,325.0*	7	17,506.1*	4
17,330.4	8	17,516.6	5
17,342.7	3	17,551.9	4
17,346.7	4	17,564.3*	1
17,356.3	10	17,587.1	1
17,369.6	9	17,596.7	1
17,374.7*	8	17,610.1	1
17,378.9	4	17,631.1	1
17,382.6	4	17,647.0	1
17,387.4	1	17,665.1	1
17,392.5	9	17,683.8	1
17,401.9*	7	17,697.6	1
17,407.7	8	17,719.6	1
17,414.4	4	17,754.5	1
17,419.5	2	17,782.9	1
17,427.7	8	17,940.9	1
17,430.7*	7		
17,445.0	7		
17,449.3	4		

If we assume the coupling between the L_i and S_i of the separated atoms to be strong in comparison with the coupling of the L_i to the internuclear axis of the molecule, the electronic angular momentum, Ω, along the internuclear axis is given by

$$\Omega = M_{J_1} + M_{J_2},$$

where $J_i = L_i + S_i$, J_i = total angular momentum of atom i, L_i = resultant orbital angular momentum of atom i, S_i = resultant spin angular momentum of atom i, and M_{J_i} = component of J_i along the internuclear axis. Hence, for $In(^2P_{1/2})$ and $Hg(^1S_0)$, $\Omega = 1/2$. But for $In(^2P_{3/2})$ and $Hg(^1S_0)$, Ω may be 1/2 or 3/2. The $In(^2P_{3/2})$ and $Hg(^1S_0)$ combination gives two unstable states corresponding to Ω equal to 1/2 and 3/2 and therefore two maxima on the long wavelength side of the indium 4511A line. But the combination $In(^2P_{1/2})$ and $Hg(^1S_0)$ yields only one unstable state and hence one intensity maximum to the long wavelength side of the 4102A line. The upper electronic state with $In(^2S_{1/2})$ and $Hg(^1S_0)$ has only one possible value of Ω, $\Omega = 1/2$.

B. The 5226A and 4994A Systems

The wave number formula for the vibrational structure of a molecule may be written

$$\nu = \nu_{00} + \omega_0' v' - \omega_0' x_0' v'^2 - \omega_0'' v'' + \omega_0'' x_0'' v''^2. \quad (1)$$

The band heads of the 5226A system can be arranged in the square array of Table I and the vibrational constants of Eq. (1) obtained. The constants are given in Table V. The v' progression $v''=0$ can be traced until it meets the 4994A system. Thus, the energy of dissociation of the upper electronic state, D_0', must be greater than 840 cm^{-1}.

An approximate limit for the energy of dissociation of the lower state is given by the formula

$$D_0'' = \omega_0''^2 / 4\omega_0'' x_0''. \quad (2)$$

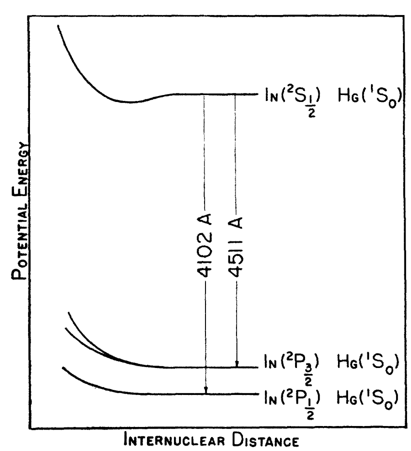

FIG. 7. Electronic states of the 4511A and 4102A bands.

[3] M. L. Guernsey, Phys. Rev. **46**, 114 (1934).
[4] W. W. Watson and A. Shambon, Phys. Rev. **50**, 607 (1936).

The vibrational constants of Table V give 169 cm^{-1} for D_0'' when substituted in Eq. (2).

Winans[5] found that the majority of mercury lines are not affected by heat; but the 5460A, 4358A, and 4047A lines are weakened, probably from collisions of the first kind which raise excited atoms to higher states. These three mercury lines have $^3S_1$ for their upper state. The 5226A system of HgIn also decreases in intensity at higher temperatures. If this system has an upper electronic state formed from Hg($^3S_1$) and In($^2P_{1/2}$) as shown in Fig. 8, it should decrease in intensity with increase in temperature because of the decrease in the number of mercury atoms in the atomic state from which the upper electronic state is formed. The extent of the band system shows that D_0' is greater than 840 cm^{-1}. This condition is satisfied if the upper electronic state is formed from Hg($^3S_1$) and In($^2P_{1/2}$) and the lower from Hg($^3P_1$) and In($^2P_{1/2}$). When the energy difference between the mercury states, the known value of D_0'', and the wave number of the (0,0) band are used, D_0' is found to be 3980 cm^{-1}. Thus D_0' is greater than 840 cm^{-1} and the upper and lower electronic states very likely dissociate into the assumed atomic states.

Since the 4511A system has excited indium and unexcited mercury for its upper state, higher indium temperatures should increase its intensity because of the greater number of excited indium atoms in the atmosphere of the discharge tube. This corresponds to observation.

The 4994A system is very likely another transition with dissociation products of the upper state the same as for the 5226A system and with lower state dissociation products Hg($^3P_0$) and In($^2P_{1/2}$). Because only a few bands are found in the 4994A system, it is difficult to construct a square array for them, but a possible arrangement is given in Table II.

C. The 5544A System

The band heads of this system can be arranged in the square array of Table III. The (0,0) and (1,1) bands have two sharp heads and one diffuse head (in brackets in Table III). The sharp heads are probably the two R heads of a $^2\Sigma \rightarrow {}^2\Sigma$ transition. The diffuse head is probably the two P branches. The bands of the $\Delta V = -2$ sequence appear to have several heads. Vibrational constants are given in Table V. The energy

TABLE V. Vibrational constants of the 5226A and 5544A systems. Measurements are in cm^{-1}

Band system	5226A	5544A
ν_{00}	19,129	18,032
ω_0'	49.3	105.5
$\omega_0'x_0'$	very small	very small
ω_0''	57.8	62.0
$\omega_0''x_0''$	4.94	0.80

[5] J. G. Winans, Phys. Rev. 39, 745 (1932).

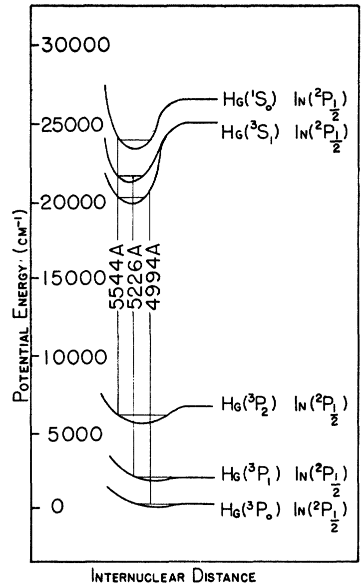

FIG. 8. Possible electronic states of the 4994A, 5226A, and 5544A systems.

of dissociation for the lower electronic state using Eq. (2) is 1201 cm^{-1}.

In Fig. 1 the 5544A system can be seen to extend to the 5226A system; hence, the energy of dissociation of the upper state must be greater than 1097 cm^{-1}. If the upper electronic state of the 5544A system is assumed to be formed from Hg($^1S_0$) and In($^2P_{1/2}$) and the lower one from Hg($^3P_2$) and In($^2P_{1/2}$), D_0' can be obtained from the equation

$$\nu_{00} + D_0' = \text{energy difference between Hg}(^1S_0) \text{ and Hg}(^3P_2) + D_0''$$

$$18{,}032 + D_0' = 19{,}885 + 1201$$

$$D_0' = 3054 \text{ cm}^{-1}.$$

D. The 5760A System

This system, shown in Fig. 6, has a majority of its bands shaded towards the violet; but several strong bands are shaded to the red. A mixture of band shading can often be correlated through the assumption of "tail bands." In the 5760A system the bands shaded to the red might be considered to be tail bands. The stronger bands fall into four distinct groups by virtue of their spacings, shadings, and intensities. These groups may be considered as progressions or as sequences, but they have not been successfully worked into a single square array. Possibly several electronic transitions between multiplet states overlap in this region.

There are several reasons for believing the 5760A and 5544A systems have upper electronic states formed from the same atomic states. Under all conditions of temperature, mercury pressure, and fading with time, they appear and disappear together. If a mercury atomic state lies slightly below the minimum of the upper electronic state of the 5760A and 5544A systems, a quenching of these systems might occur with increase in mercury pressure. This may account for the decrease in intensity of these bands with increase in mercury pressure.

A possible explanation of the fading with time of the 5760A and 5544A systems is that the molecules responsible for these systems are boiled off the amalgam at the furnace center. After a certain time all of the HgIn molecules will have boiled off leaving only indium and gaseous mercury at the center of the furnace. Since, as shown by analysis of the 4102A and 4511A bands, the ground state of HgIn is very shallow, the HgIn molecules will be dissociated a short time after evaporation. The thermal energy at the 900°C temperature is considerably greater than the energy necessary to dissociate HgIn in its ground state. The fading of some of the HgIn bands with time may thus be described.

The persistence of the 5226A system with time may mean that this system is due to molecules formed in the atmosphere of the discharge tube from excited mercury $^3S_1$ and unexcited indium $^2P_{1/2}$. It should therefore not fade with time. The difference in behavior of 5226A and of 5760A and 5544A may indicate a difference in character of the upper states for these two systems. This difference may be such that the upper state for 5760A and 5544A may not be formed from collisions between excited mercury and other atoms while the upper state for 5226A may be formed from collisions.

It is a pleasure to thank Professor J. G. Winans for suggesting the HgIn problem and for many illuminating discussions. This work was supported in part by the Research Committee of the graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

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Boson Current Corrections to Second Order

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The β-matrix formalism is applied to the Schwinger-Tomonaga method of calculating second-order current corrections for particles with spin 0 or 1 in interaction with the electromagnetic field. A rule for eliminating the troublesome "surface terms" is introduced, which makes the general formalism exactly similar to that for the electron. One other complication is the appearance in the results of an operator M which has no counterpart in the electron case; this operator can be handled without difficulty, however.

The second-order current corrections are found to diverge logarithmically for the vector meson, including the corrections to the dipole and quadrupole moments. For the scalar meson, on the other hand, the divergent terms vanish identically because of special relations between the operators. Thus to this order of calculation, the scalar meson like the electron requires only renormalization of the charge and mass, while the same is no longer true of the vector meson.

I. INTRODUCTION

THE necessary modifications in the Schwinger-Tomonaga covariant formulation[1,2] of electrodynamics in going from the case of electrons to that of bosons have been discussed by several authors.[3,4] It is found that for bosons it is necessary to introduce certain additional terms in the current and interaction Hamiltonian in order to make integrable the equations describing the development of the system in space time. These extra terms depend not only on the point under consideration, but also on the orientation of a mathematical surface σ through that point, which is expressed by the unit normal vector n_μ. On physical grounds, this surface dependence cannot appear in any calculated final quantity that is in principle measurable; explicit calculation of the first-order corrections (vacuum polarization and self-mass)[4,5] have shown that the surface-dependent parts finally cancel in the total expression. This has not been done for the higher order calculations, so that the present paper begins with a proof of a similar cancellation in the second-order corrections to the boson current. Generalizing from these examples of first- and second-order cancellation, a simple rule is given for writing expressions correct to any order without explicit introduction of the surface terms.

It is found that the β-matrix formalism of Kemmer[6] is the most convenient means of calculating electrodynamic corrections for boson fields, and is especially suited for expressing the rule for removal of the surface terms. The essential advantage of the formalism is that all expressions for particles of spins 0 and 1 become exactly similar in general structure to the corresponding

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[1] S. Tomonaga, Prog. Theor. Phys. 1, 27 (1946).
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[4] M. Neuman and W. H. Furry, Phys. Rev. 76, 1677 (1949).
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[6] N. Kemmer, Proc. Roy. Soc. (London) 173, 97 (1939).

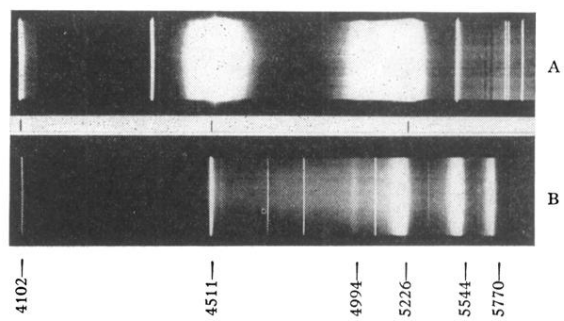

FIG. 1. Glass prism spectrograms of (A) the absorption in yellow region at high mercury pressure and (B) the band systems of HgIn.

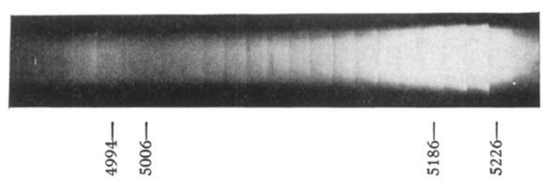

FIG. 4. Grating spectrogram of the 5226A and 4994A systems. Iron comparison lines were superimposed on all grating spectra.

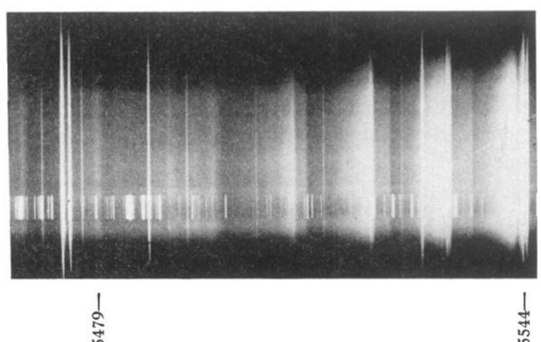

FIG. 5. Grating spectrogram of the more intense bands of the 5544A system. Higher order atomic lines also appear.

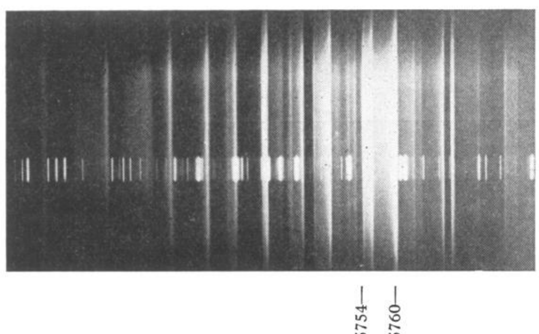

FIG. 6. Grating spectrogram of the 5760A system.