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THE EMISSION BANDS OF MERCURY VAPOUR AT 335 nm AND 485 nm

L. F. PHILLIPS

Chemistry Department, University of Canterbury, Christchurch (New Zealand)

Summary

Areas of agreement and disagreement between different investigators of the kinetics of the mercury emission bands are discussed. Certain of the existing phase shift data for pure mercury and mercury–nitrogen systems are re-interpreted in terms of the emission of the 335 nm band by a short-lived $Hg_2(^3 1_u)$ species. It is shown that both phase shift and steady state intensity data favour $Hg_2(^3 0_u^-)$ rather than Hg_3 as the emitter of the 485 nm band.

1. Introduction

The 335 nm and 485 nm emission continua of mercury vapour have been the subject of many investigations during the past 65 years, and a considerable body of experimental data and interpretation has accumulated. Until recently it appeared that the interpretations supplied by different groups of workers were converging towards a single, moderately complex reaction scheme. Lately, however, quite serious differences of opinion have appeared with regard to several features of the excitation mechanisms and even, since the advent of Hg_3, with regard to the chemical nature of the species responsible for emitting one of the bands. The purpose of the present paper is to summarize the available data and agreed points of interpretation and, where possible, to reconcile or decide between conflicting points of view.

The early results are summarized by Finkelnberg [1] and McCoubrey [2]. Probably the cleanest spectra of the bands were published by Drullinger *et al.* [3, 4, 5] who point out that the so-called 485 nm band actually has maximum intensity at 510 nm. Most theoretical discussions have been based on the interpretation of Mrozowski [6], according to which the 335 nm and 485 nm bands result from transitions to the repulsive ground state of Hg_2 from bound $^3 1_u$ and $^3 0_u^-$ states. However, Drullinger *et al.* [3] have proposed that the 485 nm band actually arises from an Hg_3^* species, rather than the

thermal equilibrium [3, 5]. The interpretation of these observations will be discussed later.

3. Areas where interpretations differ

3.1. The rate of the 335 nm emission step

The rate of the 335 nm emission step

$$Hg_2(^3 1_u) \rightarrow 2Hg + h\nu_{335} \tag{3}$$

was estimated by McCoubrey [2] as 10^7 s^{-1} on the grounds that the lifetime of $Hg_2(^3 1_u)$ should not be greater than that of the $Hg(^3 P_1)$ atom to which it dissociates at infinite internuclear distance.

To account for the much slower rise times of the 335 nm emission in a pulsed high temperature system with direct excitation into the $^3 1_u$ state, Drullinger et al. [3] postulated that the reverse of reaction (1) occurred with formation of a pool of $Hg(^3 P_0)$ which then decayed slowly by reaction (1). In subsequent work [13] they used this process as a means of generating a pool of $Hg(^3 P_0)$ for kinetic studies.

Ladd et al. [14] and Ong et al. [18] attributed the slow removal of $Hg_2(^3 1_u)$, as manifested in the phase delay of the 335 nm band relative to the 253.7 nm atomic fluorescence, to the combined effects of reactions (1), (2) and (3) with no allowance for the reverse of reaction (1). With this interpretation, extrapolation of the phase shift data to zero partial pressure of M, after removing the contribution of reaction (1), gave estimates of the lifetime of the $^3 1_u$ state which were greatly in excess of 10^{-7} s. It has been pointed out by Skonieczny [19] that such an interpretation must be highly suspect. Considering first the results of Ong et al. [18] at 373 K, we may note that if the emitter of the 335 nm band is a stabilized $Hg_2(^3 1_u)$ then the rate constant for the reverse of reaction (1) is of the order of 10^{-18} cm^3 molecule^{-1} s^{-1} (using Kuhn and Freudenberg's [21] value of 0.84 eV for the dissociation energy of the $^3 1_u$ state). Hence the dissociation of $Hg_2(^3 1_u)$ back to $Hg(^3 P_0)$ is unimportant in this system. The same is necessarily true of the reverse of reaction (2). It has been suggested [19] that trapping of 253.7 nm radiation was a source of error in these measurements; however, this is ruled out by the fact that the phase angle of the 335 nm band was measured relative to that of the 253.7 nm fluorescence. The error in the values of k_2 and k_3 given in ref. 18 actually arises from the use of an incorrect value [15] of k_1 in the analysis of the data. If all of the phase shift of the 335 nm band is attributed to reaction (1), the results yield a value of 1.2×10^{-30} for k_1, in fair agreement with ref. 17 (see Table 1). Thus the experiments of Ong et al. give no quantitative information about the rates of reactions (2) and (3) but support the view that these reactions are fast.

The data of Ladd et al. [14] were obtained at 563 K, where the reverse of reaction (1) should be much faster than at 373 K. A straightforward derivation [22] yields the results

$$\tan \delta = \frac{\omega(\omega^2 + e^2 + cd)}{(\omega^2 + e^2)b - ced}$$

$$\tan \phi = \frac{\omega(b + e)}{be - \omega^2 - cd}$$

for the phase shifts δ and ϕ of the $Hg(^3P_0)$ and $Hg_2(^31_u)$ populations respectively, where $\omega = 2\pi \times$ frequency in Hertz, the phase shifts are measured relative to $Hg(^3P_1)$ and the coefficients b, c, d and e are related to the rate constants of reactions (1) - (7):

$$Hg^0 + M \rightarrow Hg^1 + M \tag{4}$$

$$Hg^0 + Hg + M \rightarrow Hg_2{}^1 + M \tag{1}$$

$$Hg_2{}^1 + M \rightarrow Hg^0 + Hg + M \tag{5}$$

$$Hg_2{}^1 + M \rightarrow Hg_2{}^0 + M \tag{2}$$

$$Hg_2{}^1 \rightarrow 2Hg + h\nu_{335} \tag{3}$$

$$Hg^0 + wall \rightarrow Hg + wall \tag{6}$$

$$Hg_2{}^1 + wall \rightarrow 2Hg + wall \tag{7}$$

Here Hg^0 stands for $Hg(^3P_0)$, $Hg_2{}^1$ for $Hg_2(^31_u)$, $Hg_2{}^0$ for $Hg_2(^30_u{}^-)$ and Hg^1 for $Hg(^3P_1)$, and we have

$$b = k_4[M] + k_1[Hg][M] + k_6/[M]$$

$$c = k_5[M]$$

$$d = k_1[Hg][M]$$

and

$$e = (k_2 + k_5)[M] + k_7/[M] + k_3$$

If the value of k_3 is taken to be about 10^7 s^{-1}, then e is normally dominated by k_3 and is much larger than the other coefficients, including ω. Hence we have, to a good approximation,

$$\tan \phi = \tan \delta = \frac{\omega}{b - cd/e}$$

$$= \frac{\omega}{k_4[M] + k_1[Hg][M] + k_6/[M] - k_1 k_5[Hg][M]^2/k_3}$$

The final term in the denominator increases rapidly with increasing [M] and causes an increased phase delay relative to the value $\tan^{-1}(\omega/b)$ that applies at low pressure. Once again we may conclude that the phase shift results give no information about k_2 and k_3. With $k_1 = 1.6 \times 10^{-31}$, the high temperature data of Ladd [23] now yield $k_5/k_3 = 4.8 \pm 0.5 \times 10^{-19}$ cm^3 molecule^{-1} at 563 K for M = Hg.

3.2. The nature of the 485 nm emitter

Until recently it was generally believed, following Mrozowski [6], that the emitter of the 485 nm band was $Hg_2(^3O_u^-)$. However, it has been proposed [3, 4, 5] and to some degree accepted [13, 24] that the emitter is actually an Hg_3 species. The main evidence for this view is that Drullinger *et al.* [4] found that the stimulated emission process

$$Hg_2(^3O_u^-) + M' \rightarrow 2Hg + M' + h\nu_{485} \qquad (8)$$

apparently occurred only with M' = Hg. With [Hg] = 10^{17} cm^{-3} the 485 nm intensity was not enhanced by adding inert gases or nitrogen at up to a hundred times the mercury vapour pressure.

If the stimulated emission were indeed specific to M = Hg, this would indicate that an Hg_3^* species was involved. However, many observers have noted intense emission from mercury–nitrogen systems containing only about 10^{13} mercury atoms cm^{-3}; the phase shift measurements of Ong *et al.* [18] show that at high nitrogen pressures the 485 nm emitter disappears at a rate proportional to $[N_2]$, just as it disappears at a rate proportional to [Hg] in the pure mercury system [14]. The rate constant found for the reaction of the emitter with nitrogen at 373 K is less by a factor of 20 than that for the reaction with mercury at 563 K, so that in the experiments with added gases in ref. 4 it is possible that too little gas was added to bring about a significant effect. Insufficient information is given in ref. 4 to decide whether the added gases were adequately pure. A barium or magnesium getter is mentioned, but presumably this was present in the gas storage bulbs rather than in the sealed-off fluorescence cell. Impurities liberated from Pyrex during the sealing-off process can have a marked effect on 485 nm band intensity [8]. As noted in ref. 3, the spectroscopic results are all consistent with the identification of the emitter as $Hg_2(^3O_u^-)$.

The evidence given so far would appear definitely to favour $Hg_2(^3O_u^-)$ over Hg_3^*. It might be argued, in favour of Hg_3, that the removal of the 485 nm emitter by nitrogen could be a quenching step

$$Hg_2(^3O_u^-) + M \rightarrow 2Hg + M \qquad (9)$$

rather than a stimulated emission process; however, such a process should also have been observable in the experiments of Drullinger *et al.* with added gases.

To complete the mechanism we add the steps

$$Hg_2(^3O_u^-) + M \rightarrow Hg_2(^3 1_u) + M \qquad (10)$$

which is important at high temperatures, plus

$$Hg_2(^3O_u^-) + wall \rightarrow 2Hg + wall \qquad (11)$$

and

$$Hg_2(^3O_u^-) \rightarrow 2Hg + h\nu_{485} \qquad (12)$$

We can now consider the significance of the experimental observations on the ratio of steady state intensity in the two bands, as noted at the end of

Section 2. At moderately low temperatures the ratio I_{485}/I_{335} is proportional to $[\mathrm{Hg}]^2$ in the pure mercury system, changing over to $[\mathrm{Hg}]$ at temperatures where the emitters are in thermal equilibrium with one another. In the mercury–nitrogen system at low pressures the ratio I_{485}/I_{335} is proportional to $[\mathrm{N}_2]$. A steady state treatment yields

$$[\mathrm{Hg_2}^0] = \frac{k_2[\mathrm{Hg_2}^1]\,[\mathrm{M}]}{k_8[\mathrm{M}'] + (k_9 + k_{10})[\mathrm{M}] + k_{11}/[\mathrm{M}] + k_{12}}$$

so that

$$\frac{I_{485}}{I_{335}} = \frac{k_2[\mathrm{M}]\,(k_8[\mathrm{M}'] + k_{12})}{k_3(k_8[\mathrm{M}'] + (k_9 + k_{10})[\mathrm{M}] + k_{11}/[\mathrm{M}] + k_{12})}$$

or, in the case where the spontaneous emission step (12) may be neglected,

$$\frac{I_{485}}{I_{335}} = \frac{k_2 k_8[\mathrm{M}]\,[\mathrm{M}']}{k_3(k_8[\mathrm{M}'] + (k_9 + k_{10})[\mathrm{M}] + k_{11}/[\mathrm{M}] + k_{12})}$$

Here the collision partner M in reaction (8) is distinguished by a prime in case it is specifically required to be Hg. When the two emitters are in equilibrium this reduces to

$$\left(\frac{I_{485}}{I_{335}}\right)_{\mathrm{eq}} = \frac{k_2 k_8[\mathrm{M}']}{k_3 k_{10}}$$

The equilibrium ratio is proportional to $[\mathrm{M}']$ as required. If nitrogen at pressures of the order of 10 Torr can be presumed to bring about equilibrium between the two emitters, then the equilibrium intensity ratio is predicted to be proportional to $[\mathrm{M}']$ and M' can be identified with N_2, thus ruling out Hg_3. In the steady state, at pressures where $(k_9 + k_{10})[\mathrm{M}]$ is the largest term in the denominator, we again find this intensity ratio to be proportional to $[\mathrm{M}']$ and are obliged to identify M' with N_2. Only when $k_8[\mathrm{M}']$ predominates do we find the ratio proportional to $[\mathrm{M}]$ and this situation does not apply in the mercury–nitrogen system at pressures where the ratio is proportional to $[\mathrm{N}_2]$. At low pressures in pure mercury vapour the term k_{12} may predominate over $k_8[\mathrm{M}']$ in the numerator of the steady state expression, while the diffusion term $k_{11}/[\mathrm{M}]$ predominates in the denominator, in which case the intensity ratio is proportional to $[\mathrm{Hg}]^2$, as observed. However, k_{12} is small. Ong et al. [18] found $k_{12} < 500\ \mathrm{s}^{-1}$; Skonieczny and Krause [25] give $k_{12} = 46.7 \pm 3\ \mathrm{s}^{-1}$. Alternatively, at pressures where the effects of the terms in $[\mathrm{M}]$ and $[\mathrm{M}]^{-1}$ cancel each other, proportionality to $[\mathrm{Hg}]^2$ is obtained. In summary, the steady state intensity ratios also support the identification of the 485 nm emitter as $\mathrm{Hg}_2(^3 0_\mathrm{u}{}^-)$.

Smith et al. [5] cite unpublished theoretical work in support of the statement that the 6500 cm^{-1} splitting between the emitting states is too large to be the $^3 1_\mathrm{u} - {}^3 0_\mathrm{u}{}^-$ splitting of Hg_2, and also mention that the observed thermal destruction of the 485 nm radiator at temperatures above about

700 K has been successfully modelled for an Hg_3 species but not for Hg_2. Both of these statements appear less convincing than the deductions from experimental results that are outlined earlier.

4. Conclusion

Since this article is not intended as an exhaustive review, but rather as an attempt to settle some outstanding differences of opinion, a great deal of excellent non-controversial work has not been cited directly. The main points which are believed to have been settled here are the causes of the observed slow decays of the 335 nm band in the phase shift experiments and the chemical nature of the species emitting the 485 nm band.

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Note added in proof. In a current publication, Drullinger et al. (M. Stock, E. W. Smith, R. E. Drullinger, M. M. Hessel and J. Pourcin, J. Chem. Phys., 68 (1978) 1785) give a mechanism which involves a non-radiating $Hg_2(^3 0_u{}^-)$ and a radiating Hg_3 species. This mechanism accounts, more convincingly than the one given here, for the $[Hg]^2$ dependence of I_{485}/I_{335} at low $[Hg]$. Further work appears necessary to settle the question of Hg_2 versus Hg_3.

$^3 0_u^-$ state of Hg_2. This is one of the controversial points that is considered here.

There is general agreement that under most circumstances the meta-stable atomic species $Hg(^3P_0)$ serves as a reservoir of excitation energy for the bands. In experiments involving excitation by 253.7 nm resonance radiation, the $Hg(^3P_0)$ is generated in collisions involving the $Hg(^3P_1)$ that is produced initially. The collision partner may be either a ground state mercury atom or a molecule of an added gas such as nitrogen. Experiments with added gases encounter the difficulty that the metastable atoms react very rapidly with common impurities, notably oxygen for which the quenching rate constant is 2×10^{-10} cm^3 $molecule^{-1}$ s^{-1} [7 - 9]. To ensure that reaction with oxygen is negligible it is necessary, for example, to use nitrogen containing much less than 1 ppm oxygen impurity. A reliable method for scavenging the last impurities from purified nitrogen by allowing them to react with excited mercury was recently devised by Callear and Connor [10].

In Section 2 the existing experimental data will be summarized together with points of interpretation on which there is general agreement; points of disagreement will be considered in the Section 3.

2. The area of agreement

(1) In systems where excitation is by 253.7 nm radiation, $Hg(^3P_0)$ atoms are a precursor of the emission bands. This is based on the observations that $Hg(^3P_0)$ is always present is such systems and that the decay of the emission band intensity parallels the decay of the $Hg(^3P_0)$ concentration after the exciting light has been turned off. Even when the species emitting the bands are not in thermal equilibrium with one another, this implies that in the steady state the 335 nm and 485 nm bands must decay at the same rate, which is the rate of decay of the $Hg(^3P_0)$ population. The identical decay rates of the two bands under such conditions have been noted many times since the persistence times were first measured by Lord Rayleigh [11].

(2) The emitter $Hg_2(^3 1_u)$ of the 335 nm band is formed by the three-body reaction

$$Hg(^3P_0) + Hg + M \rightarrow Hg_2(^3 1_u) + M \qquad (1)$$
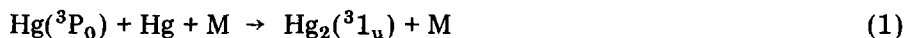
where the third body M may be another ground state mercury atom or a molecule of an added gas. The $^3 1_u$ state is able to be populated by this reaction as a result of the merging of the $^3 1_u$ and $^3 0_u^-$ potential energy curves at short internuclear distances [12]. Alternatively, the $^3 1_u$ state may be directly populated by light absorption at longer wavelengths than the 253.7 nm resonance line [3, 13]. The rate constant for reaction (1) has been measured and the results are shown in Table 1.

(3) The emitter of the 485 nm band is formed as a result of a collision of $Hg_2(^3 1_u)$ with another species. Assuming, for the moment, that this emitter is $Hg_2(^3 0_u^-)$, the process can be represented as

TABLE 1

Some measured rate constants for reaction (1)

M	Reference	k_1 (cm^6 molecule^{-2} s^{-1})	Comments
Hg	2	1×10^{-30} at $T = 473$ K	From decay of emission bands; Hg(^{3}P$_0$) not observed directly
Hg	14	$3.4 \pm 1.7 \times 10^{-31}$ at $T = 563$ K	From phase shift of 335 nm band; Hg(^{3}P$_0$) not observed directly
Hg	13	$1.6 \pm 0.2 \times 10^{-31}$ at $T = 673$ K	Hg(^{3}P$_0$) monitored by 297 nm absorption
N$_2$	15	1.3×10^{-29} at $T = 297$ K	From steady state 404.7 nm absorption; commercial N$_2$, reactive impurities $\leqslant$ 2 ppm
N$_2$	16	$\approx 10^{-30}$ at $T = 432$ K	From decay of emission bands; commercial N$_2$, reactive impurities $\leqslant$ 1 ppm
N$_2$	17	$1.55 \pm 0.16 \times 10^{-30}$ at $T = 293$ K	Hg(^{3}P$_0$) monitored by 546.1 nm fluorescence; N$_2$ purified in photochemical reactor [10]
N$_2$	This paper	$1.2 \pm 0.2 \times 10^{-30}$ at $T = 373$ K	Re-interpretation of phase shift data for 335 nm band; purified N$_2$

$$Hg_2(^31_u) + M \rightarrow Hg_2(^30_u^-) + M \qquad (2)$$
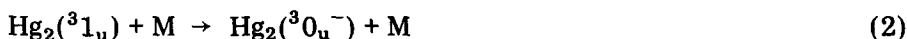
Drullinger *et al.* [3, 4] have shown that the emitting states are in equilibrium with one another in pure mercury vapour at temperatures above 575 K. In the only study of the pure mercury system that has been made over an extended temperature range, they also showed that at high temperatures the dominant emission is in the 335 nm band while at low temperatures the 485 nm band predominates. From the variation of the relative intensities with temperature at $T > 575$ K they derived a value of 6500 cm^{-1} for the energy separation of the two emitting states. They also found that in a pulsed experiment, at the low end of their temperature range, the 335 nm band rose to its maximum intensity about 25% faster than the 485 nm band. This last observation, that the time evolutions of the two bands are not always the same, is consistent with phase shift experiments which have demonstrated the presence of a phase delay of the 485 nm band relative to the 335 nm band in a modulated system, both with mercury alone [14] and with added nitrogen [18]. The assertion [19] that the existence of such a phase shift is inconsistent with the many observations that both bands decay at the same rate is based on a misunderstanding of the phase shift experiment. A phase shift exists between two signals which decay at identical rates if one begins to decay while the other is still rising to its maximum value.

(4) The steady state intensity ratio I_{485}/I_{335} is proportional to [N$_2$] in the mercury–nitrogen system at low nitrogen pressures [20, 18], to [Hg]^2 in the pure mercury system at low temperatures [2, 3, 14] and to [Hg] in the pure mercury system at temperatures where the emitting states are in