

again shortly by Mahr.¹¹ We feel sure that the fundamental importance of the questions attacked by this method, and the growing availability of tunable single mode lasers which make it practical, will com-

bine to make two-photon spectroscopy increasingly useful for finding and describing the geometrically hidden excited states of molecules.

New York, N. Y., 1968; (c) J. M. Worlock in "Laser Handbook," F. T. Arrechi, Ed., North-Holland Publishing Co., Amsterdam, 1972.

(11) H. Mahr in "Treatise in Quantum Electronics," H. Rabin and C. L. Tang, Ed., Academic Press, New York, N. Y., in press.

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Mercury-Sensitized Luminescence

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Chemical processes initiated by reactions of excited mercury atoms have been studied for many years, and several reviews are available.¹

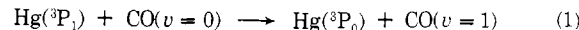
Much less attention has been given to the luminescent processes which form the subject of this Account, even though such processes were among the first reactions of excited atoms to be investigated. Thus in 1923 Cario and Franck² reported the observation of sensitized fluorescence of thallium when a mixture of thallium and mercury vapors was irradiated with the mercury 253.7-nm resonance line, and a short time later Wood and Gaviola³ and Mitchell and Dickinson⁴ described structureless emission bands which they observed during 253.7-nm irradiation of mixtures of mercury vapor with water and with ammonia. In 1928 Oldenberg⁵ described emission bands arising from short-lived excited complexes (excimers) of excited mercury atoms with rare gas atoms; analogous emission continua associated with excimers of formula Hg₂ were first reported in 1913.⁶

Current interest in the luminescent reactions of excited atoms is connected with the possible importance of luminescence as an alternative to photosensitized decomposition in systems where the quantum yield for decomposition is low,⁷ and with interest in properties such as radiative lifetimes, reactivities, and decomposition modes of the excimers themselves. A subsidiary source of interest is the possibility that excimers having repulsive ground states might form the basis of new ultraviolet laser systems.

A portion of the energy level diagram for atomic mercury is shown in Figure 1. Atoms in the ³P₁ state are readily produced by irradiating room-temperature mercury vapor with the 253.7-nm resonance line from a low-pressure mercury lamp. From the ³P₁ level an atom can return spontaneously to the

ground ¹S₀ state, emitting 253.7-nm fluorescence, with a rate constant of 9 × 10⁶ sec⁻¹.

Alternatively the excited atom may undergo a bimolecular collision, which can lead to quenching to either the ground state or to the metastable ⁶3P₀ state or can result in compound formation. Certain quenchers, notably N₂ and CO, are particularly effective at promoting spin-orbit relaxation to the ³P₀ level by processes such as



If the exciting radiation is not filtered to isolate the 253.7-nm line, the ³P₂ level may also become populated to a significant extent⁸ as a result of absorption of 404.7-nm radiation (⁷3S₁ ← ⁶3P₀) by metastable ³P₀ atoms, followed by fluorescence at 546.1 nm (⁷3S₁ → ⁶3P₂).

The work to be described has been concerned with reactions of mercury atoms in the ⁶3P₁ and ⁶3P₀ states, as studied by emission spectroscopy. Reaction rates and excimer lifetimes have been determined by rotating sector or phase-shift studies of modulated excimer luminescence.⁹

Reactions in the Mercury-Ammonia System

The emission bands observed during 253.7-nm irradiation of mixtures of mercury vapor with NH₃ and ND₃ are shown in Figure 2. The bands show no detectable fine structure at a resolution of 0.02 nm, and are believed to be perfectly continuous. An interesting feature of the emission is that its intensity is only very slightly reduced by the addition of a large excess of NH₃ or ND₃.

(1) R. J. Cvetanovic, *Progr. React. Kinet.* **2**, 39 (1964); J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

(2) G. Cario and J. Franck, *Z. Physik*, **17**, 202 (1923).

(3) R. W. Wood, *Phil. Mag.*, **50**, 774 (1925); **4**, 466 (1927); E. Gaviola and R. W. Wood, *ibid.*, **6**, 1191 (1928).

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(8) H. E. Hunziker, *IBM J. Res. Develop.*, **15**, 10 (1971).

(9) L. F. Phillips, *Progr. React. Kinet.*, **7**, Part 2, 83 (1973).

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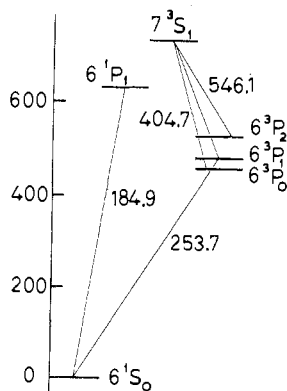
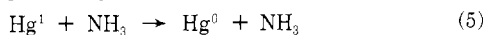
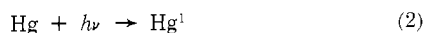


Figure 1. Low-lying energy levels of atomic mercury. (The three components of the 6^3P term differ in the value of total electronic angular momentum, given by the quantum number J which appears as a subscript in the symbols for the spectroscopic states. The 3P_0 and 3P_2 states are metastable because of the selection rules governing changes in J . To save writing, photochemists commonly put Hg^1 for $Hg(^3P_1)$ and Hg^0 for $Hg(^3P_0)$.)

In our initial studies of this system^{10,11} we proposed the following reaction mechanism



where Hg , Hg^1 , and Hg^0 stand for $Hg(^1S_0)$, $Hg(^3P_1)$, and $Hg(^3P_0)$, respectively. In this mechanism reaction 4 was included to account for the observed small yield of NH_3 decomposition,¹ reaction 5 expresses the known ability of NH_3 to quench Hg^1 to the metastable state, and reaction 6 was included because of the need to insert a slow process between the rapid removal of Hg^1 by steps 3, 4, and 5 and the fast emission step 7.

The rate of the bimolecular process 6 at low ammonia pressures, as determined by the rotating sector method, was found to be 4.3×10^{-13} and 2.0×10^{-13} cm^3 molecule⁻¹ sec⁻¹ for NH_3 and ND_3 , respectively. The overall quantum efficiency, in terms of photons emitted in step 7 per Hg^1 lost by reactions 4 and 5, was measured as 0.70 ± 0.14 for NH_3 and 1.05 ± 0.20 for ND_3 . These figures showed that the efficiency of NH_3 in converting Hg^1 to Hg^0 was considerably greater than previously believed.¹² The species responsible for the emission band was identified as a complex, or excimer, of the form indicated in reaction 7, with the bonding having a considerable amount of charge-transfer character.

Diagrammatic potential energy curves for the $Hg-NH_3$ complex are shown in Figure 3. The emission band is continuous because of the repulsive nature of the lower state. Increasing the strength of the interaction between Hg^0 and the donor molecule should result in a decrease in internuclear distance in the upper state, and therefore shift the emission band to longer wavelengths. This conclusion was

(10) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Chem. Phys. Lett.*, **5**, 555 (1970).

(11) R. H. Newman, C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Trans. Faraday Soc.*, **66**, 2827 (1970).

(12) A. B. Callear and R. E. M. Hedges, *Trans. Faraday Soc.*, **66**, 605 (1970).

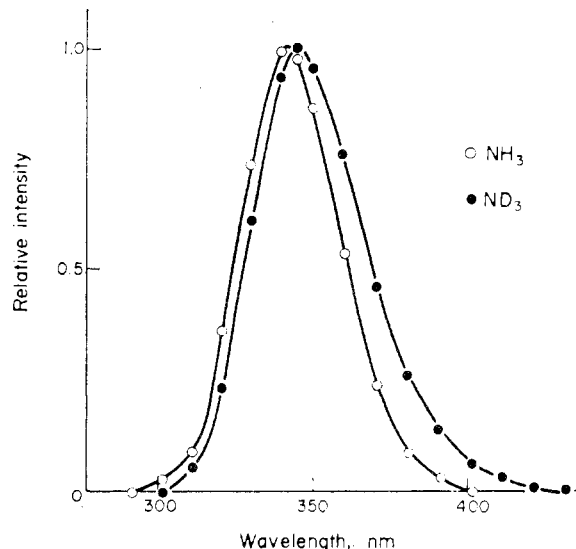


Figure 2. Emission bands observed in the mercury-sensitized luminescence of NH_3 (open circles) and ND_3 (closed circles). Intensities in photons per second.

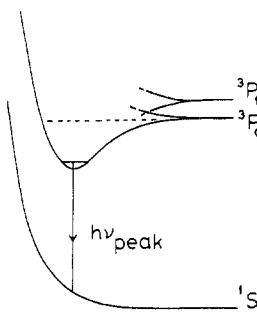
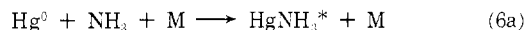


Figure 3. Diagrammatic potential energy curves for the NH_3-Hg^0 complex.

borne out by subsequent studies with water,¹³ alcohols,¹⁴ and primary amines,¹⁵ in which a correlation was found between the ionization potential of the donor and the wavelength of peak emission by the complex.

Callear and McGurk¹⁶ studied the mercury-ammonia system by flash photolysis in the presence of a large excess of a diluent gas such as nitrogen and showed that in addition to reaction 6 it was necessary to include the termolecular reaction 6a leading



to the formation of a stabilized complex. Our rotating sector technique was too slow to study the rates of the processes leading to emission at the relatively high pressures where reaction 6a was important, and to increase the available modulation frequency provision was made for the microwave-powered discharge lamp to be switched on and off electronically at frequencies up to about 150 kHz.¹⁷ With this system rate constants were determined by the phase-shift method.

It can be shown that if δ is the measured phase shift between a prompt emission from the fluores-

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(15) R. H. Newman, C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Trans. Faraday Soc.*, **67**, 1360 (1971).

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(17) L. F. Phillips, *Rev. Sci. Instr.*, **42**, 1098 (1971).

cence cell and an emission which is delayed by a process having a first-order or pseudo-first-order rate constant k (in sec^{-1}), then

$$\tan \delta = 2\pi f/k = 2\pi f\tau \quad (8)$$

where f is the modulation frequency in hertz and τ is the mean lifetime of the slow step. If two successive first-order processes give rise to phase delays δ_1 and δ_2 , the overall phase shift is simply $\delta_1 + \delta_2$. Methods are available for calculating phase shifts in more complicated reaction systems.⁹

Our results for the mercury-ammonia luminescence are shown in Figure 4.¹⁸ The phase difference between the mercury fluorescence at 253.7 nm and the complex emission at 350 nm is seen to exceed 90° at low NH_3 pressures, which implies that more than one slow step is involved in the emission process. At high NH_3 pressures the phase shift at a given frequency approaches a constant value which we associate with the finite rate of the emission step 7. From the high-pressure phase shifts the mean lifetime of the stabilized complex is found to be $1.86 \pm 0.08 \mu\text{sec}$, a result which has been verified by the flash photolysis measurements by Callear and coworkers.¹⁹

Once the phase shift δ_2 , due to the finite rate of removal of HgNH_3^* , is known from the high-pressure data it becomes possible to calculate the phase shift δ_1 , due to the finite rate of removal of Hg^0 , by subtracting δ_2 from the total phase shift δ observed at low pressures. For δ_1 we have the expression

$$\tan \delta_1 = 2\pi f / (k_6[\text{NH}_3] + k_{6a}[\text{NH}_3]^2) \quad (9)$$

From the data of Figure 4 this equation yields $k_6 = 3.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and $k_{6a} = 2.3 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ with estimated errors of about $\pm 10\%$ in each value.

It is notable that the data show no sign of any decrease in δ_2 at low pressures, as would be expected because of the availability of the reverse of reaction 6 as a mode of decomposition of the unstabilized complex.¹⁹ Later work suggests that such a decrease may occur at NH_3 pressures below about 1 Torr. Experiments in which δ_1 is determined directly, *e.g.*, by monitoring the phase of the Hg^0 absorption line at 404.7 nm, offer the interesting possibility of determining the lifetime of an excimer as a function of its degree of stabilization.

Another phenomenon which is expected to vary with the degree of stabilization of the complex is the peak wavelength of the emission band. By assuming that all of the wavelength shift observed with varying NH_3 pressure was due to varying stabilization of the complex we obtained a value of 21 kJ mol^{-1} for the dissociation energy of HgNH_3^* .²⁰ However, an alternative explanation of the wavelength shift has been provided by Callear and Connor,²¹ who concluded that at high pressures complexes with two or more NH_3 molecules attached to a single Hg^0 atom are important, and obtained stability constants for

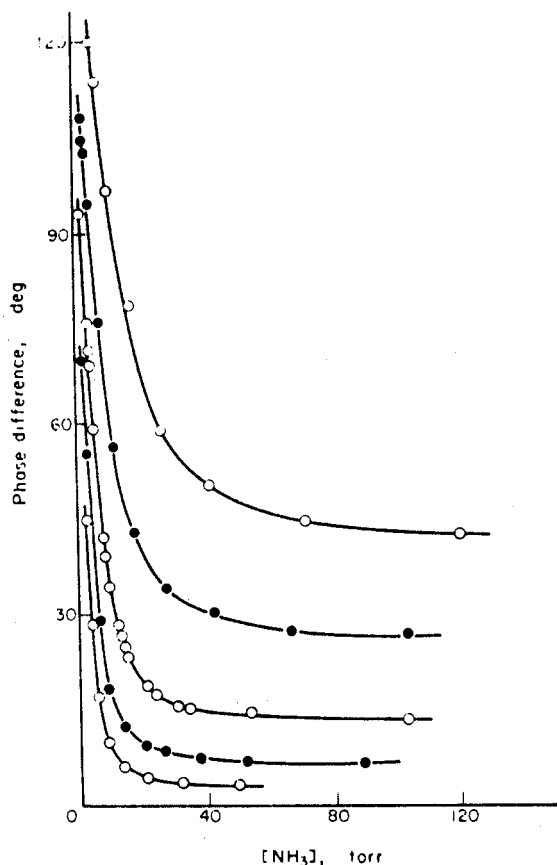
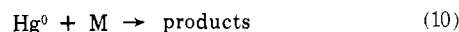


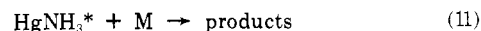
Figure 4. Variation with NH_3 pressure of the phase shift between 350-nm luminescence and 253.7-nm fluorescence. Frequencies (top to bottom) 80, 40, 20, 10, and 5 kHz.

the various complexes by deconvoluting the bands observed at NH_3 pressures up to 10 atm. This apparent willingness to form extended complexes provides an explanation for the failure of excess NH_3 to quench the emission.

In the presence of an additional reactant M the mechanism (eq 1-6) needs to be supplemented by steps 10 and 11. Reaction 11 will cause a decrease in



and



the limiting phase shift observed at high NH_3 pressures, and both (10) and (11) will act to reduce the phase shift at low pressures. It may also be necessary to take account of the presence of two different species which can act as third bodies in reaction 6a.

Experimental data for NH_3 with other gases added show some interesting differences.²² With O_2 and N_2O the phase shift is found to be reduced at both high and low NH_3 pressures, whereas with H_2 the low-pressure phase shift is greatly reduced but the high-pressure limit is almost unaffected. Rate constants for reactions 6a, 10, and 11, as derived from observations of this sort, are summarized in Table I. Values obtained for k_{10} are in fair agreement with values reported by other workers.²³⁻²⁵ It is noteworthy that k_{11} is always much smaller than k_{10} .

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(20) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Chem. Phys. Lett.*, **8**, 226 (1971).

(21) A. B. Callear and J. H. Connor, *Chem. Phys. Lett.*, **13**, 245 (1972).

(22) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Trans. Faraday Soc.*, **67**, 2004 (1971).

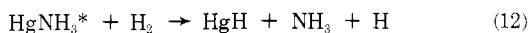
(23) A. B. Callear and J. C. McGurk, *J. Chem. Soc., Faraday Trans. 2*, **69**, 97 (1973).

Table I
Rate Constants^a Obtained from Phase-Shift
Studies Using Mixtures of NH₃ with Other Gases

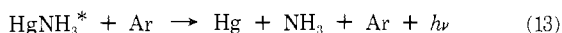
Reactant	k_{10}	k_{6a}	k_{11}
H ₂	9.2×10^{-11}		2.8×10^{-15}
O ₂	2.7×10^{-10}		8.5×10^{-13}
CO	3.9×10^{-11}		7.6×10^{-13}
NO	2.0×10^{-10}		5.7×10^{-13}
N ₂ O	5.8×10^{-11}		1.6×10^{-13}
N ₂		6×10^{-32}	$< 10^{-15}$
Ar		2.5×10^{-32}	5×10^{-15}
C ₂ H ₆ ^b	4.5×10^{-13}	4×10^{-31}	8.1×10^{-14}

^a Molecules cm⁻³ sec⁻¹. ^b Ethane containing up to 0.01% ethylene, which would make a large contribution to k_{10} .

For H₂ in particular the low value of k_{11} suggests that the reaction



is endothermic, which in turn would imply that the HgNH₃* dissociation energy is greater than that of HgH by at least 19 kJ mol⁻¹, *i.e.*, is not less than 52 kJ mol⁻¹. Very recently Callear and Connor (A. B. Callear, private communication) have obtained a value of 46 ± 4 kJ mol⁻¹ for this dissociation energy. The finite value of k_{11} obtained with argon is tentatively interpreted in terms of the collision-stimulated emission process.



Complexes of Hg(³P₀) with Water, Alcohols, and Primary Amines

Emission bands observed with these electron donors are similar to those of Figure 2, but occur at slightly longer wavelengths in the case of the amines and in the 290–300-nm region for water and alcohols.^{13–15} We did not detect sensitized luminescence with secondary amines, nor was any observed in a single experiment with diethyl ether, but Strausz and coworkers²⁶ have obtained photographic spectra of emission bands for several ethers, including dimethyl ether and furan. They also showed that an emission band obtained with xenon, which we attributed to a complex of Xe with Hg⁰,²⁷ actually involved Hg¹ rather than Hg⁰, a result which has since been confirmed in our laboratory by the finding of precisely zero phase shift between the HgXe* band and the Hg 253.7-nm fluorescence. It is likely that emission bands could be detected for secondary amines by the use of sufficiently long photographic exposures; however, for tertiary amines any excimer emission would be swamped by the strong $\sigma^* \rightarrow n$ fluorescence.²⁸

Phase shift results for water, alcohols, and amines resemble those for NH₃, and rate constants and excimer lifetimes can be derived from such data, provided the emission is sufficiently intense, just as was done for the mercury–ammonia complex. Rate constants for reactions of Hg⁰ with water, alcohols,²⁹

(24) H. Horoguchi and S. Tsuchiya, *Bull. Chem. Soc. Jap.*, **44**, 3221 (1971).

(25) G. London, A. C. Vikis, and D. J. Le Roy, *Can. J. Chem.*, **66**, 605 (1970).

(26) O. P. Strausz, J. M. Campbell, S. De Paoli, H. S. Sandhu, and H. E. Gunning, *J. Amer. Chem. Soc.*, **95**, 732 (1973).

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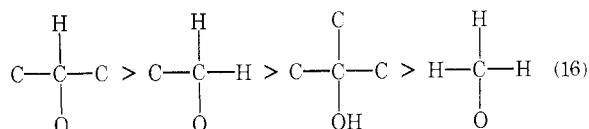
(28) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Chem. Phys. Lett.*, **8**, 77 (1971).

ammonia, and amines,³⁰ together with values of the complex lifetime, wavelength of peak intensity, and quantum efficiency of sensitized luminescence, are listed in Table II. The quantum efficiencies were determined by comparison with the intensity of emission for NH₃, allowance being made for the differing extents of quenching of the 253.7-nm fluorescence. This comparison could be made with a precision of about $\pm 10\%$ for the more intense bands, the uncertainty increasing, with decreasing quantum efficiency, to approximately a factor of two in the case of methylamine. The lifetimes, rate constants, and quantum efficiencies are seen to vary in an interesting manner with the structure of the electron-donating molecule.

Considering first the alcohols, a steady decrease in luminescent efficiency is found with increasing molecular complexity, until *tert*-butyl alcohol is reached, at which point the quantum efficiency suddenly rises by three orders of magnitude. *tert*-Amyl alcohol is also relatively efficient. This implies that the most important process competing with luminescence involves the reaction of an α hydrogen, which might occur by either eq 14, in competition with the light-emitting step, or eq 15, competing with complex formation. (The formation of HgH in these reactions is postulated by analogy with the high HgH quantum yields obtained from H₂ and several hydrocarbons.^{31–33})



Comparison of the quantum efficiencies for *n*- and isopropyl alcohols and for *n*-butyl, isobutyl, and *sec*-butyl alcohols also suggests that a lone α hydrogen is more reactive toward excited mercury than one of a pair of α hydrogens. Combining these results with the conclusion of previous workers^{34,35} that in the case of methanol the reaction occurs preferentially with the hydroxyl hydrogen, we obtain the following order of reactivity of hydrogen atoms toward excited mercury.



For methyl and ethyl alcohols it has been pointed out³⁶ that the difference of a factor of 3.5 between the “physical” and “chemical” cross sections for quenching of 253.7-nm fluorescence implies that the quenching of Hg¹ by these molecules yields mainly Hg⁰. Rate constants for quenching 253.7-nm fluores-

(29) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Trans. Faraday Soc.*, **67**, 2567 (1971).

(30) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Trans. Faraday Soc.*, **67**, 3247 (1971).

(31) A. B. Callear and J. C. McGurk, *J. Chem. Soc., Faraday Trans. 2*, **68**, 289 (1972).

(32) A. B. Callear and P. M. Wood, *J. Chem. Soc., Faraday Trans. 2*, **68**, 302 (1972).

(33) A. C. Vikis and D. J. Le Roy, *Can. J. Chem.*, **50**, 595 (1972); **51**, 1207 (1973).

(34) R. F. Pottie, A. G. Harrison, and F. P. Lossing, *Can. J. Chem.*, **39**, 102 (1961).

(35) A. R. Knight and H. E. Gunning, *Can. J. Chem.*, **39**, 1231 (1961); **39**, 2251 (1961); **39**, 2246 (1961); **40**, 1134 (1962).

(36) S. Penzes, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **43**, 4524 (1965); A. Kato and R. J. Cvetanovic, *Can. J. Chem.*, **45**, 1845 (1967).

Table II
Bimolecular and Termolecular Rate Constants for Reaction with Hg(³P₀), Lifetimes of Complexes with Hg(³P₀), and Quantum Efficiencies (φ) for Emission of Luminescence^a

Reactant	k^1	k_{6a}	τ	ϕ	Ref
H ₂ O	$(2.2 \pm 0.1) \times 10^{-14}$	$(1.2 \pm 0.4) \times 10^{-32}$	2.2 ± 0.2	0.19	13, 29
D ₂ O	$(1.35 \pm 0.15) \times 10^{-14}$	$(0.95 \pm 0.4) \times 10^{-32}$	2.2 ± 0.2	0.49	13, 29
Methyl alcohol	$(1.3 \pm 0.2) \times 10^{-12}$	$(1.5 \pm 0.7) \times 10^{-30}$	0.64 ± 0.04	0.033	14, 29
Ethyl alcohol	$(6.0 \pm 1.5) \times 10^{-12}$	$(8 \pm 4) \times 10^{-30}$	0.12 ± 0.04	0.013	14, 29
<i>n</i> -Propyl alcohol	Intensity too low		0.12 ± 0.06	0.0069	14, 29
Isopropyl alcohol	Intensity too low		0.12 ± 0.06	0.0030	14, 29
<i>n</i> -Butyl alcohol	Intensity too low		0.04 ± 0.2	0.0076	14, 29
Isobutyl alcohol	Intensity too low		0.2 ± 0.1	0.0041	14, 29
<i>sec</i> -Butyl alcohol	Intensity too low		0.07 ± 0.07	0.0021	14, 29
<i>tert</i> -Butyl alcohol	$(3.1 \pm 0.3) \times 10^{-12}$	$(7.4 \pm 2.0) \times 10^{-30}$	0.81 ± 0.04	0.26	14, 29
<i>tert</i> -Amyl alcohol	$(6.9 \pm 1.0) \times 10^{-12}$	$(1.3 \pm 0.2) \times 10^{-29}$	0.33 ± 0.03	0.042	14, 29
NH ₃	$(3.2 \pm 0.3) \times 10^{-13}$	$(2.3 \pm 0.2) \times 10^{-30}$	1.86 ± 0.08	0.70	11, 18
ND ₃	$(2.4 \pm 0.2) \times 10^{-13}$	$(3.4 \pm 0.3) \times 10^{-30}$	1.86 ± 0.08	1.0	11, 18, 19
Methylamine	Intensity too low			0.00035	15, 30
Ethylamine	$(1.8 \pm 0.6) \times 10^{-12}$	$(4.0 \pm 1.4) \times 10^{-30}$	1.85 ± 0.08	0.0115	15, 30
<i>n</i> -Propylamine	$(3.7 \pm 0.6) \times 10^{-12}$	2×10^{-30}	0.81 ± 0.09	0.018	15, 30
Isopropylamine	$(2.8 \pm 0.9) \times 10^{-12}$	3×10^{-30}	0.85 ± 0.06	0.053	15, 30
<i>n</i> -Butylamine	$(4.8 \pm 0.6) \times 10^{-12}$	$(3.0 \pm 1.0) \times 10^{-30}$	1.01 ± 0.06	0.042	15, 30
Isobutylamine	$(4.6 \pm 0.6) \times 10^{-12}$	$(3.5 \pm 1.2) \times 10^{-30}$	1.18 ± 0.06	0.023	15, 30
<i>sec</i> -Butylamine	$(8.0 \pm 2.5) \times 10^{-12}$	3×10^{-30}	1.38 ± 0.08	0.065	15, 30
<i>tert</i> -Butylamine	$(5.5 \pm 2.0) \times 10^{-12}$	$(2.3 \pm 0.2) \times 10^{-30}$	1.16 ± 0.06	0.11	15, 30

^a Units: k' , cm³ molecule⁻¹ sec⁻¹; k_{6a} , cm⁶ molecule⁻² sec⁻¹; τ , μ sec.

cence by the alcohols in Table I are all similar to one another.¹⁴ Thus it is reasonable to assume that the products of the quenching reactions, and in particular the yields of Hg⁰, are also similar, because the addition of an extra reaction channel to the Hg¹-ROH system would be expected to significantly enhance the rate of removal of Hg¹. Therefore the differences in quantum efficiency are to be understood mainly in terms of the operation of reactions 14 and 15.

On the reasonable assumption that the transition probability k_7 does not depend markedly on the nature of the groups bonded to the O atom, the variation of lifetime with structure can be attributed to the effect of k_{14} in eq 17. The lifetime variation parallels the variation of quantum efficiency, so that the inequalities (eq 16) appear also to apply to the ease with which a hydrogen atom is abstracted by a mercury atom held in a mercury-alcohol complex.

$$\tau = 1/(k_7 + k_{14}) \quad (17)$$

However, the lifetime variation alone is not sufficient to account for the whole of the variation in quantum efficiency. Differences in the values of the rate constant for removal of Hg⁰, given by

$$k' = k_6 + k_{15} \quad (18)$$

are the results of differences in k_6 (due to changes in molecular size) as well as differences in the ease of hydrogen abstraction by reaction 15. Nevertheless, on the basis of the data in Table II it would appear that the combined effect of the variations in k_{14} and k_{15} is more than enough to account for the observed quantum efficiency variation.

Now consider the amines. We note first that with methylamine the very low luminescent efficiency and relatively large rate constant¹⁵ for reaction with Hg¹ imply that Hg⁰ is unimportant in this system. For the other amines the complex lifetime varies by little more than a factor of 2 between ammonia and *n*-propylamine, so that a reaction analogous to (14) can

account for only a small part of the quantum efficiency variation. For *tert*-butylamine, *sec*-butylamine, *n*-butylamine, and isopropylamine the combined effects of decreased lifetime and increased k' value are more than sufficient to account for the low quantum efficiencies by comparison with NH₃, and we may conclude that most of the photochemical reaction probably occurs through intermediate formation of Hg⁰. For isobutylamine and *n*-propylamine, however, the k' and τ factors can account for only two-thirds of the reduction in efficiency, so direct decomposition during quenching of Hg¹ may be important. For ethylamine the k' and τ factors together account for only about 10% of the reduction, and, as for methylamine, the role of Hg⁰ must be relatively insignificant.

The Hg₂ Bands

Two structureless bands arising from bound states of Hg₂ are observed in fluorescence during 253.7-nm irradiation of pure mercury vapor at high pressures, or of room-temperature mercury vapor in the presence of excess high-purity nitrogen. One band has peak intensity at 335 nm, the other at 485 nm. Diagrammatic potential energy curves³⁷ showing the transitions involved are given in Figure 5. Supposed evidence for a ³Σ_u state, dissociating to Hg(³P₂) + Hg(¹S₀), has turned out to be spurious.³⁸⁻⁴⁰

Kinetic studies of the emission intensities⁴¹⁻⁴⁵ have shown that Hg⁰ is a precursor of the emission,

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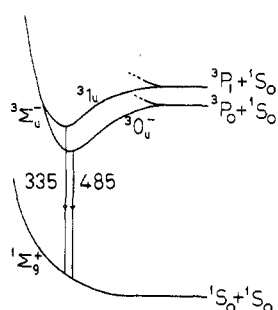
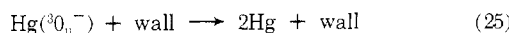
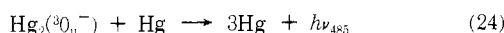
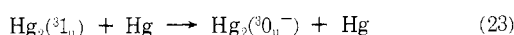
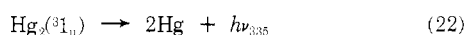
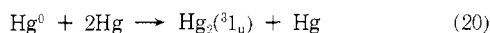
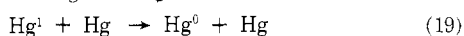


Figure 5. Potential energy curves for low-lying states of Hg_2 .

that $\text{Hg}_2(^31_u)$ is formed from Hg^0 and Hg by a three-body reaction, that the upper state of the 485 nm band can be populated when the 335 nm emission is quenched, that the ratio of intensities I_{485}/I_{335} is proportional to $[\text{Hg}]^2$ at low pressures in a pure mercury system, and that the 485- and 335-nm bands appear to decay at the same rate after pulsed excitation.

Our phase-shift studies with pure mercury vapor⁴⁴ are interpreted in terms of the following mechanism.



This mechanism has two particularly interesting features. First, although the 31_u state of Hg_2 dissociates to $\text{Hg} + \text{Hg}^1$, this state is able to be populated by reaction 20 because of the merging of the 31_u and $^30_u^-$ states at short internuclear distances (*cf.* Figure 5). In fact the 31_u state is populated preferentially, because once formed it cannot dissociate except *via* $^30_u^-$.⁴²

The second point of interest is that the radiative transition represented by reaction 24 is strongly forbidden and is therefore postulated to occur as a collision-induced process, similar to reaction 13, whose rate governs the decay of the 485-nm band. At low pressures reactions 23, 24, and 25 lead to the required dependence of I_{485}/I_{335} on $[\text{Hg}]^2$. The phase delay which we observed between the 335- and 485-nm bands results from the finite rate of reaction 24, while the delay of the 335-nm bands relative to the 253.7-nm line emission results from the combined effects of reactions 20 to 23.

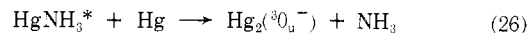
Rate constants for these reactions have been calculated from the pressure dependence of the phase shifts of the 335 nm-band relative to the 253.7-nm line, and of the 485-nm band relative to the 335-nm band, and values so obtained are listed in Table III. The rate constant values are such that the decay rates of the two bands observed in a pulsed experiment are likely to be very similar. In practice, the population of the $^30_u^-$ state would exceed that of

Table III
Rate Constant Values for Hg_2 System

k_{20}	$(3.4 \pm 1.7) \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$
k_{21}	$1.7 \times 10^{20} \text{ molecules cm}^{-3} \text{ sec}^{-1}$
k_{22}	$(2.0 \pm 0.5) \times 10^4 \text{ sec}^{-1}$
k_{23}	$(6.4 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
k_{24}	$(1.06 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

31_u , and the effect of the small difference between k_{23} and k_{24} would be partly compensated by the fact that reaction 23 populates the $^30_u^-$ state.

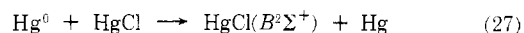
Callear and Connor²¹ have shown that the $^30_u^-$ state is able to be populated in the Hg-NH_3 system by reaction 26. (These authors refer to the 485-nm



band as the "green" band.) Huestis and coworkers⁴⁶ have shown that the Hg_2 system at 485 nm does not provide the basis of a laser, despite the repulsive ground state, because absorption to higher states of Hg_2 is more probable than stimulated emission over the wavelength range from 390 to 515 nm. (Current attempts in the author's laboratory to obtain laser action in the HgNH_3 band have been unsuccessful, presumably for an analogous reason.)

Other Studies

Vikis and Le Roy⁴⁰ have reported sensitized fluorescence of radicals, such as that of HgCl which is excited by



Hunziker has described a number of studies in which triplet states of molecules such as naphthalene, and free radicals such as HO_2 and CH_3 , are produced by mercury sensitization with a modulated light source and detected by their modulated absorption spectra. Much of this work is discussed in detail in ref 9. We have observed emission from a complex of $\text{Cd}(^3P_0)$ with NH_3 , analogous to HgNH_3^* .⁴⁷ Kinetic studies have also been made of Xe_2 fluorescence excited by 147-nm irradiation of pure xenon gas,^{48,49} which involves the reaction of metastable and ground-state xenon atoms, and of the xenon-sensitized fluorescence of CO ,^{50,51} which does not involve metastable xenon atoms, but does involve a long-lived (25 μsec) excimer of Xe and CO . Gas-phase excimers appear to constitute a large and almost unexplored group of highly interesting compounds.

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