

Finally, we should remark that Kierstead¹⁵ has shown that $(\partial V/\partial P)_T$ shows a logarithmic rise near the λ line, and that $(\partial V/\partial P)_T$ appears to begin to depart from $(\partial V/\partial P)_{T,0}$, perhaps 0.1° below the λ line. As shown in ref 7, we should expect $(\partial V/\partial T)_P$ to begin to follow the

(15) H. Kierstead, *Phys. Rev.*, **153**, 258 (1967).

specific heat much sooner than $(\partial V/\partial P)_T$; some further analysis of the situation would be in order.

Acknowledgments. I wish to thank Professor Horst Meyer for an interesting discussion and for helping me in the assembly of the data. This paper is dedicated to the memory of Professor W. D. Walters.

The Interaction of Mercury $6(^3P_1)$ Atoms with Noble Gas Atoms

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Abstract: The interaction of Hg $6(^3P_1)$ atoms with noble gas atoms results in the formation of loosely bonded diatomic van der Waals molecules. Radiative decay of these excited molecules gives rise to an intense band emission. The kinetics of band emission obey the Stern-Volmer relation, indicating that molecule formation is a second-order process (in the 0–60 Torr pressure range) and making it possible to derive rate constants and cross sections for the quenching reactions of noble gas atoms. Lennard-Jones potential energy calculations show that crossings of excited- and ground-state potential energy curves of the van der Waals molecules occur at molecular compressions with prohibitively high repulsion energies. It is proposed that quenching of Hg $6(^3P_1)$ atoms by noble gas atoms occurs exclusively by radiative dissipation of excitation energy and not by the crossing mechanism proposed by Jablonski.

The quenching of Hg $6(^3P_1)$ atoms by noble gas atoms has been studied since the early days of mercury photosensitization.^{1–3} The reaction is very inefficient, hardly measurable by the phosphorescence method, and hence reliable rate constants were difficult to determine. Olsen⁴ succeeded in obtaining rate constants from measurements of the depolarization of the mercury resonance line. The quenching cross sections found for He and Kr were “negligible” while those of Ne and Ar were 0.325 and 0.222 \AA^2 , respectively.

These reactions have been considered to be examples of total “physical” quenching of excited mercury atoms.^{5–7} According to Jablonski, the quenching occurs *via* the crossing of the repulsive potential curves representing the excited mercury atom–ground-state noble gas atom, and ground-state mercury–ground-state noble gas atom systems. The crossing would occur at potential energies slightly exceeding 112.7 kcal, the excitation energy of the mercury atom, and therefore quenching occurs only when the colliding atoms have sufficient translational energy to overcome the barrier. The crossover would be facilitated by heavy atom perturbations. After crossover the electronic excitation of the mercury atom would be converted into the translational energy of the departing atoms. This mechanism predicts a positive temperature coefficient for the quenching reactions and appears to be supported by

Oldenberg’s observation that the quenching cross section of argon increases by a factor of ~ 4 in going from room temperature to 750° .

This interpretation of the quenching mechanism does not take account of the important observation made by Oldenberg¹ that resonance irradiation of mercury–noble gas mixtures gives rise to a number of intense fluorescence bands, appearing on both sides of the mercury resonance line. With the lighter gases only one maximum appeared on the short-wavelength side of the 2537-\AA line, while the heavier gases, notably argon, krypton, and xenon, gave two broad, diffuse maxima. (More recently, a third band has been found for the Hg–Kr system.⁸) In addition to these continua, Oldenberg detected discrete band structures displaced toward the red when argon or krypton were used with mercury.

The origins of these spectra were interpreted in terms of loosely bonded van der Waals molecules formed between mercury and noble gas atoms. In a recent article, Fiutak and Frackowiak⁹ discuss the electronic correlation and potential energy relations of the Hg–Ar van der Waals molecule. The closed shells of the separate atoms [Ar + Hg] are unperturbed by molecule formation and therefore only the outer two electrons of mercury need be considered. This leads to the following electronic configurations and term types of the molecule.

$$\begin{array}{l} \text{[closed shell]} (x\sigma)^2 \text{ } ^1\Sigma^+ \text{ ground state} \\ \text{[closed shell]} (x\sigma) (y\sigma) \text{ } ^1\Sigma^+, \text{ } ^3\Sigma^+ \\ \text{[closed shell]} (x\sigma) (v\pi) \text{ } ^1\Pi, \text{ } ^3\Pi_r \end{array} \left. \vphantom{\begin{array}{l} \text{[closed shell]} (x\sigma)^2 \text{ } ^1\Sigma^+ \\ \text{[closed shell]} (x\sigma) (y\sigma) \text{ } ^1\Sigma^+, \text{ } ^3\Sigma^+ \\ \text{[closed shell]} (x\sigma) (v\pi) \text{ } ^1\Pi, \text{ } ^3\Pi_r \end{array}} \right\} \text{excited states}$$

The triplet excited states for large internuclear separations split into $\Omega = 0^-, 0^+$, and 1 states, the first of

(8) A. Michels, H. De Klavier, and D. Middlekoop, *Physica*, **25**, 163 (1959).

(9) J. Fiutak and M. Frackowiak, *Bull. Acad. Polon. Sci., Ser. Sci., Math., Astron. Phys.*, **11**, 175 (1963).

(1) O. Oldenberg, *Z. Physik*, **47**, 184 (1928); **49**, 609 (1928); **50**, 580 (1928); **51**, 40, 605 (1928); **55**, 1 (1929).

(2) H. Kuhn and O. Oldenberg, *Phys. Rev.*, **41**, 72 (1932).

(3) A. C. G. Mitchell and M. W. Zemansky, “Resonance Radiation and Excited Atoms,” Macmillan and Co., Ltd., London, 1934, p 89.

(4) L. O. Olsen, *Phys. Rev.*, **60**, 739 (1941).

(5) A. Jablonski, *Z. Physik*, **70**, 723 (1931).

(6) J. G. Calvert and J. N. Pitts, “Photochemistry,” John Wiley and Sons, Inc., New York, N. Y., p 78.

(7) P. Pringsheim, “Fluorescence and Phosphorescence,” Interscience Publishers, New York, N. Y., 1949, p 123.

which correlates with the $[\text{Ar} + \text{Hg } 6(^3\text{P}_0)]$ and the latter two with the $[\text{Ar} + \text{Hg } 6(^3\text{P}_1)]$ atomic states. All these states are slightly bonding with a very shallow potential well.

As to the nature of the spectra, several explanations have been offered. Discrete band structures have been assigned to transitions between quantized states of the van der Waals molecules;¹⁰ the short-wavelength bands have been assigned to transitions between the vibrational levels of the higher lying 0^- excited state and the 0^+ ground state and the long-wavelength bands to transitions between the vibrational levels of the lower lying $\Omega = 1$ excited state and 0^+ ground state. Alternative suggestions attribute the spectra to transitions between the repulsive branches of the ground and excited states,¹¹ to transitions between ground and excited states having auxiliary minima or maxima in the potential energy curve,¹² and to the local perturbation of the optical electron oscillation during collision.¹³ None of these interpretations are, however, entirely satisfactory.

The appearance of these so called "satellite" bands is not restricted to mercury-noble gas systems; diffuse banded spectra have also been observed from Tl, In, Zn, Cd, Na, K, Rb, and noble gases.^{14,15} Fluorescence, consisting of several red bands, has been observed from mercury-methane mixtures and assigned to Hg-CH_4 complexes.¹⁶ Similar fluorescence has been observed more recently from many paraffins.¹⁷

The transitions giving rise to these emissions can also be observed in absorption. A great deal of effort has been expended on the experimental and theoretical investigation of these and associated phenomena,¹⁸ a review of which would be out of place here.

From the above, it is evident that the "quenching" mechanism of noble gas reactions requires further study. Most often quenching measurements for the 2537-Å Hg radiation are carried out in a Zemansky-type apparatus³ which does not utilize light filters. With such an apparatus, any band fluorescence in the neighborhood of 2537 Å would be attributed to the unquenched fluorescence of excited mercury atoms. The residual quenching observed in this type of apparatus was usually referred to as "negligible" and may be due either to band fluorescence in a region relatively far from the 2537-Å line which is not registered by the photomultiplier or to Jablonski-type quenching. On the other hand, band fluorescence would be a less serious source of interference in depolarization measurements where polarization or rotation of the plane of maximum polarization is observed experimentally. Nonetheless, the quenching cross sections determined by this method could also be in serious error.

The present article describes a kinetic study of the band emission from mercury-noble gas systems and a new method for measuring quenching cross sections.

(10) J. Szudy, *Acta Phys. Polon.*, **29**, 605 (1966).

(11) H. Kuhn, *Proc. Roy. Soc., Ser. A*, **158**, 212 (1937).

(12) O. Jefimenko, *J. Chem. Phys.*, **39**, 2457 (1963).

(13) Y. Leycuras, *J. Quant. Spectrosc. Radiat. Transfer*, **6**, 131 (1966).

(14) H. Kreff and R. Rompe, *Z. Physik*, **73**, 681 (1932).

(15) W. M. Preston, *Phys. Rev.*, **51**, 298 (1937).

(16) G. Glockler and F. W. Martin, *J. Chem. Phys.*, **2**, 46 (1934).

(17) S. Penzes, O. P. Strausz, and H. E. Gunning, *ibid.*, **45**, 2322 (1966).

(18) S.-Y. Ch'en and M. Takeo, *Rev. Mod. Phys.*, **29**, 20 (1959); L. Klein and H. Margenau, *J. Chem. Phys.*, **30**, 1556 (1958).

It also presents some computational results on the Lennard-Jones potentials of mercury-rare gas atom systems.

Experimental Section

Conventional high-vacuum techniques were employed. The measurements of fluorescence intensities were carried out in a single-pass flow apparatus, which consisted of the following components along with the direction of gas flow: gas reservoir and mercury manometer, Edwards needle valve, rotameter, mercury saturator with stripper, Pirani gauge, cylindrical reaction vessel, Baratron MKS capacitor-type pressure gauge, and vacuum pumps.

The stripper of the mercury saturator was kept at 20° by circulating thermostated water through it. The reaction vessel, 120 mm long and 10 mm i.d., was made of Suprasil to minimize fluorescence from the walls. Both ends were sealed with plane 1/8 in. thick LiF windows. The cell was surrounded with a set of closely spaced, blackened brass plates to collimate the exciting light beam and to prevent scattered light reaching the photomultiplier. The output of the Baratron pressure gauge was fed into a Hewlett-Packard Model 1000 1A x-y recorder and displayed on the x axis. Both x and y input of the recorder had adjustable impedances to allow matching of the internal resistances of the potential source.

The light source in the emission study was a Hanovia low-pressure resonance lamp. In the 4047-Å absorption measurements the resonance source was a laboratory constructed low-pressure lamp with water-cooled electrodes. The emission tube was enclosed in a jacket through which a filter solution consisting of 300 g/l. of NiSO_4 and 120 g/l. of CoSO_4 in water was circulated at 24°. This filter eliminated all radiation from the lamp between 3100 and 4200 Å. The source of 4047-Å radiation was a Hanovia low-pressure lamp.

The fluorescent light emerging from the face of the resonance cell was filtered through a Baird-Atomic interference filter and its intensity measured by an RCA 1P28 photomultiplier. The output of the photomultiplier was fed onto the y axis of the x-y recorder.

The interference filters used had about 20-30% transmission with about 200-Å half-widths.

All optical parts of the apparatus were enclosed in a black box and kept at room temperature ($25 \pm 2^\circ$).

The gases used were Airco Assayed Reagent Grade sealed in Pyrex bulbs. They were used without purification.

Results

Addition of a few tenths of a Torr of noble gas to 1.2 μ of mercury resulted in the appearance of intense emission. With xenon, the long-wavelength tail of emission was estimated to lie between ~2790 and 2830 Å. Relative emission intensities were measured as a function of gas pressure for all noble gases between 0 and 15 Torr pressure and in some cases up to 60 Torr pressure using two different interference filters: (1) transmitted between 2640 Å and the emission tail end at 2830 Å; (2) transmitted between 2780 and 2830 Å. (A Pyrex filter with short-wavelength cutoff at 2830 Å removed all fluorescent radiation.) The results are depicted in Figure 1. As will be noted from the figure, the use of the shorter wavelength filter in each case resulted in considerably higher emission yields than the use of the longer wavelength filter. The ratio of emission intensities at 14 Torr pressure with filter 1 to filter 2 were 2.7 for He, 2.54 for Ne, 2.66 for Ar, and 2.88 for Kr, and the relative emission intensities with filter 1 were: 5.4:4.2:6.0:5.9:7.2 for He:Ne:Ar:Kr:Xe. These small variations in emission intensity are probably due to small changes in the spectral distribution of the fluorescence. The absolute quantum yields of the emission were not measured.

Mercury $6(^3\text{P}_0)$ atoms were looked for by 4047-Å absorption¹⁹ and 4850-Å emission²⁰ measurements;

(19) S. Penzes, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **43**, 4524 (1965); G. H. Kinbell and D. J. LeRoy, *Can. J. Chem.*, **38**, 1714 (1960); **40**, 1229 (1962).

(20) S. Penzes, H. E. Gunning, and O. P. Strausz, *J. Chem. Phys.*, **47**,

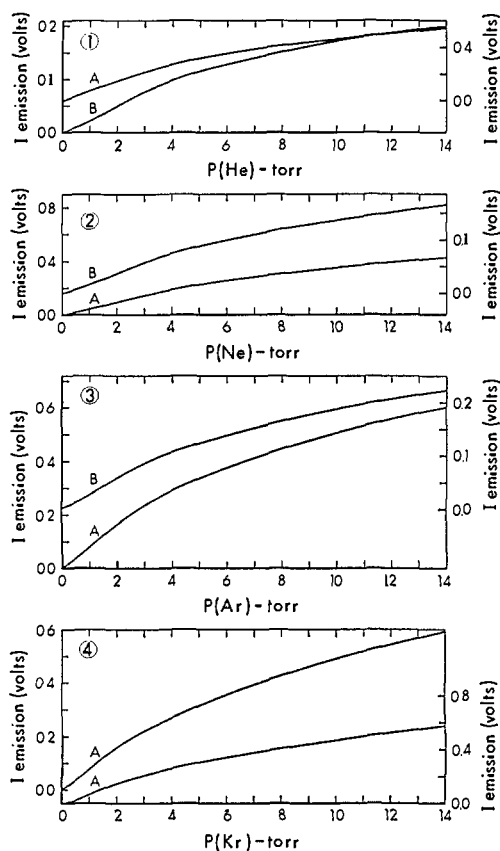


Figure 1. Emission intensities as functions of noble gas pressure: A, filter 1; B, filter 2.

neither absorption nor emission revealed a detectable concentration of metastable atoms and it was concluded that noble gas atoms are not efficient in bringing about spin-orbital relaxation of excited mercury atoms.

Simple Lennard-Jones (L-J) (twelve-six) potential energy curve calculations were carried out on the [Hg + Xe], [Hg + Kr], and [Hg + Ar] systems and their excited states to ascertain if crossings of ground- and excited-state potential curves occur at moderate energy barriers. There are several detailed potential calculations described in the literature on the [Hg-Ar] molecule.²¹ These earlier calculations were, however, mainly concerned with the shape of the attractive portion of the potential curves rather than with the question of crossing of ground and excited states.

To calculate the L-J force constants for the collision pairs the mixture rules were applied: $\epsilon_{\text{mix}} = (\epsilon_1 \epsilon_2)^{1/2}$ and $\sigma_{\text{mix}} = (\sigma_1 + \sigma_2)/2$. Values of ϵ , σ , ϵ_{mix} , σ_{mix} , ionization potentials, and polarizabilities used in the calculations are tabulated in Tables I and II.

To calculate force constants for the excited molecules we have made use of the London relationship for the attractive part of the potential

$$V(r) \approx -\frac{3}{2} \frac{\alpha_1 \alpha_2}{r^6} \frac{I_1 I_2}{I_1 + I_2}$$

4869 (1967); J. E. McDuff, D. D. Drysdale, and D. J. LeRoy, *Can. J. Chem.*, **46**, 199 (1968).

(21) L. Legowski, *Bull. Acad. Polon. Sci., Ser. Sci., Math., Astron. Phys.*, **6**, 127 (1958); W. Berdowski, *ibid.*, **11**, 227 (1963); J. Robin, R. Bergeon, L. Galatry, and B. Vodar, *Discussions Faraday Soc.*, **22**, 30 (1956).

Table I. Input Parameters for the L-J Potential Energy Curve Calculations

Atom	σ , Å ^a	ϵ/k , °K ^a	α , Å ³	I , eV ^f
Xe	4.10	221.0	4.0 ^b	12.08
Kr	3.607	171.0	2.48	13.93
Ar	3.405	119.8	1.63	15.68
Hg 6(1S ₀)	2.898	851.0	5.1 ^c	10.43
Hg 6(3P ₀)			10.0 ^d	5.85
Hg 6(3P ₁)			20.0 ^e	5.63

^a J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, pp 1110-1112. ^b H. H. Landolt and R. Bornstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, und Technik," Band I, Teil 1, Springer-Verlag, Berlin, 1950, p 401. ^c B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, *Proc. Roy. Soc., Ser. A*, **219**, 270 (1953). ^d Assumed. ^e Reference 3, p 178. ^f "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967, p E69.

Table II. Calculated Values of Lennard-Jones Force Constants^a

Collision pair	σ	σ^*	$\epsilon(1S_0)$	$\epsilon^*(3P_0)$	$\epsilon^*(3P_1)$
Hg-Xe	3.4990	3.4990	0.861	1.179	2.294
Hg-Kr	3.2525	3.2525	0.757	1.016	1.975
Hg-Ar	3.1515	3.1515	0.634	0.838	1.627
Hg-Xe	3.4990	3.1491 ^b	0.861	2.219	4.317
Hg-Kr	3.2525	2.9272 ^b	0.757	1.911	3.717
Hg-Ar	3.1515	2.8363 ^b	0.634	1.577	3.062

^a Values in Å; ϵ values in kcal/mole. ^b σ^* is 10% less than σ .

By equating this expression with the attractive term of the L-J function, we obtain

$$4\epsilon\sigma^6 = \frac{3}{2} \alpha_1 \alpha_2 \frac{I_1 I_2}{I_1 + I_2}$$

The ϵ values calculated for ground-state molecules with these approximations, using σ 's given in Table II, differed by 25-45% from the values calculated using mixture rules and reported in Table II. The calculated ϵ values for the excited molecules were then corrected using the correction factors established for ground-state molecules.

The σ values for the excited states are not known. In most previous calculations they were presumed to be somewhat larger than for the ground state. We calculated potential energy curves assuming $\sigma(\text{ex}) = \sigma(\text{gr})$ and $\sigma(\text{ex}) = 0.9\sigma(\text{gr})$. The results are compiled in Table II and the calculated potential energy curves shown in Figure 2. It is seen that crossing of ground and excited potential curves does not occur within the region of available excitation energies, even when 10% compression is assumed in the excited state.

Discussion

The computational result that crossing of potential curves occurs at molecular compressions, corresponding to prohibitively high-energy barriers, suggests that the only mode of quenching of excited mercury atoms by noble gas atoms is *via* band fluorescence, and that the fluorescence quantum yield is unity.

The width of the emission band is surprising; it extends to at least 2780 Å. Most spectroscopic studies of the mercury-noble gas systems had been done in absorption and, in the relatively few emission studies, only Oldenberg used resonance excitation, the others

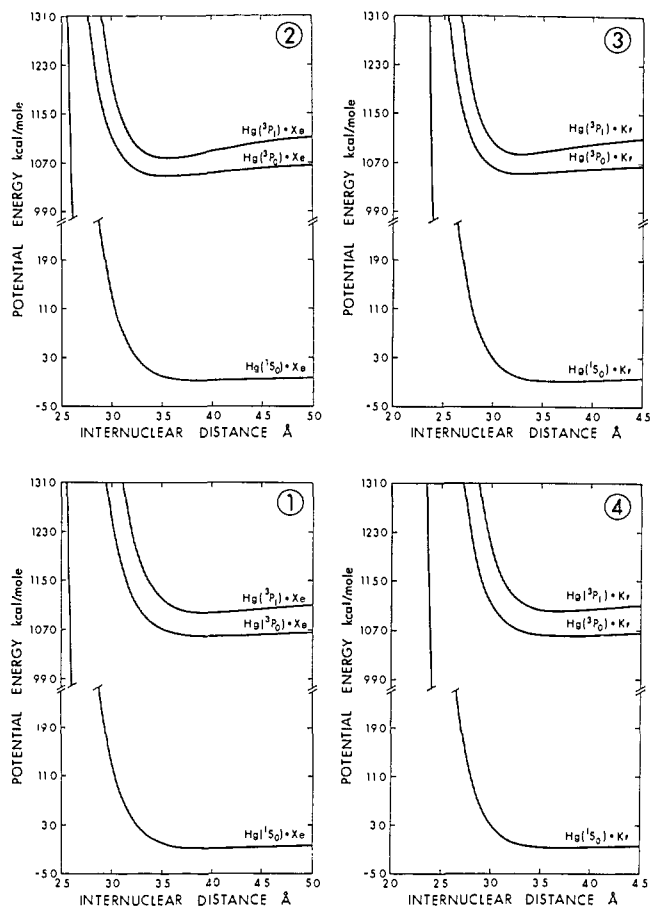
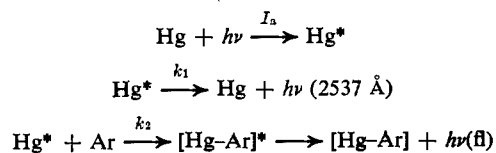


Figure 2. Calculated L-J potential energy curves: (1 and 4) $\sigma(\text{ex}) = \sigma(\text{gr})$; (2 and 3) $\sigma(\text{ex}) = 0.9 \sigma(\text{gr})$.

using discharges. It is possible that in absorption these long-wavelength transitions do not appear and in discharges they are masked by other emissions. It would be difficult to ascribe these long-wavelength emissions to transitions between quantized states of the van der Waals molecules. Evidently much more thorough studies of the emission spectra will be required for an understanding of what transpires in the Hg^* -noble gas systems.

Assuming the simple mechanism for the "quenching" reaction



steady-state treatment leads to the Stern-Volmer relation

$$\frac{I_{\text{fl}}}{I_a \phi} = \frac{k_2 P}{k_1 + k_2 P}$$

where P is the gas pressure and ϕ is the emission quantum yield. The reciprocal of this function

$$\frac{I_a \phi}{I_{\text{fl}}} = 1 + \frac{k_1}{k_2 P}$$

predicts a linear relation between the reciprocal of the emission intensity and $1/P$. Some representative plots are shown in Figure 3. It is seen that above ca. 1 Torr

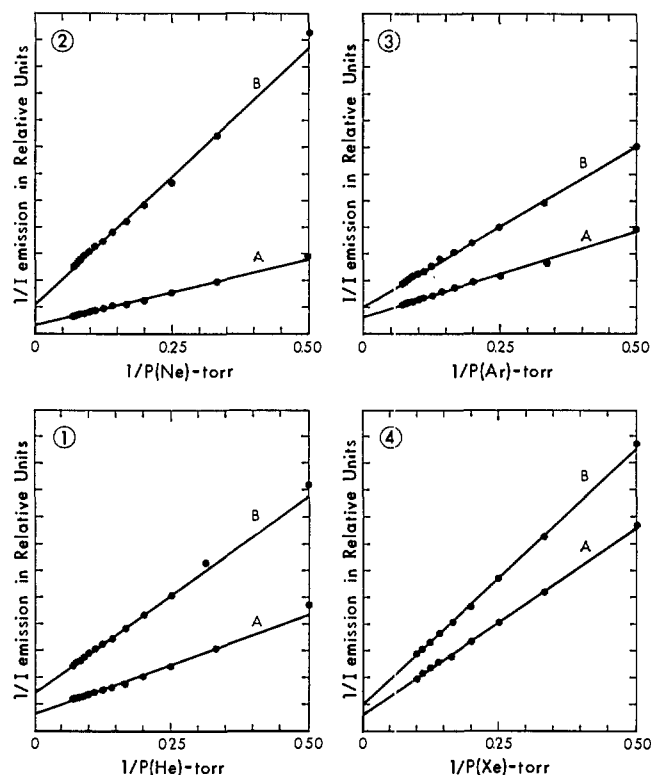


Figure 3. Reciprocal Stern-Volmer plots for emission.

pressure good straight-line relations are obtained using either filter. Taking the slopes from the plot in units of the intercepts, the value of k_1/k_2 is obtained. The value of k_1 is calculated from Holstein's imprisonment formula²² to be $3.61 \times 10^6 \text{ sec}^{-1}$ from which it is possible to obtain the rate constant and the cross section of reaction 2.

In this treatment the variations in the background emission intensities due to the "quenching" of the 2537- \AA emission, pressure broadening of the resonance line, and changes of mercury concentration with pressure have not been taken into account. The data on the rate constants and quenching cross sections presented in Table III are corrected for these effects. The values of cross sections listed in column a were derived by making allowance only for the quenching effect, while the entries in column b were derived by correcting for all three effects. The latter values are probably more reliable. Both sets of data appear to exhibit an increasing trend with increasing atomic number with the exception of xenon which appears to have somewhat lower cross section than Kr.

If the spectral distribution of fluorescence were the same for all noble gas atoms, then the trend in relative emission intensities should follow the trend in the quenching rate constants. That this is not the case (cf. Table III) is an indication that the spectra of the lighter gases are more intense in shorter wavelength radiation ($\lambda < 2640$) than the spectra of the heavier gases.

The close correlation between the experimental results and the Stern-Volmer relation discounts the possible importance of third-order processes in the formation of the van der Waals molecules. This is in marked contrast to the kinetic behavior of the analogous Hg^*

(22) T. Holstein, *Phys. Rev.*, **72**, 1212 (1947); **83**, 1159 (1951).

Table III. Rate Constant and Cross-Section Values for Quenching of Hg 6(³P₁) Atoms by Rare Gas Atoms^a

	k_2 , l. mole ⁻¹ sec ⁻¹ × 10 ⁻⁹	σ^2 , Å ²		Rel emission intensities with filter 1	$I(\text{filter 1})/$ $I(\text{filter 2})$
		a	b		
He	5.9	0.25	0.20	5.4	2.7
Ne	3.9	0.35	0.27	4.2	2.5
Ar	5.8	0.70	0.32	6.0	2.7
Kr	5.5	0.88	0.34	5.9	2.9
Xe	3.1	0.59	0.12	7.2	...

^a The error and reproducibility of measurements are within a factor of 2.

+ Hg system which has been shown to follow third-order kinetics.²⁰

Turning now to the potential energy calculations, neither our results on the Hg-Ar, Hg-Kr, and Hg-Xe

molecules nor the results reported by various authors on the Hg-Ar and Hg-He molecules^{21,23} do seem to corroborate the crossing mechanism. Also, if crossing of the ground state with either of the two excited states correlating with the Hg ³P₁-noble gas atom occurs, production of some Hg ³P₀ atoms would be expected because the state correlating with the Hg ³P₀-noble gas atom should always lie between the ground state and the states correlating with Hg ³P₁-noble gas atom. Thus the absence of metastable atoms may be taken as additional evidence against the crossing mechanism of quenching.

Acknowledgments. The authors thank the National Research Council of Canada for continuing financial support, and Dr. G. Greig and Mr. S. de Paoli for helpful assistance.

(23) J. Szudy, *Acta Phys. Polon.*, **29**, 605 (1966); **30**, 721 (1966); **32**, 359 (1967).

The Master Equation for the Dissociation of a Dilute Diatomic Gas.¹ I. A Method of Solution

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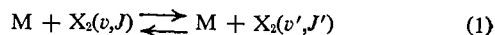
Contribution from the Centre for Research in Experimental Space Science, York University, Downsview, Ontario, Canada. Received May 2, 1969

Abstract: The master equation representing the dissociation-recombination kinetics of a dilute diatomic gas can be reduced to a system of inhomogeneous nonlinear Volterra integral equations of the second kind. Accurate solutions of these equations can be obtained using the self-consistent matrix iteration procedure proposed by Rush and Pritchard, under certain relatively unrestrictive conditions.

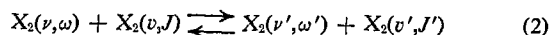
In setting up the "master equation" to represent the dissociation-recombination kinetics for a diatomic gas, three fundamental assumptions are implicit: (i) time must be considered as a continuous variable; (ii) the duration of the collisions which lead to transitions between states described in the equation must be infinitesimal compared with the time scale under consideration; (iii) the initial distribution of particle trajectories must be such that the distribution of first collision times is completely random. Thus, it is clear that the solutions of the master equation can only be valid at times which are long compared to the average time between collisions, and any attempt to deal with shorter times must appeal to more sophisticated treatments associated with the names of Bogoliubov and others.² We will assume in this work that the master equation gives a satisfactory representation of the dissociation-recombination kinetics of a diatomic gas.

We consider an idealized experiment in which a shock wave is passed through a mixture consisting of diatomic molecules X₂ and inert gas molecules M originally at a temperature of T₀. The heating process is assumed to be instantaneous, occurring at time $t = 0$, and after it

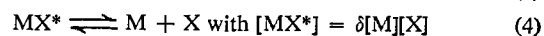
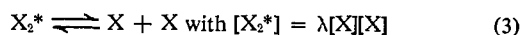
has happened, the gas is considered to have an equilibrium distribution of translational energies corresponding to a temperature T₀', but to still have internal energies characteristic of T₀. Equilibration between the internal and the translational degrees of freedom then proceeds until a final equilibrium temperature T is reached. This takes place through a series of processes of the type



and



which represent all the transitions among the rotation-vibration levels of X₂. In describing the dissociation step itself, we assume that this occurs through latent pairs, the concentrations of which are always taken to be in equilibrium with the instantaneous atom concentrations, *i.e.*



Reference should be made to our previous work³ for the definition of X₂^{*}, etc., and for the methods by which the equilibrium constants λ and δ can be calculated; it should be borne in mind that if X is an atom like H and

(1) Research supported by the Defence Research Board of Canada (Grant No. 9550-35) and the National Research Council of Canada.

(2) E. G. D. Cohen in "Fundamental Problems in Statistical Mechanics," North Holland Publishing Co., Amsterdam, 1962.

(3) D. G. Rush and H. O. Pritchard, Eleventh Symposium (International) on Combustion, Berkeley, Calif., 1967, p 13.