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Effect of Hg_2-Hg collisions on the formation and decay of excited Hg_2 molecules in Hg-N_2 mixtures*

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The effect of Hg_2-Hg collisions on the formation and decay of excited $Hg_2(^31_u)$ and $Hg_2(^30_u^-)$ molecules in Hg-N_2 mixtures was investigated in a series of delayed-coincidence experiments. $Hg(^3P_1)$ atoms, formed by irradiating the vapor-gas mixture with pulses of Hg(2537 Å) resonance radiation, were transferred collisionally to the $^3P_0$ state. The $Hg_2(^31_u)$ molecules, formed in subsequent $Hg(^1S_0) + Hg(^3P_0) + N_2$ collisions, underwent collisional $^31_u \rightarrow {}^30_u^-$ mixing. The time-decay spectra of the 3350 and 4850-Å fluorescent bands, associated with the ^31_u and $^30_u^-$ states, respectively, were studied in relation to N_2 and Hg densities and the resulting decay constants were extrapolated to zero N_2 and Hg pressures, yielding the following total cross sections $Q(A \rightarrow B)$ for collisional transfer between states A and B. For Hg_2-N_2 collisions: $Q(^30_u^- \rightarrow {}^31_u) = 2.3 \times 10^{-21}$ cm^2; $Q(^30_u^- \leftarrow {}^31_u) = 6.9 \times 10^{-17}$ cm^2; for Hg_2-Hg collisions: $Q(^30_u^- \rightarrow {}^31_u) = 2.2 \times 10^{-17}$ cm^2; $Q(^30_u^- \leftarrow {}^31_u) = 6.8 \times 10^{-14}$ cm^2. The radiative lifetime τ_4^0 of the $^30_u^-$ state was found to be 21.4 msec ± 7%.

I. INTRODUCTION

We have recently described a mechanism for the formation and decay of excited Hg_2 molecules, for which evidence was provided by delayed-coincidence studies of Hg_2 molecular fluorescent bands excited in Hg-N_2 mixtures.[1] According to the model which is consistent with Mrozowski's early postulates[2-4] and with the observations of other investigators,[5-7] the necessary condition for the formation of the ^31_u and $^30_u^-$ molecular states which are responsible for the 3350-Å ultraviolet and the 4850-Å green bands, respectively, is the presence of 6^3P_0 metastable mercury atoms. The latter are produced by collisional transfer from the 6^3P_1 resonance state which is excited directly by Hg 2537-Å resonance radiation. The ^31_u molecular state is formed first in a triple collision of an $Hg(^3P_0)$ atom, a ground-state $Hg(^1S_0)$ atom and a N_2 molecule. The $Hg_2(^31_u)$ molecule can then either decay spontaneously to the repulsive ground state with a decay constant comparable to that of the atomic 6^3P_1 resonance state,[4] or it can collide with an N_2 molecule and be transferred to the metastable $^30_u^-$ state which has a radiative life time exceeding 4.5 msec.[1] The common persistence time which was exhibited by the 3350 and 4850-Å bands, was ascribed to very efficient $^30_u^-$-^31_u mixing taking place in two-body collisions between excited Hg_2 molecules and ground-state N_2 molecules.

The relevant atomic and molecular levels of mercury, as well as the radiative and collisional processes involved in the formation and decay of the various atomic and molecular states, are shown schematically in Fig. 1. As predicted by the solutions of the rate equations describing the populations of the two atomic and two molecular states, the two bands exhibited identical decay patterns which included a slower and a faster component. The latter, which was identical with that for the decay of the 2537-Å afterglow,[8] had a negative amplitude. The decay constant Γ_b of the long-lived component was given by the following expression:

$$\Gamma_b = \tfrac{1}{2}(R_3 + R_4) - \tfrac{1}{2}[(R_3 - R_4)^2 + 4Z_{34}Z_{43}]^{1/2}, \qquad (1)$$

where $R_3 = \Gamma_3 + Z_{34}$ and $R_4 = \Gamma_4 + Z_{43}$ (Γ_3 and Γ_4 are the spontaneous decay constants for the ^31_u and $^30_u^-$ states, respectively, and the quantities Z_{34}, Z_{43} denote the frequencies of collisions per excited Hg_2 molecule, leading to transitions between the states $3 \rightarrow 4$ and $4 \rightarrow 3$ identified in Fig. 1). Γ_b was measured at various N_2 pressures but at a fixed Hg pressure which was chosen so as to effect a compromise between negligible trapping of resonance radiation and adequate intensity of the Hg_2 fluorescence. The total cross sections Q_{34} and Q_{43} as well as the lower limit of the radiative lifetime τ_4 of the $^30_u^-$ state, were calculated from the fit of Eq. (1) to the experimental data, assuming that collisions with mercury atoms did not contribute to the mixing between the ^31_u and the $^30_u^-$ states.[1]

However, some more-recent experiments indicated that Γ_b depends not only on N_2 pressure, but is also strongly affected by the density of Hg vapor in the fluorescence cell. Thus, at any given Hg pressure, the collision rates Z_{34} and Z_{43} include a significant contribution from collisions between excited Hg_2 molecules and ground-state Hg atoms. Similarly, the previously determined decay constant $\Gamma_4 = 1/\tau_4$ includes contributions from the true radiative decay ($\Gamma_4^0 = 1/\tau_4^0$) and from decay induced in $Hg_2(^3 0_u^-) - Hg(^1S_0)$ collisions.

In the present investigation, the method of delayed coincidences was employed to extend the previous studies of excited Hg_2 molecules, by monitoring, in relation to Hg pressure, the persistence times of the two molecular bands excited in Hg-N_2 mixtures, by pulses of atomic Hg resonance radiation. In this way it should be possible to determine the mixing cross sections Q_{34} and Q_{43} separately for collisions of Hg_2 molecules with N_2 molecules and with Hg atoms. In addition, the resulting extrapolation of τ_4 to zero Hg pressure should yield a more realistic value for the radiative lifetime τ_4^0.

II. EXPERIMENTAL

The apparatus and experimental technique were identical with those used by Phaneuf *et al.* in their studies of Hg_2 molecular fluorescence and Hg 2537-Å afterglow in Hg-N_2 mixtures.[1] Mercury resonance radiation emitted by a radiofrequency discharge lamp was mechanically chopped and focused into a fluorescence cell containing a mixture of Hg vapor and N_2 at a fixed temperature. The light pulses had a rise and fall time of about 40 μsec and a duration of 750 μsec. The fluorescence emitted perpendicularly to the direction of excitation was resolved by appropriate filters in series with a grating spectrometer, and was detected with a liquid nitrogen-cooled photomultiplier. A time-to-amplitude converter was used to measure the intervals between the exciting and fluorescent pulses. The "start" pulses were obtained from an auxiliary photomultiplier on to whose photocathode was reflected a small portion of the exciting light beam. The output of the photomultiplier which detected the fluorescence, provided the "stop" pulses. The resulting decay spectrum was accumulated in a 200-channel pulse-height analyzer and was recorded on punched paper tape. Particular care was taken to maintain a geometrical arrangement of the experiment similar to that described previously.[1] The density of the saturated mercury vapor in the cell was controlled by a thermostatic circulating bath and could be changed over a wide range.

III. RESULTS AND DISCUSSION

After accumulation of several decay spectra at various Hg densities but at a fixed N_2 pressure, the side-arm of the fluorescence cell was cooled and the cell evacuated for several hours, with the temperature of the cell remaining constant at 158.5 ± 1 °C. This procedure protected the cell and vacuum system against contamination by any impurities that might be adsorbed on the walls. After filling the system with a new nitrogen charge and setting a new temperature of the side-arm, a sufficient time was allowed to ensure the establishment of equilibrium in the cell. The approach to equilibrium was monitored on the recorder which registered the dc signal from the photomultiplier.

As expected, the 3350-Å uv band and the 4850-Å green band exhibited identical decay patterns. This behavior of the two bands, which has been verified over a wide range of Hg and N_2 pressures,[1,9-11] allowed all measurements of persistence times to be carried out on the uv band which, at low Hg and N_2 pressures, is much more intense than the green band.

The computer analysis of the Hg_2 molecular decay spectrum[12] yielded two exponential components, the faster of which had a negative amplitude and was identical to that measured in the 2537-Å afterglow.[1] The latter component was found to decrease with increasing mercury pressure and, at a Hg pressure of 7×10^{-2} torr, its decay constant became comparable to the decay constant Γ_b of the Hg_2 molecular bands. This behavior of the 2537-Å afterglow, which was probably due to the increase in the imprisonment time of the Hg 2537-Å resonance radiation in the cell, put a limit on the Hg pressure which could be used in the experiment because when the two decay constants became comparable, the computer analysis could no longer be used to separate them with satisfactory precision.

Figure 2 shows the variation of the decay constant Γ_b with Hg pressure for several fixed N_2 pressures. Each measured rate constant was corrected for diffusion effects using an experi-

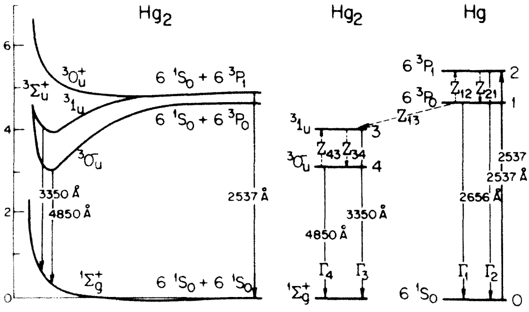

FIG. 1. Schematic diagram of atomic and molecular levels and processes involved in the sensitized fluorescence of Hg_2 molecules. The molecular potential-energy curves are drawn according to Mrozowski (Ref. 4).

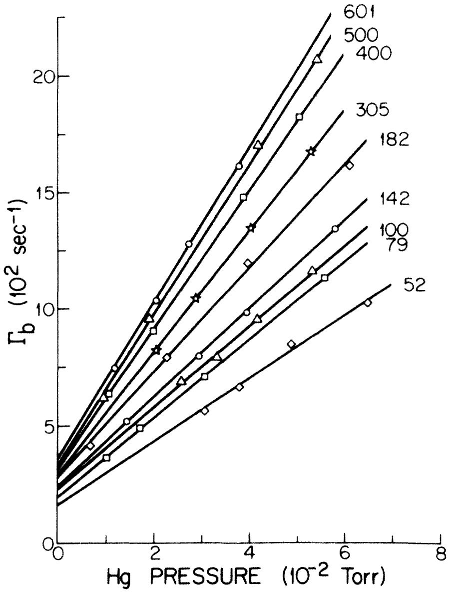

FIG. 2. Variation of the decay constant Γ_b with Hg pressure for various values of N_2 pressure which are indicated (in torr) in the vicinity of each plot. The points are experimental and the lines represent linear least-squares fits to the experimental data.

mentally determined diffusion correction.[1,8] The solid lines represent linear least-squares fits to the experimental data. Assuming that the plots of Γ_b against N_2 pressure are linear below 0.5 × 10^{-2}Torr, each intercept resulting from extrapolation to zero Hg pressure, represents a Γ_b value which is unaffected by the decay of excited Hg_2 molecules, induced in two-body collisions with ground state Hg atoms.

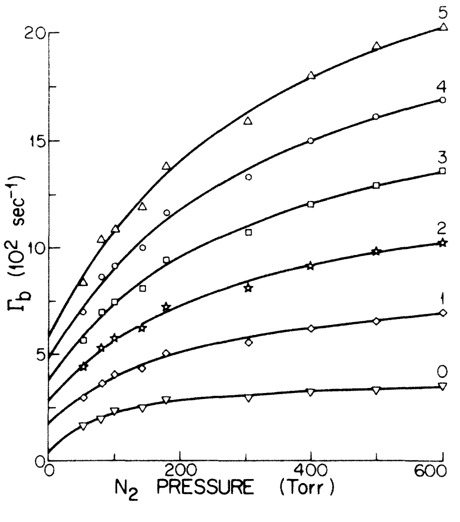

FIG. 3. Variation of the decay constant Γ_b with N_2 pressure for various values of Hg pressure which are indicated (in 0.01 torr) in the vicinity of each plot. The points have been read off the graphs in Fig. 2 and the curves represent least-squares fits of Eq. (1).

Figure 3 shows several plots of Γ_b against N_2 pressure, each plot corresponding to a particular Hg pressure. The points on the curves were calculated from the slopes and intercepts obtained from the linear least-squares analyses of the experimental data shown in Fig. 2. The solid curves in Fig. 3 represent least-squares fits of Eq. (1) with the assumption that Z_{34} and Z_{43} depend only on N_2 pressure. This simplification permitted a reduction in the number of parameters used in the least-squares analysis. The lowest curve corresponds to zero Hg pressure and, consequently, the rates Z_{34} and Z_{43} associated with it are appropriate to collisions in which only N_2 molecules are involved as a second body. The intercept of this curve corresponds to the purely radiative decay constant Γ_4^0 of the $Hg_2(^3 0_u^-)$ state, and does not include any contributions from collisional processes. It should be noted that the various curves in this figure are similar in character to the curve shown by Phaneuf *et al.* who, however, ignored the contributions of collisions with Hg atoms on the experimentally determined cross sections and decay constants.[1]

The total inelastic cross sections Q_{34} and Q_{43}, defined analogously to the gas-kinetic cross sections, were obtained from the collision numbers Z_{34} and Z_{43}, by the application of the expression

$$Z_{ij} = N Q_{ij} v_r , \tag{2}$$

where N is the N_2 density and v_r is the relative velocity of the colliding partners. The results are listed in Table I, which also shows cross sections derived from other curves in Fig. 3. Since, in fitting the data to Eq. (1), any influence

TABLE I. Effective cross sections for $^3 0_u^- \longleftrightarrow {}^3 1_u$ mixing, induced in Hg_2-N_2 collisions, and decay constant Γ_4, obtained from least-squares fits of Eq. (1) to data in Fig. 3. Effects of Hg_2-Hg collisions have been ignored.

Mercury pressure (10^{-2} Torr)	$Q_{43}(^3 0_u^- \rightarrow {}^3 1_u)$ (10^{-21} cm^2)	$Q_{34}(^3 0_u^- \leftarrow {}^3 1_u)$ (10^{-17} cm^2)	Γ_4(sec^{-1}) (from intercept)
0	2.3 ± 1.0	6.9 ± 3.5	37 ± 68
0.25	2.4 ± 1.0	4.8 ± 1.8	81 ± 46
0.5	2.4 ± 1.2	3.8 ± 1.6	115 ± 51
1.0	2.5 ± 0.7	3.0 ± 1.6	172 ± 70
1.5	2.8 ± 0.7	2.4 ± 0.7	234 ± 44
2.0	2.9 ± 0.9	2.2 ± 0.6	284 ± 47
2.5	3.1 ± 0.7	2.1 ± 0.6	334 ± 50
3.0	3.4 ± 0.7	2.0 ± 0.5	384 ± 55
3.5	3.8 ± 0.8	1.9 ± 0.5	432 ± 56
4.0	4.1 ± 0.8	1.8 ± 0.5	479 ± 62
4.5	4.5 ± 0.9	1.8 ± 0.4	528 ± 65
5.0	4.8 ± 0.9	1.8 ± 0.5	577 ± 72

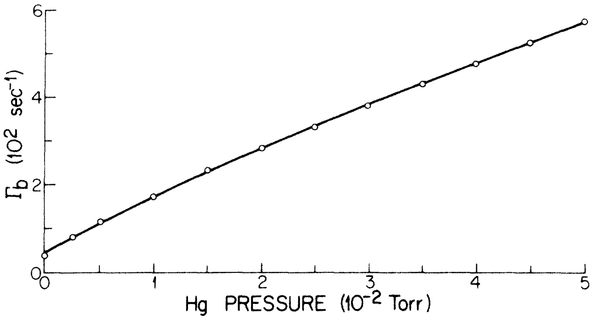

FIG. 4. Variation with Hg pressure of the decay constant Γ_b, extrapolated to zero N_2 pressure. The points correspond to the intercepts of the curves in Fig. 3 and of other similar curves (not shown). The curve represents a least-squares fit of Eq. (1).

of Hg_2-Hg collisions on the inelastic processes involving ^31_u and $^30_u^-$ molecules was disregarded, only results corresponding to zero Hg pressure in Table I do, in fact, represent true Hg_2-N_2-collision cross sections and a true radiative decay constant. Values derived from data obtained at higher Hg pressures, which are obviously Hg pressure-dependent, include indeterminate contributions to the mixing cross sections and to the decay constant Γ_4, arising from Hg_2-Hg collisions.

Figure 4 represents the variation with Hg pressure of the decay constant Γ_b, at zero N_2 pressure. The Γ_b values were obtained from the intercepts of the curves shown in Fig. 3 (and of several additional such curves not shown for the sake of clarity), and are listed in the last column of Table I. The solid curve represents a least-squares fit of Eq. (1) to the data. Here the collision rates Z'_{34} and Z'_{43} depend only on Hg pressure, and the cross sections Q'_{34} and Q'_{43}, calculated from Eq. (2), refer to transfer between the Hg_2 states $^30_u^-$ and ^31_u, induced in two-body collisions with ground-state Hg atoms. The intercept corresponds to the true radiative-decay constant Γ_4^0 of the $^30_u^-$ state. This value for Γ_4^0 is more accurate and reliable than that derived from the lowest curve in Fig. 3. The results obtained from the analysis are listed in Table II.

It may be seen that the cross sections Q'_{34} and Q'_{43} for Hg_2-Hg collisions are some four orders of magnitude larger than the cross sections for Hg_2-N_2 collisions, even though the same ^31_u-$^30_u^-$ mixing process results in both cases. This difference is not altogether unexpected and might be ascribed to the possible presence of exchange forces in the Hg_2-Hg interaction. Such exchange forces which are absent from Hg_2-N_2 interactions, are considered responsible for the large sizes of the cross sections for ^2P mixing in Na **atoms,** induced in Na(^2P)-Na(^2S) collisions, as compared with similar cross sections for collisions with noble gas atoms or with molecules.[13]

An attempt was made to reproduce the straight-line plots of the experimental data in Fig. 2, by substituting in Eq. (1) the values Γ_4^0, Q'_{34}, and Q'_{43} from Table II and the values Q_{34} and Q_{43}, corresponding to zero Hg pressure, from Table I. It was found that this could be done satisfactorily only by including in Eq. (1) another term, corresponding to the dissociation of the $Hg_2(^30_u^-)$ molecule in a three-body collision involving an N_2 molecule and a ground-state Hg atom. The complete Eq. (1), which accounts for Hg_2-N_2 and Hg_2-Hg two-body collisions as well as for the three-body process, may now be written

$$\Gamma_b = \tfrac{1}{2}(R'_3 + R'_4) - \tfrac{1}{2}[(R'_3 - R'_4)^2 + 4(Z_{34} + Z'_{34})(Z_{43} + Z'_{43})]^{1/2}, \tag{3}$$

where

$$R'_3 \equiv \Gamma_3 + Z_{34} + Z'_{34},$$

$$R'_4 \equiv \Gamma_4^0 + Z_{43} + Z'_{43} + Z_{40}.$$

The three-body collision rate Z_{40} represents the frequency of dissociative collisions per $Hg_2(^30_u^-)$ molecule, and may be represented as

$$Z_{40} = k_{40} N(N_2) N(Hg), \tag{4}$$

where k_{40} is the three-body-collision-rate constant and $N(N_2)$ and N(Hg) are the densities of N_2 molecules and Hg atoms, respectively.

As Eq. (3) was fitted to the data obtained at N_2 pressures above 200 Torr, it became apparent that, although the plots in Fig. 2 could be reproduced quite faithfully, the effective value of k_{40} decreased with increasing N_2 pressure, from 2.4×10^{-31} $cm^6\,sec^{-1}$ at 79 Torr to 1.1×10^{-31} cm^6

TABLE II. Cross sections Q' for $^31_u \longleftrightarrow {}^30_u^-$ mixing, induced in Hg_2-Hg collisions, and the radiative decay constant Γ_4^0 extrapolated to zero Hg and N_2 pressures, from data in Fig. 4.

$Q'_{43}(^30_u^- \rightarrow {}^31_u)$	$Q'_{34}(^30_u^- \leftarrow {}^31_u)$	Γ_4^0 (from intercept)	$\tau_4^0 = 1/\Gamma_4^0$
$(2.2 \pm 0.1) \times 10^{-17}$ cm^2	$(6.8 \pm 1.2) \times 10^{-14}$ cm^2	46.6 ± 3.6 sec^{-1}	21.4 ± 1.5 msec

sec^{-1} at 601 Torr. With k_{40} kept strictly constant, Eq. (3) predicts a linear dependence of Γ_b on Hg pressure, with the slopes of the individual plots directly proportional to N_2 pressure. In Fig. 2, the slopes of the straight lines do not increase proportionally with N_2 pressure, but rather tend to approach some limiting value as the pressure is increased. This decrease in k_{40} at higher N_2 pressures is not fully understood, but it should be considered that, at higher N_2 densities, the Hg_2 molecules might well collide simultaneously with more than one N_2 molecule. In this way, some of the two- or three-body collisions would effectively become three-or four-body collisions, respectively, with effective collision rates increasing less rapidly with N_2 pressure than would be expected from a strictly linear dependence. A similar saturation effect at high buffer-gas densities has been noted in the course of experiments on $4^2P_{1/2}$-$4^2P_{3/2}$ mixing in potassium atoms, induced in K-Ar and K-Kr collisions.[14]

In spite of this difficulty associated with the proper fitting of the three-body rate constant to the experimental data, there is no question but that the model for the formation and decay of excited Hg_2 molecules,[1] is fully consistent with experimental observations. It might be of interest to remark on the convergence of Γ_4^0, the radiative decay constant for the $Hg_2(^3 0_u^-)$ state, towards the value of 20 sec^{-1} determined by McCoubrey[11] who, however, reported it as the spontaneous radiative decay constant of the 3350-Å band which he associated with this state. It should be borne in mind that McCoubrey carried out his measurements in pure Hg vapor, where the excited Hg_2 molecules must necessarily be formed by a mechanism which does not involve the participation of N_2 molecules.

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