Chemiluminescent Reaction Channel Opened by Photon Absorption During Collision

Peter Hering,[a] Philip R. Brooks, R. F. Curl, Jr., Richard S. Judson, and R. S. Lowe[b]
Rice Quantum Institute and Chemistry Department, Rice University, Houston, Texas 77001
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The reaction exoergicity of $K + HgBr \rightarrow KBr + HgBr$ ($\Delta D_0 = -0.86 \pm 0.09$ eV) plus the energy of a photon of $\lambda < 606 \pm 26$ nm provides sufficient energy to open the channel to HgBr* ($\tilde{B}^2\Sigma^+$). Although neither reagents nor products absorb near 595 nm, luminescence at 500 nm is observed from the crossing region of beams of K, $HgBr_2$, and photons ($\lambda \sim 595$ nm). This emission is attributed to HgBr* formed by light absorption during reactive collision. The cross section is $\sim 10^{-17}$ cm^2 at ~ 2 MW/cm^2.

At some point in the course of chemical reaction, new bonds are forming, old bonds are breaking, and one has neither "reagents" nor "products." Chemists have come to regard this stage as a "transition state" (which we will not define further). If we could study this "transition state," it would be possible to obtain direct information about the bond-making–bond-breaking process. We have sought to excite such a transient state with a laser which is *not* resonant with the asymptotic states of either reagents or products, and we report here our initial experiments.

Nonreactive analogs are well known in that species which normally do not absorb can be induced to do so during a collision.[1] Until very recently observations of collision-allowed absorption were restricted to nonreactive and almost elastic collisions in which the photon absorbed was nearly resonant with an energy-level separation of one member of the colliding pair. The collision serves to break down some selection rule which normally prevents absorption. A new kind of collision-allowed absorption was recently observed[2-4] in which the photon absorbed in not resonant with an energy-level separation for either collision partner, but instead provides the difference in internal energy required to allow energy transfer between the atoms. These photon-assisted inelastic collisions are now well established, and for the Ca:Sr system of Harris,[2,3] the inelastic cross section is 10^{-16} cm^2 at laser intensities of 1 MW/cm^2.

The process under study here is schematically shown in Fig. 1. K and $HgBr_2$ react on nearly every collision to form KBr and ground electronic state ($\tilde{X}^2\Sigma^+$) HgBr.[5] The exoergicity, $\Delta D_0 = -0.86 \pm 0.09$ eV,[6,7] is insufficient to form HgBr* ($\tilde{B}^2\Sigma^+$), lying at $T_0 = 2.91$ eV.[8] The $\tilde{B}^2\Sigma^+$ state is energetically accessible if a photon with $\lambda < 606(26)$ nm is absorbed by the system. This reaction was chosen because no single-photon absorptions are known for $\lambda \sim 590$ nm for either reagents or products,[8,9] because the $\tilde{B}^2\Sigma^+$ state of HgBr is easily detectable in fluorescence ($\tilde{B} \rightarrow \tilde{X}$), and because the threshold photons in the yellow near 590 nm can be easily supplied from a rhodamine 6G dye laser.

A schematic diagram of the apparatus is shown in Fig. 2. Beams are formed by heating solid

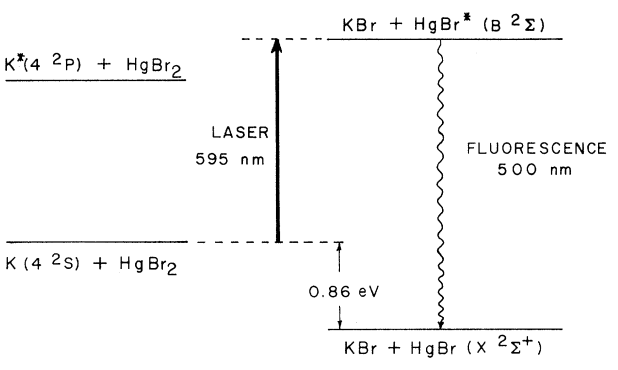

FIG. 1. Schematic diagram of the process being studied. The laser is resonant with neither the reactants nor the products of the reactions. Formation of HgBr* is highly endoergic in the absence of the photon.

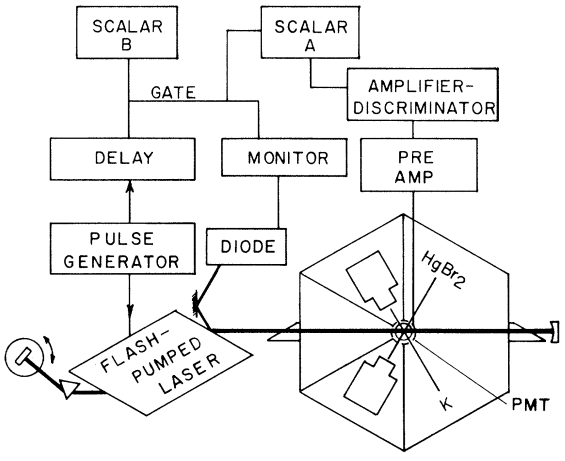

FIG. 2. Experimental apparatus. The light collecting telescope, filter, and photomultiplier are situated directly above the beam intersection region.

reagents in stainless steel ovens located ~5 cm from the crossing point. Typical operating conditions are shown in Table I. Beam intensities for $HgBr_2$ are measured with an ionization gauge obtained inside a heated (100 °C) glass envelope, and K intensities are measured by ionizing K on a W surface and measuring the resulting K^+ ion current.

The collimated molecular beam cross inside the laser cavity at an angle of 120°; the laser beam lies in the plane of and bisects the angle between the molecular beams. Fluorescence from about 5 mm of the three-beam crossing region is collected and collimated by an $f4.2$ lens, passed through a 500-nm interference filter (Oriel G572-5000) with a bandpass [full width at half maximum (FWHM)] of 10 nm, and imaged. Suitable masking of the image greatly reduces scattered light. Light passed by the mask is detected by an RCA 8575 photomultiplier operated at room temperature in the pulse-counting mode.

The prism-tuned, flash-pumped dye laser (FPDL) used a Chromatix CMX-4 dye head and a cavity 2.4 m long. Typically, a $1.4\times10^{-4}M$ solution of rhodamine 6G in ethanol and water is pumped with a 20-J flash at a repetition rate of ~1 Hz, resulting in a laser pulse 1 μs long (FWHM). The laser performance is seriously degraded by mirror vibration in the long cavity, and the peak circulating power inside the cavity is roughly estimated as 2 MW/cm^2 over an area of 0.01 cm^2 at the beam crossing. An external pulse triggers the flash, and the same pulse delayed 0.5 μsec enables the scaler during the laser pulse. This delay minimizes rf pickup from the flash but still permits the scaler to be gated on for a time period (1 μsec) encompassing in the laser pulse. Since the radiative lifetime for HgBr* ($\tilde{B}^2\Sigma^+$) is 23 nsec,[10] all HgBr* formed during the laser pulse should fluoresce during the gate time period and also inside the imaged beam-crossings region.

TABLE I. Typical operating conditions.

Beam	T (°C)	P (Torr)	Nozzle diameter (cm)	Flux ($s^{-1}sr^{-1}$)
K	400	3[a]	0.04	4×10^{17}
$HgBr_2$	200	24[b]	0.04	2×10^{18}

[a] An. N. Nesmeyanov, *Vapour Pressure of the Elements* (Academic, New York, 1963).

[b] *Gmelin Handbuch der Anorganischen Chemie* (Verlag Chemie, Weinheim, 1967), Vol. 34, Part B, No. 2.

The reaction channel to HgBr* opened by the laser should be manifested by an increased number of fluorescent counts when all three beams are present. Typical counting rates on different dates are displayed in Table II for two different laser wavelengths. There is a reproducible and statistically highly significant difference between the signal observed with all three beams on and that with one of the molecular beams flagged off. The observed counting rate is very low and arises mainly from light scattered from slits and windows. To discern a small three-beam signal, counts were collected for alternate combinations of beam flags open and closed. Drift was negligible compared to fluctuations in the scattered light.

Qualitatively similar results were obtained for other wavelengths in the range 585–600 nm, but we are as yet unable to comment on the quantitative wavelength dependence of the signal. Qualitatively similar results were also obtained if the fluorescence was observed through a 480-nm interference filter, or through two 500-nm filters which strongly reject fluorescence at frequencies outside the pass band. (Two filters also strongly attenuated the signal of interest indicating that several different fluorescent transitions are involved.)

The presence of a three-beam signal is established, but this could equally well arise from a resonant absorption in one beam followed by a

TABLE II. Counts measured on different days for two laser wavelenths. Δ is the difference between the three-beam signal (K, $HgBr_2$, $h\nu$) and the signal with $HgBr_2$ flagged off (K, $h\nu$); Δ_{avg} is the difference between the three-beam signal and the average of the other signals; and denotes the standard deviation.

shots/entry	K, $HgBr_2$, $h\nu$	K, $h\nu$	$HgBr_2$, $h\nu$	$h\nu$
600 nm, $\Delta = 0.122$ counts/shot; $\sigma = 0.011$				
1000	491	294		
1500	590	437		
1500	652	487		
1500	559	405		
Total	2292	1623		
595 nm, $\Delta_{avg} = 0.091$ counts/shot; $\sigma = 0.018$				
500	215	150	155	
500	216			165
500	207	183	209	162
250				72
500	223	184	148	165
500	205			
Total	1066	517	512	564

collision with some species in the other beam. Two auxiliary experiments were performed to eliminate possible interfering processes.

(1) The wavelength range encompasses the Na *D* lines. Possible interference from resonant excitation of Na impurities in the beam followed by the reaction $Na^* + HgBr_2 \rightarrow NaBr + HgBr^*$ was eliminated by exciting a pure Na beam. For this experiment the beam crossing is extracavity, but the Na fluorescence is still saturated. A signal (~ 2 counts per shot) was observed through the 500-nm filter, but was independent of the presence of the $HgBr_2$ beam and disappeared when a second 500-nm filter was added. This indicates that the signal is due to leakage through the filter of the strong Na *D* fluorescence. No signal was observed when the laser was tuned off resonance, but the power is not high enough to indicate anything about the nonresonant process $Na + HgBr_2 + h\nu \rightarrow NaBr + HgBr$.

(2) The possible participation of two or more photons was probed with the much higher peak power and smaller bandwidth of a dye laser pumped with the frequency-doubled output of a *Q*-switched neodymium-doped yttrium aluminum garnet laser (Nd:YAlG DL). With focused 20-mJ, 5-ns pulses having a bandwidth of ~ 0.1 nm, two-photon transitions to the $9d\,^2D$ and $10d\,^2D$ states of K (Ref. 9) at 595.7 and 590.8 nm could be detected by observing fluorescence to $4p\,^2P$ at 487 and 481 nm, respectively. The counting rate for the bound-bound transition at 595.7 nm was 20/shot even though the transmission of the 500-nm filter is < 5% at 487 nm. When the $HgBr_2$ beam flag was opened, this signal was unaffected or slightly decreased. When the Nd:YAlG DL was tuned off the K two-photon resonance, a three-beam signal was observed which was comparable to that observed with the FPDL at the same fluence/pulse. Since the peak intensity of the Nd:YAlG DL is 200 times greater than the FPDL at the same fluence, multiphoton causes of the three-beam signal can be ruled out. This signal decreased as the gate was delayed (varied ~ 50 ns) but was independent of gate length (50 ns–1 μsec). This behavior is expected for a short-lived emitter formed during the laser pulse.

Emission near 500 nm is observed in the collision region of K atoms, $HgBr_2$ molecules, and 595-nm photons. No single-photon transitions in K or $HgBr_2$ are known in the wavelength region under study. Potassium dimer is known to be present in the beam (~ 1%) and K_2 absorbs in this region, but all single-photon processes involving K_2 can be ruled out because the bond dissociation energy of K_2 (0.55 eV)[11] must be supplied. Direct laser excitation of vibrationally excited HgBr product to the $\tilde{B}\,^2\Sigma^+$ state is not possible because the HgBr dissociation energy (0.74 eV)[7] is so low that a sufficient amount of energy cannot be stored in HgBr to allow 595-nm light to excite the $\tilde{B}\,^2\Sigma^+$ state. Experiment (1) rules out the participation of resonant absorption from possible Na impurity. Experiment (2) demonstrates that the signal cannot arise from direct two-photon absorptions. It also shows that the three-beam signal does not arise from a sequence of photon absorption followed by collision since the signal from such a process would be decreased by a short gate. The emitter lifetime seems comparable to that of HgBr*, 23 ns.[10]

We can think of no other process leading to a blue shift under molecular beam conditions and conclude that we have observed the laser-driven chemical reaction

$$K + HgBr_2 + h\nu \rightarrow KBr + HgBr^*.$$

Confirmation of this conclusion will, of course, require line-shape measurements and identification of the emitter. For the beam conditions of Table I and the estimated circulating power in the cavity, the estimated cross section for reaction is $\sim 10^{-17}$ cm^2 at a laser intensity of 2 MW/cm^2 [under the assumptions of f4.2 collection optics, 15% quantum efficiency of the photomultiplier tube, an interaction volume of 5 mm^3 and a relative speed of 600 m/sec, and convoluting the filter transmission and Franck-Condon factors[12] for HgBr* ($v = 0,1$)].

Many important questions remain unanswered. So far it has not been possible to measure quantitatively the dependence on the exciting laser frequency to answer questions regarding line shapes, nor has it been possible to measure the power dependence of the signal, except to note that it disappears at low powers.

The estimated cross section is only about one order of magnitude less than the energy-transfer cross section found by Harris and White.[3] The cross section may be enhanced because $HgBr_2K$ forms a fairly long-lived complex[5] (3 or 4 psec). It should be borne in mind that this cross section is for forming HgBr *in the excited state*. Other exit channels for the system are dark. If these other exit channels were statistically populated the overall laser-driven cross section could easily be several orders of magnitude larger than that estimated for just the chemiluminescent

channel.

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[a]Present address: Max-Planck Gesellschaft, Projektgruppe für Laserforschung, 8046 Garching bei München, West Germany.

[b]Present address: Herzberg Institute for Astrophysics, National Research Council, Ottawa K1A 0R6, Canada.

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ERRATUM

MEASUREMENT OF ω-MESON PHOTOPRODUCTION ON PROTONS FROM 46 TO 180 GeV. R. M. Egloff, P. J. Davis, G. J. Luste, J. F. Martin, J. D. Prentice, D. O. Caldwell, J. P. Cumalat, A. M. Eisner, A. Lu, R. J. Morrison, S. J. Yellin, and T. Nash [Phys. Rev. Lett. 43, 1545 (1979)].

On page 1548, the two references to Fig. 4 should be to Fig. 5.

The cross sections presented in Table I were corrected for $\rho^0 \rightarrow \pi^0\gamma$ events (a factor of 0.98), but not for ρ^0-ω interference. This correction may be estimated by assuming that the ρ^0 and ω are produced in phase, and utilizing simple Breit-Wigner decay amplitudes. An average ρ^0 production cross section of 9.2 μb over the energy range in question is obtained from Ref. 1, and a mass cut of ± 200 MeV is imposed (to match the spectrum of Fig. 3).

Using a $\rho \rightarrow \pi\gamma$ branching ratio of $(0.024 \pm 0.007)\%$ [from C. Bricman *et al.*, Phys. Lett. 75B, 1 (1978)], we estimate that an additional correction factor of 0.88 ± 0.04 is required. If on the other hand one uses a branching ratio of $0.043 \pm 0.005\%$ [see A. N. Kamal and G. L. Kane, Phys. Rev. Lett. 43, 551 (1979); and the new data of D. Berg *et al.*, to be published], the additional correction required (beyond the 0.98 factor) is 0.83 ± 0.02. Quoted uncertainties are based only on the cross sections and branching ratios utilized. An additional uncertainty of ± 0.02 can be included to allow for the possibility that the ρ^0 branching ratio might, as a consequence of ρ^0-ω mixing, not equal the measured ρ^+ branching ratio (D. Geffen, private communication). The values of A in Table II must be correspondingly scaled. Using the 0.83 correction, $\gamma_\omega^2/4\pi$ becomes 6.5 ± 0.5.

We are indebted to D. Geffen for pointing out the large size of this correction, and for bringing to our attention the new measurement of the ρ branching ratio.