Production efficiencies of electronically excited states of barium monohalides

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Diatomic barium monohalides (BaX) have been produced in the gas-phase reaction of Ba, entrained in a flowing inert carrier gas, with F_2, SF_6, Cl_2, Br_2, and I_2. Bright green chemiluminescent flames were observed at pressures from 0.1–10 torr. Emission spectra were obtained from 300–1200 nm. Near infrared emission from BaBr and BaI has been ascribed to transitions to the ground state from previously unobserved electronic states analogous to A and B states in BaF and BaCl. In BaBr, electronic state energies for B $^2\Sigma^+$, A $^2\Pi_{3/2}$, and A $^2\Pi_{1/2}$ have been found to be 11 325, 10 604, and 9980 cm^{-1}, respectively; in BaI, corresponding values are 10 417, 9921, and 9268 cm^{-1}. BaX molecules are produced with moderate efficiency into lower lying electronic states (80%–98% in A and B) with an absolute efficiency of approximately 1 photon for each 100 reacted barium atoms. There is a small dependence on pressure with maximum yields occuring near 4 torr. Spectra of C $^2\Pi$–X $^2\Sigma^+$ transitions show Boltzmann distributions in both vibration and rotation corresponding to population temperatures of approximately 3000 K for BaF and 2000 K for BaBr, BaCl, and BaI. Electronic population temperatures show trends similar to those observed in vibration and rotation.

INTRODUCTION

Reactions of barium metal vapor with halogens in a flowing inert carrier gas stream at pressures near 1 torr form bright chemiluminescent flames. Visible green emission is due to BaX C $^2\Pi$–X $^2\Sigma^+$ electronic transitions.[1-3] The reaction of Ba with N_2O in a similar flow system[4,5] produces bright chemiluminescence with a large photon production efficiency. Interest in production efficiencies is motivated by the search for visible chemical laser candidates as well as a desire to understand formation of electronically excited states by chemical reactions.

Here we report measurements of photon distributions among electronic states of the barium monohalides (BaX) produced by the reaction of barium vapor with F_2, Cl_2, Br_2, and I_2. These reactions are all exoergic and produce molecules directly into electronically excited states. However, in BaCl, BaBr, and BaI, some high-lying states are formed which cannot be populated directly.

Under single collision conditions, Jonah and Zare[6] have found continuum emission in the reaction of Ba $+ Cl_2$ which they ascribe to two-body radiative recombination, i.e., Ba $+ Cl_2 \rightarrow$ BaCl$_2^*$ $+ h\nu$. Menzinger and Wren[7-10] have studied reactions of Ba $+X_2$ at low pressure (10^{-3} to 10^{-6} torr) and proposed a radiative three-body recombination scheme in which there is collisional stabilization of a long-lived collision complex. Continua intensities from Ba $+ Cl_2$, Br_2 and I_2 reactions were found to have a quadratic pressure dependence on halogens, indicating a three-body process in which there is rapid collision stabilization of a very long-lived collision complex BaX$_2^*$.

EXPERIMENTAL

Apparatus

Photon yields are determined by spectroscopic measurements of chemiluminescence produced by reactions of barium atoms with halogen molecules. Reactions take place in a low pressure flow system which has have been described previously.[1-5,11] Ba vapor, produced by heating the metal in an alumina crucible via a surrounding tungsten wire basket heater, is entrained in an argon carrier which cools and transports it into the reaction region. Halogens are injected through a stainless steel tube perpendicular to the barium flow. Resultant flames are studied in the carrier gas pressure range of 0.1–10 torr with flow rates near 5 liter (NTP)/sec. Partial pressures of barium are from 1–10 mtorr while halogen pressures are 10 times greater.

Flame emission is viewed through a quartz window with a scanning monochromator, photomultiplier tube, and picoammeter system. Photocurrent vs wavelength is displayed on a strip-chart recorder and is also digitized and recorded for computer analysis. The total wavelength region from 300–1200 nm is observed by the use of three different photomultiplier-grating combinations.

Relative instrument response of each detector system is measured by scanning and digitizing emission of a quartz–iodine standard lamp over the desired wavelength region. Using a digital computer, the lamp spectrum is divided point by point with intensity vs wavelength data provided by the lamp manufacturer. The resultant calibration curve is then used to correct spectral data for instrument response.

Most spectra are taken with a 1-m Czerny-Turner spectrometer with 0.75 nm resolution. This coarse resolution is used to allow a convenient data record size for computer analysis. Flames are sufficiently intense to allow observation at 0.02 nm resolution (e.g., Fig. 3).

Extended red detection to 1200 nm is attained through the use of a 750 nm blaze grating and an S-1 response photomultiplier cooled to 200 K to reduce dark-current noise. With the same grating, a GaAs extended red response photomultiplier is used to cover the region from 500–850 nm. Finally, a 300 nm blaze grating is used with an S-5 response photomultiplier for the scans from 300–500 nm.
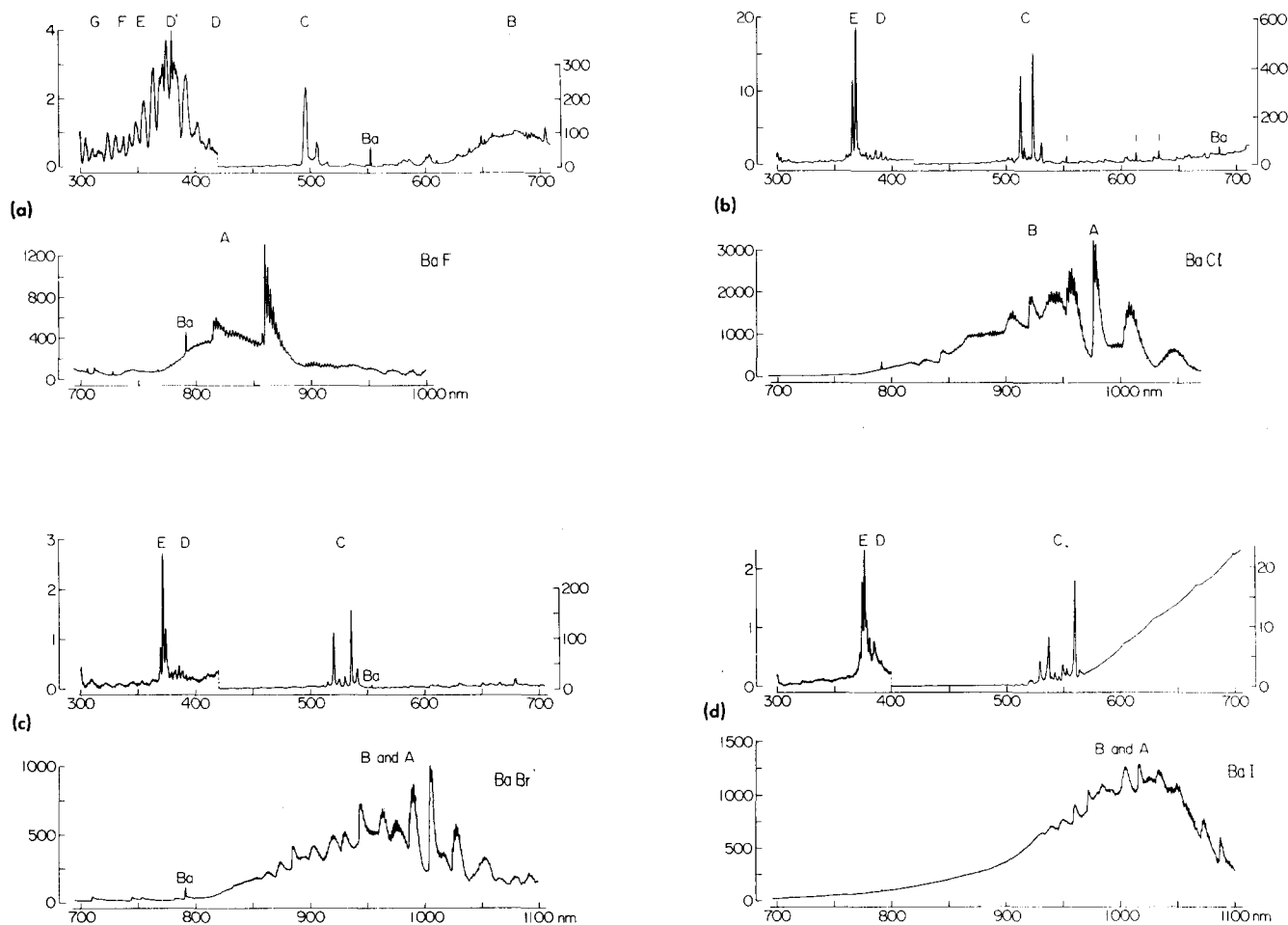
FIG. 1. Survey spectra (0.75 nm resolution) of BaX formed in reactions Ba + X_2. Electronic transition origins are indicated by the letter of the upper state (e.g., A denotes the $A-X$ transition.) Numerous Ba and Ba⁺ lines appear throughout the spectrum; however, (6 $^1P^0$–6 ^1S) at 553.55 nm and (6 $^3P^0$–6 ^1S) at 791.14 nm are most prominent. Intensities have been corrected for instrument response and are absolute where 1000 units = 10^{14} photons/nm/sec/Ba atom. Each spectrum is on the same absolute scale. Scale changes are denoted by a vertical dotted line. (a) BaF at 5 torr; (b) BaCl at 3 torr. Weak band structure from 550–800 nm is due to BaO contamination. Several Ba lines are observed as in BaF. The F and G states are very weak and have not been labeled; (c) BaBr at 8 torr. Newly discovered $A-X$ and $B-X$ transitions are shown in the region 800–1100 nm. Ba lines also appear throughout the spectrum. Weak band structure from 550 to 800 nm is due to BaO contamination; (d) BaI at 4 torr. Previously unobserved $A-X$ and $B-X$ transitions are shown in the region 800–1100 nm.

Photon yields

Photon yields, the number of photons emitted by a given electronic state per reacted barium atom, are obtained by comparison with yields previously measured for the reaction of Ba + N_2O.[4,5] Owing to the corrosive nature of halogens, barium flow measurement and oxidizer mixing techniques used in the Ba + N_2O experiments are not practical for Ba + X_2. Emission is recorded for Ba + N_2O and then for Ba + X_2. For constant metal atom flow and carrier gas pressure, the area (in photons/sec) of the nearby, convenient BaO $A-X$ (7, 0) band is compared with the total area of the $C-X$ transition of BaX. $C-X$ photon yields are found by multiplying the photon yield for the selected BaO band by the ratio of the area of the BaX $C-X$ transition to the area of the BaO band.

Relative photon yields for other electronic transitions are found by comparing areas of the transitions to the $C-X$ transition, accounting for both spectral response of the detector system and wavelength dependence of

photon energy. Using the absolute yield of the $C-X$ transition as determined by comparison with BaO and the relative rates, absolute yields for each upper state are found.

RESULTS

Spectra

Visible BaX chemiluminescence consists of two types of electronic transitions: $^2\Pi-^2\Sigma^+$ and $^2\Sigma^+-^2\Sigma^+$. In the wavelength region from 300–1200 nm, emission is observed from the A and C $^2\Pi$ as well as B, D, E, F, G, H $^2\Sigma^+$ states in BaF, analogous A through G states of BaCl, and A through E states of BaBr and BaI. All emission observed terminates on the X $^2\Gamma$ ground state. Vibrational frequencies and internuclear separations for all electronic states of a given BaX molecule are almost equal, resulting in appearance of strong $\Delta v = 0$ vibrational sequences and with much weaker $\Delta v = \pm 1$ sequences. Spacing between adjacent vibrational bands
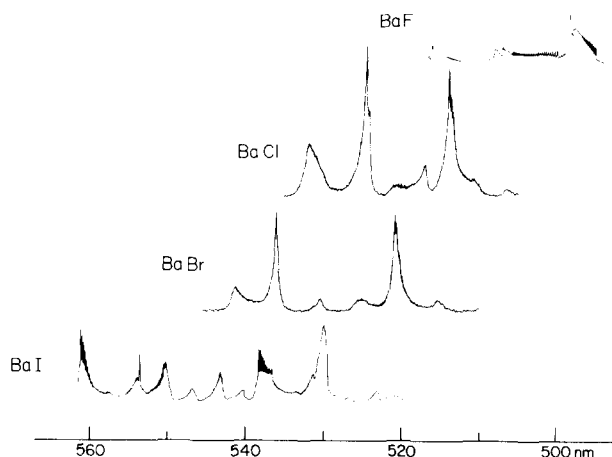
FIG. 2. $C\,^2\Pi-X\,^2\Sigma^+$ BaX spectra from the reactions of Ba+X$_2$ at pressures near 1 torr. The resolution is 0.02 nm.

FIG. 4. Plot of $I_{v'v'}/\nu^4$ vs $G'(v')$ for BaX $C-X$ vibrational transitions. The slope is $-hc/kT$, and observed temperatures are indicated. Each curve has been displaced vertically for clarity.

is on the order of 0.1 nm. Vibrational levels as high as $v'=27$ in the $C-X$ transitions of BaF have been identified and the "head of heads" appears at $v' > 50$.

Computer corrected spectral scans for each BaX molecule are shown in Fig. 1. Ba resonance emission $(6\,^1P^0-6\,^1S)$ at 553.5 nm is seen in each BaX spectrum, while numerous barium atom and ion lines are seen throughout the spectrum from the reaction of Ba + F$_2$. In obtaining survey BaX spectra, two new electronic states analogous to A and B have been found in both BaBr and BaI. Assignment of spectra and determination of molecular constants are in progress.[12]

Differences in appearance exist among the spectra of the various BaX species. For example, in BaX $C-X$ transitions, the direction of the vibrational progressions differs. In BaF, sequential members of these progressions move to the red, while in BaCl, BaBr, and BaI they move to the blue (see Fig. 2). Figure 3 illustrates spectra of BaF produced by two different reactants, F$_2$
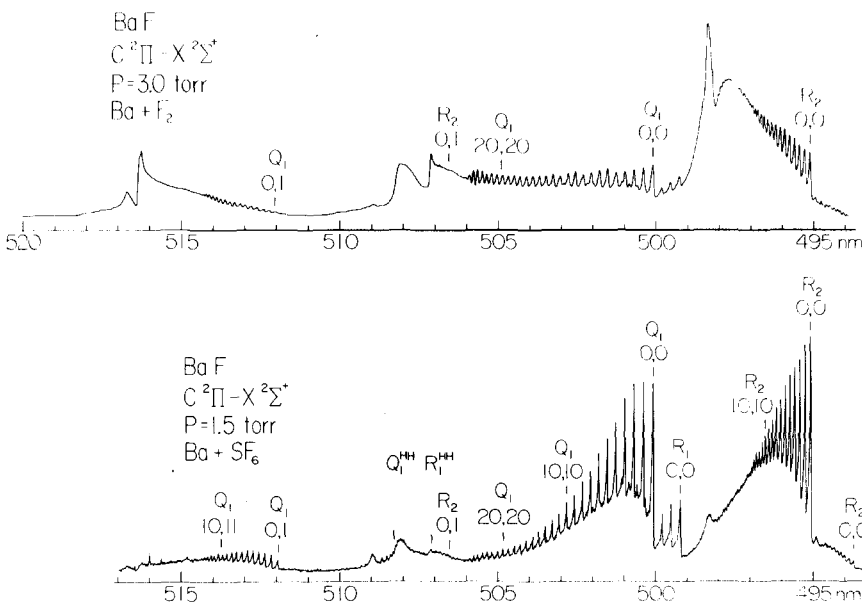
and SF$_6$. Vibrational temperatures are quite different for each reaction and will be discussed in the next section.

Each Ba + X$_2$ reaction is exoergic for BaX ground electronic state production. If reactions are characterized by the simple channel, Ba + X$_2 \rightarrow$ BaX* + X, then there is some difficulty in explaining the energy balance. If the simple channel is the major reaction, then literature values for the bond strengths[7,13-15] for BaX are too low, since there is not enough energy to populate higher-lying electronic states of BaCl, BaBr, and BaI. If the bond strengths are correct, then there must be additional channels for BaX* production. In contrast to single collision work, continua at pressures near 1 torr are a very minor part of the chemiluminescent spectra, sug-

FIG. 3. Comparison $C\,^2\Pi-X\,^2\Sigma^+$ spectra of BaF produced by reactions of Ba with F$_2$ and with SF$_6$. Resolution of the upper and lower spectrum is 0.04 and 0.02 nm, respectively. Argon carrier pressures were 1.5 and 4.0 torr, respectively.
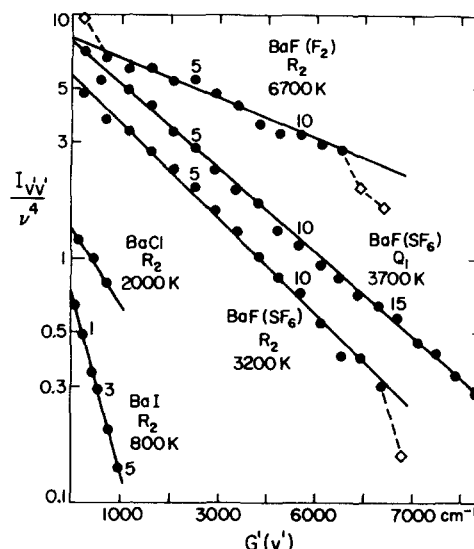
TABLE I. Relative BaX photon yields as a function of pressure, molecule, and electronic state for the reaction of Ba+X₂. Due to overlap, $A-X$ and $B-X$ transitions are counted together for BaCl, BaBr, and BaI.

Molecule	Transition	Relative yields (%)		
		1	4	16 torr
BaF	$A-X$	80.9	78.6	85.4
	$B-X$	12.5	15.6	12.4
	$C-X$	6.1	5.6	2.2
	$D-X$	0.1	0.2	...
	$E-X$	0.3	0.04	...
	$F-X$	0.06	0.02	...
	$G-X$	0.01	0.01	...
BaCl	$A-X$, $B-X$	99.8	99.9	99.8
	$C-X$	0.2	0.1	0.2
	$D-X$	...	0.001	...
	$E-X$	...	0.003	...
BaBr	$A-X$, $B-X$	99.9	99.9	99.9
	$C-X$	0.1	0.08	0.06
	$D-X$	...	...	0.001[a]
	$E-X$	...	...	0.008[a]
BaI	$A-X$, $B-X$		99.7	
	$C-X$		0.3	
	$D-X$		0.004	
	$E-X$		0.006	

[a]10 torr.

gesting that a different excitation mechanism exists in this pressure region. $C-X$ spectra show small pressure effects between 0.1 and 10 torr as well as little dependence on carrier gas type. At low Ba flow rates, the peak intensity of $C-X$ emission formed in the reaction of Ba + Cl is about 100 times that of $E-X$. As the Ba flow rate is increased, the ratio of $C-X$ to $E-X$ peak intensity decreases to near unity at the highest flows. This behavior can possibly be explained by the reaction Ba + BaX₂* → BaX* + BaX or 2Ba + X₂ → BaX* + BaX.

Vibrational temperatures

The expression relating intensities of vibrational bands to vibrational temperature[16] is given by

$$\log \sum_{v''} I_{v'v''}/v^4 = C - G'(v')[hc/kT], \qquad (1)$$

where I is the vibrational band intensity, v the frequency of the transition, C a constant, and $G(v)$ the vibrational energy. Assuming that each Δv = constant sequence has the same vibrational distribution, only diagonal sequences need be included in the sum, so that

$$\log I_{v'v'}/v^4 = C - G'(v')[hc/kT]. \qquad (2)$$

Taking the intensity of each band to equal its peak height over the background and dividing by v^4, then graphing on a semilog plot vs $G'(v')$, a straight line is obtained with slope $-hc/kT$.

Using spectra similar to that shown in Fig. 2, vibrational temperatures of BaX molecules have been found with ±20%. Figure 4 is a semilog plot of $I_{v'v'}/v^4$ vs $G'(v')$ for each molecule. In the reaction of Ba + F₂, the temperature is 6700 K for the R_2 branches, while for Ba+SF₆, temperatures of 3700 K and 3200 K are ob-

served for the Q_1 and R_2 branches, respectively. Ba +Cl₂ shows a temperature of 2000 K for the R_2 branches, and Ba+I₂ is lower yet at 800 K. BaBr is not shown, since band overlap is too great to permit proper determination of intensities.

Rotational temperatures

Since individual rotational lines are not observed in $C-X$ spectra, it is difficult to obtain a rotational temperature; however, the profile of a vibrational band can give a good indication. The most promising band for profile analysis is R_2 (0, 0) in BaF (Ba +SF₆) since there is minimal overlapping. Using both line position and line intensity expressions[16,17] for R_1 along with a simulated instrument width of 0.4 cm⁻¹, the band shape is generated for several temperatures with the aid of a computer[3] using molecular constants given by Cruse et al.[18] By comparing the generated profile with actual spectra, the BaF rotational temperature is found to be 3000 ± 200 K.

Photon yields

Relative photon yields as measured from spectra similar to those shown in Figs. 1–4 are listed as a function of pressure by molecule and electronic transition in Table I. It is evident that the largest fraction of the photons arise from $A-X$ and $B-X$ transitions.

Absolute yields in photons per reacted barium atom are given in Table II. These yields are probably within ±60%, with one-third of the error due to optical power measurements. Since absolute yields are computed from the C state which is a small part (< 6%) of the total emission, slight errors in its determination may lead to somewhat larger errors in derived yields. The total photon yield for BaF agrees fairly well with the value 0.012 reported by Eckstrom and co-workers.[19] However, their value for BaCl is low, since spectra was observed only to 900 nm, beyond which there is a large contribution to the yield.

Although yields peak at 4 torr, there is not a strong pressure dependence and BaCl gives a somewhat higher yield than the other halogens. Carrier effects, measured only for $C-X$ transitions, show little dependence on gas type (Ar, N₂, He).

Electronic temperatures

The population of a given electronic state is proportional to the relative photon yield from that state times

TABLE II. Absolute BaX photon yields in photons emitted per reacted barium atom as a function of pressure and molecule for the reactions of Ba+X₂.

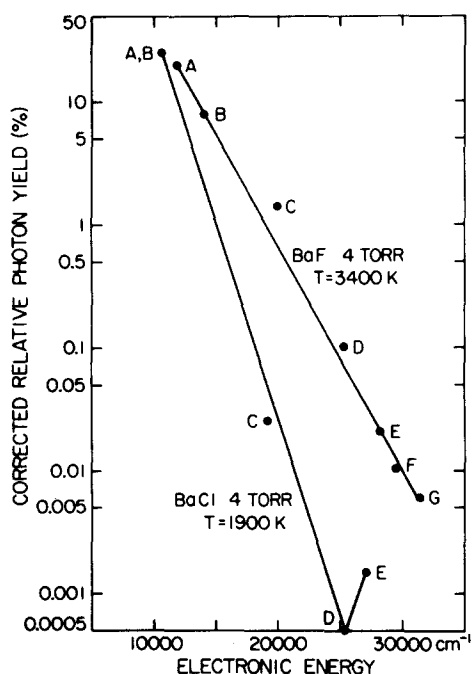| Molecule	1	4	16 torr
BaF	6.6×10^{-3}	7.3×10^{-3}	1.4×10^{-3}
BaCl	4.0×10^{-2}	5.0×10^{-2}	6.0×10^{-3}
BaBr	9.5×10^{-3}	2.3×10^{-2}	1.3×10^{-2}
BaI	...	3.6×10^{-2}	...

FIG. 5. Semilog plot of relative photon yield vs electronic energy for BaF and BaCl at 4 torr. The slope is $-hc/kT$, from which the electronic temperature is obtained. BaBr and BaI also show characteristic temperatures of around 1800 K. Electronic degeneracies have been taken into account.

the radiative lifetime, which is probably quite similar for each electronic state and therefore enters only as a scale factor. Assuming a Boltzmann distribution of electronic states, a semilog plot of relative photon yield divided by the appropriate electronic degeneracy factor, vs energy (ν_{00}, the electronic state origin) will yield a straight line with slope $- hc/kT$. Sample plots for BaF and BaCl at 4 torr as shown in Fig. 5 indicate that this is a good assumption. Temperatures of 3400, 1900, 1600, and 2300 K within ±20% were found for BaF (Ba + F_2), BaCl, BaBr, and BaI, respectively. Similar temperatures are obtained at 1 and 16 torr.

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