

Chemiluminescent spectra of alkali-halogen reactions

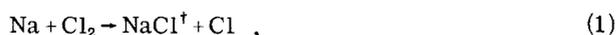
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Using a beam-gas arrangement, we have obtained the chemiluminescence spectra of alkali-halogen reactions at pressures less than 1 mtorr. The spectra in general are characterized by a broad molecular feature on which are superimposed sharp atomic alkali transitions. Under higher resolution (better than 5 Å) the molecular feature consists of a single progression of regularly spaced peaks extending over several thousand angstroms. Spectra are presented for the chemiluminescent reactions $M_2 + X_2(XY) \rightarrow MX^* + MX(MY)$, where $M_2 = K_2, Rb_2, Cs_2$ and $X_2(XY) = Cl_2, Br_2, I_2, IBr, ICl, ClF$. The MX^* emitter is identified by comparison of the vibrationally resolved spectra with previous absorption and emission studies of the alkali halides. The spectra consist of transitions from the bound or quasisubvibrational levels of a shallow homopolar excited state to high-lying vibrational levels of the ionic ground state. Differences in the onsets and cutoffs between our spectra and those of flame studies are noted and rationalized in terms of the different effective rotational potentials describing the MX^* emitters produced under the single-collision conditions employed here and under the conditions prevailing in flame studies. For the mixed halogen reactions, the MY ground state is the more stable salt molecule that can be formed from the halogen atoms of the XY pair. A four-center mechanism is deduced from the dependence of the chemiluminescent intensity on reagent concentrations. The observed atomic emission apparently results from a different mechanism. While the alkali reactions with F_2 do not yield appreciable molecular emission, atomic transitions from high Rydberg levels are prominent for these reaction systems. Both atomic and molecular chemiluminescence are shown to be consistent with electron-jump mechanisms.

INTRODUCTION

The history of alkali-halogen reactions, sparked by the beautiful diffusion flame studies of M. Polanyi,¹ is a long one with many unexpected twists. In the 1930's, intense sodium *D*-line emission was found to occur when chlorine gas is injected into sodium vapor. Based on the observation of strong quenching of Na^* emission by the addition of inert gases, Polanyi and subsequent diffusion flame investigators² postulated the following multistep mechanism for the production of sodium chemiluminescence:



where the asterisk and dagger denote, respectively, electronic and vibrational excitation. In the above, step (1) liberates free chlorine atoms, while step (2) has the necessary exothermicity to excite Na atoms to the $3p^2P$ level through the vibrational-electronic energy transfer shown in step (3). Polanyi also considered the possibility that step (2) produced direct excitation,



Although (4) is energetically feasible, this reaction was rejected because it was not consistent with the quenching data. Nevertheless, calculations by Magee³ in 1940 indicated that direct excitation through step (4) should occur, and subsequent calculations by Pechukas, Light, and Rankin⁴ in 1966 suggested that steps (3) and (4) were of comparable importance.

This question was clarified experimentally through the elegant triple beam studies of Moulton and Herschbach⁵ in 1966 and the crossed beam chemiluminescence studies of Struve, Kitagawa, and Herschbach⁶ in 1971.

These experiments show not only that vibrational-electronic energy transfer occurs rather efficiently but also that direct excitation occurs with a comparable cross section. Hence, as theoretical arguments had predicted, these molecular beam experiments demonstrate that both excitation mechanisms can play a significant role in the observed atomic emission.

Recent studies, independently conducted by Ham,⁷ Herschbach *et al.*^{6,8} and ourselves⁹ have now shown that direct atomic excitation via step (4) occurs with other alkali-dimer-halogen-atom combinations producing high-lying atomic excited states whose energies approach the reaction exothermicity. These observations have been made both in diffusion flames and under beam conditions.

Although most attention has been directed in the past to the atomic emission accompanying alkali-halogen reactions, molecular chemiluminescence has also been observed. Shortly after Polanyi's original flame studies, Levi¹⁰ photographed chemiluminescent emission from lithium, sodium, and potassium halide molecules in diffusion flames similar to those of Polanyi. She also studied these same molecules through absorption and emission spectroscopy of the vapor, the latter being performed using an electrical discharge. The spectra varied somewhat as a function of different conditions employed in each study. Potassium halide chemiluminescence has also been observed by Tewarson¹¹ when admitting halogen gas into a bulb filled with alkali metal vapor and several torr of argon. The resulting spectra are similar, though not identical, to those presented by Levi. In an interesting (if not tantalizing) footnote to the letter of Struve, Kitagawa, and Herschbach,⁶ we find mention of a "molecular continuum" accompanying the sodium-chlorine reaction. Recently, Ham¹² has observed molecular emission from mixtures of sodium with

fluorine and chlorine in a dilute gas flow system. The spectra, which show several vibrational modes, are qualitatively different from those of previous flames studies. Their behavior with the variation of various experimental parameters lead Ham¹² to assign the source of the emission to the electronically excited triatomic molecules NaF_2^* and NaCl_2^* formed in termolecular collisions.

Previously, we have applied the technique of crossed-beam chemiluminescence to a number of other reaction systems producing electronically excited molecules.¹³⁻¹⁵ We began the present study with the hope that its application to the alkali-halogen reactions might shed some light on the molecular excitation mechanism in much the same way that molecular beam studies of the atomic chemiluminescence have helped to clarify the production of excited atoms. We have investigated the molecular chemiluminescence produced in the reactions of the alkali dimers, $M_2 = \text{K}_2, \text{Rb}_2, \text{ and } \text{Cs}_2$ with the halogen molecules, $X_2 = \text{Cl}_2, \text{Br}_2, \text{ and } \text{I}_2$, and $\text{XY} = \text{ClF}, \text{IBr}, \text{ and } \text{ICl}$. From the chemiluminescent spectra we have identified the emitter as MX^* . Based on the dependence of the intensity of the chemiluminescence on the metal flux and halogen pressure, we have found that the process responsible for the production of MX^* is a bimolecular reaction between M_2 and X_2 or XY . Based on energetic grounds we conclude that a four-center reaction of the type that might have pleased Bodenstein¹⁶ is responsible for the production of MX^* ,



and



where Y corresponds to the halogen atom forming the more stable ground state salt molecule. Similar studies have been independently conducted by Struve, Krenos, McFadden, and Herschbach (SKMH).¹⁷ With their magnetic deflection apparatus and with their well-defined crossed beams, they are better equipped to study the detailed dynamics of these interesting four-center reactions. Consequently, we focus our attention here on presenting the spectroscopic identification and analysis of the chemiluminescence.

EXPERIMENTAL

The beam apparatus, LABSTAR, has been described previously.^{13,14} Alkali metals are heated in a molybdenum effusive oven, located in a differentially pumped source chamber. This chamber has been modified for the alkali metal studies with the addition of a liquid-nitrogen-cooled collimator, which forms the boundary between the source and reaction chambers. This proved necessary because previous room temperature collimators did not have sufficient pumping speed for the relatively volatile alkali metals and the "cloud" formation tended to destroy the beam. Oven temperatures are monitored with a chromel-alumel thermocouple whose potential is measured with a Digitec 266 dc voltmeter. The alkali metal beam, whose flux is typically 10^{17} – 10^{18} particles/sec, traverses a scattering chamber where it

intersects a tenuous atmosphere of halogen gas, typically at pressures 2 – 4×10^{-4} torr, as determined by an uncalibrated ionization gauge. Those halogens that are solids or liquids at room temperature are heated in a molybdenum oven external to the reaction chamber in order to produce sufficient vapor pressure. The halogen flow is controlled by a Whitey needle valve. The visible chemiluminescence is detected using a 1 m Interactive Technology scanning spectrometer with a Centronic S-20 photomultiplier tube inside a cooled housing attached to its exit slit.¹⁵

The cesium and rubidium metals are obtained from Kawecki-Berylco with a stated purity of better than 99% where the main contaminants are other alkali metals and calcium. Even with this high purity, atomic emission lines from the alkali contaminants are observed. For most experiments involving potassium, only lump metal is used with the consequence that a prominent feature of the chemiluminescence is the Na *D* lines. Normally the interference of the *D* lines with the molecular spectra is minimal, except in the case of the reactions involving I_2 , ICl , and IBr . For these reactions, high purity potassium (~ 150 ppm Na) obtained from Alfa Products is used. The sources for the halogen reagents are for chlorine, Matheson; bromine, Mallinckrodt; iodine, Fisher Scientific; ICl and IBr , Matheson, Coleman, and Bell; and ClF , K & K Laboratories. All halogen reagents are of standard purity and are used without any additional purification.

RESULTS

Appearance of chemiluminescent spectra

Figures 1–3 show the chemiluminescent spectra obtained from the gas-phase reaction of potassium, rubidium, and cesium with Cl_2 , Br_2 , and I_2 . The spectra are characterized by a broad molecular feature that extends throughout most of the visible spectrum upon which are superimposed sharp atomic emission lines. The molecular feature is resolvable into what is apparently a long vibrational progression from a single vibrational level or, as is more likely, a narrow band of closely spaced levels in the excited electronic state. The exact onset and intensity contour of the molecular feature and the exact positions and spacings of the vibrational band structure vary with respect to the particular alkali metal and halogen molecule reaction pair. The spacings of the peaks increase in going from I to Cl and in going from Cs to K. The magnitudes of the largest spacings are between 0.65–0.95 of the ω_e values of the corresponding alkali halide, and the spacings regularly decrease to the red. The individual peaks have definite reproducible features that vary from one peak to the next.

No comprehensive investigation was made of either the sodium-halogen or lithium-halogen chemiluminescence since these systems are currently being studied elsewhere by Ham.¹² However, exploratory runs made on the sodium-bromine and sodium-chlorine reactions gave evidence for molecular emission in the region 5800–7000 Å qualitatively similar to those of the other

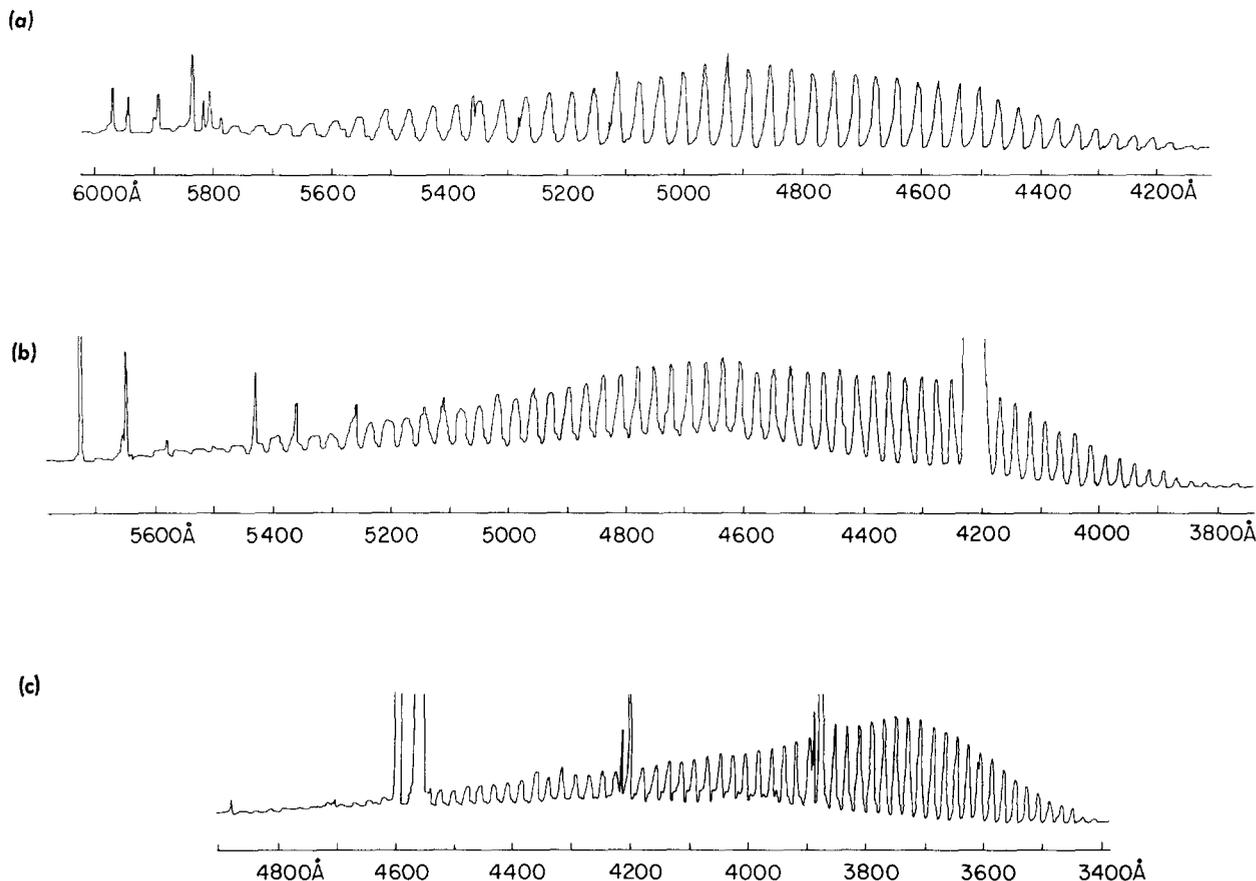


FIG. 1. Chemiluminescent spectra of (a) KCl, (b) RbCl, (c) CsCl, with a resolution of 5 Å or better. Also present in each trace are atomic (alkali) lines, some of which are off scale.

alkali halides, although of weaker intensity. Since Na_2 is known to emit in this spectral region,¹¹ emitter identification is difficult and was not pursued. The alkali-fluorine reactions gave no detectable molecular emission, except in the case of cesium, which yielded a very weak apparently unstructured continuum between 4100–4800 Å.

The halogens, bromine and chlorine, and the alkali metal, rubidium, have more than one isotope in significant natural abundance. Examination of Figs. 1(b), 1(c), 2(b), 2(c), and 3(b) reveal that each band is split in a manner suggestive of an isotope effect. Because the reduced masses of the alkali halides containing rubidium, bromine, and chlorine are so large, isotope splittings would be expected normally to be quite small. The effect, which is explained more fully in a later section, is a result of the relatively high ground state vibrational levels to which emission occurs. The splittings increase in magnitude with increasing wavelength, corresponding to transitions to higher v' levels.

The various alkali metal beams have also been crossed with several mixed halogen molecules. Reactions of IBr and ICl with any of the alkali metals yield the same molecular emission as the reactions involving I_2 , with no trace of any other molecular emission. Similarly, ClF yields the same molecular emission as Cl_2 . The peaks lie at identical wavelengths to within our spectral resolution, and the spectra have similar over-all intensity

distributions. Consequently, no additional figures are presented for these alkali-mixed-halogen reactions.

Atomic emission lines appear in the spectra of all reactant pairs studied. All the atomic lines have been identified as alkali atom transitions. Most transitions belong to the various Rydberg series of the particular alkali metal being studied. However, transitions are also seen from the lowest levels of other alkali atoms that are present in the beam as impurities. The Rydberg series observed consist of transitions from the various 2P levels to the ground state 2S level, the various 2D levels and 2S levels to the lowest 2P level, and the various 2F levels to the lowest 2D level. The number of Rydberg states populated depends on the reactant pair in the following manner: the extent of the Rydberg series increases in going from Na to Cs; it also increases in going from I to F where $\text{I}_2 \approx \text{ICl} \approx \text{IBr} < \text{Br}_2 < \text{Cl}_2 \approx \text{ClF} < \text{F}_2$. The case of the cesium-fluorine reaction system is particularly spectacular, as shown in Fig. 4. Rydberg transitions originate from levels closely approaching the ionization limit of the cesium atom. Indeed, some of the highest members of the $nf^2F - 5d^2D_{5/2,3/2}$ and $nd^2D - 6p^2P_{3/2,1/2}$ Rydberg series appear not to have been observed previously.¹⁸ An attempt was made to determine the steady-state populations of the atomic excited states in hopes that this reaction might have potential as a visible chemical laser system. However, no significant population inversions were

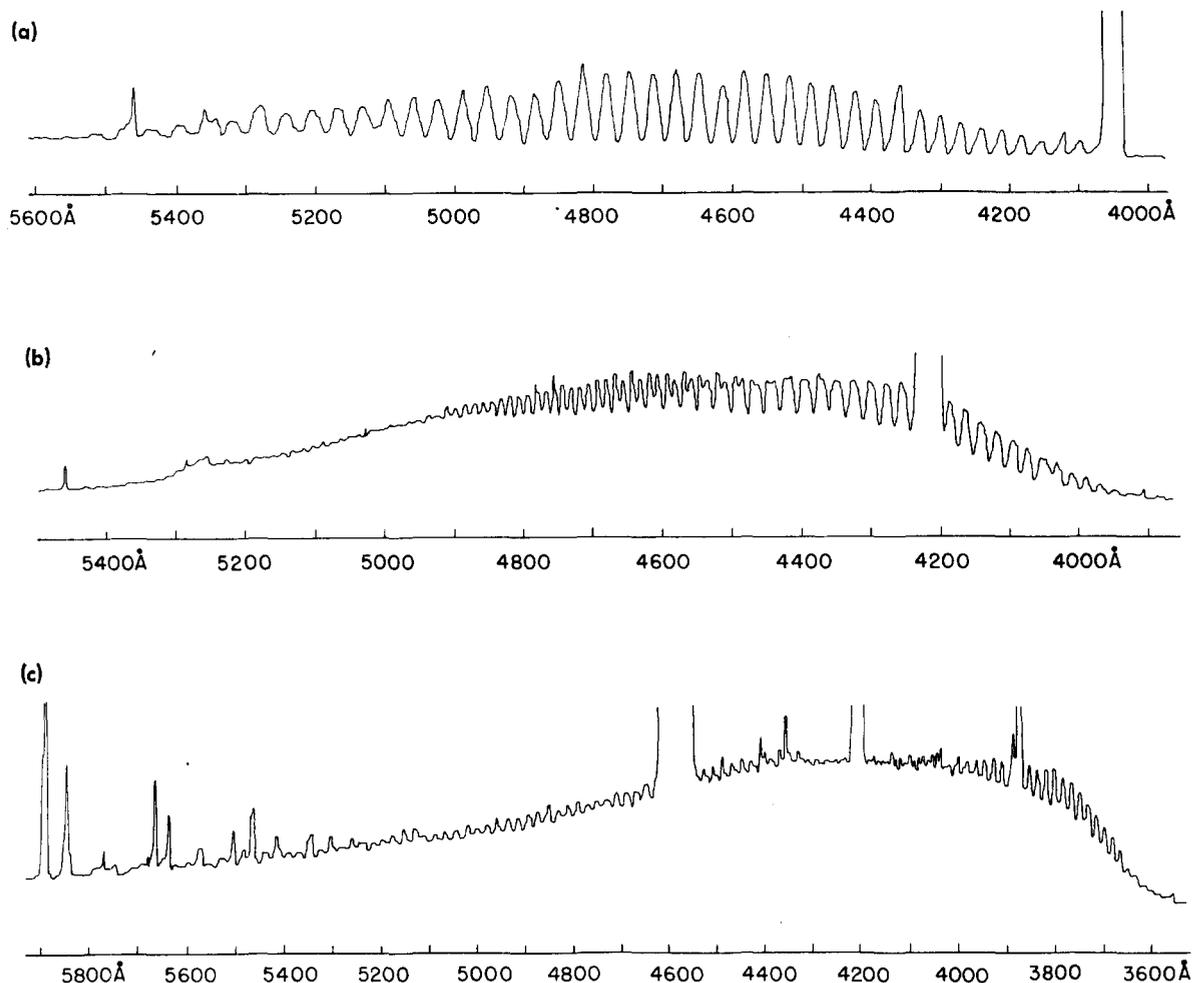


FIG. 2. Chemiluminescent spectra of (a) KBr, (b) RbBr, (c) CsBr, with a resolution of 5 Å or better. Also present in each trace are atomic (alkali) lines, some of which are off scale.

found.

Intensity dependence on reagent flux

In order to determine the mechanism responsible for the molecular chemiluminescence, an investigation was made of the variation of its intensity with reagent concentrations. The process producing the molecular chemiluminescence is found to be first order with respect to both alkali dimers and halogen molecules, and has no dependence on alkali atoms. The order with respect to halogen molecules is determined by fitting the molecular chemiluminescent intensity to the expression $p^n \exp(-\alpha p)$ where n is the reaction order and p is the halogen pressure.¹³ The exponential factor corrects for the attenuation of the metal beam which occurs prior to its crossing of the observation zone. This correction is necessary since no effort is made to collimate the halogen "beam" and therefore the halogen vapor fills the scattering chamber. The order with respect to the alkali metal is determined by studying the chemiluminescent intensity as a function of source oven temperature. A plot of the logarithm of the intensity vs inverse temperature yields a straight line whose slope represents the sum of the heat of vaporization of the participating species and the reaction activation energy (Clausius-

Clapeyron relation). However, alkali-halogen reactions are typically initiated by electron-jump mechanisms and consequently have large cross sections and nearly zero activation energies. Therefore, the slope is expected to approximate closely the heat of vaporization. Figure 5 illustrates the relation between the intensity of the 5142 Å peak of the potassium-iodine chemiluminescence and source oven temperature. The dashed lines represent the source oven vapor pressures of the potassium atoms and potassium dimers. As seen in Fig. 5, data points lie close to the dashed line corresponding to potassium dimer pressures. Slight curvature of the actual data points is found at the higher temperatures. This is caused by the fact that the flow is not strictly effusive in this temperature region, i.e., the oven pressures are less than the vapor pressures at the corresponding temperatures. Nevertheless, such plots allow us to conclude that the molecular chemiluminescent reaction depends linearly on only the alkali dimer component of the beam. Struve, Krenos, McFadden, and Herschbach¹⁷ have seen similar intensity-temperature dependences in the molecular "continua" they observed.

Using the same technique we have investigated the atomic chemiluminescence accompanying the alkali-halogen reactions. No exhaustive study was attempted, but

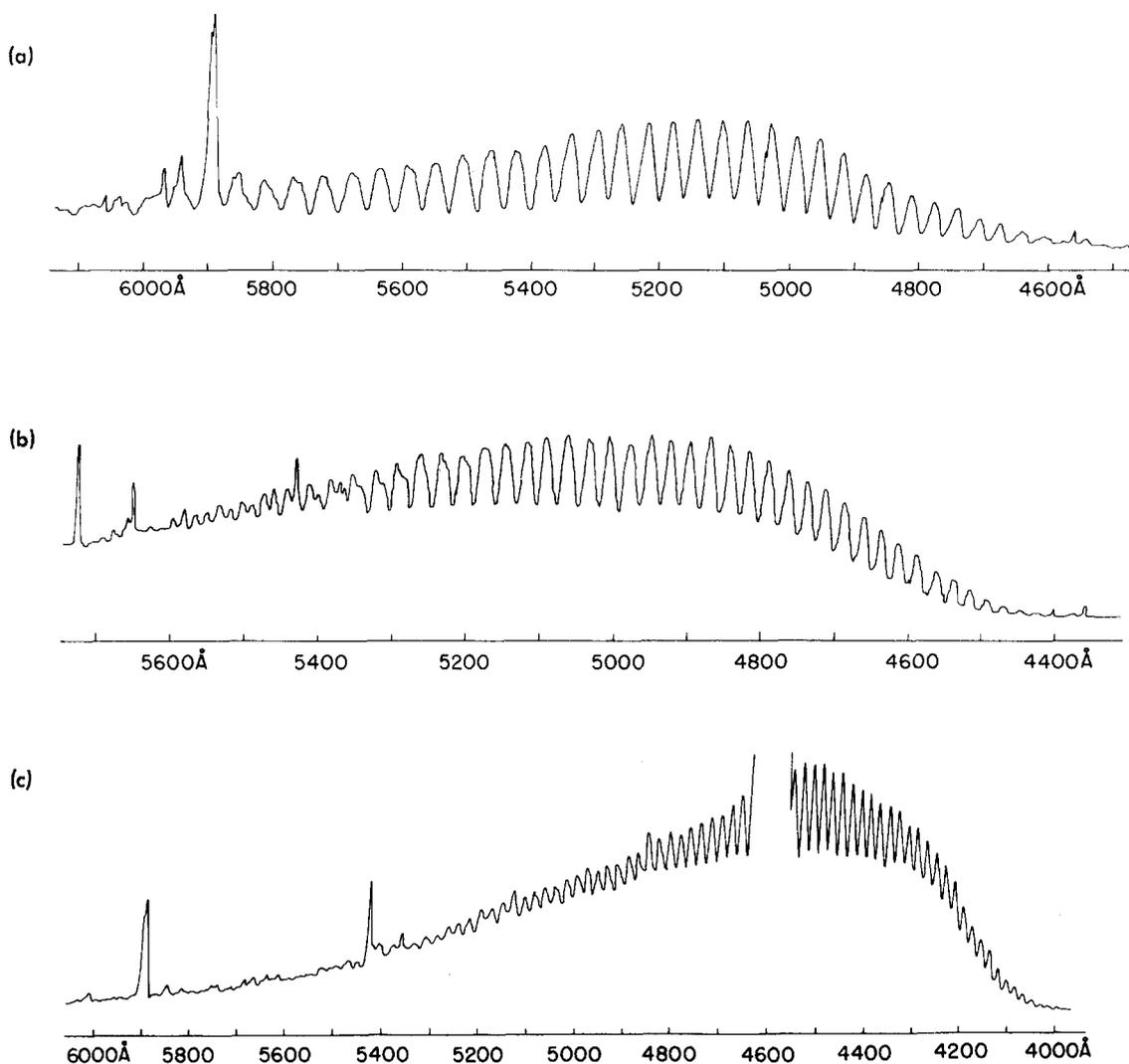


FIG. 3. Chemiluminescent spectra of (a) KI, (b) RbI, (c) CsI, with a resolution of 5 Å or better. Also present in each trace are atomic (alkali) lines, some of which are off scale.

for the few Rydberg transitions studied, the dependence on alkali metal flux appears to be consistent with a linear dependence in *both* alkali atoms *and* alkali dimers. There is also a linear dependence on halogen molecules. Thus the pressure dependence we have observed is consistent with Reaction (1) followed by Reaction (4), i. e., direct excitation of the alkali atom by reaction of the halogen atom with alkali dimers. The Rydberg transitions for which the pressure dependence was studied were for intermediate members of the series. We did not assess the role of vibrational-electronic energy transfer from vibrationally excited ground-state alkali halide molecules in populating the Rydberg states via Reaction (3).

Spectral identification

The exact position and spacings of the band structure observed depend on the particular alkali metal and halogen reactant pair, indicating that the emitting species must contain at least one alkali and one halogen atom. The pressure dependence studies are consistent with a

bimolecular reaction of an alkali dimer with a halogen molecule. These two facts limit our choice of possible emitters to the following: MX^* , M_2X^* , MX_2^* , and $M_2X_2^*$. The alkali-mixed-halogen reaction results are clearly inconsistent with an emitter containing more than one halogen atom, thereby ruling out the last two choices.

We have concluded that MX^* , rather than M_2X^* , is the emitter responsible for the chemiluminescence based on the following three reasons. First, the molecular beam studies by Kwei and Herschbach¹⁹ on the reactions of alkali atoms with the mixed halogen molecules ICl and IBr have shown that the principal product contains the halogen atom forming the more stable ground state salt molecule. By analogy, if our emitter is M_2X^* , our reaction of an alkali dimer with, for example, ICl, would be expected to yield the chloride product (M_2Cl) rather than the iodide as is observed. Second, while no known spectra exist for the M_2X molecule, the MX molecule has been certainly seen in absorption, and also reported in emission. These known spectra are similar to our chemiluminescent spectra. Finally, the short wavelength limits of our chemiluminescent spectra set lower

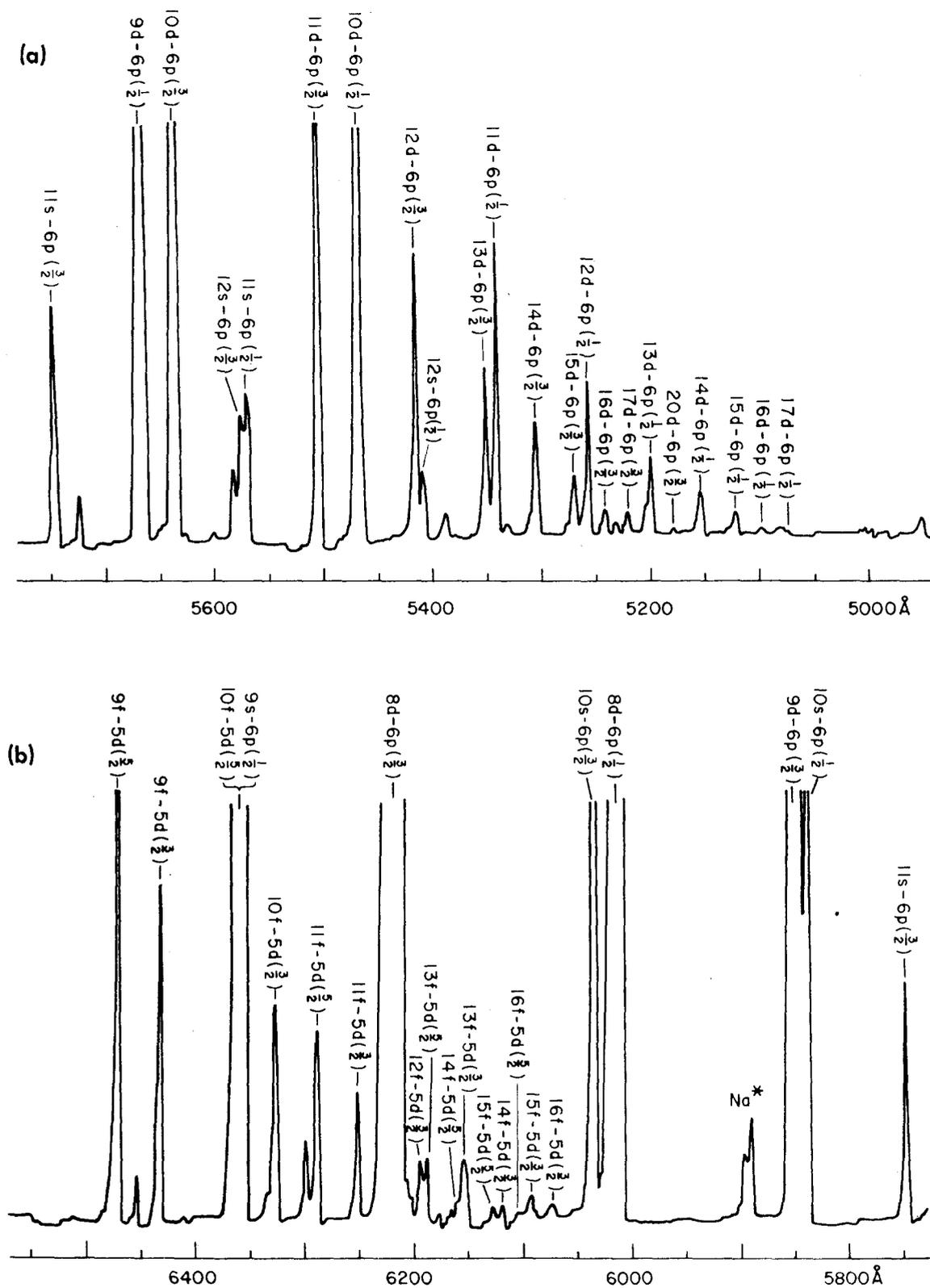


FIG. 4. Portions of chemiluminescent spectra resulting from the $F + Cs_2$ reaction. Highest energy transitions terminating on (a) $6p\ ^2P$ fine structure levels and (b) $5d\ ^2D$ fine structure levels.

limits on the reaction exothermicities. To explain the observed spectra, the heat of atomization of the M_2X molecule in all cases would be of necessity at least 30–40 kcal/mole greater than the corresponding diatomic MX molecule. This would make the M_2X molecule unex-

pectedly stable.

The electronic absorption spectrum of an alkali halide vapor generally consists of a strong continuum in the near uv followed by a progression of much weaker bands

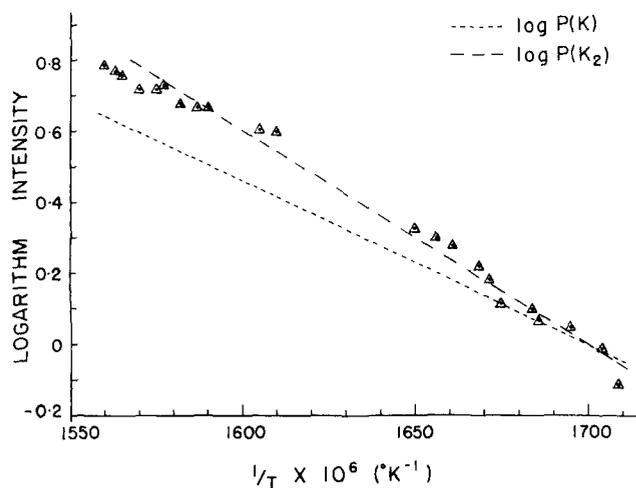


FIG. 5. Intensity of the KI 5142 Å emission peak vs potassium source oven temperature. The dashed lines show the expected dependence of potassium atom and dimer source pressures.

extending to longer wavelengths and into the visible region of the spectrum. The continuum is interpreted as resulting from transitions from several of the lowest vibrational levels of the ground electronic state to a steep repulsive wall of the excited state curve. Fluctuations occur in the continuum intensity at longer wavelengths caused by the constructive and destructive overlap between the ground-state and excited-state vibrational wavefunctions. The maxima of these fluctuations have been measured by Levi¹⁰ for the potassium halides and Barrow and Caunt²⁰ for the cesium and rubidium halides.

In general our shortest wavelength emission peaks lie to the red of the maxima reported in the alkali halide absorption studies. Only for the salts KI and CsI is there some portion of the absorption and emission spectra in the same wavelength region. Agreement with the published positions of the absorption maxima in this overlap region is reasonably good, i. e., to within 10 Å, except for two or three of our shortest wavelength emission bands of KI. However, measurement of our first few KI band positions is complicated by their low intensities and by the presence of several strong atomic lines in this spectral region. Thus these discrepancies are regarded as unimportant.

Potassium halide chemiluminescence has been observed previously by Levi¹⁰ and by Tewarson.¹¹ Spectra consist of a progression of peaks which blend into continua at short wavelengths as in absorption. The peaks cover much the same region of the spectrum as in absorption studies, and in addition extend further to the red. Maxima positions were measured in these flame studies, and the reported values are consistent with the results of Levi's own absorption study.

Our potassium halide spectra show a long progression of peaks similar to the emission spectra of Levi and of Tewarson, but have two very noticeable differences. Our spectra do not blend into continua at short wavelengths, and our over-all intensity contours are considerably shifted to longer wavelengths. The short wave-

length onsets of our spectra lie approximately in the center of these flame spectra. Our long wavelength cut-offs for KI and KBr are similar to those of Tewarson's spectra, but our KCl spectrum extends to much longer wavelengths than previously observed.

The positions of our peaks in the region where the spectra overlap do not coincide exactly with those reported by previous workers, but the agreement in the peak positions is considered to be good because of the large measurement uncertainties. For KBr and KCl, all our peaks lie within 10 Å of the corresponding maxima reported by both Levi and Tewarson (for comparison the peak widths are $\cong 20$ Å). This is also true for KI, but there are larger deviations toward the long and short wavelength limits of the spectrum. However, as mentioned above, the intensity of the peaks drops off towards these limits (see Figs. 1-3), and this makes their measurement less certain. These differences are therefore not believed to be unreasonable. The spacings of our peaks in the overlap region appear to be slightly smaller and more evenly spaced than those previously observed.

Despite the differences between our spectra and those of flame studies (which we feel are significant), we are confident that the spectral similarities, combined with the other reasons mentioned earlier, justify our conclusion that the emitter is the diatomic alkali halide molecule. All that remains is to rationalize the discrepancies between our spectra and those from the flame chemiluminescence studies. It is our contention that those differences may be understood as a consequence of variations in rotational excitation. All previous chemiluminescence spectra were taken at relatively high pressure (1-2 torr) of argon, allowing enough collisions within a radiative lifetime for nearly complete rotational thermalization. However, in our experiments, the pressure regime (10^{-4} torr) is low enough to make secondary collisions rare and rotational thermalization impossible. Product rotational distributions are determined only by the energy partitioning of the reaction in which they are formed. Very high product rotational "temperatures" are therefore possible, and considering the electron-jump mechanism, likely.

Kaufmann and Kinsey²¹ have recently proposed a technique for the analysis of alkali halide spectra utilizing molecular beam scattering data. In an accompanying paper, Kaufmann, Kinsey, Palmer, and Tewarson (KKPT)²² have analyzed the KI flame spectra using the reflection method. An accurate ground-state potential was obtained by splicing a Dunham potential, constructed using accurate microwave data,²³ to a Rittner potential at larger internuclear distances. Rotational excitation was taken into account by solving for the energy levels in the effective rotational potential. Tewarson placed a thermocouple in the center of his dilute flame which indicated a temperature of 1000 °K. An effective (most probable) J of 100 was chosen in the above analysis assuming that complete rotational thermalization occurred before emission. Vibrational numbering was varied so that the rotationless excited state potential would have a well depth consistent with the scattering data of Kauf-

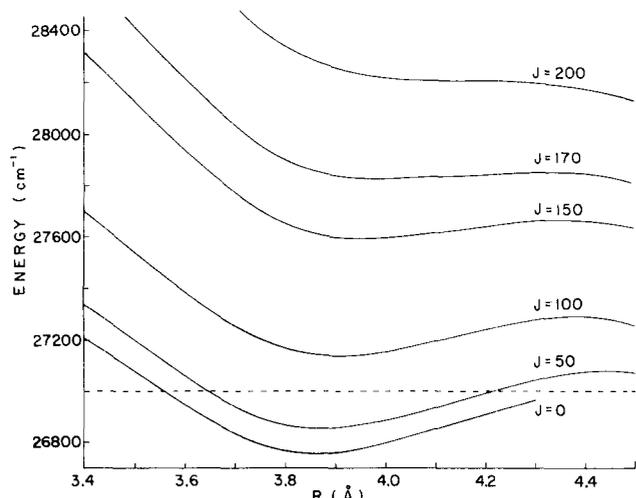


FIG. 6. Effective excited state potential curves for KI constructed from the rotationless potential of Kaufmann, Kinsey, Palmer, and Tewarson, assuming a dissociation asymptote of $27\,000\text{ cm}^{-1}$.

mann, Lawter, and Kinsey²⁴ and a limit at large internuclear distance consistent with dissociation into ground-state potassium and iodine atoms. The rotationless excited state KI potential that KKPT deduced was smoothed of experimental fluctuations and shown in Fig. 6.

Also shown in Fig. 6 are rotationally excited potential curves for selected values of J , which we have obtained by adding the term $E(J, R) = \hbar^2 J(J+1)/2\mu R^2$ to the rotationless potential given by KKPT. We note that the repulsive wall of the resulting "effective" excited state potential rises at larger internuclear distances as the value of J increases, the potential becoming essentially repulsive for a value of $J \approx 200$. The location of the potential minimum is forced to larger R and the well depth decreases with increasing J . We also note the appearance of a maximum or "rotational barrier" at the outer edge of the well. The position of this maximum moves inward and upward with increasing J and finally at $J \approx 200$ coincides with the position of the potential minimum, reducing the potential "well" to a mere point of inflection in the curve.

We wish to consider how the appearance of the chemiluminescent spectra changes with the effective rotational potential. The spectra consist of transitions from the bound or quasibound vibrational levels of the excited state to the outer turning points of high-lying ground-state vibrational levels. Therefore, the short wavelength onset of the spectrum is determined by the lowest v'' level which has an appreciable vibrational overlap with the bound or quasibound v' levels. This, in turn, is a function of how far the v' levels extend to small internuclear distances. Figure 6 shows the pronounced effect of rotational excitation on the position of the repulsive wall of the excited state curve. It is evident that the smaller the J value, the further to the blue the short wavelength onset will lie. In the flame studies, where rotational relaxation is significant spectra can be expected to extend further to the blue, which is exactly what is observed. If we assume that transitions only occur from the bound part of the potential, then we es-

timate from Fig. 6 that the onset of our KI chemiluminescence spectrum is consistent with a rotational distribution peaked at a J value of 150–160. (For a Boltzmann rotational distribution, a most probable J of 150 corresponds to a rotational temperature of $\approx 2500\text{ }^\circ\text{K}$ in the excited state.) If we adopt the vibrational numbering of the previous analysis (KKPT), then our shortest wavelength peak corresponds to a transition to $v'' = 25$. The fact that our emission is to such high ground-state vibrational levels explains the observed isotope splittings discussed in the Results section.

The dependence of the long wavelength cutoff on the rotational energy of the emitter is not as straightforward, but nevertheless yields a possible explanation of the observed differences. The radial extent of the occupied v' levels to large internuclear distances determines the highest v'' level which has appreciable vibrational overlap, and therefore the long wavelength intensity cutoff. The upper-state potential at the outer limb is a slowly varying function of both internuclear distance and rotational excitation. Therefore the distribution of vibrational energy within the narrow band of excited state levels plays a critical role in determining the cutoff position. (This distribution is only of minor importance in determining the short wavelength onset since its role is overshadowed in that case by the radical changes in the potential curve with J .) This can be seen by comparing two effective curves of different J values. If they are both "filled," i. e., all bound vibrational levels significantly populated, the emission from the rotational potential with smaller J would extend to longer wavelengths, since the potential maximum moves outward with decreasing J . However, if two different effective rotational potentials have equal amounts of vibrational energy, then the potential curve with the lower J value will not necessarily have all its vibrational levels occupied since it is deeper. Examination of the curves (Fig. 6) indicates that the emission from the rotational potential with larger J may therefore extend to longer wavelengths. In flame studies, molecules are presumably produced in high J states and rotationally relaxed via subsequent collisions to the J levels from which emission occurs. The extent to which the vibrational levels of the potential are occupied depends on: (1) the initial mechanism of formation, which may populate the vibration levels differently, (2) the rotational relaxation of the emitters, which causes the final effective rotational potential to be deeper than the initial effective rotational potential, and (3) the degree of alteration of the vibrational energy content, which occurs during the rotational thermalization. Therefore, a comparison between the long wavelength cutoffs of beam and flame spectra is not a direct measure of the variations in rotational excitation of the emitters, and such a comparison would be expected to vary among different sets of reactants studied and under different operating conditions.

One should also consider the effect of rotational excitation on the peak positions and spacings. The separation between the ground- and excited-state potentials is not changed by rotational excitation. However, rotational excitation does decrease the depth and distort the

shape of both wells. In particular this has the effect of decreasing the spacing of the ground-state vibrational levels. The fact that our peaks show slightly smaller spacings than those in flame spectra is again consistent with our emitter's higher rotational excitation.

Although the upper-state potential curve of KKPT was used as a basis for the above discussion, the detailed shape of the curve is not critical to the arguments presented here. Rather, our conclusions depend only on the essentially shallow nature of the curve and should therefore apply to other alkali halides with electronic states similar to those of KI. An analysis of our data similar to that of KKPT would be interesting but at best difficult. Although the most probable rotational level for each of Tewarson's upper-state vibrational levels is nearly the same because of the rotational thermalization, our rotational distribution is determined solely by reaction exoergicity partitioning, and the most probable rotational state can vary considerably from one upper state level to the next.

In conclusion, we believe that the difference between the flame and beam chemiluminescence spectra can be understood solely by consideration of the variations in rotational excitation of the emitting molecules and that such variations are indeed to be expected. However, we do not wish to imply that there are no other factors influencing these differences. We, therefore, do not pursue further the interpretation of the differences in the various chemiluminescence spectra.

DISCUSSION

Comparison with crossed-beam studies (SKMH)

Struve, Krenos, McFadden, and Herschbach¹⁷ have observed visible chemiluminescence "continua" under low resolution when crossing well-defined molecular halogen beams with alkali metal beams from a nozzle oven. They postulate the mechanism



where the emitter is tentatively identified as the alkali halide. We believe that our spectra result from the same chemiluminescent reaction since kinetic studies show our chemiluminescent emission has a linear dependence on the same reactants (and no others) and our spectra have the same over-all intensity contours as their "continua." By resolving the "continua," we are able to identify the emitter as the electronically excited alkali halide. An additional ground-state alkali halide product is necessary for energy conservation. Thus our studies confirm the mechanism which SKMH postulate.

Mixed halogen reactions

The fact that the alkali-dimer-mixed-halogen reactions only yield chemiluminescence from the alkali halide containing the less electronegative halogen atom [Reaction (6)] invites speculation about the detailed reaction mechanism. Since the ionization potential of an alkali dimer is even lower than that of the alkali atom, analogy to alkali-atom-halogen-molecule reactions¹⁹ indicates that the reaction proceeds by an electron-jump mecha-

nism. Following the electron jump, the electron must migrate to the more electronegative halogen atom of the mixed halogen molecule. This atom then combines with an alkali ion to preferentially form an ionic ground state alkali halide ($M^+ Y^-$) which is the more stable of the two possible salt products. The less electronegative halogen atom X and the remaining alkali atom M are both neutral. Barring a second electron jump, which can only occur at large internuclear distances, the M and X atoms find themselves on a homopolar (excited state) curve. The experimental evidence of Foreman, Kendall, and Grice²⁵ and of SKMH indicate that most M and X atoms separate. Presumably, some M and X collision partners are trapped in bound or quasibound levels of the homopolar potential curve from which they later radiate. What role the $M^+ Y^-$ product plays as a chaperon in this trapping process is unknown.

Absence of molecular emission in reactions involving Na_2 or F_2

There is a conspicuous absence of molecular emission in the sodium-halogen and alkali-fluorine reactions. However, the intensity of the atomic lines accompanying these reaction systems attests to the fact that this absence is not a consequence of variations in experimental conditions. Rather, it can result from the following three considerations.

First, the absence of molecular emission may indicate that the reaction producing the emitter [Reaction (5)] has a significantly slower rate (smaller cross section) for these reactants. Examination of the corresponding cross sections for the analogous alkali-atom-halogen-molecule reactions shows that reactions involving sodium atoms have cross sections that are approximately a factor of 2 smaller than those of potassium, rubidium, and cesium atoms. This may then contribute to the weakness of molecular emission in sodium-halogen reactions, although this alone could not account for its absence.

Second, the absence may indicate that the rates of competing processes are an important factor in these reaction systems and are therefore depleting the reactants. The dynamics of alkali-dimer-halogen-molecule reactions have been studied in conventional molecule beam devices.^{17,25,26} The following reactions have been shown to occur:



Angular distributions of alkali halide reaction products are forward peaked in the center-of-mass frame which demonstrates Reaction (7a) to be the dominant reaction pathway at large impact parameters. Angular distributions of reactively scattered alkali atoms give evidence that Reaction (7b) becomes important at small impact parameters, although (7a) may still remain dominant. The extent to which (7b) becomes significant clearly depends on the facility with which a second electron jump

may occur. This is related to the magnitude of the ionic-homopolar potential curve crossing radius. Reactions (7c) and (7d) occur with extremely small cross sections and therefore are not expected to be competitive for reactants.

Reaction (7a) most likely predominates at large impact parameters over the reaction path we observed for all reaction pairs studied. At small impact parameters, Reaction (7b) is unimportant for the potassium-, rubidium-, and cesium-halogen systems because the curve crossing radius²⁷ is large. However, for the sodium-halogen systems, this distance is much smaller. Reaction path (7b) therefore probably occurs significantly and could alter the branching ratio so as to deplete reactants which might otherwise yield chemiluminescent products.

The third possible reason for the absence of molecular emission is that the electronically excited products from certain reactions might be unstable and dissociate before emission is possible. In the previous section we demonstrated the high rotational excitation in the product emitter and also noted that extensive rotational excitation leads to an effective curve that has no bound levels, i. e., no potential minimum. If the energy partitioning is similar in all reactions studied, then highly exothermic reactions might produce electronically excited products too rotationally hot to hold together long enough to emit. The alkali-fluorine reactions are considerably more exothermic than those of the other halogens since the alkali fluoride bond strengths are relatively large and the molecular fluorine bond relatively weak. Therefore, this might be particularly important in explaining the absence of molecular emission in the reactions involving fluorine.

Speculation on the mechanism of atomic Rydberg state production

The necessary energy required to populate the observed high-lying Rydberg states could only be provided by the highly exothermic reaction between an alkali dimer and a halogen atom. However, as pointed out before, we do not know whether the atomic Rydberg states are directly populated by this chemical reaction or indirectly populated via vibrational-electronic energy transfer from MX^\dagger formed in this reaction. Indeed our pressure dependence studies are somewhat ambiguous on this point and even suggest that both processes are operative. The production of Rydberg states, where an electron is promoted to a distant, loosely bound orbital, is somewhat unusual. We are led to wonder what mechanism facilitates such a process.

The similarity between chemi-ionization and the production of Rydberg states encourages speculation on what role ionic intermediates might play. Both the direct reaction $\text{M}_2 + \text{X} \rightarrow \text{MX} + \text{M}^*$ and the vibrational transfer $\text{MX}^\dagger + \text{M} \rightarrow \text{MX} + \text{M}^*$ are expected to proceed through an M_2X complex which may live for several vibrations or more, based on the behavior of the alkali-alkali halide exchange reactions²⁸ and on semiempirical calculations.^{29,30} As pointed out by Magee, the *p*-orbital degeneracy of the halogen atom allows only one-third of the collisions to form an intermediate which can dis-

sociate to $\text{M}^+ \text{X}^- + \text{M}$, whereas two-thirds of the collisions form intermediates which either correlate to $\text{M}^+ \text{X}^- + \text{M}^*$ or $\text{MX}^- + \text{M}^+$. In particular, the later ionic intermediate, in which the complex insists on dissociating into ion pairs, crosses the homopolar curves for $\text{M}^+ \text{X}^- + \text{M}^*$. The possibility therefore exists for the MX^- partner to return the electron as the M^+ ion attempts to depart from the M_2X complex. As the separation between MX^- and M^+ increases, the electron "falls into" increasingly higher Rydberg states of the M atom. In this picture, then, the population distribution of the atomic Rydberg states is not just a consequence of sufficient energy, but involves as well the branching probability at numerous curve crossings. If this mechanism proves to be a correct description, then careful studies of the production of Rydberg states could yield useful information on the dynamics of curve crossings.

Some remaining problems

A number of questions remain unanswered about the nature of the covalent alkali halide potentials. First, there is both a $^1\Sigma^+$ and a $^1\Pi$ covalent potential curve arising from $\text{M}(^2\text{S})$ and $\text{X}(^2\text{P}_{3/2})$ atoms. We do not know their relative location, whether one or more are bound, and which one (if not both) is responsible for the observed spectra. Moreover, we are also ignorant about the covalent potential curves arising from $\text{M}(^2\text{S})$ and $\text{X}(^2\text{P}_{1/2})$, although it does not seem necessary to invoke their existence to explain our chemiluminescence spectra. Finally, we have little spectroscopic information about the well depths of these potential curves although molecular beam scattering data provide some estimate. From the evidence presented here for the existence of bound states of covalent MX^* molecules, it might be hoped that fluorescence studies would be possible. Such studies combined with the isotope information available, would lead to a better understanding of these curious states.

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