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Citation: *The Journal of Chemical Physics* **91**, 2834 (1989); doi: 10.1063/1.456952

View online: <http://dx.doi.org/10.1063/1.456952>

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Chemiluminescent reactions of ground and metastable states of the group IV A elements with halogens

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(Received 25 April 1989; accepted 26 May 1989)

Earlier work on chemiluminescent beam-gas reactions of the ground states (3P_J) of Si, Ge, and Sn with F_2 and of both ground and metastable states (1D , 1S) of Sn with Cl_2 , Br_2 , and I_2 is extended to include reactions of both ground and metastable states of Si, Ge, and Sn with F_2 , Cl_2 , Br_2 , I_2 , and ICl . Chemiluminescent products of metal halides and/or dihalides were observed in all of these reactions, although attempts to observe that in the similar reactions of Pb were unsuccessful. In ICl reactions with Si, Ge, and Sn, both monochloride and dichloride emission occurs, confirming the previously proposed mechanism for creating dihalide emission in Sn reactions with Br_2 and I_2 via a monohalide intermediate.

I. INTRODUCTION

The gas-phase chemiluminescent (CL) reactions of group IV A elements provide an interesting example of reactions of atoms with relatively high ionization potentials with a p^2 valence electronic configuration, which may be compared to those well-studied CL reactions of group II A elements¹ which have lower ionization potentials and an s^2 valence electronic configuration. Most such studies involving the ground states of group IV A elements and F_2 have been carried out in flame and flow experiments,²⁻⁶ where the CL products SiF , GeF , and SnF were observed. In order to study the dynamics of these CL reactions, they were carried out in a molecular beam apparatus in this laboratory⁷ along with the reactions of metastable Sn with F_2 .⁸

Although the reactions of the ground states of the IV A elements with F_2 to form monofluorides are sufficiently exothermic to populate the electronically excited CL states, it is not the case for other halogens or mixed halogens like ICl . For example, no CL was observed in the reaction of ground state Sn with Cl_2 . However, the reaction of metastable Sn with Cl_2 to form an electronically excited $SnCl$ is energetically allowed and, indeed, the CL product in this reaction was observed.⁸

On the other hand, CL was observed in the reactions of the ground state of Sn, e.g., with Br_2 and I_2 ,⁹ where the CL products were determined to be dihalides rather than monohalides which are energetically forbidden as mentioned earlier and a two-step reaction mechanism was proposed.⁹

In the present study, reactions of ground and metastable states of Si, Ge, and Sn with F_2 , Cl_2 , Br_2 , I_2 , and ICl to form monohalides and/or dihalides are reported. Also, an attempt has been made to study the reactions of Pb with these halogens, but no measurable CL was observed.

II. EXPERIMENTAL

The method and procedure utilizing a beam-gas arrangement in this study are similar to those used in the previous studies.⁷⁻¹⁰

Briefly, the metals were vaporized in a high temperature beam source in a molecular beam apparatus. Typical source temperatures were 1750, 1850, and 2000 K for Sn, Ge, and Si, respectively. The metal vapors were collimated upon entering a separately pumped chamber filled with halogens. The pressure of the halogen was typically about 10^{-4} Torr, and was measured with a capacitance manometer.

Most metal atoms entering the reaction chamber were thermally populated in the ground states. However, substantial amounts of the metastable states of Pb, Sn, and Ge, for example, can be and were generated by an electric discharge in front of the metal oven orifice with a typical discharge current of 50–100 mA at 150–250 V. Efforts to produce a discharge in a Si beam were unsuccessful. The metastable states produced in the discharge are mostly a combination of both 1S and 1D states having the p^2 valence electronic configuration. However, it was determined in the case of Sn that the 1D state is the major contributor to the CL product for the following two possible reasons⁸: (a) the population of the 1S state is only about 1% of that of 1D ; and (b) the cross section for the CL reaction of Cl_2 with the 1S state is smaller than that of the 1D state.

Chemiluminescence from the products was viewed at 90° to the beam through a 3/4 meter Spex monochromator with a spectral band pass of 3 nm followed by an RCA C31034 photomultiplier tube. The monochromator was controlled by a microcomputer and scanned to obtain the emission spectra, which were corrected later for spectral response using calibrated deuterium and quartz-halogen lamps.

All the chemicals were used directly from the suppliers without further purification.

III. RESULTS AND DISCUSSION

The chemiluminescent reactions of F_2 with ground-state group IV A elements^{7,9} and with metastable Sn⁸ have been studied previously. In this paper, we report extensions to metastable Ge reactions, as well as reactions of ground-state group IV A elements (Si, Ge, and Sn) with Cl_2 , Br_2 , I_2 , and ICl .

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A. Tin

No significant amount of CL was detected in the reaction of Cl_2 with ground state Sn, which was known to react with Br_2 and I_2 to form the corresponding tin dihalides.⁹ It was observed in this study that ground state Sn reacts with ICl to form a chemiluminescent product. Shown in Fig. 1 is the CL emission spectrum of the aforementioned reaction, which has two noted spectral peaks around 350 and 425 nm. The ICl pressure dependence study at the wavelengths of both maxima shows that the reaction is second order in ICl, which suggests⁹ that dihalide is the CL product formed in a two-step mechanism involving a vibrationally excited tin monohalide intermediate. In order to identify the CL product, the three possible dihalides were considered. This spectrum is obviously different from that of the CL reaction of Sn with I_2 ,⁹ which therefore essentially rules out the possibility of SnI_2 formation. Another possible dihalide product is, of course, the mixed halide, i.e., SnICl . If, in the two-step mechanism, the choice of abstracting I or Cl from ICl by Sn in the first step or by SnI/SnCl in the second step is random, it is expected that 25% of the products would be SnI_2 with emission in the vicinity of 550 nm.⁹ The fact that no emission was observed in that region, therefore, not only rules out SnI_2 as a product but also suggests that a random choice of I or Cl in the reaction is unlikely. Hence, we can also rule out the possibility of SnICl as a CL reaction product. On the other hand, the emission of SnCl_2 at 322 and 450 nm has been assigned to $^1B_1-^1A_1$ and $^3B_1-^1A_1$ transitions,^{11,12} respectively. It is then reasonable to attribute the observed CL primarily to the emission from the 3B_1 and 1B_1 states of SnCl_2 . This is also consistent with the fact that the production of SnCl_2 is the most favorable path, energetically, among all three possibilities.

When the electric discharge was turned on, metastable states of Sn, mostly $\text{Sn}(^1D)$, were generated in the metal beam. While the added population of more energetic metastable states of Sn apparently did not affect the CL emission spectra for the reactions with Br_2 and I_2 , it did make big differences for the reactions with F_2 , Cl_2 , and ICl. In the reaction of $\text{Sn}(^1D)$ with F_2 , the product spectrum was similar to the spectrum of $\text{Sn}(^3P)$ reaction product, but the in-

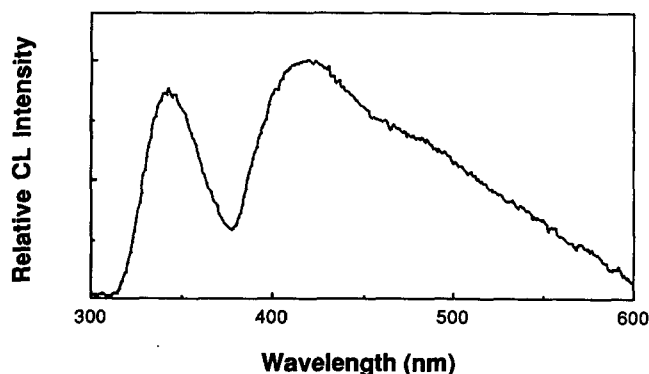


FIG. 1. CL of ground state Sn with ICl at 0.35 mTorr. The peaks are assigned from shorter wavelength to emission of 1B_1 and 3B_1 states of SnCl_2 .

tensity was greatly enhanced.⁸ For $\text{Sn}(^1D)$ with Cl_2 , the CL reaction to form the $\text{SnCl } A'(^2\Sigma)$ state is energetically allowed, and emission observed in the spectral region between 370 and 570 nm was assigned to formation of that state. In the present study, the improved detection sensitivity allowed the spectral scan for the reaction with Cl_2 to be extended to 300 and 750 nm, as shown in Fig. 2. While there is no doubt that emission with wavelength longer than 500 nm is mostly due to the $A'(^2\Sigma)$ state as evidenced by the vibrational structure in the spectrum, it is uncertain, though, whether the weak emission in the region of 350 nm is due to the $A(^2\Delta)$ state,¹³ which is not energetically accessible in the reaction of $\text{Sn}(^1D)$ with Cl_2 . Rather, this weak emission should probably be interpreted as the minor production of $\text{SnCl}_2(^1B_1)$ in a two-step mechanism. Because the ICl bond is weaker than the Cl_2 bond, formation of SnCl in the $A(^2\Delta)$ state in a single collision is energetically allowed in the reaction of $\text{Sn}(^1D)$ with ICl based on $D^0_0 = 98 \text{ kcal mol}^{-1}$ for SnCl ¹⁴ and the availability of twice the average thermal energy of $5.2 \text{ kcal mol}^{-1}$ in the reactants. Indeed, the A state of SnCl was observed in the reaction with ICl in addition to emission from both 1B_1 and 3B_1 states of SnCl_2 as shown in Fig. 3. More specifically, the two sharp peaks in the spectrum can be attributed to the transitions $A^2\Delta_{5/2}-X^2\pi_{3/2}$ and $A^2\Delta_{3/2}-X^2\pi_{1/2}$.¹⁵ It is, therefore, reasonable to conclude that, in the reaction of metastable Sn with ICl, both SnCl and SnCl_2 can be readily formed, uncharacteristic of the reactions with other halogens.

B. Germanium

As for Sn, the cross section for the reaction of ground state Ge with Cl_2 to form electronically excited products seems to be quite small, since no CL was observed. Likewise, its reactions with Br_2 , I_2 , and ICl did produce CL products. Figures 4–6 are the CL emission spectra for the aforementioned three reactions. The CL was determined to be second order in Br_2 , I_2 , and ICl in the pressure dependence studies and, therefore, it is believed that the major CL products are the corresponding germanium dihalides. In the case of Br_2 and I_2 , to the best of our knowledge, no emission from GeBr_2 or GeI_2 in this spectral region has been reported be-

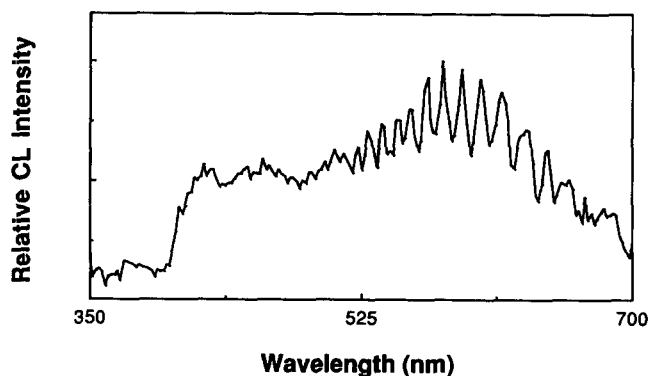


FIG. 2. CL of discharged Sn with Cl_2 at 0.3 mTorr. The longer wavelength structured region is assigned to $\text{SnCl } A'(^2\Sigma^+)$ emission. The shorter wavelength peak may include $\text{SnCl}_2(^1B_1)$ emission.

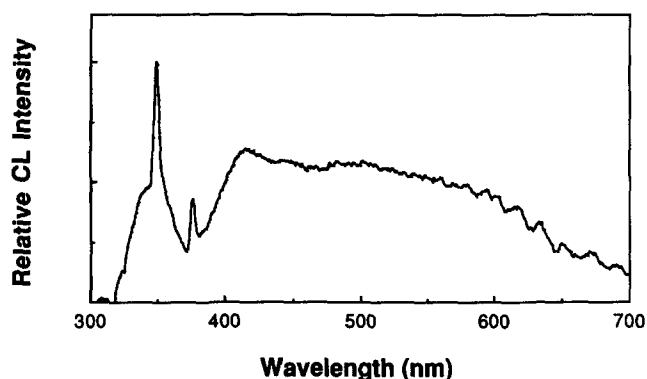


FIG. 3. CL of discharged Sn with ICl at 0.4 mTorr. Note the structure due to SnCl which was absent in Fig. 1. The sharp peaks are assigned from shorter wavelength to $A^2\Delta_{3/2}-X^2\pi_{1/2}$ and $A^2\Delta_{5/2}-X^2\pi_{3/2}$ transitions, and the longer wavelength structure to $A'^2\Sigma^+-X^2\pi$.

fore. However, it is believed that the CL observed in the present study is due to 3B_1 states of the dihalides for the following three reasons. First, the reactions are second order in the halogens, which suggests⁹ that the products are not likely to be monohalides, but dihalides formed in the two-step abstraction mechanism. Second, the emission spectra are broad and quasicontinuous with no characteristic diatomic vibrational structures and the spectra are not in the region of known emission of the monohalides.¹³ Third, their spectral shifts from the known spectrum of GeCl_2 ^{11,16} show the same trend as observed in the Sn series. (See Table I).

By the same arguments given earlier in the discussion of Sn, the CL observed in the reaction of ground state Ge with ICl can be attributed to the formation of the 3B_1 and 1B_1 states of GeCl_2 , which is consistent with the available spectroscopic data.^{11,16}

When the Ge metastables, mostly in the 1D state, are produced in the metal beam by an electric discharge, no significant change in the CL emission spectra was observed for the reactions with Br_2 and I_2 . However, changes were obvious in the case of F_2 , Cl_2 , and ICl, as shown in Figs. 7–9, respectively.

For F_2 , the emission due to the $A(^2\Sigma^+)$ state of GeF

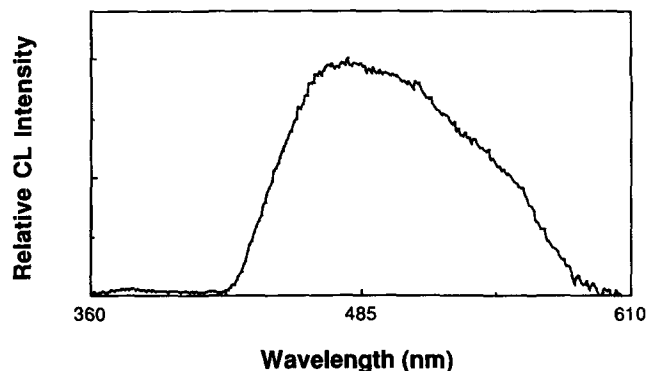


FIG. 4. CL of ground state Ge with Br_2 at 0.37 mTorr. The major peak is assigned to GeBr_2 (3B_1) emission. The minor peak at short wavelength may be due to the 1B_1 state.

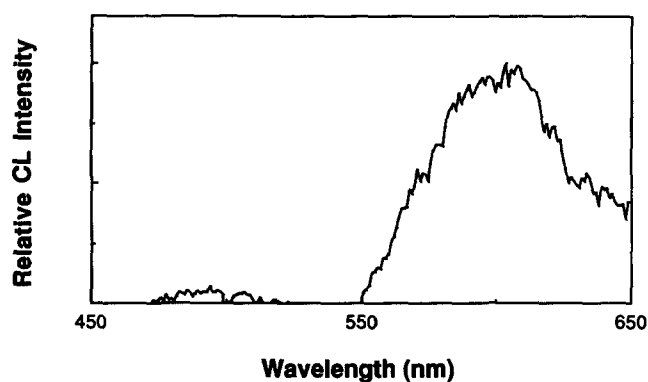


FIG. 5. CL of ground state Ge with I_2 at 0.3 mTorr. The peaks are assigned from shorter wavelength to emission of 1B_1 and 3B_1 states of GeI_2 .

was enhanced and extended to slightly higher frequency than with reaction of $\text{Ge}(^3P)$ alone. Also, weak emission was observed from the $B(^2\Sigma^+)$ state. Both of these changes are understandable given the extra energy of the 1D state. Attenuation of the 1D state by H_2 was used in the same manner as for Sn⁸ to show that the enhanced CL reaction is assignable to it. Just as for Sn, the 1D state and the CL emission are more strongly attenuated by H_2 than is the 3P , or 1S state. The absolute value for the CL cross section of the 1D state with F_2 was not obtainable because of uncertainty in the 1D population, but estimates of the 1D to 3P ratio indicate that the 1D CL cross section is larger by a factor of ~ 50 , which is similar to the $85\times$ enhancement in the analogous Sn process.

For Cl_2 , formation of the $\text{GeCl}A(^2\Sigma^+)$ state¹³ appears to be responsible for most of the CL emission. This is consistent with the reaction being first order in Cl_2 . For ICl, the most striking features in the CL emission spectra are the sharp peaks in the spectral region of previously reported emission of GeCl from the $A'(^2\Delta)$ state to the $X(^2\pi)$ state.^{13,17} In addition to them, the broad band emission from GeCl_2 is also present as in the ground state Ge reaction. It is not surprising at all, of course, since more of the Ge atoms in the beam are in the ground state even with the electric dis-

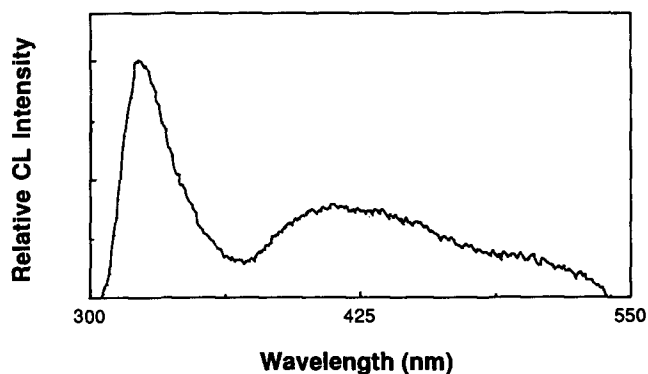


FIG. 6. CL of ground state Ge with ICl at 0.9 mTorr. The two major peaks are assigned from shorter wavelength to emission of 1B_1 and 3B_1 states of GeCl_2 .

TABLE I. Electronic transitions of selected group IV A dihalides.

Molecule	${}^3B_1-{}^1A_1$ (nm)	Ref.	${}^1B_1-{}^1A_1$ (nm)	Ref.
SnCl ₂	449	12	322	11
SnBr ₂	435	9	365	22
SnI ₂	550	9	...	
GeCl ₂	441	16	322	11
GeBr ₂	480	this work	...	
GeI ₂	600	this work	...	
SiCl ₂	437	11	330	18,19,20
SiBr ₂	...		362	21
SiI ₂	...		490	this work

charge.⁸ Again, as in the case of Sn, only the reaction of metastable Ge with ICl produces both monohalide and dihalide emission. Based on $D_0^0 = 101.5 \text{ kcal mol}^{-1}$ for GeCl¹³ the A' state is just accessible in the reaction of Ge(¹D) with ICl if twice the average thermal energy of $6.0 \text{ kcal mol}^{-1}$ in the reactants is available, but is not energetically accessible in the reaction with Cl₂.

C. Silicon

Unlike Sn and Ge, ground state Si does react with Cl₂ to produce CL products. Figure 10 is the emission spectrum for this reaction. It was determined in a pressure dependence study that the reaction is second order in Cl₂ and, therefore, the CL product is believed to be SiCl₂. Furthermore, the ¹B₁ state of SiCl₂ has been found to have an emission peak around 330 nm¹⁸⁻²⁰ and, indeed, that was what we observed in this reaction. Thus, the singlet SiCl₂ is a major product of this reaction, although there is no reason to exclude the triplet state as another product since the lifetime of the triplet state of SiCl₂ may be long enough to prevent its observation in the $\sim 10^{-5}$ s that it spends in the observation region.

Like Sn and Ge, CL from the reactions of Si with Br₂ and I₂, as shown in Figs. 11 and 12, are consistent with the similar conclusion that the formation of silicon dihalides are

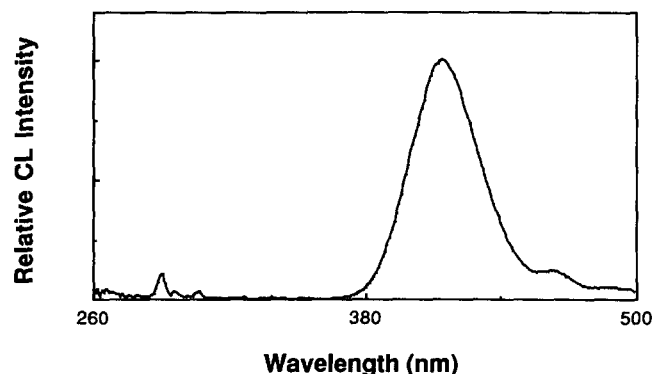


FIG. 7. CL of discharged Ge with F₂ at 0.36 mTorr. The $A'{}^2\Sigma^+ - X{}^2\Pi$ transition of GeF observed at longer wavelength is shifted to slightly shorter wavelength than displayed in Ref. 7 for the reaction of ground state Ge with F₂. The shorter wavelength structure is due partly to the $B'{}^2\Sigma^+ - X{}^2\Pi$ transition and partly to Ge transitions in the discharge region.

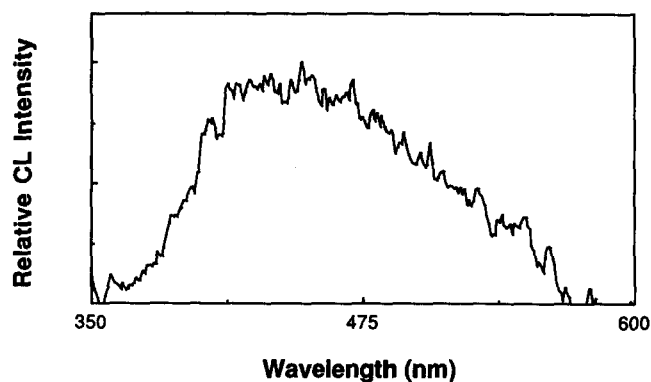


FIG. 8. CL of discharged Ge with Cl₂ at 0.2 mTorr. The structure is attributable to GeCl ($A'{}^2\Sigma^+$) emission.

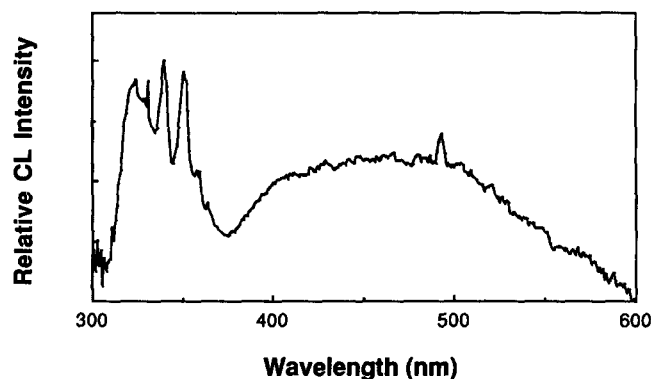


FIG. 9. CL of discharged Ge with ICl at 0.9 mTorr. Note the structure due to GeCl which was absent in Fig. 6. The sharp peaks are assigned from shorter wavelength to $A'{}^2\Delta_{3/2} - X{}^2\Pi_{1/2}$ and $A'{}^2\Delta_{5/2} - X{}^2\Pi_{3/2}$ transitions, and the longer wavelength structure to $A'{}^2\Sigma^+ - X{}^2\Pi$.

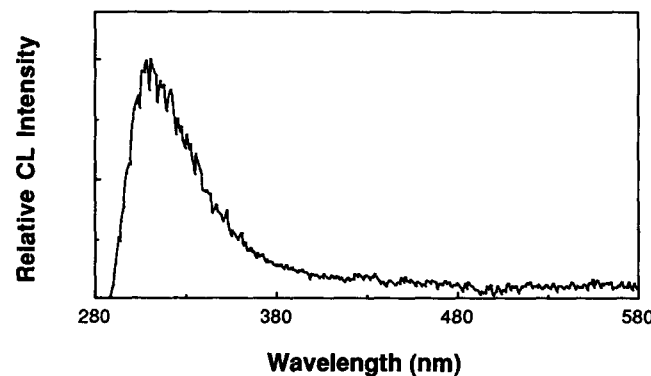


FIG. 10. CL of ground state Si with Cl₂ at 0.3 mTorr. The peak is assigned to SiCl₂ (¹B₁) emission.

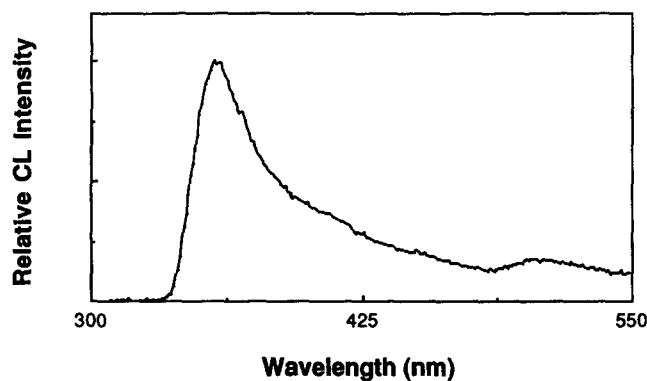


FIG. 11. CL of ground state Si with Br_2 at 0.35 mTorr. The shorter wavelength peak is assigned to SiBr_2 (1B_1) emission. The longer wavelength peak may be due to SiBr_2 (3B_1).

primarily responsible for the observed CL. While only the $^3B_1-^1A_1$ transition was observed for SnBr_2 , SnI_2 , GeBr_2 , and GeI_2 , in the case of SiBr_2 and SiI_2 , the $^1B_1-^1A_1$ transition was observed, but not the $^3B_1-^1A_1$ transition. The $^1B_1-^1A_1$ transition has been reported previously for SiBr_2 but not for SiI_2 . However, by analogy to the Sn and Ge series, the emission from SiI_2 can be safely assigned to the 1B_1 state (see Table I). Although a transition for the monohalide SiI is known to appear around 472 nm,²³ the fact that there is not enough energy to produce the excited state of SiI in a single collision and the observation that the reaction is second order in I_2 rule out the possibility that the emission was due to SiI .

Again, for the reaction of Si with ICl , only the 1B_1 state of the dihalide was produced, which is believed to be SiCl_2 for the same reason as in the case of Sn and Ge. In addition, the transition has been reported before to be in the same spectral region of 330 nm as observed in the present study, which is shown in Fig. 13(a). This spectrum was taken at relatively high ICl pressure, namely, 5×10^{-4} Torr, where only the emission of the dihalide appeared. However, another spectrum taken at $P_{\text{ICl}} = 1 \times 10^{-4}$ Torr [Fig. 13(b)] shows additional sharp features in the 390 nm region suggestive of possible diatomic transitions. The possibility that the sharp features were quenched at higher pressures by collisional relaxation was explored by taking the CL emission

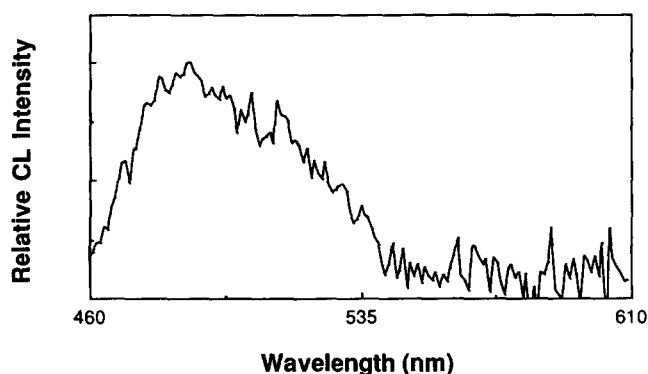


FIG. 12. CL of ground state Si with I_2 at 0.2 mTorr. The major peak is assigned to SiI_2 (1B_1) emission.

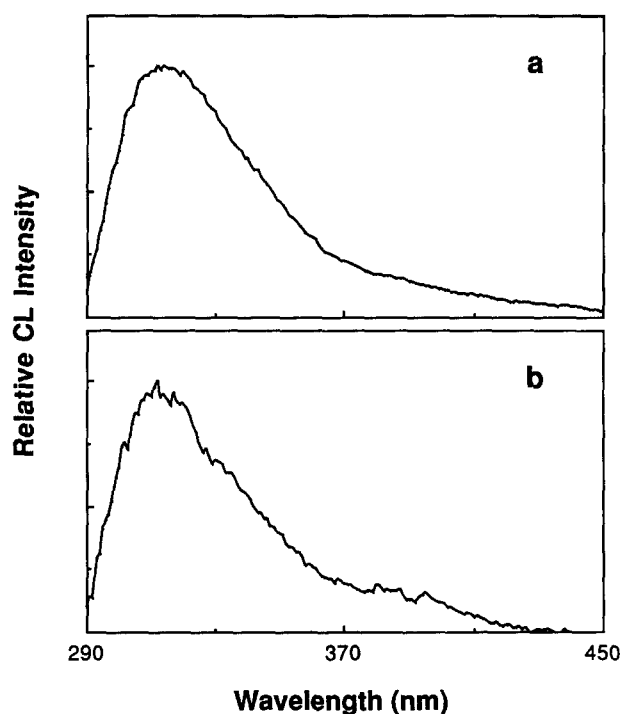


FIG. 13. CL of ground state Si with ICl at (a) 0.5 mTorr and (b) 0.1 mTorr. The major peak is assigned to SiCl_2 (1B_1) emission. Note the increased structure in the lower pressure spectrum which is attributable to SiCl ($A^2\Sigma^+$) emission, which may be collisionally quenched in the higher pressure spectrum.

spectrum in the presence of N_2 . A spectrum taken at $P_{\text{ICl}} = 1 \times 10^{-4}$ Torr and $P_{\text{N}_2} = 4 \times 10^{-4}$ Torr was identical to that taken with ICl only with $P_{\text{ICl}} = 1 \times 10^{-4}$ Torr. Therefore, the CL product with emission at about 390 nm is most likely quenched at higher ICl pressure by reaction to form SiCl_2 . Thus, we seem to have identified a system undergoing the two-step abstraction mechanism in which direct observation of the intermediate monohalide is possible.

IV. CONCLUSIONS

Group IV A elements react with halogens to produce a variety of CL states, dictated largely by the available energy. Monohalide emission from a single-step abstraction can be produced or enhanced by employing the 1D atomic states in the more exothermic reactions with F_2 , ICl , and Cl_2 . Dihalide emission following a two-step abstraction occurs with all of the halogens except F_2 . The tendency for ICl to give more monochloride, as well as dichloride, emission than Cl_2 can be attributed to the greater exoergicity of both abstraction reactions. Finally, the lowest excited triplet and singlet states of the Ge and Sn dihalides are readily observable, but apparently the radiative lifetimes of the triplet Si dihalides are too long for observation in our apparatus.

ACKNOWLEDGMENT

Support of the National Science Foundation under Grant No. CHE-8611966 is gratefully acknowledged.

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