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Chemiluminescence of alkaline earth monohalides in the collisions of ground state Ca, Sr, and Ba atoms with Cl_2, Br_2, I_2, ICl, and IBr

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Abstract. Formation of electronically excited alkaline earth monohalides MX^* in the reactions of ground state Ca, Sr, and Ba atoms with Cl_2, Br_2, I_2, ICl, and IBr was studied in a beam-gas arrangement. The MX^* spectra were observed for all the reactive systems with the exception of Ca, Sr + I_2. The energy balance indicates that MX^* can be formed in a single-collision exchange reaction; also the dependence of MX^*-chemiluminescence intensity on halogen gas pressure is typical of a bimolecular process. The MX^*-chemiluminescence cross sections and lower limits of photon yields are estimated.

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1 Introduction

Chemiluminescent reactions of ground state alkaline earth atoms $M(^1S_0)$ with diatomic halogens X_2 were first reported by Jonah and Zare [1]. The $M + X_2$ systems were later studied intensively [2–29]; results published before 1980 were reviewed in references [30–33].

The reactions of ground state Ca, Sr, and Ba atoms with diatomic halogens lead to the following product channels [1–27,29,34]:

$$\begin{aligned} M(^1S_0) + X_2 \rightarrow\ & MX(X^2\Sigma^+) + X, & (1)\\ & MX^*(A\,^2\Pi, B\,^2\Sigma^+, C\,^2\Pi) + X, & (2)\\ & MX^+(^1\Sigma^+) + X^-, & (3)\\ & MX_2^* \rightarrow MX_2 + h\nu, & (4)\end{aligned}$$

where equation (1) represents formation of ground state monohalide products, channel (2) gives electronic chemiluminescence (CL) of MX molecules, equation (3) describes chemi-ionization, and channel (4) corresponds to the radiative two-body recombination of M and X_2. The present work concentrates on the process (2).

Recently it was reported [24,27] that in the reactions of $M(^1S_0)$ with X_2, the MX^* emission for MCl, MBr, and MI may result from the dissociation of MX_2^* collision complex and therefore the MX-bond energy determinations based on observation of chemiluminescence of the monohalides (given the energy balance of Eq. (2)) are not reliable. This claim was supported by the examples of Sr + Cl_2, Br_2 reactions, which yield $SrCl^*$ or $SrBr^*$, respectively, although channel (2) for these systems was found to be endoergic. The conclusions of references [24,27] cast a doubt on a widely accepted method of estimation of dissociation energies of MX radicals. The present work attempts to clarify this problem by recording chemiluminescence spectra for 15 different $M + X_2$ systems under single-collision conditions and investigating if there is any MX^* chemiluminescence that can not be explained by the energy balance of equation (2).

Absolute rates of formation of electronically excited products (chemiluminescence cross-sections σ_{CL}) can be derived from chemiluminescence spectra by cross-calibration of the measured signals to a chemiluminescent reaction with known σ_{CL} value. The $Mg^*(^3P_J) + I_2$ reaction can serve as a reference, as its σ_{CL} value was obtained rather precisely [22] using the experimental procedure of references [35,36].

2 Experimental

The experiments were performed in a beam-gas arrangement. The stainless steel oven of the beam source was equipped with an iron-sheath insulated heater. Electrical connections of the oven were carefully screened to prevent production of alkaline earth atoms in the metastable states. The temperature of the oven was $T_0 = 1080$ K for Ca, 1030 K for Sr, and 1130 K for Ba, as measured with a chromel-alumel thermocouple. All metals were supplied by Aldrich. The scattering cell ($T = 350$ K) with a quartz window was mounted above the beam source. Halogens (Aldrich) were put into a Pyrex trap and processed

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twice in a freeze-pump-thaw cycle. For scanning of chemiluminescence spectra, the containers were thermostated and gases were admitted *via* a manometer-controlled valve (Granville-Phillips model 245) to the scattering cell at pressure of 0.16 Pa, as measured with a capacitance manometer (MKS Baratron model 120AD-00001RAU). Chemiluminescence spectra were recorded using a Carl Zeiss Jena SPM-2 grating monochromator (focal length 0.4 m; 651 l/mm grating, blazed for $\lambda_B = 570$ nm) and a photon counting system (type SR-400 with an SR 445 preamplifier) equipped with a Burle C31034 phototube in a cooled housing ($T = 250$ K). All spectra were accumulated in a microcomputer and corrected for the wavelength-dependent sensitivity of the detecting system, determined with an Osram Wi 17/G tungsten band lamp. The measurements of pressure dependence of the chemiluminescence intensity were made using a mask mounted on the window of the scattering cell; this mask fixed the beam path length in the gas at $x = (21 \pm 1.5)$ mm. The latter measurements were performed with a monochromator selectively ($\Delta\lambda = 6$ nm) transmitting the strongest band of a given monoiodide emission; the pressure dependence of the background pseudo-continuum emission was also recorded using proper glass filters (Andover) instead of the monochromator.

For calibration of the chemiluminescence cross-sections, the $Mg^*(^3P_J) + I_2$ reaction was used, because the $Mg(^3P_1{-}^1S_0)$ transition probability is well-known (see Ref. [37]). To produce the metastable $Mg^*(^3P_J)$ atoms, we struck a discharge (8 V; 0.8 A) between the tip of the oven and a hot tungsten wire cathode mounted a few millimeters above the beam source. The power supplies of the discharge and of the cathode could be switched off or on, varying the beam composition from the pure ground state $M(^1S_0)$ to that with a metastable content. For a similar beam source as that used in the present work, the fraction of $Mg^*(^3P)$ metastables was found to be 20% [38] and this value is used here because we lack facilities to measure the metastable conversion efficiency. The temperature of magnesium beam source was $T_0 = 900$ K. The relative concentrations in the beams of different alkaline earth atoms were determined under the assumption that the field of number density distribution of the atoms depends only on the number density of atoms in the oven, *i.e.* it is scaled like (p_0/T_0) [39]. The temperature of the oven, T_0, could be determined with precision ±10 K, however, the metal vapor pressure inside the oven, p_0 (derived from the T_0 value using formulas of Ref. [40]), has a rather large error. The σ_{CL}-values were obtained from spectrally corrected chemiluminescence recordings by integration of photon counts corresponding to a given spectral MX^*-feature (with background pseudo-continuum MX_2^*-emission subtracted). The sums of counts were compared with the total of photon counts of the corrected CL emission observed for the reference $Mg^* + I_2$ reaction. It is estimated that the uncertainty of the chemiluminescence cross sections is about the factor of 2, when comparing the data for Ca, Sr, and Ba. The uncertainty is much lower when comparing σ_{CL} values for the same metal reacting with different gases. The relative proportions of light production in the $M + X_2$, XY reactions were compared in a single experimental run for a given M, when all target gases studied were put one after another into the scattering cell and the CL signals were recorded; this procedure was repeated three times and the relative light intensities were consistent within 15%.

Table 1. Average reactant energies in the experiment, $\langle E_{tr}\rangle + \langle E_{int}\rangle$, (in kJ/mol).

	$\langle E_{tr}\rangle + \langle E_{int}\rangle^{(a)}$		
Reactants	Ca	Sr	Ba
Cl_2	15	13	12
Br_2	17	15	14
I_2	17	16	16
ICl	17	16	16
IBr	17	16	16

(a) uncertainty ≤ 3 kJ/mol.

Table 2. Dissociation energies of alkaline earth monohalides MX used in the present work (all values in kJ/mol).

M X	Ca	Sr	Ba
Cl	$406 \pm 10^{(a)}$	$401 \pm 13^{(b)}$	$445 \pm 12^{(c)}$
Br	$348 \pm 10^{(a)}$	$333 \pm 10^{(d)}$	$400^{(c)}$
I	$281 \pm 8^{(e)}$	$286 \pm 6^{(f)}$	$319 \pm 6^{(e)}$

(a) Ref. [43]; (b) Ref. [44]; (c) Ref. [45] the value is given without uncertainty limits; (d) Ref. [46]; (e) Ref. [47]; (f) Ref. [48].

3 Energetics

The sums of average collision and internal energies of the reactants, $\langle E_{tr}\rangle + \langle E_{int}\rangle$, are given in Table 1. The values were calculated as described in reference [41]. The bond strengths $D_0(X_2)$ of Cl_2, Br_2, I_2, ICl, and IBr are 243, 194, 153, 211, and 179 kJ/mol, respectively (all data from Ref. [42]; uncertainties ≤ 0.4 kJ/mol). The literature values of dissociation energies of alkaline earth monohalides vary in a wide range. For the specific purpose of this work we do not use the data obtained from the observation of MX^* chemiluminescence. Table 2 collects the most reliable (in our opinion) $D_0(MX)$-values obtained by laser spectroscopy or mass spectroscopy. Electronic energy terms $T_{0i}(MX)$ were taken from reference [44].

4 Results and discussion

Chemiluminescence spectra from collisions of ground state Ca, Sr, and Ba atoms with Cl_2, Br_2, I_2, ICl, and IBr, recorded at the target gas pressure of 0.16 Pa, are shown in Figure 1 (for homonuclear targets) and in Figure 2 (for heteronuclear targets). Spectra of this kind were reported

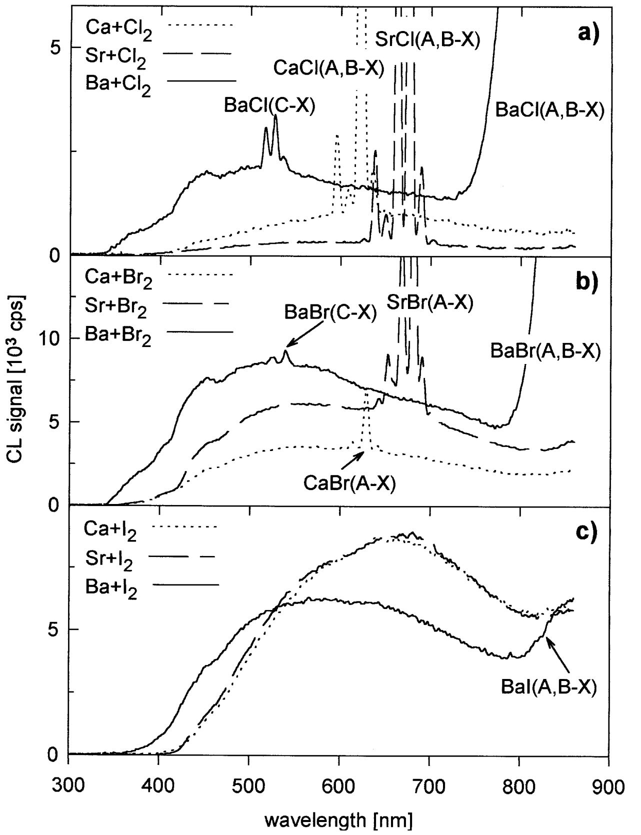

Fig. 1. Chemiluminescence spectra in the $\lambda = 300-870$ nm range for Ca, Sr, Ba + X_2 reactions at X_2-pressure of 0.16 Pa. Target gas: (a) Cl_2; (b) Br_2; (c) I_2. Spectral resolution: 6.0 nm. The contours are corrected for the spectral sensitivity of the detection system.

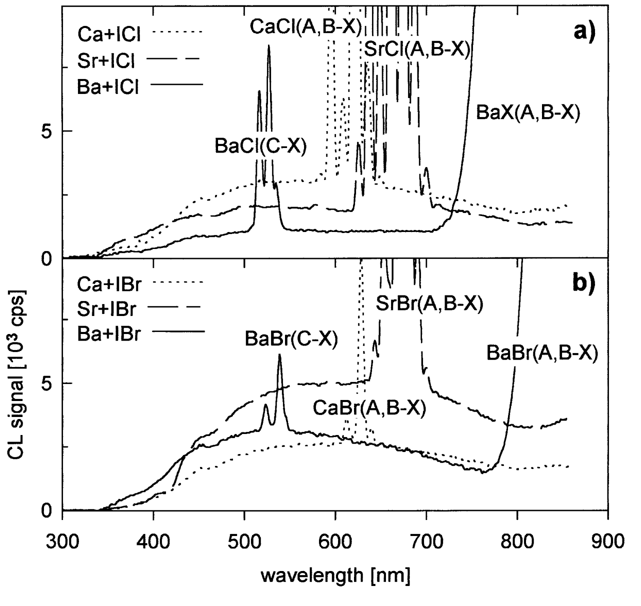

Fig. 2. Chemiluminescence spectra in the $\lambda = 300-870$ nm range for Ca, Sr, Ba+XY reactions at XY-pressure of 0.16 Pa. Target gas: (a) ICl; (b) IBr. Spectral resolution: 6.0 nm. The contours are corrected for the spectral sensitivity of the detection system.

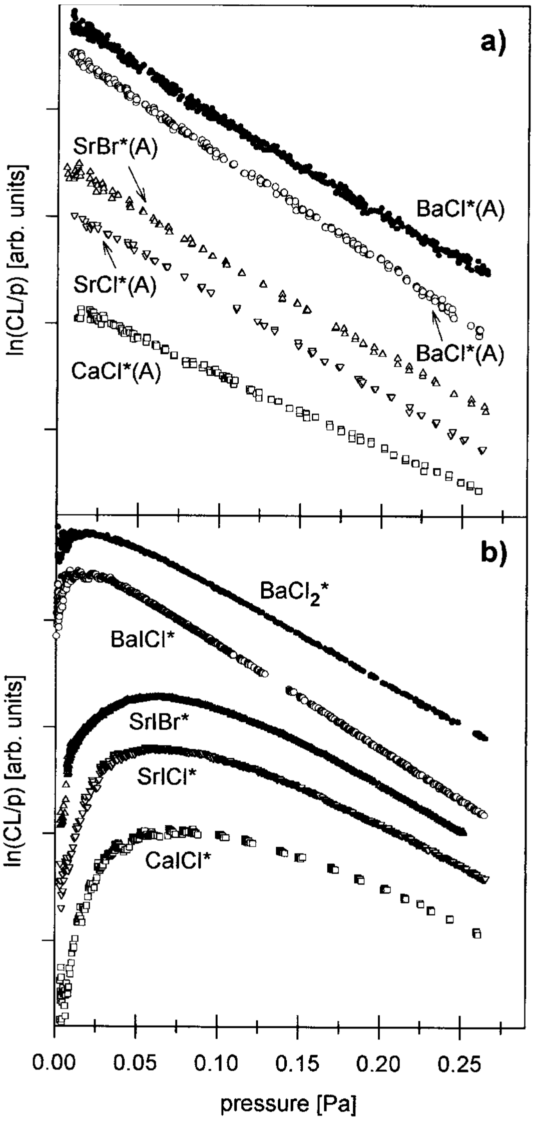

Fig. 3. Semilogarithmic plots of pressure dependence of chemiluminescence intensity per unit pressure for selected reactive systems: (a) $MX^*(A\,^2\Pi - X\,^2\Sigma^+)$ chemiluminescence; (b) MX_2^* (or MXY^*) chemiluminescence pseudo-continuum. Shown from the top in the same order in both boxes for: Ba + Cl_2 reaction (full circles), Ba + ICl (circles), Sr + IBr (triangles), Sr + ICl (reversed triangles), and Ca + ICl (squares). The plots are arbitrarily shifted up and down for clarity.

previously for some systems belonging to the MX_2 family, but they were usually recorded in the spectral region limited to the visible (see *e.g.* [1,13]) until the recent systematic study [23]. The spectra in Figures 1 and 2 cover 15 combinations of reactants, compared with 12 systems presented in reference [23] (where they were not recorded consistently in the same wavelength region and were shown without correction for the spectral response of the detection system).

With the exception of the chemiluminescence for M + I_2 systems, the spectra in Figures 1 and 2 consist of rather narrow bands of alkaline earth monohalides

Table 3. Exoergicity ΔE_i (in kJ/mol) of the ith electronic state of MX^* product formed in the $M(^1S_0) + X_2$, XY reactions$^{(a)}$.

Target	Product/State		CaX*	SrX*	BaX*
Cl_2	MCl^*	A $^2\Pi$	-15 ± 13 (*)	-6 ± 16 (*)	90 ± 15 (*)
		B $^2\Sigma$	-24 ± 13 (*)	-17 ± 16 (*)	72 ± 15 (*)
		C $^2\Pi$	-139 ± 13	-131 ± 16	-14 ± 15 (*)
Br_2	MBr^*	A $^2\Pi$	-19 ± 13 (*)	-22 ± 13 (*)	101 (*)
		B $^2\Sigma$	-25 ± 13	-30 ± 13	85 (*)
		C $^2\Pi$	-132 ± 13	-137 ± 13	-3 (*)
I_2	MI^*	A $^2\Pi$	-41 ± 11	-24 ± 9	71 ± 9 (*)
		B $^2\Sigma$	-43 ± 11	-28 ± 9	57 ± 9 (*)
		C $^2\Pi$	-134 ± 11	-122 ± 9	-31 ± 9
ICl	MI^*	A $^2\Pi$	-99 ± 11	-82 ± 9	13 ± 9 (*)
		B $^2\Sigma$	-101 ± 11	-86 ± 9	-1 ± 9 (*)
		C $^2\Pi$	-192 ± 11	-180 ± 9	-89 ± 9
	MCl^*	A $^2\Pi$	19 ± 13 (*)	29 ± 16 (*)	126 ± 15 (*)
		B $^2\Sigma$	10 ± 13 (*)	18 ± 16 (*)	108 ± 15 (*)
		C $^2\Pi$	-105 ± 13	-96 ± 16	22 ± 15 (*)
IBr	MI^*	A $^2\Pi$	-67 ± 11	-50 ± 9	45 ± 9 (*)
		B $^2\Sigma$	-69 ± 11	-54 ± 9	31 ± 9 (*)
		C $^2\Pi$	-160 ± 11	-148 ± 9	-57 ± 9
	MBr^*	A $^2\Pi$	-4 ± 13 (*)	-6 ± 13 (*)	118 (*)
		B $^2\Sigma$	-10 ± 13 (*)	-14 ± 13 (*)	102 (*)
		C $^2\Pi$	-117 ± 13	-121 ± 13	14 (*)

$^{(a)}$ based on the average reactant energies, $\langle E_{\rm tr}\rangle + \langle E_{\rm int}\rangle$, from Table 1, bond strengths from Table 2, and the molecular energy terms from reference [44]; a positive value of ΔE_i means that the channel is exoergic; an asterisk in parentheses labels emissions observed in this work.

superimposed on a broad pseudo-continuum emission. As identified in references [1,23,24], the latter is due to the triatomic MX_2^* (or MXY^*) molecules which, as found in references [22,29], are formed simultaneously in two different ways, by radiative two-body recombination [1]:

$$M + X_2 \rightarrow MX_2^* \tag{5}$$

and by the two-step chemiluminescent reaction *via* vibrationally excited $MX^\dagger$ [30]:

$$M + X_2 \rightarrow MX^\dagger + X, \tag{6}$$

$$MX^\dagger + X_2 \rightarrow MX_2^* + X, \tag{7}$$

where the second step (7) is much faster than the first one (6). The long-wavelength limit of the pseudo-continuum always extends above 870 nm. One can note that of the known CaX^* and SrX^* emissions in the visible, these associated with monoiodides are generally absent. For the barium reactions (with the exception of $Ba + I_2$), there is a very strong BaX(A, B–X) spectrum and a much weaker BaX(C–X) emission. Other than reported in reference [13], no BaI(C–X) emission was observed from $Ba+I_2$ collisions; a possible explanation of this discrepancy is that in reference [13] a small admixture of Ba atoms in the metastable states disturbed the chemiluminescence spectrum for the ground state Ba reaction with I_2.

Reactions exoergicities ΔE_i were calculated from the equation:

$$\Delta E_i = D_0(MX) + \langle E_{\rm tr}\rangle + \langle E_{\rm int}\rangle - D_0(X_2) - T_{0i}(MX). \tag{8}$$

The results are collected in Table 3. The observed MX^*-emissions are marked by an asterisk next to the channel exoergicity. One has to keep in mind that the values in Table 3 are valid for the *average* reactant energies, while some reactants have higher collision energies due to the Maxwellian velocity distribution in the atomic beams. We estimate that there can be a detectable contribution to the chemiluminescence from reactant pairs for which $\langle E_{\rm tr}\rangle$ is exceeded by (12 ± 1) kJ/mol, (11 ± 1) kJ/mol, and (9 ± 1) kJ/mol in the reactions of Ca, Sr, and Ba, respectively (the values have an uncertainty bracket, because they slightly depend on the $M + X_2$ combination). Taking this into account while examining Table 3, one finds that there is no MX^* chemiluminescence violating the energy balance of equation (2) and therefore there is no need to introduce a mechanism of MX^* production other than a single-collision exchange reaction (2). The contrary conclusions of references [24,27] were based in part on some older values of the dissociation energies of MX, in particular those from reference [6] which are presently known to be distorted by the reactions involving metastable alkaline earth atoms [30]. The idea of references [24,27] that MX^* radicals are formed by dissociation of a long-lived

Table 4. Chemiluminescence cross-sections σ_{CL} (in 10^{-20} m^2) and photon yields Φ_{CL} (in %) of alkaline earth monohalides MX* produced in the $\mathrm{M}(^1\mathrm{S}_0) + \mathrm{X}_2$, XY reactions.

Reaction	σ_{CL}		Φ_{CL}	
	This work	Previous	This work	Previous
$\mathrm{Ca} + \mathrm{Cl}_2 \rightarrow \mathrm{CaCl}^*(\mathrm{A{+}B}) + \mathrm{Cl}$	0.008		0.008	$0.03^{(\mathrm{c})}$
$\mathrm{Ca} + \mathrm{Br}_2 \rightarrow \mathrm{CaBr}^*(\mathrm{A{+}B}) + \mathrm{Br}$	0.001		0.001	$0.03^{(\mathrm{c})}$
$\mathrm{Ca} + \mathrm{I}_2 \rightarrow \mathrm{Cal}^*(\mathrm{A{+}B}) + \mathrm{I}$	0	$0^{(\mathrm{d,e})}$	0	$0^{(\mathrm{d,e})}$
$\mathrm{Ca} + \mathrm{ICl} \rightarrow \mathrm{CaCl}^*(\mathrm{A{+}B}) + \mathrm{I}$	0.04	$0.045^{(\mathrm{f})}$	0.03	$0.034^{(\mathrm{f})}$
$\mathrm{Ca} + \mathrm{IBr} \rightarrow \mathrm{CaBr}^*(\mathrm{A{+}B}) + \mathrm{I}$	0.004	$0.011^{(\mathrm{f})}$	0.003	$0.011^{(\mathrm{f})}$
$\mathrm{Sr} + \mathrm{Cl}_2 \rightarrow \mathrm{SrCl}^*(\mathrm{A{+}B}) + \mathrm{Cl}$	0.014		0.009	$0.07^{(\mathrm{g})}$
$\mathrm{Sr} + \mathrm{Br}_2 \rightarrow \mathrm{SrBr}^*(\mathrm{A{+}B}) + \mathrm{Br}$	0.02		0.01	$0.06^{(\mathrm{g})}$
$\mathrm{Sr} + \mathrm{I}_2 \rightarrow \mathrm{SrI}^*(\mathrm{A{+}B}) + \mathrm{I}$	0	$0^{(\mathrm{d,e})}$	0	$0^{(\mathrm{d,e})}$
$\mathrm{Sr} + \mathrm{ICl} \rightarrow \mathrm{SrCl}^*(\mathrm{A{+}B}) + \mathrm{I}$	0.07		0.04	
$\mathrm{Sr} + \mathrm{IBr} \rightarrow \mathrm{SrBr}^*(\mathrm{A{+}B}) + \mathrm{I}$	0.025		0.015	
$\mathrm{Ba} + \mathrm{Cl}_2 \rightarrow \mathrm{BaCl}^*(\mathrm{A{+}B}) + \mathrm{Cl}$	> 0.14		> 0.08	$5.0^{(\mathrm{h})}$
$\mathrm{BaCl}^*(\mathrm{C}) + \mathrm{Cl}$	0.001			
$\mathrm{Ba} + \mathrm{Br}_2 \rightarrow \mathrm{BaBr}^*(\mathrm{A{+}B}) + \mathrm{Br}$	> 0.10		> 0.06	$2.3^{(\mathrm{h})}$; $0.6^{(\mathrm{i})}$
$\mathrm{BaBr}^*(\mathrm{C}) + \mathrm{Br}$	0.0002		0.0001	$0.011^{(\mathrm{i})}$
$\mathrm{Ba} + \mathrm{I}_2 \rightarrow \mathrm{BaI}^*(\mathrm{A{+}B}) + \mathrm{I}$	> 0.01		> 0.005	$3.6^{(\mathrm{h})}$
$\mathrm{BaI}^*(\mathrm{C}) + \mathrm{I}$	0	$> 0^{(\mathrm{k})}$	0	$> 0^{(\mathrm{k})}$
$\mathrm{Ba} + \mathrm{ICl} \rightarrow \mathrm{BaX}^*(\mathrm{A{+}B}) + \mathrm{I}$	> 0.36		> 0.18	
$\mathrm{BaCl}^*(\mathrm{C}) + \mathrm{I}$	0.005		0.002	$> 0^{(\mathrm{m})}$
$\mathrm{Ba} + \mathrm{IBr} \rightarrow \mathrm{BaX}^*(\mathrm{A{+}B}) + \mathrm{I}$	> 0.10		> 0.05	
$\mathrm{BaBr}^*(\mathrm{C}) + \mathrm{I}$	0.003		0.002	$> 0^{(\mathrm{m})}$

[a] determined using the experimental method of Refs. [35,36]; [b] $\Phi_{\mathrm{CL}} = \sigma_{\mathrm{CL}}/\sigma_{\mathrm{T}}$, the total collision cross-sections σ_{T} are taken from Ref. [29]; [c] Ref. [9] (flow system); [d] Ref. [22]; [e] Ref. [23]; [f] Ref. [25]; [g] Ref. [12] (flow system); [h] Ref. [11] (flow system); [i] Ref. [2] (flow system); [k] Ref. [13]; [m] Ref. [19].

MX$_2^*$ complex receives no support from the comparison of pressure dependence of chemiluminescence intensities for MX* and MX$_2^*$ (see Fig. 3). For these MX* emissions which provide sufficient light intensity for the measurement, the semilogarithmic plots of $[I_{\mathrm{CL}}(p)/p]$ *vs.* pressure (p) are all linear (Fig. 3a); this indicates (see Eq. (7) in Ref. [41] or the Appendix of Ref. [21]) a single-collision exchange reaction (in the plots of Fig. 3a, the underlying pseudo-continuum was subtracted from the total intensity recorded at the position of MX* bands). The pressure dependence of the MX$_2^*$ chemiluminescence (Fig. 3b) is quite different from that of the corresponding MX* and it denies the supposed parentage.

As described in the experimental section, the absolute cross-sections for chemiluminescence, σ_{CL}, were obtained by cross-calibration of the observed light intensity to that recorded from the reference reaction $\mathrm{Mg}^*(^3\mathrm{P}_J) + \mathrm{I}_2$. The results are given in the second column of Table 4 together with available literature data.

Dividing the chemiluminescence cross-sections, σ_{CL}, by the total collision cross-sections, σ_{M}, one obtains an estimate of the chemiluminescence yield. The results are shown in the third column of Table 4. The photon yields are all rather small, due to dynamical reasons presented in references [31–33]. The literature data of Φ_{CL} in Table 4 are all larger (sometimes even by an order of magnitude) than the ones obtained in the present work, however, in the past they were obtained mostly in the flow systems, where the rates of chemiluminescence could be overestimated due to a contribution from the reactions of alkaline earth atoms in the metastable states, $\mathrm{M}^* + \mathrm{X}_2$. The photon yields of the latter can be as high as 40% [36] and even a tiny fraction of M*-metastables can easily distort the results for $\mathrm{M} + \mathrm{X}_2$.

5 Conclusion

In the past, electronic chemiluminescence of alkaline earth monohalides, MX*, was observed on numerous occasions when a beam of alkaline earth atoms in the ground state met a low-density dihalogen gas target, X$_2$. Recent reports [24,27] attributed the light emission (at least for some MX*) to the dissociation of MX$_2^*$ collision complex. The present work proves the contrary, namely that the MX* radicals are formed in a single collision exchange reaction $\mathrm{M} + \mathrm{X}_2 \rightarrow \mathrm{MX}^* + \mathrm{X}$. This conclusion is based on a chemiluminescence study supported by consideration of energy balance for 15 systems belonging to the $M + X_2$ family. In addition, the MX^* photon yields are estimated.

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