# Electronic Energy Partitioning in the Reactions of Metastable Mg*($^3P_J$) Atoms with $F_2$, $Cl_2$, $Br_2$, $I_2$, ICl, IBr

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Chemiluminescent reactions of metastable Mg*($^3P_J$) atoms with $F_2$, $Cl_2$, $Br_2$, $I_2$, ICl, IBr molecules were studied in a beam-gas experiment. For all homonuclear targets the MgX(A $^2\Pi$ - X $^2\Sigma^+$) emission was observed, but for ICl and IBr reactants the MgI(A-X) emission was absent and only MgCl(A-X) or MgBr(A-X) spectra were found. In addition, for the $I_2$, IBr, ICl, $Br_2$ reactions, broad pseudocontinua extend from above 400 nm into the infrared. These pseudocontinua are tentatively attributed to the MgI, MgBr (B' $^2\Sigma^+$ - X $^2\Sigma^+$) transition. The total attenuation cross sections, chemiluminescence cross sections and quantum yields were measured. The quantum yields are all below 5%. The results are analyzed using information theory. The low yields for the Mg* + $F_2$ system are explained by a barrier in the entrance channel. For other reactions the low yields are most probably caused by predissociation of the MgX*(A $^2\Pi$) products.

*Key words:* Chemiluminescence; Energy Transfer; Atomic Collisions; Molecular Collisions; Luminescence.
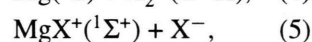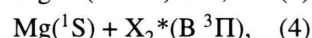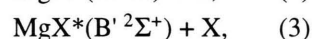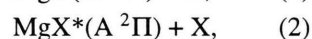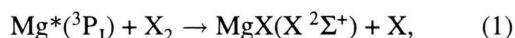
## 1. Introduction

Chemiluminescent (CL) reactions of metastable Mg*($^3P_J$) atoms with diatomic halogens $X_2$ in a beam-gas arrangement were reported previously for X = F [1, 2], for X = Cl [3 - 5], for X = F, Cl [6], for X = F, Cl, Br [7, 8] and for X = I [9, 10]. The systematic studies presented in [7, 8] served to construct a general model of the alkaline earth atom – halogen molecule reactions [11 - 13]. The present paper extends the previous works to the iodine-containing interhalogen targets IBr, ICl, apart from a renewed study of the homonuclear $F_2$, $Cl_2$, $Br_2$, $I_2$. The collisions of Mg*($^3P_J$) with $X_2$ or XY may produce MgX and MgY products in the electronic groundstate, different electronically excited CL emitters and MgX$^+$+X$^-$ chemi-ions.

The present work concentrates on the ground state and chemiluminescent states, neglecting chemi-ions whose contribution in the Mg* + $F_2$, $Cl_2$, $Br_2$ systems was found to be minor [7, 8]. An upper limit of the total reactive cross section is given by the total Mg* attenuation cross section $\sigma_T$, which can be readily determined. The rates of formation of the electronically excited products (CL cross sections, $\sigma_{CL}$)

can be derived with relatively high precision using the experimental procedure of [14, 15], if the transition probability of the Mg*($^3P_1$ - $^1S_0$) atomic line is known. This atomic line serves as an internal standard for measuring the number density of metastables.

Apart from the readily identifiable emission spectra from the MgX(A$^2\Pi$) state, the reactions with $Br_2$, $I_2$, IBr and ICl produce intense pseudocontinua extending from > 400 nm into the infrared, and a goal of this paper is to identify the processes responsible for these features.

The following bimolecular processes are energetically allowed:

$$Mg^*(^3P_J) + X_2 \rightarrow MgX(X\ ^2\Sigma^+) + X, \qquad (1)$$
$$MgX^*(A\ ^2\Pi) + X, \qquad (2)$$
$$MgX^*(B'\ ^2\Sigma^+) + X, \qquad (3)$$
$$Mg(^1S) + X_2^*(B\ ^3\Pi), \qquad (4)$$
$$MgX^+(^1\Sigma^+) + X^-, \qquad (5)$$

where (1) is the ground state channel, (2) corresponds to well known narrow-band chemiluminescence and (5) represents chemi-ionization. For X = I it was reported [10] that an additional chemiluminescence

channel (3) may be open, which accounts for the intense pseudocontinuum emission. Another possibility is the electronic energy transfer process (4), which will be considered below. The generalization of (1 - 5) to richer reactions involving heteronuclear targets is obvious.

When [6 - 8] were written, we believed that the proper value of the transition probability for magnesium is $A_{ki}(^3P_1 - {}^1S_0) = 455$ s$^{-1}$ (recommended in [16]) and this value served for the determination of $\sigma_{CL}$. As discussed already in [17], this value has a systematic error (pointed out in [18]) and the correct value of the transition probability is 225 s$^{-1}$. This change of the $A_{ki}$-value causes subsequently that for Mg*($^3P_J$) reactions with $F_2$, $Cl_2$, and $Br_2$ our previous $\sigma_{CL}$ data from [6 - 8] must be scaled down by a factor of two. The revised values of the $\sigma_{CL}$ as well as of photon yields are given here. In addition, the results of measurements performed later for the $Cl_2$ and $Br_2$ targets at somewhat higher collision energy are reported. Further, the investigation is expanded to the Mg* + interhalogen molecules ICl, IBr. The photon yields for all reactions are compared with prior expectation values obtained by the information theoretic approach [19].

A puzzling result of previous studies was the fact that the MgX* chemiluminescent channels, for which adiabatic correlations from reactant to product states exist, have relatively small quantum yields. This was originally explained as due to a barrier in the entrance channel. In the present paper, an alternative explanation is offered for the systems other than Mg* + $F_2$, based on the now well established predissociation in the MgX(A $^2\Pi$) state for X = Cl, Br, I.

## 2. Experiments

The experiments were performed at two laboratories, one in Toronto and another one in Gdansk. The Toronto experiment is described in detail in [7]. The beam source of metastable atoms was based on the original idea given in [20]. The oven was made of molybdenum and was surrounded by a cylindrical carbon heater. The temperature of the oven was 850 K. An electrical discharge (5 V, 0.8 A), struck between the grounded oven and a hot tungsten cathode mounted 5 mm above the beam orifice, produced an estimated fraction (as found for similar sources [20]) of 20% of magnesium atoms in the metastable $^3P_J$ states. Assuming a statistical

population of the Mg*($^3P_J$) levels in the discharge and using the radiative lifetime of the Mg*($^3P_1$) state, it was estimated that the radiating fraction of the $^3P_J$ reactants in the observed zone was equal to 0.33. A scattering cell with a quartz window was mounted 5 cm above the last collimating slit of the beam source. For cross section measurements, the window was covered, except for a slit that determined the effective scattering path length $L = (22 \pm 1.75)$ mm. Target gases ($F_2$, $Cl_2$, $Br_2$) were supplied from reservoirs via a line made of Monel alloy and were admitted to the scattering cell ($T = 300$ K) through a calibrated leak. The gas pressures used in the cell were in the 0 - 0.27 Pa range, as calculated from the leak conductance and backing pressures, measured with a Baratron capacitance manometer in the 0 - 133 Pa range. Chemiluminescence spectra were recorded by a 3/4 m SPEX monochromator equipped with an RCA-C31034 photomultiplier; for cross section measurements, a 0.3 m MINISPEX monochromator (spectral slitwidth 5 - 20 nm) was used. The spectral response of the detection system was calibrated with a standard tungsten lamp. The chemiluminescence cross sections were determined by graphic integration of the contours of the spectral features plotted.

In Gdansk, the experimental setup was very similar, with a few exceptions. The Monel gas-feeding line was substituted by teflon tubes. The oven of the metastable beam source was heated by an iron-sheath insulated heater (Selfa Poland) and had the temperature of 900 K. The operating conditions of the beam source discharge were identical to the Toronto experiment. The scattering cell ($T = 370$ K) was mounted above the beam source, and the effective scattering path length was $L = (28 \pm 1.75)$ mm. The chemicals were supplied by Aldrich. They were put into a pyrex trap, placed in liquid nitrogen, and pumped. The pump-freeze procedure was repeated several times. After this initial preparation, the chemicals were thermostated and admitted via a manometer-controlled valve (Granville-Phillips model 245) to the scattering cell at pressures up to 0.27 Pa as measured directly with a capacitance manometer (MKS Baratron model 120AD-00001RAU). The chemiluminescence spectra were recorded with a Carl Zeiss Jena SPM-2 grating monochromator (focal length 0.4 m; 651 l/mm grating, blazed at 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 scanned spectra

Table 1. Dissociation energies, $D_0{}^\circ$, electron affinities, E. A., of target molecules, reactant collision energies, $\langle E_{tr}\rangle$ + $\langle E_{int}\rangle$, (all values in kJ/mol) and effective collision temperatures $T_{eff}$ (in K) for the Mg* + X$_2$, XY systems studied.

| Molecule | $D_0{}^\circ$ [a] | E.A. [b] | $\langle E_{tr}\rangle$ + $\langle E_{int}\rangle$ | $T_{eff}$ |
|---|---|---|---|---|
| F$_2$ | 155 | 297 ± 10 | 10 | 635[c] |
| Cl$_2$ | 239 | 230 ± 10 | 11 | 710[c]; 765[d] |
| Br$_2$ | 190 | 246 ± 10 | 12 | 777[c]; 830[d] |
| I$_2$ | 149 | 246 ± 5 | 15 | 854[d] |
| ICl | 208 | 274 ± 15[e] | 13 | 831[d] |
| IBr | 173 | 246 ± 10 | 14 | 844[d] |
| MgF | 458 | | | |
| MgCl | 325[f] | | | |
| MgBr | 316[g] | | | |
| MgI | 282 | | | |

[a] from [21], if not indicated otherwise; [b] from [22]; if not indicated otherwise; [c] in the Toronto laboratory, where $T$(Mg) = 850 K, $T$(X$_2$) = 300 K; [d] in the Gdansk laboratory, where $T$(Mg) = 900 K, $T$(X$_2$, XY) = 370 K; [e] from [23]; [f] from [5]; [g] [21] gives $D_0{}^\circ$ < 323 kJ/mol, while [7] gives $D_0{}^\circ$ > 287 kJ/mol; we take $D_0{}^\circ$ = 315 kJ/mol, because this value fits best the trends in predissociation of the A $^2\Pi$ state and in the dissociation energies of MgX (X = Cl → Br → I).

were accumulated in a microcomputer and corrected for the wavelength-dependent sensitivity of the detecting system. This calibration was done with an Osram Wi 17/G tungsten band lamp. The measurements of the pressure dependence of the intensity of CL were performed using either the monochromators with wide open slit (for the MgX(A-X) emission) or using proper glass filters (Andover) and a bare InGaAs photomultiplier (for the pseudocontinuum); during the measurements, the data points were stored together with automatized pressure readings. The background light signal from the cathode of the metastable beam source increased with wavelength and constituted ~50% of the total signal at 870 nm, at the target gas pressure of 0.26 Pa. This background signal was always subtracted from the spectra or from the overall signal of CL intensity.

## 3. Energetics

Table 1 contains the dissociation energies of the reactant and product molecules involved, the electron affinities for calculating the harpooning cross sections, the sums of average collision and internal energies of the target gases (determined as described in [7]) and the effective collision temperatures. The electronic energy terms of alkaline earth monoiodides were taken from [21], the energy levels of magnesium from [24].
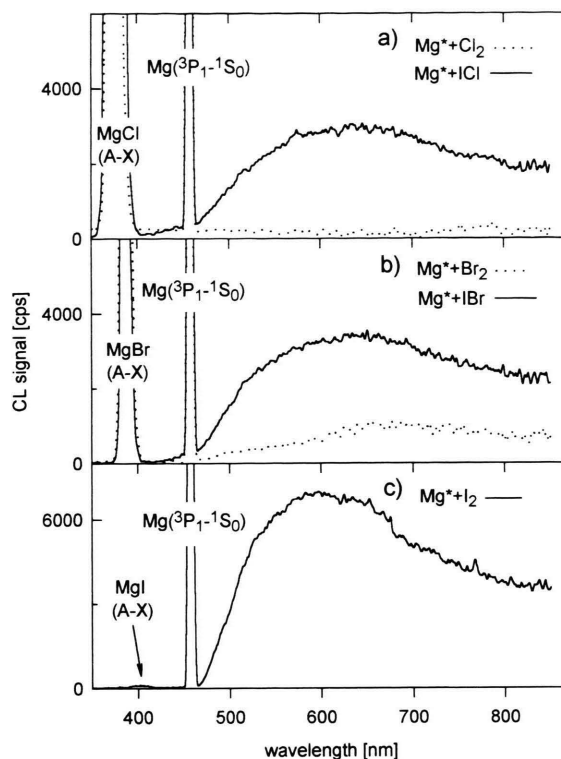


Fig. 1. Chemiluminescence spectra from Mg*($^3$P$_J$) + ICl, IBr, I$_2$ reactions in the $\lambda$ 350 - 870 nm range at target gas pressure of 0.16 Pa. Spectral resolution: $\Delta\lambda$ = 6 nm. The contours are corrected for the spectral response of the detection system.

## 4. Results and Discussion

The CL spectra of the Mg* + Cl$_2$, Br$_2$, I$_2$, ICl, and IBr systems are shown in Figure 1. The dominant features of the spectra obtained with I$_2$, ICl, and IBr are broad pseudocontinua extending from ca. 400 nm into the infrared. The continuum is weaker for the Mg* + Br$_2$ reaction, where the maximum is shifted to longer wavelengths, and it does not appear at all in the Mg* + Cl$_2$, F$_2$ systems [7].

Pseudocontinua of similar appearance were previously observed in the related reactions M($^1$S) + X$_2$ of groundstate alkaline earth atoms with dihalogens [25 - 27], where the dependence of the emission intensity on target gas pressure in the pressure range of 0.1 - 10 mPa indicated the presence of bimolecular and third order contributions through terms linear and quadratic in pressure. The possible nature of the surprisingly fast third order processes was discussed in [11, 12, 26 - 28]. In the present experiments, how-
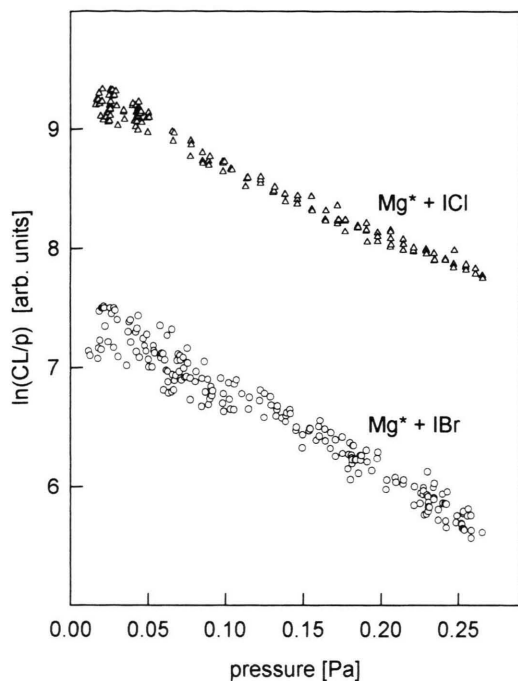
Fig. 2. Semilogarithmic plots of the pressure dependence of the chemiluminescence intensity per unit pressure for the pseudocontinuum resulting from Mg*($^3P_J$) + ICl and Mg($^3P_J$) + IBr reactions.

ever, there is no evidence of third order processes. As reported in [10], the broadband emission from Mg* + $I_2$ shown in Fig. 1c depends linearly on $I_2$ pressure below 50 mPa. The same is true for Mg* + ICl and Mg* + IBr systems, as shown in Figure 2. A high light background from the cathode of the beam source prevented reliable measurements of the Mg* + $Br_2$ pressure dependences.

Bimolecular processes that could produce the continuum emitters are: (a) formation of MgI, MgBr in new (B' $^2\Sigma^+$) states, (b) electronic energy transfer to the $X_2^*$(B $^3\Pi_{O+}$) state, and (c) formation of $MgX_2^*$ by radiative two-body recombination. R2BR can be excluded for two reasons. First, the relatively large cross sections for forming the continuum emitter from $I_2$, IBr, ICl, $Br_2$ (Table 2) is inconsistent with reasonable estimates of cross sections for $MX_2^*$ complex formation and its unimolecular and radiative lifetimes. The second reason is the energetics of the process [10]: magnesium dihalides are more weakly bound than the other alkaline earth dihalide molecules.

The non-reactive electronic energy transfer (4) to the halogen molecule is energetically allowed in all

present systems. Among the known bound states, the $X_2^*$(B $^3\Pi_{O+}$) state appears to be the most suitable receptor state that would, if sufficiently excited vibrationally, emit over a broad wavelength range due to a substantial difference of equilibrium internuclear distances and vibrational constants relative to the groundstate. Energy conservation predicts for the $X_2^*$(B $^3\Pi_{O+}$) state the following maximum values of vibrational energy (in kJ/mol), vibrational state $v'$ and minimum wavelength of emission $\lambda_{min}$ (in nm), respectively, for: $F_2^*$ (137; 27; 440), $Cl_2^*$ (66; 20; 438), $Br_2^*$ (84; 42; 437), $I_2^*$ (88; 59; 432), IBr* (83; 48; 434), ICl* (67; 26; 435). Given the difference in spectroscopic constants between upper and lower states and the possible high levels of vibrational excitation, it is plausible that the expected emission spectra would be as broad as the observed ones. However, the absence of the pseudocontinua from the Mg* + $Cl_2$ and Mg* + $F_2$ systems casts some doubt on this energy transfer mechanism, since the same receptor states are readily available in the $Cl_2$ and $F_2$ molecules. Also, the observed short wavelength cutoffs for IBr and ICl lie somewhat below the calculated ones.

As discussed [10] for the Mg* + $I_2$ system, the pseudo-continuum may also be due to the MgX(B' $^2\Sigma^+$ - X $^2\Sigma^+$) transition, similar to that observed earlier for HgX [29] or group IIIA monohalide cations [30]. It should be noted that the emitting B' $^2\Sigma^+$ state (labelled B $^2\Sigma^+$ in the isoelectronic group IIIA monohalide cations AX$^+$) is *not* the analog of the well known, lowest (B $^2\Sigma^+$ - X $^2\Sigma^+$) transition in alkaline earth molecules [30]. But its presence in MX is required by correlation rules. A schematic diagram of potential energy curves for the MgI molecule is given in Figure 3. The B' $^2\Sigma^+$ state arises from the ionic ground state asymptote Mg$^+$($^2$S) + I$^-$($^1$S) and has a minimum due to the avoided crossing with the Mg($^1$S) + I($^2$P) potential curve. The equilibrium distance $r_e$ of the MgI(B' $^2\Sigma^+$) state is considerably larger than that of the MgI(X $^2\Sigma^+$) state, and for this reason the emission from the minimum of the B' $^2\Sigma^+$ state of MgI can be expected in the infrared. In fact, it has never previously been observed in emission in the visible or UV, when conventional spectroscopic sources were used, and was only observed in absorption around 270 nm for MgCl and around 370 nm for MgBr [31]. It seems that chemiluminescence experiments in which some very high vibrational states are often populated, offer the best way to excite this emission in the visible, although, as our results suggest, not for every MgX

Table 2. Exoergicity $-\Delta E_i$ (in kJ/mol), total attenuation cross sections $\sigma_T$ (in $10^{-20}$ m$^2$), harpooning cross sections (calculated, in $10^{-20}$ m$^2$), electronic channel cross sections $\sigma_i$ (in $10^{-20}$ m$^2$) and quantum yields $\Phi_i$ (in %).

| Reactant/Product | $-\Delta E_i$ | $\sigma_T$ M* atten. | from CL | $\sigma_h$ a) | $\sigma_i$ | $\Phi_i$ |
|---|---|---|---|---|---|---|
| Mg*($^3$P) + F$_2$ → | | 103±9 b) | | 187 | | |
| MgF(X) + F | 575 | | | | | |
| MgF*(A) + F | 242 | | 105±16 | | 0.22±0.04 | 0.21±0.07 c) |
| MgF*(B) + F d) | 131 | | | | <0.05 e) | <0.05 e) |
| MgF*(C) + F | 67 | | | | <0.05 e) | <0.05 e) |
| Mg*($^3$P) + Cl$_2$ → | | 102±9 | | 99 | | |
| MgCl(X) + Cl | 359 | | | | | |
| MgCl*(A) + Cl | 42 | | 104±13 | | 0.94±0.09 f) | 0.91±0.17 f) |
| Mg*($^3$P) + Br$_2$ → | | 118±10 | | 113 | | |
| MgBr(X) + Br | 399 | | | | | |
| MgBr*(A) + Br | 90 | | 123±12 | | 1.5±0.2 g) | 1.3±0.3 g) |
| MgBr*(B') + Br | | | | | 0.4±0.1 | 0.3±0.1 |
| Mg*($^3$P) + I$_2$ → | | 100±10 h) | | 113 | | |
| MgI(X) + I | 410 | | | | | |
| MgI*(A) + I | 119 | | | | 0.013±0.002 h) | 0.013± 0.003 h) |
| MgI*(B') + I | | | | | 4.2±0.6 i) | 4.2±0.9 i) |
| Mg*($^3$P) + ICl → | | 101±7 | | 147 | | |
| MgCl(X) + I | 392 | | | | | |
| MgI(X) + Cl | 349 | | | | | |
| MgCl*(A) + I | 75 | | 102±7 | | 3.8± 0.2 | 3.7±0.4 |
| MgI*(A) + Cl | 58 | | | | <0.001 e) | <0.001 e) |
| MgI*(B') + Cl | | | | | 1.0±0.2 | 1.0±0.3 |
| Mg*($^3$P) + IBr → | | 112±8 | | 113 | | |
| MgBr(X) + I | 418 | | | | | |
| MgI(X) + Br | 385 | | | | | |
| MgBr*(A) + I | 109 | | 111±8 | | 0.7± 0.1 | 0.6±0.2 |
| MgI*(A) + Br | 94 | | | | <0.001 e) | <0.001 e) |
| MgI*(B') + Br | | | | | 1.3±0.2 | 1.2±0.3 |

a) theoretical harpooning cross section, calculated from $\sigma_h = \pi r_c^2$, where $r_c = 14.35$ / (I.P.(Mg*) – E.A. (XY)) (in $10^{-10}$ m); b) [2] gives $(84\pm10) \times 10^{-20}$ m$^2$; c) [2] gives $(12\pm3)$% for an emission containing also bands of Mg$_2^*$ and of MgF$_2^*$ molecules; d) this molecular state originates from the Mg$^+$($^2$P) + F$^-$($^1$S) asymptote and therefore is different from the states designated as B' $^2\Sigma^+$ for all other molecules in this table; e) chemiluminescence not observed, this is an upper limit estimate resulting from detection sensitivity; f) this value was obtained for $T_{eff}$ = 765 K, while for $T_{eff}$ = 710 K the values $\sigma_{CL} = (0.25\pm0.05) \times 10^{-20}$ m$^2$ and $\Phi_{CL} = (0.24\pm0.08)$% were obtained ([6 - 8], with correction for $A_{ki}$); g) this value was obtained for $T_{eff}$ = 830 K, while for $T_{eff}$ = 777 K, the values $\sigma_{CL} = (0.9\pm0.2) \times 10^{-20}$ m$^2$ and $\Phi_{CL} = (0.8\pm0.3)$% were obtained ([6 - 8], with correction for $A_{ki}$); h) from [9]; i) from [10].
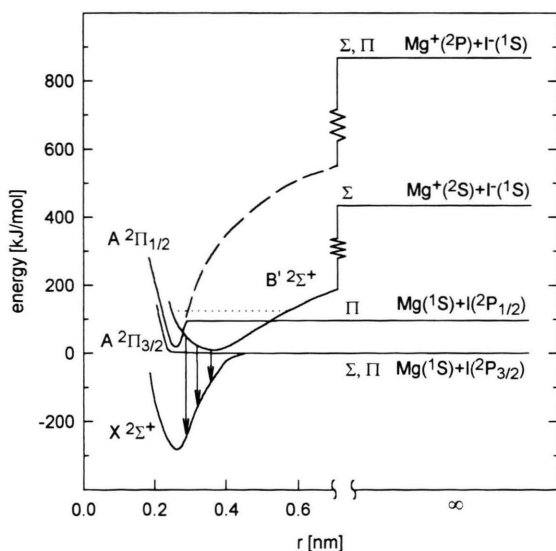


Fig. 3. A schematic diagram of potential energy curves for the magnesium iodide molecule. The horizontal dotted line corresponds to the highest vibrational level of the B' $^2\Sigma^+$ state that can be populated in the Mg*($^3$P$_J$) + I$_2$ reaction.

molecule. An analysis of trends based on an approximate determination of the attractive parts of the MgX potential curves and other energy considerations sug-

gests that: (a) The difference $\Delta r_e = r_e(\text{B' }^2\Sigma^+) - r_e(\text{X }^2\Sigma^+)$ for MgX should increase in the order X = I, Br, Cl, F. Therefore, the emission from the minimum of the MgX(B' $^2\Sigma^+$) curve should be shifted further and further into the IR in the same order. (b) If one assumes that the minimum of the MgX(B') potential energy curve has approximately the same energy as the Mg($^1$S) + X asymptote, then the available energy $\Delta E_i'$ in the Mg*($^3$P$_J$) + X$_2$ reactions allows vibrational levels of the B' $^2\Sigma^+$ state to be populated up to ~125 kJ/mol, ~80 kJ/mol, ~30 kJ/mol, and ~110 kJ/mol above the minimum for MgI, MgBr, MgCl, and MgF molecules, respectively. The highest populated $v'$ level is shown as a dotted line for MgI in Figure 3. Larger exoergicity increases the chance of observing the pseudocontinuum in the visible.

The CL spectra for the Mg*($^3$P$_J$)+X$_2$ reactions seem to reflect this interplay between the two factors: only for MgI and MgBr are the $\Delta r_e$ values small enough and simultaneously the exoergicity large enough to allow the MgX(B-X) emission in the visible.

For heteronuclear XY halogen targets one can note that: for the Mg*($^3$P$_J$) + IBr reaction, the exoergicity available for vibrational excitation in the B' $^2\Sigma^+$ state is ~100 kJ/mol for MgI (or MgBr) products, i. e.

| Reactant/Product | $f_i$ [a] | $p_i$ [b] | $p_i^{o}$ [c] | $-I_i$ [d] | $p_i^{o}$(corr) [e] | $-I_i$(corr) [f] |
|---|---|---|---|---|---|---|
| Mg*($^3$P) + F$_2$ → | | | | | | |
| MgF(X) + F | 0.0 | 0.99 | 0.79 | 0.22 | | |
| MgF*(A) + F | 0.58 | 0.0021 | 0.18 | −4.45 | | |
| MgF*(B) + F | 0.77 | < 0.0005 | 0.020 | < −3.69 | | |
| MgF*(C) + F | 0.88 | < 0.0005 | 0.0073 | < −2.68 | | |
| Mg*($^3$P) + Cl$_2$ → | | | | | | |
| MgCl(X) + Cl | 0.0 | 0.99 | 0.99 | 0.00 | | |
| MgCl*(A) + Cl | 0.88 | 0.0091 | 0.0094 | −0.03 | 0.0092 | 0 |
| Mg*($^3$P) + Br$_2$ → | | | | | | |
| MgBr(X) + Br | 0.0 | 0.99 | 0.95 | 0.04 | | |
| MgBr*(A) + Br | 0.77 | 0.013 | 0.046 | −1.26 | 0.013 | 0 |
| Mg*($^3$P) + I$_2$ → | | | | | | |
| MgI(X) + I | 0.0 | 0.96 | 0.92 | 0.04 | | |
| MgI*(A) + I | 0.71 | 0.00013 | 0.083 | −6.46 | 0.0 | 0 |
| Mg*($^3$P) + ICl → | | | | | | |
| MgCl(X) + I | 0.0 | | 0.42 | | | |
| MgI(X) + Cl | 0.11 | | 0.55 | | | |
| MgCl*(A) + I | 0.81 | 0.037 | 0.014 | 0.97 | 0.011 | 1.2±0.2 |
| MgI*(A) + Cl | 0.85 | < 10$^{-5}$ | 0.012 | < −7.09 | 0.0 | 0 |
| Mg*($^3$P) + IBr → | | | | | | |
| MgBr(X) + I | 0.0 | | 0.44 | | | |
| MgI(X) + Br | 0.08 | | 0.50 | | | |
| MgBr*(A) + I | 0.74 | 0.006 | 0.030 | −1.61 | 0.008 | −0.3±0.3 |
| MgI*(A) + Br | 0.78 | < 10$^{-5}$ | 0.030 | < −8.00 | 0.0 | 0 |

Table 3. Information theoretic analysis of branching ratios.

[a] $f_i = E'_i / E'_{tot}$, where $E'_{tot}$ is the total energy available to products, $E'_{tot} = D_0{}^{\circ}(MX) - D_0{}^{\circ}(XY) + E(Mg*(^3P)) + \langle E_{int}\rangle + \langle E_{tr}\rangle$ and $E'_i = E'_{tot} - T_{oi}$; [b] $p_i = \sigma_i/\sigma_T$, where for the excited i-th state of the products $\sigma_i = \sigma_{CL}(i)$, and for the ground state of the products $\sigma_i = \sigma_T - \Sigma\sigma_{CL}(i)$; [c] $p_i{}^{\circ} = \sigma_i{}^{\circ} / \Sigma\sigma_i{}^{\circ}$, where $\sigma_i{}^{\circ} \approx g_i A_{ab} (1 - f_i)^{2.5}$; statistical weight $g_i = 24$ for the $^2\Pi$ states and $g_i = 12$ for the $^2\Sigma^+$ states, structural factors $A_{ab}$ for chemical branching in the reactions with ICl and IBr were estimated from the data in [21]: $A_{MgI/MgCl} = 1.75$, $A_{MgI/MgBr} = 1.40$; [d] surprisal: $-I_i = \ln(p_i / p_i{}^{\circ})$; e) after being corrected for predissociation of the MgX(A) state: $p_i{}^{\circ}(\text{corr}) = p_i{}^{\circ}(E'_i) - p_i{}^{\circ}(E'_i - E_v)$, where $E'_i$ is the same as in the footnote (a) and $E_v$ is the energy at which predissociation starts, measured with regard to that of the $v' = 0$ level of the MgX(A) state; [f] surprisal corrected for predissociation of the MgX(A) state: $-I_i$ (corr) = $\ln(p_i / p_i{}^{\circ}(\text{corr}))$.

less than the ~125 kJ/mol for Mg* + I$_2$. Therefore the corresponding pseudocontinuum in Fig. 1b has a lower intensity and the emission maximum is shifted slightly to the longer wavelengths compared to the MgI(B'-X) spectrum for the Mg*($^3$P$_J$) + I$_2$ system (Fig. 1c). For the Mg*($^3$P$_J$) + ICl system, the exoergicity available to populate vibrational levels of the MgX(B') state is even lower (only ~65 kJ/mol); as a result, the intensity of the pseudocontinuum is still lower than that of the IBr target.

Weighing the above arguments for the energy transfer X$_2$*(B $^3\Pi_{0+}$) channel (4) and the CL exchange channel MgX*(B' $^2\Sigma^+$) (3), those of the latter are more consistent with the observed decrease of continuum emission in the visible in the order I$_2$ → IX → Br$_2$ → Cl$_2$ → F$_2$. While the X$_2$*(B $^3\Pi_{0+}$) channel cannot be rigorously excluded without detailed spectroscopic work, the exchange channel MgX*(B' $^2\Sigma^+$) appears to be more likely.

The experimental data on collision cross sections and photon yields are collected in Table 2. Also the exoergicities, $-\Delta E_i$, of product channels are given in the second column. The values of $-\Delta E_i$ are absent for the MgX*(B) states because the exact values of the electronic energy terms are unknown. One can expect that they are approximately the same as for the A $^2\Pi$ state, see Figure 3. The total collision cross sections, $\sigma_T$, were determined from the attenuation of the metastable Mg* beam (denoted as

$\sigma_T(M*)$) and when possible also from the attenuation of the MgX(A-X) chemiluminescence ($\sigma_T(CL)$). The agreement between $\sigma_T(M*)$ and $\sigma_T(CL)$ is very good, confirming the quality of the measurement. All the values are around $100 \times 10^{-20}$ m$^2$, indicating that the electron transfer (harpooning) model applies to these systems. Harpooning was observed earlier also for the ground state Mg($^1$S) + Cl$_2$ reaction [32]. The harpooning cross sections were calculated according to [33], using the ionization potential I.P.(Mg*($^3$P$_J$)) = 476 kJ/mol [24] and electron affinities of target molecules as given in Table 1. Except for F$_2$ and ICl targets, the agreement between measured $\sigma_T$ and theoretical $\sigma_h$ is excellent.

The last two columns in Table 2 give the experimental values of chemiluminescence cross sections (determined as in [14, 15]) and quantum yields [7]. For the continuum emitter, labelled MgX(B' $^2\Sigma^+$), these data constitute only the lower limits, since the emission $\lambda > 870$ nm was not recorded. All the measured quantum yields are rather low. They were already found in the past to be so surprisingly low that they prompted a discussion of a disagreement between these data and the adiabatic correlation of electronic states [6]. This discussion did not take into account the possibility that the MgX(B' $^2\Sigma^+$) states may lie slightly below the MgX(A $^2\Pi$) states (in view of the present work this seems very probable). If this were the case, then the Mg*($^3$P) + X$_2$ reactants would correlate adi-

abatically with the MgX(B' $^2\Sigma^+$) state, and not with the MgX(A $^2\Pi$) state. This would explain the low production rate of MX in the A$^2\Pi$ state, as being due to a non-adiabatic process.

In Table 3 we compare the experimental results with the prior values [19] based on an information theoretic approach. In general, the surprisal values for MgX(A) are rather large. This led to the formulation of the hypothesis [7] of a barrier in the entrance valley. Today this survives as a plausible explanation only for the Mg* + F$_2$ system, since it is known that for MgCl*(A), MgBr*(A) and MgI*(A) these large negative surprisals could also arise from the predissociation in the MgX*(A $^2\Pi$) states.

Predissociation in the MgX(A$^2\Pi$) states has been reported in [4, 5, 9, 34]. It is known that MgCl (A $^2\Pi$) dissociates above $v'$ = 6 (which has the energy E$_v$ = 33 kJ/mol above that of $v'$ = 0), MgBr dissociates above $v'$ = 3 (energy $E_v$ = 13 kJ/mol above $v'$ = 0) and MgI already in the $v'$ = 0 ($E_v$ = 0). The observed quantum yields can be readily explained along these lines. Assuming that there is a loss of A $^2\Pi$ products due to predissociation, one can try to estimate how much the prior is reduced due to predissociation. The prior values corrected in this way are $p_i^\circ$(corr) = $p_i^\circ(E_i)$ − $p_i^\circ(E_i - E_v)$. The results are given in the sixth column of Table 3. One finds that in the reactions of Mg*($^3$P$_J$) with Cl$_2$, Br$_2$ and I$_2$, the corrected prior values agree very well with the experiment. For the reactions of Mg*($^3$P$_J$) with ICl and IBr, the correction procedure

is insufficient for the ICl target. Nevertheless, for all other systems in which predissociation plays a role, surprisal values become zero after the correction. In general, one gets the impression that the Mg*($^3$P$_J$) + X$_2$, XY reactions have a statistical outcome, similarly to that observed for the Ca($^3$P$_J$) + X$_2$, XY systems [8, 35]. This impression is supported by comparing the measured photon yields for the MgX(B') state (although these are only lower limits, since emission in the IR is not accounted for) with approximate prior expectations for this state. A rough estimate of the priors for MgX(B') can be found immediately. If we assume that the electronic energy terms are the same for the MgX(A) and MgX(B') states (see discussion above), then the prior for the B' state is one half of the value for the A state. Comparing quantum yields $\Phi_i$ for the MgX(B') states (the last column in Table 2) with the $p_i^\circ$-values for MgX(A) states (fourth column in Table 3; remember that in this comparison the latter values have to be multiplied by 0.5), one finds that the measured populations of the MgI(B') state in the reactions of Mg* with I$_2$, ICl, and IBr are very close to statistical. For Mg* + Br$_2$ the population is somewhat lower than statistical − perhaps because this latter system has a stronger emission in the IR.

### Acknowledgements

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