

CHEMILUMINESCENT EMISSION IN THE REACTION



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The chemiluminescence of BaO in the range 600–800 nm has been observed for the first time in the reaction between Ba(6s6p¹P₁) and CO₂ in a crossed beam experiment under single collision conditions. The observed spectrum is attributed to the emission from the A¹Σ⁺ state of BaO and no emission from the A¹Π is visible under our experimental conditions. The distribution of low ν' in the A¹Σ⁺ state appears statistical at low collision energy and, at higher collision energy, the ν' = 1 appears less populated than statistically predicted.

KEY WORDS: Ba, CO₂, chemiluminescence, crossed-beam, distribution of vibrational energy.

INTRODUCTION

The reactions of alkali and alkaline earth metal atoms with molecules have attracted a considerable attention over the past years.¹ More recently, the combination of lasers with crossed beams apparatus has allowed the study of the reactivity of these atoms when excited to short lived electronic states.^{2–6} It turns out that the reaction mechanism may then be substantially different than for the reacting atom in its ground state.⁵

Electronic excitation in alkaline earth atom-molecule collisions opens several reactive and inelastic channels which compete one with each other. A complete dynamical picture of such collisions requires the study of each of these channels as a function of a dynamical parameter such as the collision energy. A systematic experimental study of this type has been initiated in our laboratory using a crossed beam apparatus combined with laser excitation technique.

The present paper reports on preliminary results concerning the first observation of chemiluminescence in the reaction between Ba(6s6p¹P₁) and CO₂ and its dependence with the collision energy. The reaction of a ground state barium atom with a CO₂ molecule has already been investigated for collision energies varying between 0.1 and 0.3 eV.^{7–9} The measured angular distribution as well as the internal energy distribution of the ground state BaO product molecule suggest that this reaction

proceeds through the formation of a long-lived complex intermediate. It is therefore interesting to examine, when excited Ba is reacting, if the large amount of energy contained in the $\text{Ba}(6s6p^1P_1) + \text{CO}_2$ system is shared statistically between the various exit channels and conforms the mechanism of long-lived complex. Besides the chemiluminescent channel this includes inelastic energy transfer to other states of the barium atom, one of which is observed here too, namely the $\text{Ba}(6s6p^1P_1 \rightarrow 6s6p^3P_1)$ energy transfer.

EXPERIMENT

The experimental setup and its use for the measurement of chemiluminescence has been described elsewhere.^{10,11} Briefly, it consists in crossed molecular beams of barium and CO_2 . The Ba beam originates from an oven heated at 1070 K and expands through a 0.8 mm nozzle. The molecular CO_2 beam can be seeded into helium and expands through a 0.2 mm nozzle followed by a 0.5 mm skimmer and a 1.5 mm collimator. Its velocity is measured by a time-of-flight system. By changing the concentration of the helium seeding gas, the collision energy is varied between 0.12 and 0.45 eV. The expansion conditions are chosen so that the formation of CO_2 clusters can be neglected and the CO_2 molecules are produced vibrationally cold.¹¹

The barium atoms are laser photoexcited in the collision zone. The beam of a CW single frequency ring dye laser is focused onto the entrance of a single mode optical fiber and the output of this fiber is imaged in the collision volume. The fluorescence light is collected by a lens and focused onto the entrance slit of a monochromator followed by a RCA 31034 photomultiplier (PMT). A red filter (Schott OG 590) is placed in front of the PMT in order to reduce the intense fluorescence due to the barium resonance line. The signal of the PMT is sent to a photon counting system followed by a multiscaler.

The chemiluminescent emission is recorded by sweeping the wavelength of the monochromator between approximately 600 and 800 nm. It is limited towards the blue by the cut-off of the band pass filter and towards the red by the spectral response of the PMT. The background is subtracted by recording a spectrum with the CO_2 beam flagged off. The spectra are then corrected from the spectral response as estimated with a tungsten lamp.

RESULTS

The chemiluminescent spectrum obtained at low collisional energy (0.12 eV) with a spectral resolution of 4 nm is presented in Figure 1. Several vibrational bands are clearly visible. The dissymmetry of each band towards the red is mainly due to the rotational excitation of the BaO molecule. The emission at the red end of the spectrum (791 nm) which is about 10 times more intense than the rest of the spectrum has been truncated for clarity. It originates from the intercombination line

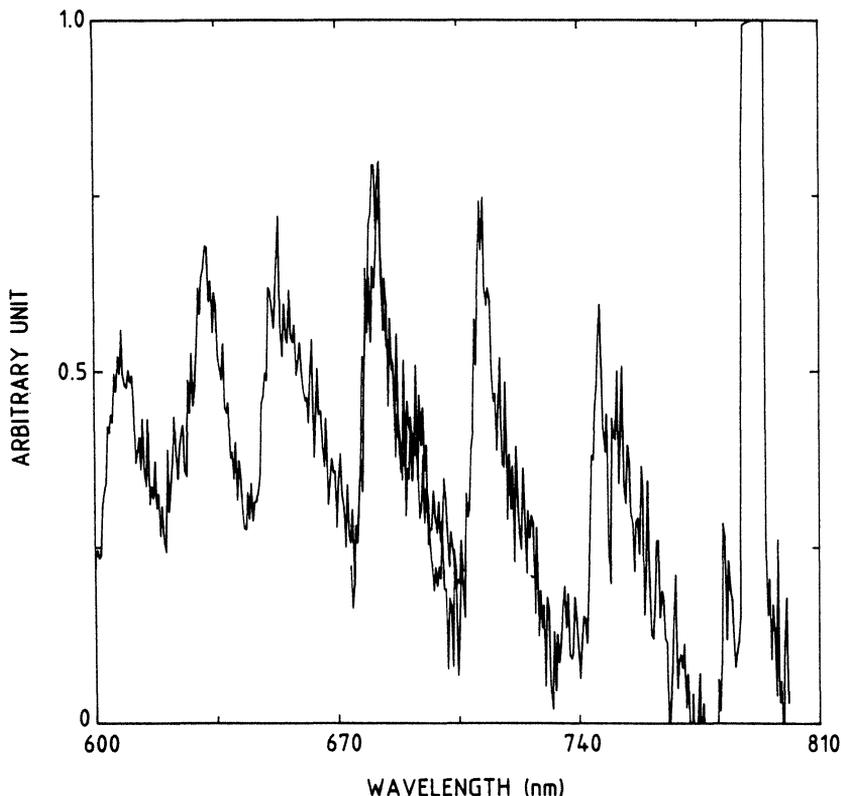
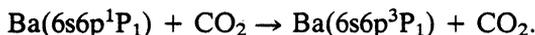


Figure 1 Chemiluminescent emission of the reaction Ba(1P_1)+CO₂ at a collision energy of 0.12 eV recorded with a spectral resolution of 4 nm. The intense emission in the red (791 nm) is due to the Ba $^3P_1 \rightarrow ^1S_0$ transition and has been truncated for clarity.

$6s^2S_0 - 6s6p^3P_1$ which is strongly enhanced when the CO₂ beam is on. The collisions with the CO₂ molecules thus induce significantly the energy transfer:



The chemiluminescent spectrum has also been recorded at a lower resolution of 10 nm for three different collision energies 0.12, 0.28 and 0.45 eV. The results are presented in Figure 2 together with the results of a simulation which will be discussed later on. Due to the 10 nm resolution the peaks appear more symmetrical. The important feature appearing in this figure is that the modulation decreases when the collision energy is enhanced.

DISCUSSION

The reaction between a ground state barium atom and CO₂ is exoergic by 0.33 eV.^{1,7,12} When an energy of 2.24 eV is added to the system as electronic excitation in

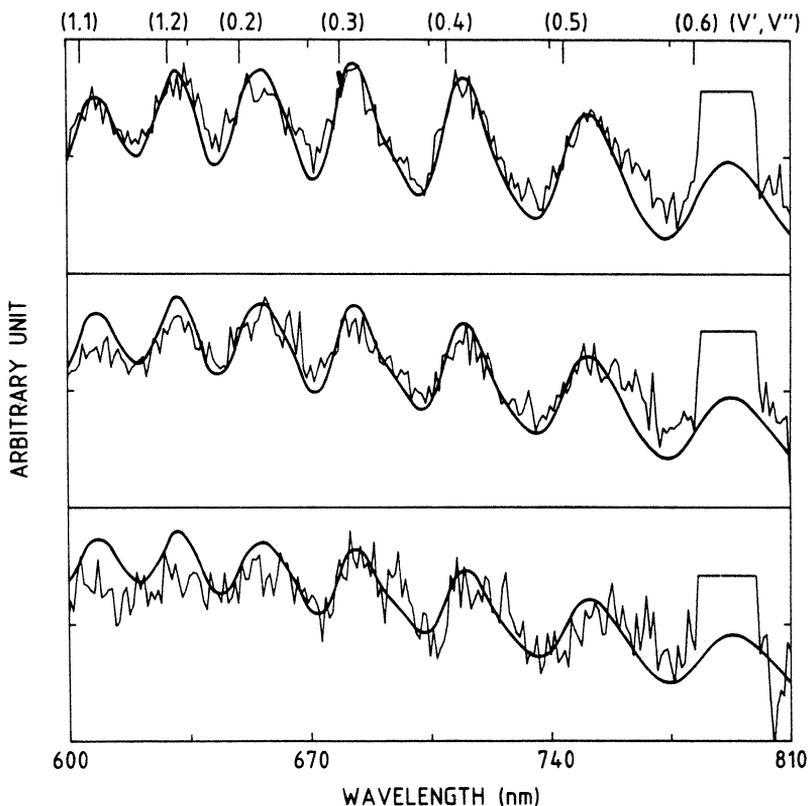


Figure 2 Same as Figure 1, but with a spectral resolution of 10 nm. The three parts correspond to three different collision energies 0.12 (upper part), 0.28 (middle part) and 0.45 eV (bottom part). The full curves result from a simulation of the emission of BaO excited in the $A^1\Sigma^+$ state with a statistical distribution of ro-vibrational states. The upper part of the figure indicates the origins of the main v' , v'' bands contributing to the calculated spectrum.

Ba, the exit channels leading to a BaO molecule excited in the low lying excited states ($a^3\Sigma^+$, $A^1\Sigma^+$, $b^3\Pi$, and $A'^1\Pi$) become energetically allowed.¹³ Only the singlet states are optically coupled to the $X^1\Sigma^+$ ground state of BaO and can be responsible for the observed emission.

In Figure 3, together with the experimental spectrum of Figure 1, is also plotted the result of simulations of the BaO spectrum. The calculation was performed using the SIML program developed by M. Prisant¹⁴ and the spectroscopic data of Gottscho *et al.*¹³ The chosen ro-vibrational distribution is the so called prior distribution introduced by Levine in his Information Theory.¹⁵

A very good agreement is observed in Figure 3 between the experimental spectrum and the simulated $A^1\Sigma^+$ emission alone. This leads to two conclusions. First, the emission from the $A'^1\Pi$ state is not observed. This is particularly evident in the red part of the spectrum around 780 nm where the simulation of the $A'^1\Pi$ emission predicts a maximum when a minimum is experimentally observed. The

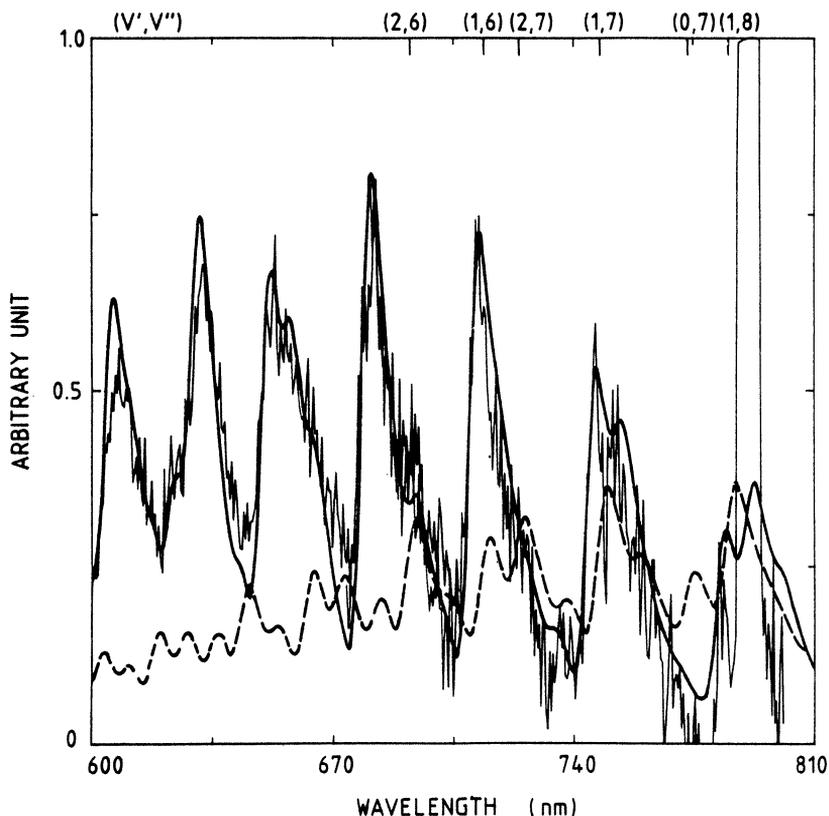


Figure 3 Same as Figure 1. The experimental spectrum is compared with simulations of the emission of BaO excited in the $A^1\Sigma^+$ (full curve) and in the $A'^1\Pi$ (dashed curve) state, respectively. In both cases, the ro-vibrational distribution is assumed to be a prior distribution. The spectrum corresponding to A emission is normalized to the experimental spectrum at 710 nm. The ratio of the A to A' populations is assumed to be statistical and equal to 1/2; the A' spectrum has then been divided by a factor of 2 to take into account the loss due to thermal escape. The upper part of the figure indicates the origins of the main v' , v'' bands contributing to the calculated A' spectrum.

second conclusion is that, at the collision energy of 0.12 eV, the population of the observed levels of the $A^1\Sigma^1$ state is adequately described by the prior distribution. The reaction $\text{Ba}(6s6p^1P_1) + \text{CO}_2 \rightarrow \text{BaO}(A^1\Sigma^1) + \text{CO}$ is exoergic by about 0.5 eV. This means that 0.62 eV are shared into the products. The prior model considers that this energy is shared equally into the internal modes of the products. Therefore, a mean energy of 0.11 eV is going into the notation and the vibration of BaO, and the rotation and the vibration of CO, and the rest corresponds to the mean relative kinetic energy. Consequently, the good agreement between experimental and calculated spectra with the prior model suggests the internal modes of the CO product are significantly populated and that the CO bond is not simply a spectator in the reaction.

In Figure 2, the curves which are compared to the experimental spectra are the results of the same simulation of the emission of $\text{BaO}(A^1\Sigma^+)$, but taking into account

the lower resolution and the changes in collision energy. As in Figure 3, the agreement is good for the low collision energy, but at higher energy, there is a deviation in the blue part of the spectrum: the simulated curve is higher than the experimental points.

The upper part of Figure 2 shows the position of the band origins of the main transitions contributing to the simulated spectrum. It can be seen that most of the spectrum is due to transitions originating from the $\nu' = 0$ level of the $A^1\Sigma^+$ state and that the blue part has a significant contribution from the $\nu' = 1$. The evolution of the shape of the spectrum with the collision energy can be interpreted in the following way: at low collision energy the $\nu' = 0$ and $\nu' = 1$ states are statistically populated and, when the energy increases, the rotational distribution of the $\nu' = 0$ state remains statistical but the $\nu' = 1$ is less populated than predicted by the Prior model.

No fluorescence from the $A'^1\Pi$ state is observed. This does not mean that no population is present in this level but that there is an absence of preferential production in the $\text{BaO}(A'^1\Pi)$ state. The main reason is that, the $A'^1\Pi$ level has a longer lifetime ($\approx 10\mu\text{S}$) than that of the $A^1\Sigma^+$ level^{16,17} and part of the fluorescence from the A' state is lost due to thermal escape. An estimate of this loss is rather complex, but, considering the geometry of the detection system, it is at least a factor 2. This factor has been included in the statistical calculation in Figure 3 to scale the A and A' spectra. This shows that if the ratio of the A to A' population is statistical (1/2) the contribution of A' to the spectrum would be weak.

The last point that is discussed concerns the energy transfer from the $\text{Ba}(6s6p^1P_1)$ to the $\text{Ba}(6s6p^3P_1)$ state due to the collision with the CO_2 molecules. Such energy transfers have been studied in the collision $\text{Ba}(6s6p^1P_1) + \text{He}$ and have been shown to be highly state selective forming only $\text{Ba}(6s6p^3P_2)$.¹⁸ The present experiment shows the cross section for production of $\text{Ba}(6s6p^3P_1)$ is much higher with CO_2 than with He . It will be interesting to examine the other inelastic channels and in particular whether these inelastic channels can compete efficiently with the reactive channels. Such an experiment is in progress.

CONCLUSION

The chemiluminescence of BaO has been observed in the reaction between $\text{Ba}(6s6p^1P_1)$ and CO_2 in a crossed beam experiment under single collision conditions. The observed spectrum can be assigned to the emission from the $A^1\Sigma^+$ state of BaO and no emission from the $A'^1\Pi$ is visible under our experimental conditions. The distribution of low ν' in the $A^1\Sigma^+$ state appears statistical at low collision energy and, at higher collision energy, the $\nu' = 1$ appears less populated than statistically predicted. This contrasts with what is observed for the reaction between the ground state Ba and CO_2 where the existence of a long-lived intermediate leads to a statistical distribution of products. A more complete study of this chemiluminescent reaction as a function of the collision energy and of the laser polarization together with the comparison with the results obtained in other systems will be the subject of a forthcoming article.

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