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Elastic scattering of Sm in collision with He, Ne, Ar, Kr and Xe and relative cross-sections for intramolecular electronic energy transfer in SmO

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Abstract

Using the molecular beam chemiluminescence technique for the reaction of samarium with N_2O, the averaged elastic scattering cross-section of samarium with different closed-shell inert gases is measured and the relative probability for the collision-assisted intramolecular energy transfer (CAIMET) from metastable to radiative SmO states has been estimated. The relative CAIMET probability represents a gross average value for undefined metastable states to radiative states of SmO. © 1997 Elsevier Science S.A.

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1. Introduction

Chemiluminescent reactions of samarium metal atoms with various oxidant molecules, e.g. N_2O, O_3, SF_6, are of considerable interest owing to their high photon yields at torr-level pressures [1–3]. Although the photon yields at such pressures are very high [3] compared to those in the millitorr region, extraction of dynamic parameters at higher pressures is very difficult due to the complexity of the environment. The high photon yields at higher pressures are attributed to the collision-assisted intramolecular energy transfer (CAIMET) process or energy pooling type of reactions and the participation of non-radiating states which crossover to the radiating states in the high-pressure region [4]. The reactions are interesting due to the high multiplicity of the atomic ground state of samarium leading to a large number of low-lying states of samarium oxide [5]. In simple ligand field argument, the ionically bonded $Sm^{2+}O^{2-}$, the ground state configuration, gives 72 low-lying states, and out of these many states are either metastable or non-radiating, with the possibility of crossover to the radiating states on collision with heavy atomic gases, thus increasing the photon yields. The scattering cross-sections of samarium with various oxidants have been determined by different groups [1–4,6,7]. The interaction of samarium with closed-shell inert gases to our knowledge has not been studied before. Moreover, study of the interaction of open-shell atoms in the ground state with closed-shell atoms, i.e. rare gases, is important for understanding van der Waals forces in such types of systems. Aquilanti and co-workers [8,9] have studied the interaction of ground state oxygen $O(^3P)$ atoms with rare gases and measured the integral cross-section for these systems. The integral cross-section can be utilised to derive the potential of different states that governs the interaction forces, when the cross-section is measured as a function of collision energy. The non-radiative crossover from one electronic state to another is an interesting phenomenon and it is quite general [10–13]. Recently, Ottinger et al. [14] have obtained the crossover cross-section for the $CO(a^3\Pi) \rightarrow CO(a'^3\Sigma^+), CO(d^3\Delta)$ transitions in molecular beam experiments. In the present work, averaged elastic cross-sections of samarium with different non-reactive closed-shell gases and relative probabilities of crossover from metastable SmO to radiating states have been measured using the molecular beam chemiluminescence technique.

2. Experimental

The molecular beam machine used in this work has been described previously [3]. Briefly, it consists of two chambers, a lower chamber containing the resistively heated oven for the effusive metal atom source and an upper chamber for scattering metal atoms by different gases. The background

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pressures in the lower and upper chambers are in the range 10^{-4} and 10^{-6} torr respectively. Experiments were carried out in the beam–gas configuration. The metal atom beam effuses through a 1 mm orifice and is further collimated by a 4 mm diameter slit positioned on the partition plate between the two chambers. The oxidant gas was introduced into the scattering chamber through a mass flow controller (MKS). The resulting chemiluminescence from the observation zone located at 5.25 cm from the collimation slit was collected and focused on the slit of a stepper motor-driven monochromator (Jarrel–Ash model 82-140, 0.3 m provided with two gratings, one for the 200–400 nm and the other for the 400–800 nm range). The dispersed light was measured by a photomultiplier (S-11 response) and an electrometer amplifier (Keithley 617) combination. Buffer gas was also introduced into the scattering chamber through the mass flow controller. The total pressure (buffer gas + oxidant gas) was measured by the capacitance manometer (Datametics) and the chemiluminescence intensities were measured at various flow rates of buffer gas. All experiments were carried out in the pressure range 0.5–2.5 mtorr. The partial pressures of the gases were calculated by their respective flow rates and the total pressure.

3. Method

The total scattering cross-sections of samarium with different buffer gases were measured employing the chemiluminescence (CL) technique, utilising the well-studied chemiluminescence reaction $Sm + N_2O \rightarrow SmO + N_2$ as reference. The observed chemiluminescence intensity (I_0), in the absence of buffer gas, for the reaction of Sm with N_2O is given by [3,6,7]

$$I_0 = C[Sm][N_2O]v_r\sigma_{cl}V\exp(-\alpha_0 p_{N_2O}) \quad (1)$$

where C is a constant factor which includes a geometry factor for collection and detector efficiency, v_r is the relative velocity of the reactants, σ_{cl} the chemiluminescence cross-section, V the volume of the observation zone, p_{N_2O} the pressure of N_2O in torr, α_0 the attenuation parameter in $torr^{-1}$ for the attenuation of the Sm atom beam by N_2O, [Sm] the concentration of samarium metal atoms (atoms cm^{-3}) at the entrance to the scattering chamber and [N_2O] the concentration of N_2O (molecules cm^{-3}).

In the presence of the inert gas the CL intensity (I_0) will decrease to I_1 as a result of additional attenuation of the metal atom beam by the buffer gas from the port of entry to the viewing zone in the scattering chamber. Assuming that there is no emission arising from the crossover phenomena (explained later), the intensity becomes

$$I_1 = C[Sm][N_2O]v_r\sigma_{cl}V \times \exp(-\alpha_0 p_{N_2O})\exp(-\alpha_1 p_{inrt}) \quad (2)$$

where p_{inrt} is the pressure of the inert gas in torr and α_1 is the attenuation parameter in $torr^{-1}$ for the attenuation of the Sm atom beam by the inert gas.

The attenuation parameters α_0 and α_1 are related to the total phenomenological cross-section for metal atom removal σ in $Å^2$ by

$$\alpha = (1.33 \times 10^{-13}\sigma l)/kT$$

where l is the path length of the samarium beam in the scattering chamber up to the viewing zone, k (erg K) is the Boltzmann constant and T is the absolute temperature of the oxidant/buffer gas. The constant 1.33×10^{-13} has units of dyne $torr^{-1}$ $Å^{-2}$.

From Eqs. (1) and (2), we get

$$\ln(I_1/I_0) = -\alpha_1 p_{inrt} \quad (3)$$

The plot of $\ln(I_1/I_0)$ vs. p_{inrt} (the inert gas pressure) will give a negative slope of α_1, the attenuation coefficient for Sm by inert gases in the path length l. The equation holds good if the inert gas scatters only the samarium atom and not the emitting species from the viewing zone and there is no significant contribution from the crossover from the non-radiative state to the radiative state. The probability of scattering of the emitting species SmO from the viewing zone is negligible due to its short lifetime (≈ 180 ns). The latter condition holds good only at very low pressures, especially for the heavier buffer gases. In the $Sm + N_2O$ reaction, a large number of metastable states are populated and there is a probability of crossover from these states to the radiative states through collision-assisted intramolecular energy transfer thus increasing the intensity and deviating from the above equation. Jones and Broida [15] have observed similar behaviour in the reaction of Ba atoms with N_2O. The changes in the emission spectra of BaO with pressure have been attributed to the collision-assisted crossover phenomena, which are dominant in a system like BaO where the electronic states have many degenerate vibronic couplings with the rotational perturbations. On the similar basis the contribution to the chemiluminescence intensity from the crossover from metastable SmO to radiating states can be included in Eq. (2) as follows.

The rate of formation of total metastable SmO in the viewing zone is given by

$$R_{ms} = d[SmO^*]/dt = [Sm][N_2O]v_r\sigma_{ms}V \times \exp(-\alpha_0 p_{N_2O})\exp(-\alpha_1 p_{inrt}) \quad (4)$$

where σ_{ms} is the total cross-section for metastable SmO formation in the reaction $Sm + N_2O \rightarrow SmO + N_2$.

The CL intensity from the radiative states populated via crossover from metastable state can be given by

$$I_{cross} = CR_{ms}[1 - \exp(-Qp_{inrt})] \quad (5)$$

where Q is the probability of crossover per torr of buffer gas pressure and is proportional to the cross-section for the collision-assisted intramolecular energy transfer from the metastable to the radiative states of SmO. From Eqs. (1) and (5) the total measured CL intensity I is

$$
\begin{aligned}
I &= I_1 + I_{\text{cross}} \\
&= C\{[\text{Sm}][\text{N}_2\text{O}]v_r V\sigma_{\text{cl}}\exp(-\alpha_0 p_{\text{N}_2\text{O}}) \\
&\quad \times \exp(-\alpha_1 p_{\text{inrt}}) + [\text{Sm}][\text{N}_2\text{O}]v_r V\sigma_{\text{ms}} \\
&\quad \times \exp(-\alpha_0 p_{\text{N}_2\text{O}})\exp(-\alpha_1 p_{\text{inrt}})(1-\exp(-Qp_{\text{inrt}}))\} \\
&= C\{[\text{Sm}][\text{N}_2\text{O}]v_r\sigma_{\text{cl}} V\exp(-\alpha_0 p_{\text{N}_2\text{O}}) \\
&\quad \times \exp(-\alpha_1 p_{\text{inrt}})\{1+\sigma_{\text{ms}}/\sigma_{\text{cl}}(1-\exp(-Qp_{\text{inrt}}))\}
\end{aligned} \tag{6}
$$

Combining Eqs. (6) and (1)

$$
\begin{aligned}
\ln(I/I_0) &= -\alpha_1 p_{\text{inrt}} + \ln[1 + (\sigma_{\text{ms}}/\sigma_{\text{cl}}) \\
&\quad \times (1-\exp(-Qp_{\text{inrt}}))]
\end{aligned} \tag{7}
$$

The above Eq. (7) reduces to Eq. (3) if the probability of crossing over cross-section Q is zero. In the limiting condition of Qp_{inrt} tending to zero at very low p_{inrt}, the term $\exp(Qp_{\text{inrt}}) \approx 1 - Qp_{\text{inrt}}$ and we have,

$$
\ln(I/I_0) = -\alpha_1 p_{\text{inrt}} + \ln[1 + (\sigma_{\text{ms}}/\sigma_{\text{cl}})Qp_{\text{inrt}}] \tag{8}
$$

Taking $(\sigma_{\text{ms}}/\sigma_{\text{cl}})Q = k$, Eq. (8) reduces to the simple form

$$
\ln(I/I_0) = -\alpha_1 p_{\text{inrt}} + \ln[1 + kp_{\text{inrt}}] \tag{9}
$$

In the low-pressure region the contribution from the second term is negligible and α_1 can be obtained from the plot of $\ln(I/I_0)$ vs. p_{inrt}. With α_1 thus obtained from the low-pressure region, on substitution in Eq. (9) and fitting the data for the entire pressure region studied, the value for k can be determined. k gives the probability of formation of radiative states by crossover from metastable SmO. The averaged elastic scattering cross-section values obtained from α_1 represent the lower limit of the cross-section due to non-consideration of the contribution from crossover phenomena and also because some of the Sm atoms which are scattered by the buffer gas will contribute to the observed chemiluminescence intensity by reacting with N_2O molecules in the viewing zone and thus contribute to the lowering of the measured cross-section. This contribution depends on the volume of the viewing zone. To minimise the contribution mentioned above the viewing zone volume should be kept as small as possible, but there is a practical difficulty in doing so as the signal-to-noise ratio will decrease. We have kept the viewing zone volume of about 1.3 cm^3 to get a good signal-to-noise ratio. The error introduced in the cross-section values can be minimised by taking the relative cross-section values instead of the absolute cross-section values.

4. Results and discussion

Typical plots of $\ln(I/I_0)$ vs. pressure of inert gases for He, Ar and Xe are shown in Fig. 1(a) and for Ne and Kr in Fig. 1(b). For the light gas He (Fig. 1(a)) the plot is almost linear, but for the heavier gases Ne, Ar, Kr and Xe a pronounced non-linearity is seen in increasing order. Since it is improbable that a rare gas atom could supply or remove energy much more than kT from SmO, collision-induced intramolecular energy transfer (CAIMET) must occur between the nearby vibronic levels of different electronic states. Cross-sections for such types of collision-induced crossover from one electronic state to another could be unusually large and strongly rotation and vibration dependent. Such processes are known to occur via perturbed rotational levels with cross-sections comparable to those for rotational relaxation [16,17].

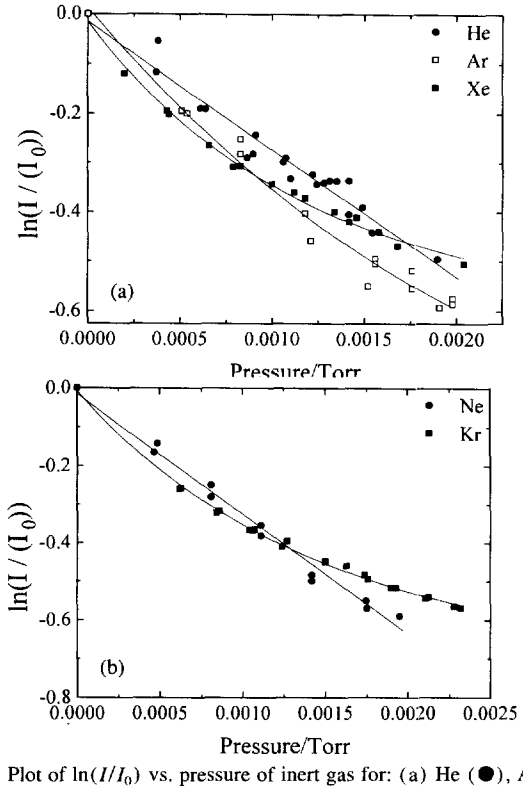

Fig. 1. Plot of $\ln(I/I_0)$ vs. pressure of inert gas for: (a) He (●), Ar (□) and Xe (■); (b) Ne (●) and Kr(■).

The crossover phenomenon responsible for the enhanced intensity has also been observed by Irvine and Dagdigian [4]. They have observed the difference in the chemiluminescence spectra by increasing the pressure of oxidant gases up to 1 torr. Similar results in many chemiluminescent systems have been obtained by Gole and Pace [18]. We have not observed any significant change in spectra by increasing the pressure of inert gases up to 2.5 mtorr for all the five gases studied. This may be due to the relatively small contribution from the crossover phenomena in the pressure range studied. In our typical experimental conditions the maximum rate of product (SmO) formation in the viewing zone of volume of 1.3 cm^3 is estimated to be 4.4×10^{11} s^{-1}, by taking the reactive cross-section equal to the total scattering cross-section. Assuming a spherical observation zone and taking the thermal velocity of the species, the average residence time of thermal SmO in the observation zone is approximately 35 μs. With this upper limit for the concentration of SmO and average

Table 1
Comparison of hard sphere cross-section, experimental elastic scattering cross-section and Massey–Mohr cross-section of samarium metal with different inert gases [a]

Atom	Radius/Å	Hard sphere cross-section/Å^2	Experimental values/Å^2	Massey–Mohr (Eq. (11)) cross-section/Å^2	Relative probability for CAIMET [b]	T_{eff}/K
Sm	1.80	–	–	–	–	–
He	1.33	30.7	91.8	189.5	Undetected	313
Ne	1.19	28.0 (1.00)	101.4 (1.00)	328.41 (1.00)	1.0	348
Ar	1.47	33.6 (1.20)	110.4 (1.10)	616.9 (1.87)	1.2	406
Kr	1.58	35.8 (1.28)	124.8 (1.23)	777.4 (2.36)	12.6	476
Xe	1.72	39.0 (1.39)	142.2 (1.40)	960.0 (2.92)	17.5	533

[a] Relative values are given in parentheses taking the value for Ne as 1.
[b] Collision-assisted intramolecular energy transfer.

residence time of SmO in the viewing zone, the collision frequency of SmO with buffer gas (pressure = 2.5 mtorr) is estimated to be 9.0×10^{11} s^{-1} cm^{-3} in the observation zone. Hence, on average, SmO encounters about two collisions with buffer gas molecules in its residence in the viewing zone volume. Some of these encounters are fruitful for the metastable states to crossover to the radiating states and emit in the viewing zone volume. In the pressure range of 0.0 to 1.0 mtorr, the average number of encounters of SmO with buffer gas is less than 1 and the contribution from the crossover from metastable to radiating state is negligible. The elastic scattering cross-section values obtained from Eq. (3) in the low-pressure region are given in Table 1. The above estimated cross-sections are for the average mean collision energy having a typical Maxwell–Boltzmann distribution. The effective temperature of encounter, T, and the collision energies for the different collision partners have been estimated. The experimental conditions are also given in Table 1.

The hard-sphere cross-sections for the different collision partners have been estimated from the van der Waals constant b [19], for comparison and are also given in Table 1. Since the hard sphere cross-section arises from the short-range repulsive potential it has very little to do with the elastic scattering which normally arises from the long-range attractive potentials. At long range the leading term for the potential of the system is the van der Waals $-C_6r^{-6}$ term. Since both the interacting partners are atoms the C_6 term can be estimated by the use of an appropriate formula in terms of polarisabilities of the atoms involved, due to Slater and Kirkwood [20]. The C_6 term can be written as

$$C_6=\frac{3e\hbar}{2\sqrt{m_e}}\frac{\alpha_1\alpha_2}{[(\alpha_1/N_1)^{1/2}+(\alpha_2/N_2)^{1/2}]} \quad (10)$$

where m_e and e represent the electronic mass and charge respectively and $\hbar$ is Planck's constant. For the above type of potential the Massey–Mohr [21] expression for the total elastic cross-section becomes

$$Q=b(C_6/v_r)^{2/5} \quad (11)$$

where $b=4.66\times10^{11}$ erg cm^6 and v_r is the relative velocity of the colliding partners (Sm and inert gases).

The average elastic scattering cross-sections of different types of atomic partners thus calculated are given in Table 1. The relative experimental elastic cross-sections match fairly well with the relative hard sphere cross-sections, whereas the absolute values lie in between the hard sphere model and the Massey–Mohr expressions, but closer to the hard sphere model. The above condition in the present case may be due to the geometry of the detection system used in the experiments. The geometry used here, which is a large detector volume, is very unsuitable for the measurement of the attractive small angle scattering. The lower value of the elastic cross-section in the present case may in fact pertain largely to the repulsive wide angle scattering.

Fig. 1(a) and (b) show linear behaviour at very low pressure, for all the buffer gases used. The non-linearity in Fig. 1(a) and (b) at higher buffer gas pressure, i.e. the upper trend, may be due to (1) slowing down of diffusion of the radiating species out of the viewing zone, and (2) CAIMET from metastable states to the emitting states. Irvin and Dagdigian [4] have estimated the percentage decrease of diffusional loss and found it to be only 11% for the increment of pressure from 10 to 75 mtorr. In the present experiment, from 0.7 to 2.5 mtorr pressure, the percentage decrease of the diffusional loss is negligible ($<15\%$). To account for the non-linearity, the percentage decrease of the diffusional loss by increasing the pressure from 0.7 to 2.5 mtorr should be greater than 73%, which is highly improbable. The relative values of CAIMET are given in Table 1 with respect to Ne values. The increasing trend for the intramolecular energy transfer can be attributed to the size of the collision partner as well as the kinetic energy associated with the partner, since both the atomic diameter as well the kinetic energy increases in the series from He to Xe.

In a simple ligand field argument the SmO molecule is represented by the ionically bonded $Sm^{2+}O^{2-}$ configuration. The ground state will result from the $4f^5 6s$ configuration of Sm^{2+} and the lowest state from the f^5 core will be $^6H_{5/2}$. The ground state is 0^- [5]. The ground state configuration f^5s will give 72 states with the lowest states being those with low Ω, where Ω is the projection of total angular momentum on the internuclear axis. The detailed calculations predict that

there will about 50 states, all with Ω between 0 and 5 and lying below 5000 cm^{-1} [5]. Dickson [22] reported that Laser induced fluorescence (LIF) excitation and the chemiluminescence spectrum of SmO are identical. From the lifetime measurement he concluded that the red band system (500–700 nm) terminates on the ground state and suggested that only one upper electronic state participated in the transition. Contrary to this, Hannigan [23] found biexponential radiative decay which indicates the presence of more than one band systems in the red region of the SmO spectrum. Spectra taken at the variable delay between excitation and observation not only differ in intensity but also in spectral distribution, thus directly demonstrating the possibility of participation of more than one band system. Bujin and Linton [24] have reported high-resolution analysis of many low-lying states of SmO. Due to the complexity of the energy states of SmO and the poor resolution in our chemiluminescence spectrum, we are unable to assign the relative CAIMET probability to any particular pair or group of energy states.

5. Conclusion

The average, relative elastic scattering cross-sections of the samarium atom with different inert gases, namely He, Ne, Ar, Kr and Xe, were measured and found to be 91.8, 101.4, 110.4, 124.8 and 142.2 $Å^2$ respectively. These values are the lower limit of the true values. The relative cross-section values agree well with the relative hard sphere cross-section values. The probability for the collision-assisted intramolecular energy transfer process from metastable SmO to the radiative state has been estimated to be 1.0:1.2:12.6:17.5 for Ne, Ar, Kr and Xe respectively.

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