

VACUUM ULTRAVIOLET LUMINESCENCE IN THE FLASH PHOTOLYSIS OF CARBON SUBOXIDE

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Summary

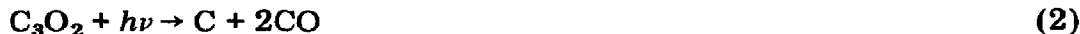
Previously unreported chemiluminescence ($\lambda = 120$ nm) has been observed in the vacuum UV photolysis of C_3O_2 ($\lambda < 170$ nm) and tentatively identified as the CO (B \rightarrow X) transition. Arguments are presented suggesting the formation of CO(B $^1\Sigma^+$) via an energy pooling mechanism involving CO(a $^3\Pi$).

1. Introduction

The photochemistry of carbon suboxide has been reviewed by Filseth [1]. Photolysis in the near UV has been examined in both low intensity product analysis studies [2] and in flash photolysis-kinetic absorption spectroscopy experiments [3]. The primary process for $\lambda > 200$ nm is reasonably well established as



In the vacuum UV ($\lambda < 200$ nm), low intensity product analysis studies [4] and flash photolysis-kinetic absorption spectroscopy experiments [5] have also been performed. It was suggested by Stief and DeCarlo [4] and established by Braun *et al.* [5] that the major process in this wavelength region is



A modification of this technique using resonance absorption detection has been extensively used by Husain and Kirsch [6 - 10] to measure absolute rate constants for reactions of atomic carbon.

Chemiluminescence has been observed in the reaction of atomic oxygen with C_3O_2 in discharge flow systems [11] and in a combination flash photolysis-low pressure flow system [12]. This luminescence has been attributed to the reaction sequence



Emission in the vacuum UV (140 - 210 nm) has been identified as the fourth positive band system of $\text{CO}(\text{A}^1\Pi \rightarrow \text{X}^1\Sigma)$ while weak emission in the red is associated with the CO triplet bands ($\text{d}^3\Delta \rightarrow \text{a}^3\Pi$) and the Herman bands [13] ($\text{e}^3\Sigma \rightarrow \text{a}^3\Pi$).

We have observed a previously unreported luminescence in the vacuum UV after the flash photolysis of carbon suboxide at $\lambda < 170$ nm and have accumulated a number of interesting results including both qualitative trends and quantitative data.

2. Experimental

The observations were made employing the flash photolysis-resonance fluorescence apparatus described previously [14]. In the experiments reported here, the resonance lamp was not employed. In a typical experiment dilute flowing mixtures of C_3O_2 in helium (about 1 part in 10^5) at a total pressure of 100 Torr were subjected to microsecond pulses of vacuum UV radiation. The resulting luminescence was detected at a right angle to the incident light beam using an EMR 542-G-08-18 photomultiplier. The luminescence was observed to decay exponentially with time. A typical pseudo first order rate constant was 120 s^{-1} . The decay was followed over at least two lifetimes, *i.e.* for about 20 ms. This is approximately 10^3 times longer than the decay of the flashlamp and thus the luminescence decay was recorded essentially free of any contribution due to scattered light from this source.

A variety of window materials (*e.g.* LiF, MgF_2 , CaF_2 , SrF_2 , BaF_2 , sapphire and suprasil quartz) could be placed between the flashlamp and the reaction cell and between the reaction cell and the detector thus allowing for an approximate determination of excitation spectra and for an initial attempt at dispersal of the emitted radiation. Several attempts were made to obtain the spectra of the luminescence in more detail using a combination of lens and 0.3 m monochromator described previously [15]. Unfortunately, the signal was too weak to be detected and the block spectrum (Fig. 1) was the best we could obtain.

Carbon suboxide was prepared by dehydration of malonic acid with P_2O_5 at 140°C [16]. The product was immediately purified by low temperature distillation and stored at liquid N_2 temperature. Mass spectrometric analysis indicated that the purified sample was better than 99% C_3O_2 . The only detectable impurity was CO_2 . Helium (Airco, 99.9999%), argon (Matheson, 99.9995%), oxygen (Matheson, 99.99%), nitrogen (Matheson, 99.9995%) and carbon dioxide (Matheson, 99.8%) were used without further purification.

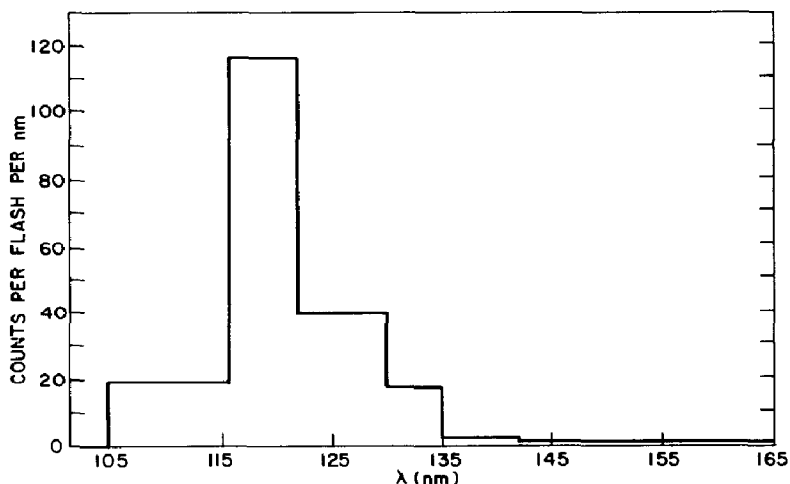


Fig. 1. Block spectrum of the vacuum UV luminescence observed in the flash photolysis of C_3O_2 under the following conditions: 1 mTorr C_3O_2 , 100 Torr He, 298 K, CaF_2 filter on flashlamp, flash energy 225 J.

3. Results

The spectrum of the vacuum UV luminescence obtained using the series of windows with different short wavelength limits is shown in Fig. 1. For each wavelength interval, the intensity of the luminescence, expressed as initial counts per pulse per nanometer, was determined by difference. For example, the intensity for the interval 105 - 116 nm was obtained by subtracting the signal obtained with a MgF_2 window in front of the photomultiplier from that obtained with LiF. This difference was then corrected for the efficiency of the photomultiplier tube as a function of wavelength. It should be noted that, if corrections are not applied for the efficiency of the photomultiplier, the intense peak centered around 120 nm would be even more pronounced since this is the region of the tube's maximum efficiency.

In addition to obtaining information on the spectral distribution of the luminescence, we also examined the effect of temperature, C_3O_2 concentration, total pressure (He), intensity and wavelength of the incident radiation, the addition of CO_2 , O_2 and N_2 as well as the substitution of argon for helium on both the initial intensity of the undispersed luminescence I and its decay rate R . In general, the effect of these parameters on the intensity of the luminescence was much more pronounced than the effect on its rate of decay. The observations may be summarized as follows.

3.1. Temperature. In the range 300 - 223 K, I increased with decreasing temperature by a factor of 10^3 and R increased by a factor of 6 (Table 1).

TABLE 1

Dependence of the decay rate R and intensity I of the luminescence on temperature, diluent gas and added gas^a

| T (K) | Gas (pressure in torr) | | R (s ⁻¹) | I (relative) |
|---------|------------------------|---|---------------------------|-------------------|
| | Diluent | Added | | |
| 223 | He(100) | — | 753 | 1000 |
| 248 | He(100) | — | 594 | 100 |
| 273 | He(100) | — | 360 | 10 |
| 300 | He(100) | — | 120 ± 10 | 1.00 |
| 300 | Ar(100) | — | 76 | 1.04 |
| 300 | He(100) | CO ₂ (2 × 10 ⁻³) | 114 | 0.94 |
| 300 | He(100) | O ₂ (3 × 10 ⁻³) | 127 | 20 |
| 300 | He(100) | O ₂ (6 × 10 ⁻³) | 130 | 10 |
| 300 | He(100) | O ₂ (3 × 10 ⁻²) | 224 | 3 |
| 300 | He(90) | N ₂ (10) | 76 | 0.36 |
| 300 | He(53) | N ₂ (47) | 55 | 0.11 |

^a 1 mTorr C₃O₂ was used for all experiments.

3.2. [C₃O₂]. For a constant pressure (100 Torr He), the intensity is essentially linear with respect to [C₃O₂] (Fig. 2) while R is approximately constant.

3.3. Total pressure. For a constant C₃O₂ pressure (1 mTorr), the intensity varies approximately as the square of total pressure in the range 100 - 500 Torr (Fig. 2) while R is again nearly constant.

3.4. Incident radiation. Both I and R were maximized using a CaF₂ window ($\lambda > 122$ nm) on the flashlamp. In this condition the intensity of the luminescence increased as the square of the incident flash intensity (Fig. 3). Again R is relatively unaffected by a twenty-fold change in this parameter.

3.5. Addition of O₂, CO₂ and N₂ (Table 1). Small amounts of O₂ (comparable with the C₃O₂ pressure) result in a dramatic increase in I by an order of magnitude or more but there is no significant change in R . Addition of a larger amount of O₂ (30 mTorr) is much less effective in enhancing I but does lead to a significant increase in R . The addition of N₂ to the reaction mixture results in a decrease in both I and R . The addition of 2 mTorr CO₂ (a possible impurity in our C₃O₂) had no measurable effect on either I or R .

3.6. Diluent gas — Ar versus He. No effect on I and only a small decrease in R was observed (Table 1).

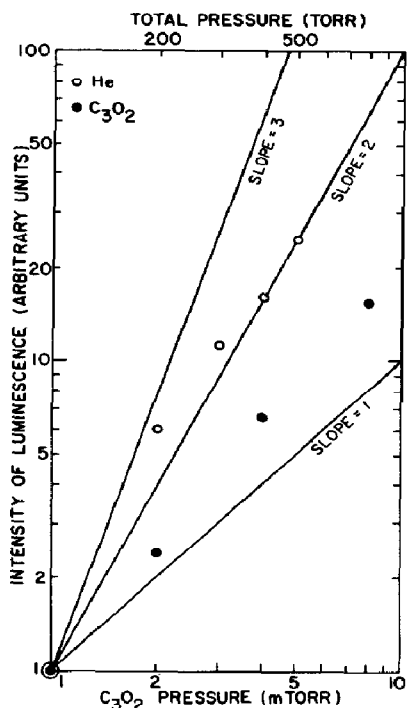


Fig. 2. Dependence of the luminescence intensity on C_3O_2 pressure (filled circles) and total pressure (open circles): ●, lower scale, total pressure = 100 Torr He; ○, upper scale, C_3O_2 pressure = 1 mTorr. All other conditions same as for Fig. 1.

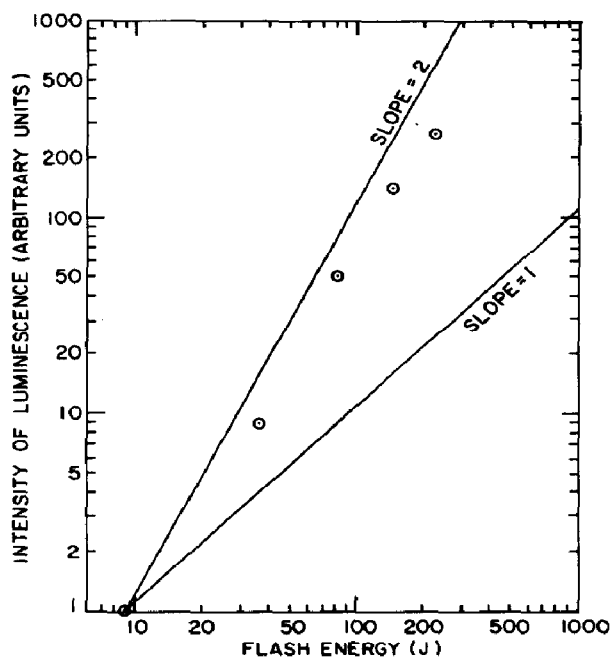


Fig. 3. Dependence of the luminescence intensity on flash energy. All conditions other than flash energy are the same as for Fig. 1.

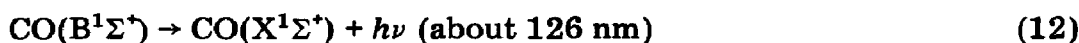
Using an EMR-542-F-08-18 photomultiplier and various windows (Suprasil, Pyrex and Quartz) we observed a second emission in the near UV centered around 250 nm. Unfortunately the signal was even weaker than the 120 nm system and was therefore also too weak to disperse.

4. Discussion

In the absence of a more detailed spectrum of the luminescence, positive identification of the emitter is not possible. It is, however, worthwhile to consider briefly circumstantial evidence which leads to a plausible interpretation of the experimental observations. The observations of emission peaking near $\lambda = 120$ nm (about 10 eV) in a system containing only carbon and oxygen suggests that the emitter may be an excited state of CO since this is the only molecular species capable of being formed in such a system which has bound states in the 10 eV range. A likely candidate for the origin of the observed luminescence would be the $B(^1\Sigma^+) \rightarrow X(^1\Sigma^+)$ transition of CO. The more familiar $A(^1\Pi) \rightarrow X(^1\Sigma^+)$ transition (4th positive system) is not

consistent with the spectrum shown in Fig. 1 since this system has an intense 0,1 band around 160 nm [17]. The emission observed near 250 nm may tentatively be identified as the Cameron bands [18] ($a^3\Pi \rightarrow X^1\Sigma^+$) thus implicating the participation of CO in both the $B^1\Sigma^+$ and $a^3\Pi$ states.

With these preliminary comments in mind we present a possible, but not necessarily unique, series of reactions as an explanation for the observations reported above:

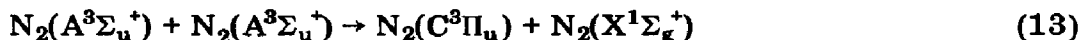


Primary process (5) is certainly the major process based on both product analysis experiments [4] and on direct observation of carbon in flash photolysis experiments [5]. There is no evidence for the occurrence of reaction (6) in C_3O_2 but a low quantum yield ($\phi \approx 0.01$) would easily suffice. It is also possible that the photolysis of a very low level O_2 impurity (about 1 ppm) in the helium or argon diluent could be the source of $O(^3P)$. The observation that I increases by an order of magnitude or more upon addition of O_2 in very small quantities (30 ppm) is consistent with either hypothesis.

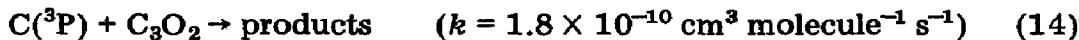
The insensitivity of the intensity to the addition of small amounts of CO_2 (the principle impurity in C_3O_2) demonstrates that this is not a significant source of $O(^3P)$ in this system.

Competition between stabilization and decomposition of CO^* (reactions (8) and (7)) would account for the large increase in the intensity of the luminescence with decreasing temperature. The observed rate of decay (about 120 s^{-1}) of the luminescence and the observation that this rate is constant over a wide range of conditions implies that process (9) is the dominant loss process for $CO(a^3\Pi)$. The lifetime ($\tau = 1/k$) calculated from the decay rate is 8.3 ms. This is consistent with the lifetime of $CO(a^3\Pi)$ calculated by James [19] to be 8.75 ms and with Lawrence's [20] experimental value of 7.5 ms. This implies that, under these conditions, the energy pooling process (11), followed immediately by reaction (12) which produces our observed luminescence, is a minor process. It should be noted that $N_2(A^3\Sigma_u^+)$, the

lowest triplet state of N_2 , is nearly isoenergetic with $CO(a^3\Pi)$ and that a comparable energy pooling process has been reported for this species [21]:



Here it should also be noted that reaction (7) must compete with the fast reaction [22]



since $[C_3O_2]$ was typically $3 \times 10^{13} \text{ molecule cm}^{-3}$ and the concentration of transient species probably never greatly exceeded $10^{10} - 10^{11} \text{ cm}^{-3}$. Therefore, even if reactions (7) and (8) occurred on every collision, less than 1% of the $C(^3P)$ formed in the flash would react with a transient species such as $O(^3P)$. Reactions (11) and (12) are therefore very minor processes in the overall photolysis of C_3O_2 .

The observed luminescence is proposed to result from the energy pooling process (11) and hence the intensity at $t = 0$ should be dependent upon the square of $[CO(a^3\Pi)]$. $CO(a^3\Pi)$ in turn should be pseudo first order with respect to $O(^3P)$ and hence be linearly dependent on flash intensity since it is formed in reaction (7) and $[C(^3P)] \gg [O(^3P)]$ initially. This is consistent with the observed dependence of the intensity of the luminescence on the square of the flash intensity (Fig. 3). Similarly, $CO(a^3\Pi)$ should be linearly dependent on the total pressure via reaction (8). Thus the intensity of the luminescence should vary as the square of the total pressure. Again, this is consistent with observation (Fig. 2).

It might be argued that the reaction



could be the source of the observed luminescence. Although C_2O has been identified in the near UV photolysis of C_3O_2 , the reaction (15) is only $8.8 \pm 0.2 \text{ eV}$ exothermic [13] and therefore could not directly populate the B state. In fact, the absence of the CO 4th positive system argues against the presence of a significant concentration of C_2O since reaction (15) is known to yield primarily 4th positive emission [13]. The related reaction



is however energetic enough (about 10.8 eV) to populate the B state directly. This reaction can be discounted for the following reason. Argon is an efficient deactivator of $O(^1D)$ ($k_{Ar} = 7.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [23] whereas helium is not ($k_{He} < 7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [23]. Therefore, the substitution of argon for helium as the diluent gas should drastically decrease the intensity of the luminescence if reaction (16) were important. As can be seen from Table 1, the substitution of argon for helium has essentially no effect on intensity.

5. Summarizing remarks

The observed far UV chemiluminescence (120 nm) is attributed to the $B(^1\Sigma^+) \rightarrow X(^1\Sigma^+)$ transition in CO. The B state is thought to be formed in an energy pooling reaction involving $CO(a^3\Pi)$. This reaction, and hence the far UV luminescence, represent a relatively minor process in the vacuum UV flash photolysis of C_3O_2 . Speculations concerning the mechanism of formation of $CO(a^3\Pi)$ are presented which are qualitatively consistent with the observations. This has been done to provide a framework for an initial attempt at understanding the experimental observations and in the expectation that this might stimulate further work on the system.

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