

AD737392

SEMI-ANNUAL TECHNICAL REPORT

July 1st - December 31st, 1971

ARPA ORDER NUMBER 1482 Amdt 2

PROGRAM CODE NUMBER OE20

Name of Grantee
COLUMBIA UNIVERSITY
NEW YORK, NEW YORK

Effective Date of Grant
30 JUNE 1970

Grant Number
DA-ARO-D-31-124-70-G103

Amount of Grant: \$50,000

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Short Title of Work
METAL OXIDE INFRARED EMISSION

Sponsored by
ADVANCED RESEARCH PROJECTS AGENCY
ARPA ORDER No. 1482 Amdt 2

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some of the recent work has been
described in

SUMMARY

1. Reactions of the Group II A metals (except Be) and of aluminum have been carried out with O_3 under single-collision conditions; In the case of the Group II A metals, the spectra are quite complex in appearance and include previously identified singlet-singlet transitions terminating on what is supposed to be the ground state of the metal oxide molecule, and unanalyzed triplet-triplet transitions which may terminate on the actual ground state of the MO molecule.

2. Reaction of $Sr + O_2$ yields both vacuum UV emission as well as emission in the visible (red); The emitter is tentatively identified as the SrO_2 (strontium peroxide) molecule which is believed to result from two-body radiative recombination. and

3. The distribution of vibrational-rotational levels (v'' , J'') populated in the oxidation of metals which may exert a large influence on their subsequent radiative and/or reactive fate. We have crossed Ba with O_2 and observed the (v'' , J'') population distribution of the newly-formed BaO product, using the new technique of laser-induced fluorescence. The nature of the

(v'' , J'') (double prime)

Such as in the crossing of Ba and O_2

reaction, $\text{Ba} + \text{O}_2$, is discussed in the light of these findings. The radiative lifetime of the $\text{BaO A } ^1\Sigma$ state has been measured and found to be 350 ± 50 nsec.

I. M + O₃ CHEMILUMINESCENCE

A. Al + O₃

Preliminary investigations have been carried out on the AlO emission bands obtained from the crossing of aluminum atoms and ozone beams. Evidence has been found for the formation of AlO in the first excited A state (the blue-green band system) and, to some extent, in the second excited B state. From a study of these spectra a lower limit on the AlO ground state dissociation energy may be placed. Investigation of Al atom reactions with other oxidizer gases is now in progress.

B. Ca + O₃

Spectra corresponding to transitions involving the X¹Σ and the B¹Π and C¹Σ states have been tentatively identified. The A¹Σ - X¹Σ transition also appears in chemiluminescence. A complicated region of the spectrum similar to that found in BaO and SrO is believed to correspond to a triplet-triplet transition in CaO. This suspicion is supported by L. Brewer and J. Wang's recent matrix isolation work (unpublished) on CaO showing that some of these unidentified bands are seen in

absorption, implying that the ground state is not the $X \ ^1\Sigma$ state in CaO. The band observed at the short wavelength limit of the $C \ ^1\Sigma - X \ ^1\Sigma$ spectrum is assigned to the (2, 1) band. This places a lower limit of 4.64 eV on the dissociation energy of the CaO $X \ ^1\Sigma$ state.

C. Sr + O₃

The chemiluminescence spectrum from the reaction $Sr + O_3$ begins at approximately 3,800 Å, becomes very strong from 5,000 to 6,000 Å, and extends with decreasing intensity far into the red. The linear O₃ pressure dependence and Sr beam flux dependence indicate that SrO is the emitter, i.e. the chemiluminescence is due to the direct reaction $Sr + O_3 \rightarrow SrO^* + O_2$. With the assumption that at the threshold for chemiluminescence the total energy of the reaction goes into internal energy of the SrO molecule and the further assumption that the electronically excited SrO radiates to the ground state of SrO, we get a lower limit for the dissociation energy of SrO : 4.25 eV. The chemiluminescence spectra taken with low resolution (20 Å) show, in the short wave length region, a fairly regular structure with approximately 100 Å spacing, but above 5,200 Å this structure becomes more irregular. Yet it seems to be due to vibrational

transitions. With 2 Å resolution, definitely red, degraded band heads become apparent (in the region 4,600 - 5,300 Å). An attempt to identify these heads with the well known also red degraded heads of the blue system B ${}^1\Pi - X {}^1\Sigma$ [P. C. Mahanti, Phys. Rev. 42, 609 (1932); I. Kovács and A. Budó, Ann. Phys. (Leipzig) 6, 17 (1953)] was not successful. Obviously, the chemiluminescence is due to another SrO transition which has not been identified before.

D. Ba + O₃

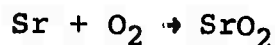
The Ba + O₃ chemiluminescence begins at approximately 3,350 Å (450 Å below the corresponding Ba + N₂O chemiluminescence). A comparison of the Ba + O₃ and Ba + N₂O chemiluminescence shows that both reactions give rise to the same chemiluminescence spectra. Spectra taken with 0.5 Å resolution agree in the position of the maxima, only the intensities are different. Except for the fact that the Ba + O₃ chemiluminescence contains a very small fraction corresponding to the BaO A ${}^1\Sigma - X {}^1\Sigma$ transition, the chemiluminescence spectrum is very complicated. The main part of the Ba + O₃ and Ba + N₂O chemiluminescence is very likely to be due to an excited BaO triplet state. This is supported by the fact that many perturbations were found in the BaO A ${}^1\Sigma -$

$X^1\Sigma$ spectrum [A. Lagerqvist, E. Lind, and R. F. Barrow, Proc. Phys. Soc. A 63, 1132 (1950); I. Kovács and A. Lagerqvist, Arkiv Fisik 2, 411 (1950)], but unfortunately, even the relative positions of these perturbing states is unknown.

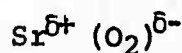
II. $M + O_2$ CHEMILUMINESCENCE



Previous and concurrent work has indicated that the dissociation energy of strontium oxide is definitely less than that of O_2 (≤ 5.0 eV for SrO vs. 5.1 eV for O_2), and therefore, the reaction of strontium atoms and oxygen molecules is unlikely to yield SrO molecules. We have, however, noted and measured light emission from the reaction



where we believe SrO_2 to be the only possible reaction product. The spectrum observed occurs in the region above 6,000 Å and has been tentatively assigned as a progression in the O-O stretching and Sr-O-O bending mode for the ground states. The reaction is found to be first order in both metal flux and oxygen gas pressure implying the formation of SrO_2 via a quite unusual two body radiative association process. The probable structure of SrO_2 is



since one of the characteristic features of the emission bands is an $1,180\text{ cm}^{-1}$ separation indicative of O_2^- .¹ Hence, the

radiative association is correlated with a probable electron jump mechanism. The formation of $\text{Sr}^{\delta+}-\text{O}_2^{\delta-}$ brings to mind the possibility that emission of vacuum ultraviolet radiation occurs, since the heat of formation for the process (1) is ≈ 6.7 eV.² Tentative measurements have indicated that this is indeed the case, confirming the probable formation of the SrO_2 molecule.

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1. J. Rolfe, J. Chemical Physics, 40, 1664 (1964).
 2. I. I. Vol'vov, Peroxide, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals, Plenum Press, New York, 1966 pg. 66.

III. LASER-INDUCED FLUORESCENCE:
A NEW METHOD TO STUDY INTERNAL STATES OF REACTION PRODUCTS

In the semi-annual technical report, June 30th - December 31st, 1970, we proposed to cross a beam of metal atoms (M) with a beam of O₂ molecules and observe the MO products by laser-induced fluorescence. A feasibility study was then presented for the prototype system $Ba + O_2 \rightarrow BaO + O$ in which it was concluded that this technique was sufficiently sensitive to detect the v" distribution of the BaO products, if not the (v", J") distribution, itself.

During the last year, we have assembled the necessary equipment, and a few weeks ago, we carried out the first experimental studies along the lines proposed. Using the LABSTAR apparatus, a beam of barium atoms traverses a scattering chamber containing O₂ molecules. Simultaneously, the output of an AVCO Dial-A-Line dye laser is passed through the reaction zone. As the wavelength of the dye laser is scanned, the BaO molecule is excited to the (v', J') level whenever the laser wavelength coincides with an allowed v" J" \rightarrow v' J' transition in the A-X band system. This is detected by viewing the fluorescence at right angles to

the laser beam using a combination of a sharp cutoff Corning filter (which blocks the laser wavelength) and a fast-response photomultiplier. Because the laser is pulsed, i.e. because the laser is off most of the time, gated detection electronics is employed. For this purpose, we used a Princeton Applied Research Boxcar Integrator, on loan to us from Dr. Howard Schlossberg, AFCRL. The boxcar is triggered by the laser pulse. The variable gate (window) is maintained open from the start pulse to about five times the BaO radiative lifetime. Because the boxcar is an analog device its use permits many single shots to be averaged together. The dye laser is pumped, in turn, by a nitrogen-pulsed laser. Consequently, the duration of the dye laser pulse is less than 10 nsec. Thus, provided the radiative lifetime of the A state of BaO exceeds 10 nsec, it can be measured by using the boxcar with its narrow gate-window to observe, directly, the exponential decay. This was done.

Figure 1 shows a portion of the vibrational structure in a fast scan whereas Figure 2 shows the resolved rotational structure of a single band in a slow scan. In the latter, the assignment is that of Lagerqvist et al.¹ A preliminary analysis of Figs. 1 and 2 allows a temperature of about $T_v = 1,500^\circ\text{K}$ to be assigned to the vibrational distribution and $T_r = 500^\circ\text{K}$

to the rotational distribution of the BaO product if a Boltzmann distribution is assumed.

Several other groups²⁻⁶ have also investigated the reaction



using crossed beams. Based on the BaO dissociation energy of 5.74 eV which we determined⁷ and on the O₂ dissociation energy of 5.08 eV, the above reaction is exothermic by about 0.66 eV. This excess energy of reaction must appear as translational energy and as internal energy of the products. Based on their angular distribution studies, Batalli - Cosmovici and Michel concluded that most of the exoergicity is found in the internal states of the products. Our direct measurement of the population of individual (v", J") levels of BaO contradicts the work of Batalli-Cosmovici and Michel. Recently, Herschbach and Loesch have repeated Batalli - Cosmovici and Michel's angular distribution measurements with quite different results. Herschbach and Loesch concluded from the double-peaked angular distribution of reactively scattered BaO that at least at higher collision energies (0.3 - 0.7 eV) a collision complex is formed. Our measurement of the (v', J") population distribution is consistent with the formation of a collision complex and provides direct information about the nature of this reaction process. A more elaborate

investigation is in progress.

As mentioned, the use of the boxcar integrator also gives us the opportunity to measure the BaO lifetime directly. Our first rough lifetime measurements for $v' = 3, 4, 5, \dots$ give a value 350 ± 50 nsec, which is somewhat larger than the values reported recently by Johnson.⁸

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FIGURE CAPTIONS

Fig. 1. Fast scan giving the vibrational distribution of the BaO product. The relative energy of the reaction partners is 0.05 eV. The Ba atom density is $5 \times 10^9 \text{ cm}^{-3}$; the O_2 pressure is about 10^{-3} torr.

Fig. 2. Slow scan giving the rotational distribution of the $v'' = 0$ vibrational level. The experimental conditions are the same as for Fig. 1. Those two lines marked by an asterisk are a known perturbation.

Laser-induced fluorescence
for the reaction $\text{Ba} + \text{O}_2 \rightarrow \text{BaO} + \text{O}$

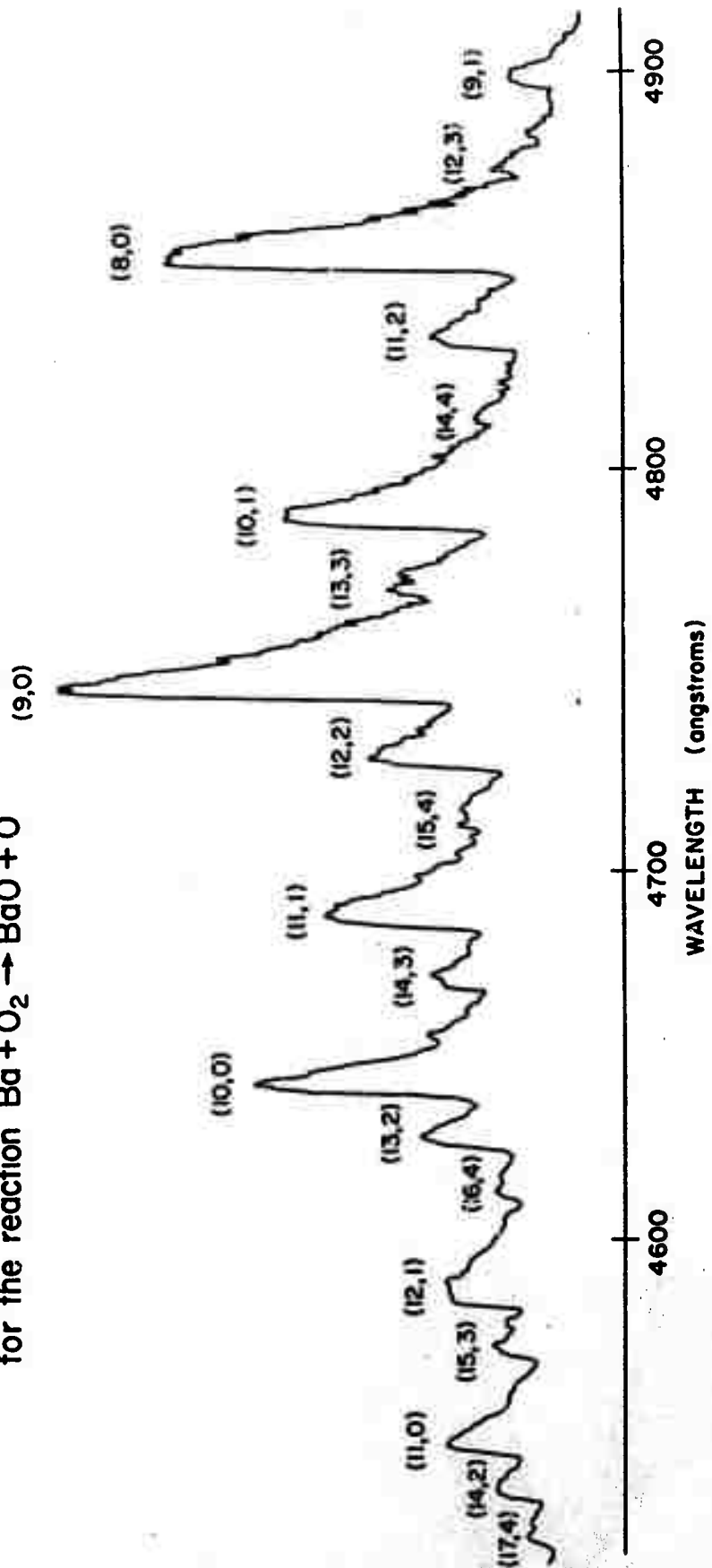


Figure 1.

(3.0) BAND
BaO A-X

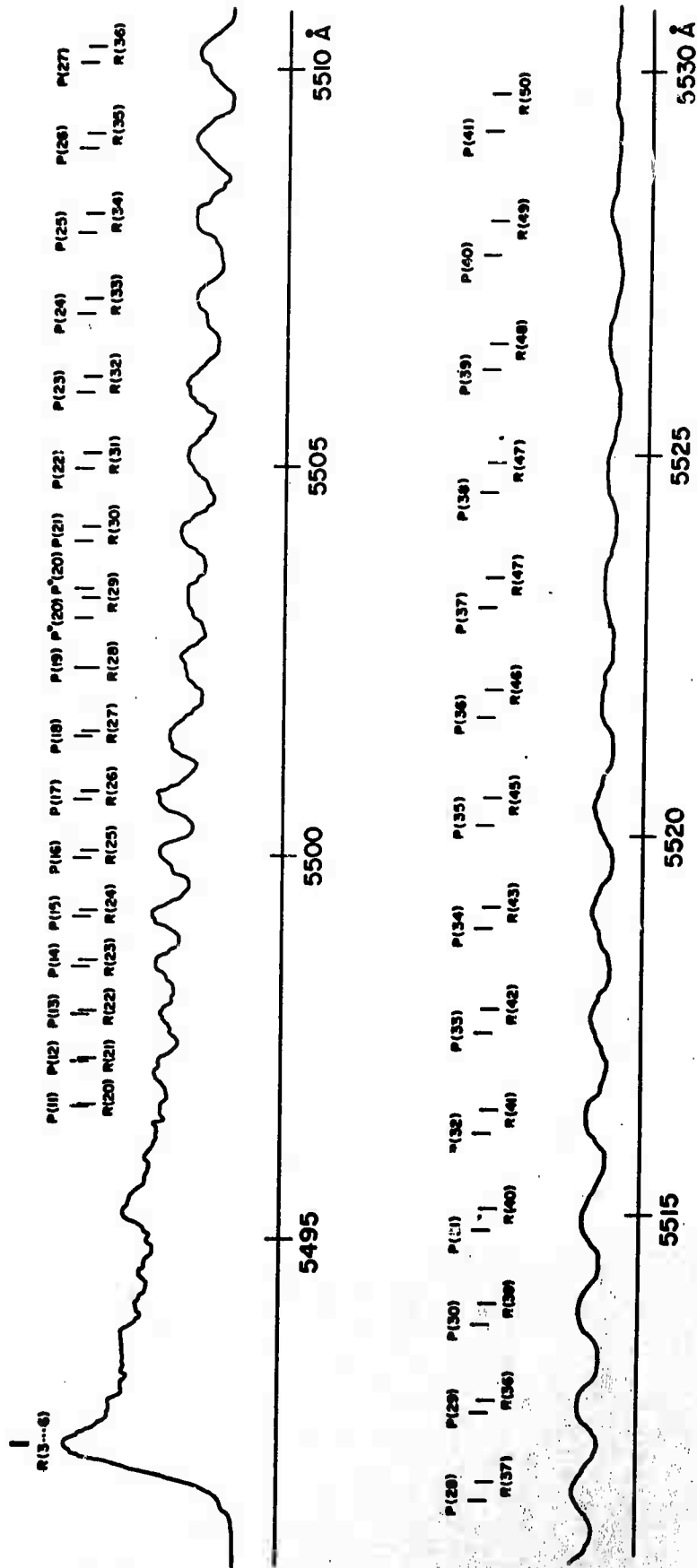


Figure 2.