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METAL OXIDE INFRARED EMISSION

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Summarized is work dealing with the following topics:-

SUMMARY

1. Reactions of magnesium, calcium, strontium, and barium with NO_2 and N_2O ~~have been~~ carried out under crossed beam conditions;

2. A spectral study of the chemiluminescence from these reactions-- ~~has been made and~~ in the case of Ba + NO_2 the spectra is assigned to the A - X blue-green band system of the BaO emitter;

3. In this latter case, the rotational structure has been resolved for each vibrational band. The rotational structure is characterized by temperature but it is found that with increasing v' excitation the J' population distribution decreases.

4. Use of a new technique, namely, laser-induced fluorescence, is discussed with application to the detection of vibrationally excited metal oxide molecules. ( )

I. INTRODUCTION

We are engaged in a research program to study primarily the formation of metal oxide molecules by reactions of metal beams with various oxidizer gases. For this purpose a crossed-beam apparatus has been constructed, named LABSTAR, for its ability to achieve metal source temperatures characteristic of coal-type stars. Presently, we are carrying out experiments with LABSTAR whereby the reactions are monitored by their visible chemiluminescence. Accordingly, this method restricts us to investigating highly exoergic processes that produce electronically excited fragments. The majority of chemical reactions of interest, however, yield vibrationally-excited ground state products. During this period we have evaluated various means of detecting these products. A detailed study was made of the possibility to use infrared chemiluminescence much in the same way we presently employ visible chemiluminescence. Signal-to-noise calculations, though, rule out this technique for our experimental configuration. Instead, we are planning to use laser-induced fluorescence as a probe of the vibrational population distribution.

In this report we shall first describe our present efforts to understand the visible chemiluminescent spectra from group IIA metals with various oxidizer gases, and then present the signal-to-noise considerations which prompt us to pursue the laser-induced fluorescence technique as a new potential molecular beam detector.

II. CROSSED-BEAM CHEMILUMINESCENCE

The dynamics of chemical reactions can be studies most directly by crossed-beam experiments whereby reactions may be carried out "molecule-by-molecule." Since the first pioneering experiments[1] more than ten years ago, the field has blossomed rapidly and provided us with much detailed information about the angular distribution of the products, the partitioning of excess chemical energy into translational, and all other degrees of freedom, and the variation of the reaction cross section with velocity, impact parameter, and orientation.[2]

Because molecular beam detectors, such as hot-wire surface ionizers or "universal" mass spectrometers, are fairly insensitive to the internal energy state of the species being detected, molecular beam experiments generally can only infer with difficulty the distribution of energy among the various internal degrees of freedom of the freshly formed products. To increase the number of reactions in which the internal product excitation can be studied, we are attempting to marry the techniques of molecular beams with molecular spectroscopy. To accomplish this, we have chosen to study a special class of highly exothermic reactions, namely, those that yield electronically excited products that subsequently fluoresce. By observing the chemiluminescent spectrum of these reactions under single-collision conditions, we are able to discover how the excess energy of reaction is divided among vibration, rotation, and electronic excitation of the products. The success of this technique of course presupposes that the emission spectrum can be assigned to the (v', J')

levels of the emitter and that vibrational band strengths and rotational line strengths are known or can be calculated thus permitting the spectral intensity features to be reduced to relative population distribution.

Previously, information on the population of (v, J) levels of newly formed products in chemical reactions has been obtained through infrared chemiluminescence studies, first initiated by J. C. Polyani and coworkers.[3] Because the vibrational lifetime of the molecular products are typically of the order of 10^{-3} sec or longer, it is necessary to correct for the effects of collisional relaxation on the observed population distribution. Another consequence of the long vibrational lifetime is that only a small fraction of the excited products are detected. It also should be mentioned that the signal-to-noise problems associated with the use of infrared detectors, particularly with increasing wavelength, has so far almost exclusively limited infrared emission studies at low pressures to products containing hydrogen bonds.

Visible chemiluminescence studies are quite complimentary to infrared chemiluminescence studies since the former do not suffer from some of the disadvantages found in the latter. Because electronic lifetimes are typically of the order of 10^{-6} sec or shorter, collisional degradation of the initial (v', J') population distribution can be neglected at much higher pressures than in infrared chemiluminescence. Also, all excited products will radiate in the field of view of the detector. Moreover, detectors in the visible portion of the spectrum are superior to their counterparts in infrared. Thus, visible chemiluminescence studies, when applicable, offer a much more sensitive means of detection. It must be stressed, though,

that both techniques are "blind" to different types of reactions. For example, infrared chemiluminescence requires that the vibrationally excited products have an electric dipole moment, and cannot detect products in the v=0 vibrational level; while visible chemiluminescence studies detect only electronically excited products and consequently information about " invisible" reactions, e. g. such as the formation of vibrationally excited ground state products, can only be inferred.

The first attempts to observe visible chemiluminescence of molecular species formed under crossed beam conditions were the efforts of Harrison and Scattergood.[4] They investigated the reactions of O_3 with NO, CO, H_2O and CS_2 but found no chemiluminescent signal above the " background light" resulting from O_3 reaction on the walls of the vacuum chamber. About two years later, Ackerman[5] reported detecting visible chemiluminescence from the reaction O_3 + NO in the spectral range 5500 to 8000 Å. He used a combination of broadband interference filters (750 Å FWHM) and different red-sensitive photographic films. The first spectroscopic studies were carried out on the reaction of group IIA metals with various oxidizer gases,[6] in particular NO_2 and N_2O. We report here a continuation of these visible chemiluminescent studies.

III. EXPERIMENTAL

Experiments are performed with a crossed-beam apparatus named LABSTAR for its ability to obtain the temperatures of late-type stars in the laboratory. Figure 1 shows a schematic diagram of LABSTAR. Basically, the experiments are carried out as follows. A beam of metal atoms effuses from a hot-oven source surrounded by numerous heat shields. This beam then enters a differentially pumped chamber through a small hole (1 cm in diameter) in its bulkhead where it intersects an uncollimated beam of the oxidizer gas which flows into the reaction chamber through an orifice (0.3 cm in diameter). The chemiluminescence is viewed at right angles to both beams through a quartz window mounted on a flange at the side of the reaction chamber.

The oven chamber of LABSTAR has attached to its bottom a 4" oil diffusion pump (750 liters/sec) with a water-cooled baffle. The reaction chamber of LABSTAR is evacuated by a 6" oil diffusion pump (1500 liters/sec) without a baffle. In addition, there is a blank flange on the reaction chamber to which another 4" oil diffusion pump may be attached. Provisions were made for this extra pumping speed so that chemiluminescent reactions with cross sections much less than gas kinetic could be studied at higher gas throughputs. However, this additional pumping speed was unnecessary for the studies reported here.

A. VACUUM SYSTEM

The diffusion pumps of the oven chamber and the reaction chamber share a common foreline which is evacuated by means of a 1397 Welch forepump (425 liters/min). To avoid attack of the forepump oil by oxidizer gases, particularly NO_2, a demountable liquid-nitrogen-cooled glass trap is inserted in the foreline immediately before the forepump.

The pressure is monitored by two Veeco ionization gauges, one located in the reaction chamber, the other in the oven chamber. With a pressure of 1 millitorr in the reaction chamber, the pressure of the oven chamber is better than 5×10^{-6} torr. Exuberant differential pumping is necessary to maintain a well-defined metal atom beam as well as to avoid destruction of the hot oven by the oxidizer gases.

B. METAL SOURCE

The metal beam was formed by effusion from a molybdenum oven heated with a high current (50-60 A) molybdenum-wire resistance winding. A molybdenum heat shield and a water-cooled copper heat shield surround the oven and provide part of the collimation of the beam. The oven is a closed cylinder 10 cm high and 4 cm in diameter. It has a 3 mm hole in the top through which the beam effuses. Occasionally the orifice of the oven clogged when high metal fluxes of Mg, Ca, and Sr were used. This difficulty was never encountered with Ba, which unlike the other group IIA metals is a liquid at the operating temperatures necessary for forming a sufficiently intense beam. Molybdenum was chosen as the oven wall material because of its resistance to chemical attach by the group IIA metals.

Previously, the metal source in LABSTAR was a crucible placed inside a resistance-heated graphite cylinder.[4] Although this permits much higher temperatures, the capacity of the crucible prevented extended runs.

Magnesium ribbon, calcium turnings, and discs of strontium and barium (cut from a metal bar with a bandsaw) were used. The metal oxide coating is scraped off and the metal (of the order of a few grams) was placed inside the molybdenum oven and LABSTAR was pumped down as quickly as possible.

A Granville-Phillips film thickness monitor (see Fig. 1) was used to measure the beam flux and monitor its long-term stability. This device responds to the change in period of oscillation of a quartz crystal oscillator during deposition of the metal. Typical beam fluxes correspond to 10^{15} atoms/sec.

C. GAS SOURCE

The NO_2 or N_2O gas was held in a stainless steel ballast tank and was leaked into the system through a micrometer needle valve. The NO_2 and N_2O are Matheson reagent grade gases and they were used without further purification. The gas orifice contains coarse crinkly-foil and consequently there is very little collimation of the gas flow so that the oxidizer gas tends to fill the entire reaction chamber. Occasionally it was useful to be able to switch rapidly between NO_2 and N_2O. This is accomplished by the use of a second gas orifice in the reaction chamber not shown in Fig. 1.

D. LIGHT DETECTION SYSTEM

All spectra are taken in first order with a $\frac{3}{4}$-m Spex 1702 spectrometer with a grating blazed at 5000 Å. An EMI 6256 QA photomultiplier with a "S" (Q) response is used with no cooling, and the current from the photomultiplier was measured with a Keithley 417 picoammeter and a Leeds and Northrup strip-chart recorder. None of the spectra were corrected for the wavelength response of the detection system. One quartz lens is used to gather and focus the chemiluminescence on the entrance slits of the spectrometer.

IV. CHEMILUMINESCENT SPECTRA

We investigated the reactions of Mg, Ca, Sr, and Ba with NO_2 and N_2O. For both oxidizer gases, the light yield was found to increase from Mg to Ba. The reaction Mg + NO_2 yielded no detectible visible chemiluminescence and the reaction Mg + N_2O yielded chemiluminescence of such low intensity that little effort was made to pursue the study of this process. The low-resolution spectra of the chemiluminescence from the reaction of Ca and Ba with NO_2 and N_2O are presented in Fig. 2.

An examination of Fig. 2 permits us to classify these spectra into three types. In the case of Ca and Sr with NO_2, the spectra are featureless even at high resolution. In the case of Ca, Sr, and Ba with N_2O the spectra at low-resolution appear dense and " noisy," but at higher-resolution, these spectra re shown to be highly structure and comb-like in appearance. Figure 3 illustrates the closely-packed structuring for the case of Ba + N_2O. Finally, in the case of Ba + NO_2, the spectrum has readily distinguishable band-like features. Indeed, a majority of its bands have been assigned to the A - X blue-green band system of BaO.[6] At higher resolution, as seen in Fig. 4, the rotational structure (partially resolved) is apparent, showing the formation of the bandhead. The shading to the red is characteristic of the BaO A - X system.

Bandheads result from the piling together of a large number of rotational lines.[7] In the case of the BaO A - X system, the bandhead occurs at very low J values ($4 \leq J \leq 6$), so that the bandhead is very close to the band origin[8] and thus, the width and the rate of degradation (falling

off) of the band is a measure of the J' distribution of the v' level. Figure 4 shows four traces of unoverlapped, or weakly overlapped, (v', v''=0) bands. It is seen that the slope is greatest for (v'=6) and decreases with decreasing v'. Since the exact shape of the band depends on the v' level of the excited state. computer simulations of the shapes of the four bands were carried out with the same J' distribution for each band. We found that the shape of the bands (v'=6, v'' =0) to (v'=3, v''=0) were essentially the same for the same J' distribution. Thus we conclude that the band shadings shown in Fig. 4 result from the population of higher J' levels for lower v' levels in the reaction product.

Note that this conclusion is not what could be expected from a phase space argument,[9] but indicates a negative correlation between vibrational and rotational excitation of the BaO product. Similar conclusions have been drawn from the infrared chemiluminescence studies of $F + H_2 \rightarrow HF + H$,[10] and $Cl + H_2 \rightarrow HCl + Cl$,[11] where the rate of formation contours in the vibration-rotation plane show a negative slope.

An " effective" rotational temperature may be assigned to the bands shown in Fig. 4, e. g. (v'=6, v''=0) corresponds approximate to 800° K. Note that the rotational distribution of RbBr products formed in the reaction $Rb + Br_2$ is also well characterized by a rotational temperature.[12] For Maxwell-Boltzmann beams and reactions with large cross sections an " effective" rotational temperature may be expected in general based on very simple reaction models.

V. LASER-INDUCED FLUORESCENCE

We propose to cross a beam of metal atoms (M) with a beam of O_2 molecules and observe the MO products by laser-induced fluorescence. The following calculations are an estimate of the signal to be expected under the most pessimistic assumptions using a N_2 laser pumped dye laser. We consider the prototype system $Ba + O_2 \rightarrow BaO + O$ where about 0.67 eV is the excess energy of reaction.

Using a Granville-Phillips thin film monitor we have found in our system that the barium beam has a flux of 2×10^{14} atoms cm^{-2} sec^{-1}, corresponding to a density of 4×10^{9} atoms cm^{-3}. We assume that the O_2 pressure is adjusted so that one barium atom in 10 reacts. For a 1 cm path legth and a reaction cross sections of 10^{-15} cm^2 this requires an O_2 concentration of 10^{-3} torr. Thus 4×10^{8} BaO molecules cm^{-3} are formed in the reaction region.

We assume that there are approximately 10^3 vibrational rotational levels (vJ) available to the BaO molecule and that they are equally populated (worst case). Hence there are 4×10^{5} BaO molecules cm^{-3} in a particular v, J level.

The AVCO dye laser produces a 20 μ J pulse of 1×10^{-8} sec duration with a bandwidth of 5A. Moreover, the repetition rate is 25 to 100 pps. We will take the lower figure in the subsequent calculations.

Let us assume an oscillator strength of 10^{-3} corresponding to a radiative lifetime of 4×10^{-6} sec. We believe this to be a lower bound.

The number of excited BaO molecules per pulse coming from one (v, J) level is found from the relation

$$\Delta N = N B \rho \Delta t \tag{1}$$

where N is the number within the reaction volume of BaO molecules in the N, J level, B is the Einstein absorption coefficient ($ergs^{-1}$ cm^3 sec^{-2}), ρ is the radiation density per unit bandwidth (erg cm^{-3} sec), and Δt is the pulse duration. For our proposed experiment we estimate

$$N = 4 \times 10^5$$

$$B = 1 \times 10^{18} \text{ erg}^{-1} \text{ cm}^3 \text{ sec}^{-2}$$

$$\rho = 1 \times 10^{-13} \text{ erg cm}^{-3} \text{ sec}$$

$$\Delta t = 1 \times 10^{-8} \text{ sec}$$

From Eq. (1) we obtain

$$\Delta N = 4 \times 10^2 \text{ per pulse.}$$

Taking into account quantum efficiency of the detector and losses due to the collection optics, we estimate that we will observe 4 photoelectrons per pulse. This corresponds to 100 photoelectrons per second.

The success of the detection scheme depends critically on our ability to reject scattered laser light. We propose to use a pockels cell to blank off the photomultiplier during the laser pulse. We also plan to gate the photomultiplier output so that it is on only during the time immediately after molecular excitation. Because of the short

duration of the AVCO dye laser pulse we will be able to turn the photomultiplier off while the laser is on and still observe almost all of the (slower) molecular fluorescence. Of course, a right angle geometry will be employed and care will be taken to properly baffle both the viewing direction and the direction of the laser beam. In this manner we believe we can detect this signal.

Note that the magnitude of the signal is grossly underestimated. We expect the Ba atom density can be increased by 10 to 100 times its present value. Also we expect to concentrate our attention on the prominent band heads where many $v'', J'' \rightarrow v' J'$ transitions merge. This is estimated to give us another factor of 100 in sensitivity. We are thus quite optimictic that this method will permit us to monitor the vibrational levels of the newly formed metal oxide molecules. Accordingly, an AVCO dye laser has been ordered.

REFERENCES

1. See, for example, T. H. Bull and P. B. Moon, Disc. Farad. Soc. 17, 54 (1954(; E. H. Taylor and S. Datz, J. Chem. Phys. 23, 1711 (1955); E. F. Greene, R. W. Roberts, and J. Ross, J. Chem. Phys. 32, 940 (1960); D. R. Herschbach, G. H. Kwei, and J. A. Norris, J. Chem. Phys. 34, 1842 (1961).

2. For recent reviews consult D. R. Herschbach, Advan. Chem. Phys. 10, 319 (1966); M. J. Henchmann, Ann. Rept. Chem. Soc. (London) 62, 39 (1966); A. R. Blythe, M. A. D. Fluendy, and K. P. Lawley, Quart. Rev. (London) 20, 465 (1966); E. F. Greene and J. Ross, Science 159, 587 (1968); J. P. Toennies, Ber. Bunsenges Physik. Chem. 72, 927 (1968).

3. See K. G. Anlauf, P. E. Charters, D. S. Horne, R. G. Macdonald, D. H. Maylotte, J. C. Polyani, W. J. Skrlac, D. C. Tardy, and K. B. Woodall, J. Chem. Phys. 53, 4091 (1970) and references cited therein.

4. H. Harrison and D. M. Scattergood, Bull. Am. Phys. Soc. 10, 1211 (1965); Boeing Technical Document D1-82-0480 (Boeing Scientific Research Laboratories, Seattle, Washington, 1966).

5. M. Ackerman, Bulletin de l'Académie royale de Belgique 53, 1311 (1967).

6. Ch. Ottinger and R. N. Zare, Chem. Phys. Letters 5, 243 (1970).

7. G. Herzberg, Spectra of Diatomic Molecules 2nd ed. (Van Nostrand Reinhold Co., New York, 1950).

8. A. Lagerqvist, E. Lind, and R. F. Barrow, Proc. Phys. Soc. London 63A, 1132 (1950).

9. P. Pechukas and J. C. Light, J. Chem. Phys. 42, 3281 (1965).

10. J. C. Polyani and D. C. Tardy, J. Chem. Phys. 51, 5717 (1969).

11. K. G. Anlauf, P. J. Kuntz, D. H. Maylotte, P. D. Pacey, and J. C. Polyani, Disc. Faraday Soc. 44, 183 (1967).

12. R. Grice, J. E. Mosch, S. A. Safron, and J. P. Toennies, J. Chem. Phys. 53, 3376 (1970).

FIGURE CAPTIONS

Fig. 1. Schematic diagram of LABSTAR.

Fig. 2. Chemiluminescent spectra.

Fig. 3. High-resolution trace of the light emission from the reaction Ba + N_2O.

Fig. 4. Selected (v', v"=0) bands of the BaO $A^1\Sigma$ - $X^1\Sigma$ electronic system. The rotational structure represents individual lines or in some cases the blend of two P and R lines.

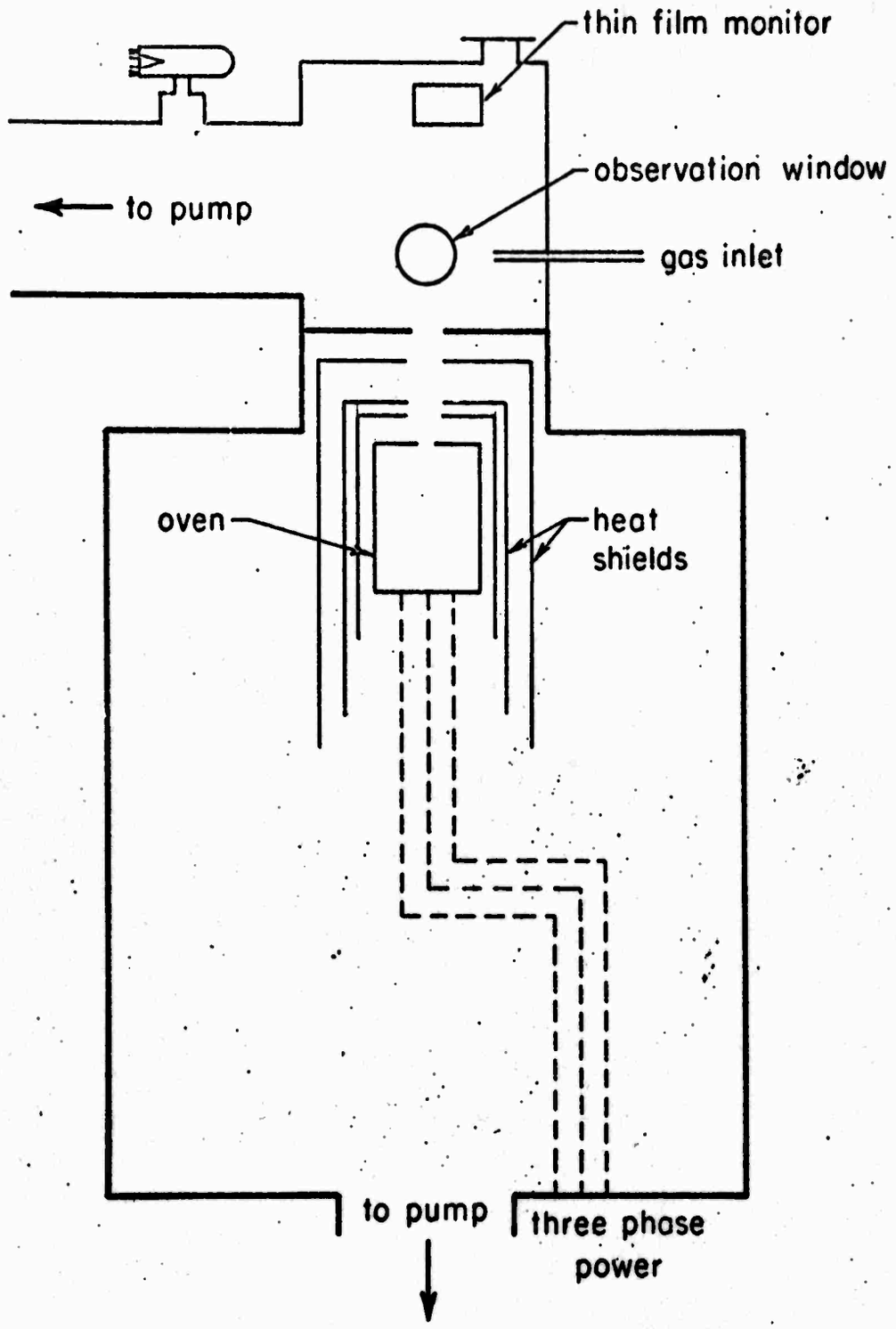
thin film monitor
observation window
to pump
gas inlet
oven
heat
shields
to pump
three phase
power

Figure 1.

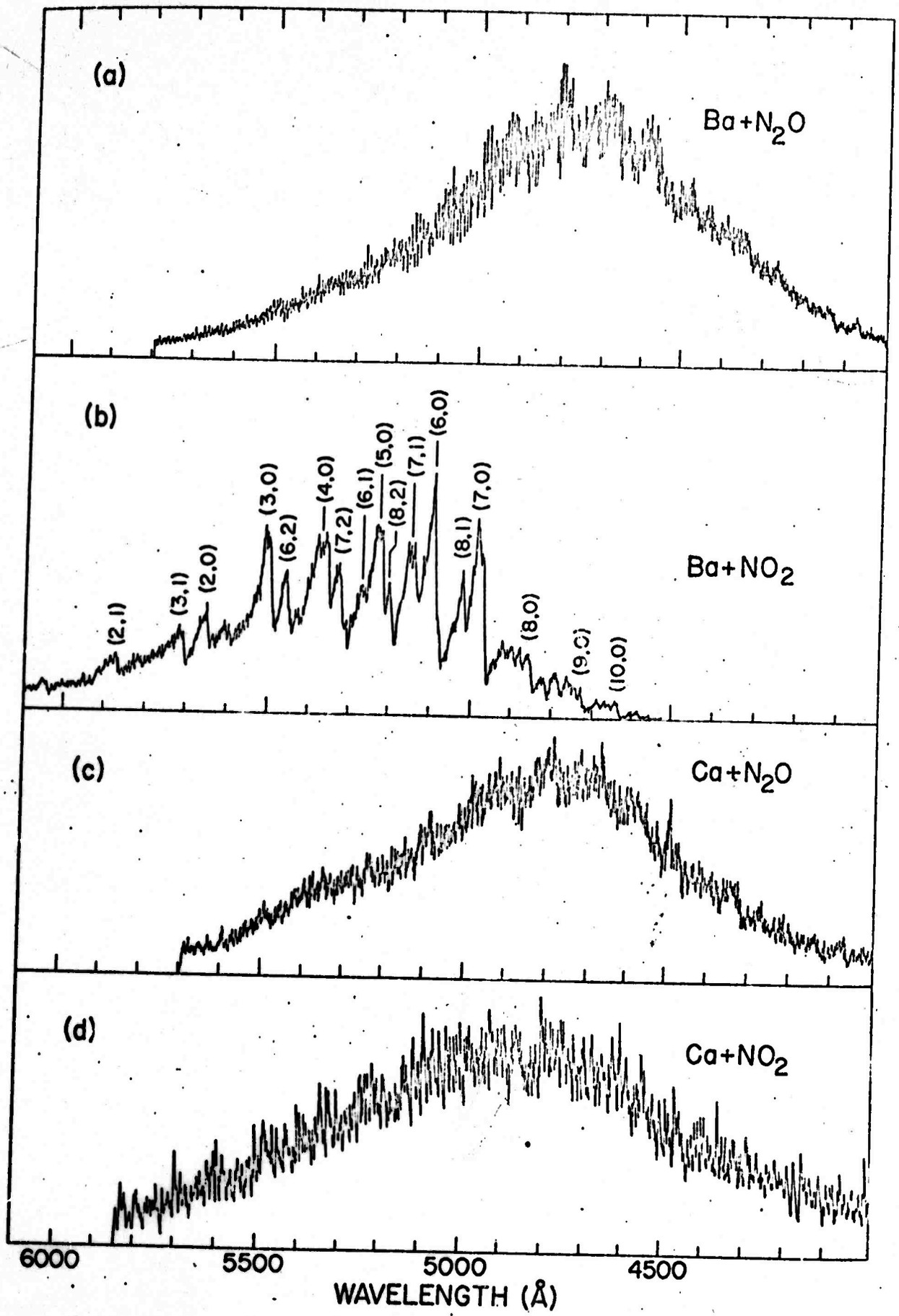
(a)
Ba+N2O
(b)
(2,1)
(3,1)
(2,0)
(3,0)
(6,2)
(4,0)
(7,2)
(6,1)
(5,0)
(8,2)
(7,1)
(6,0)
(8,1)
(7,0)
(8,0)
(9,0)
(10,0)
Ba+NO2
(c)
Ca+N2O
(d)
Ca+NO2
6000
5500
5000
4500
WAVELENGTH (Å)

Figure 2.

RK

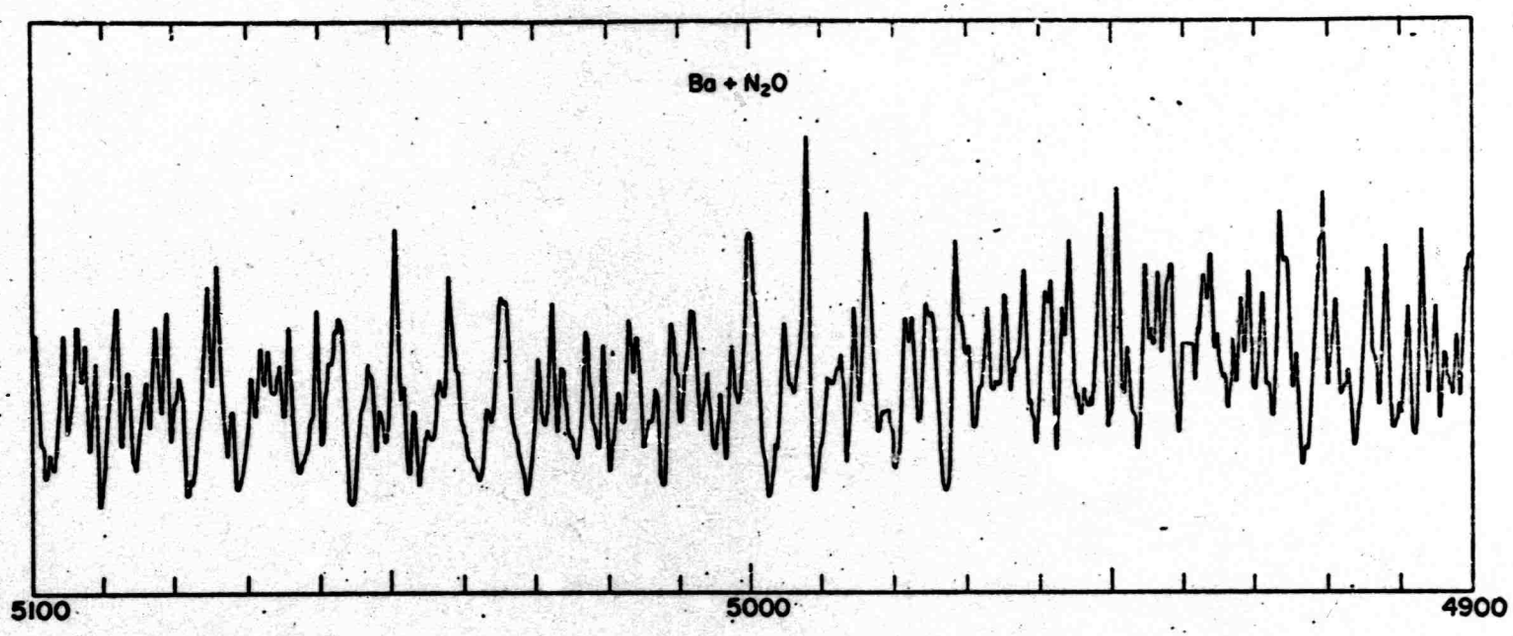

Figure 3.

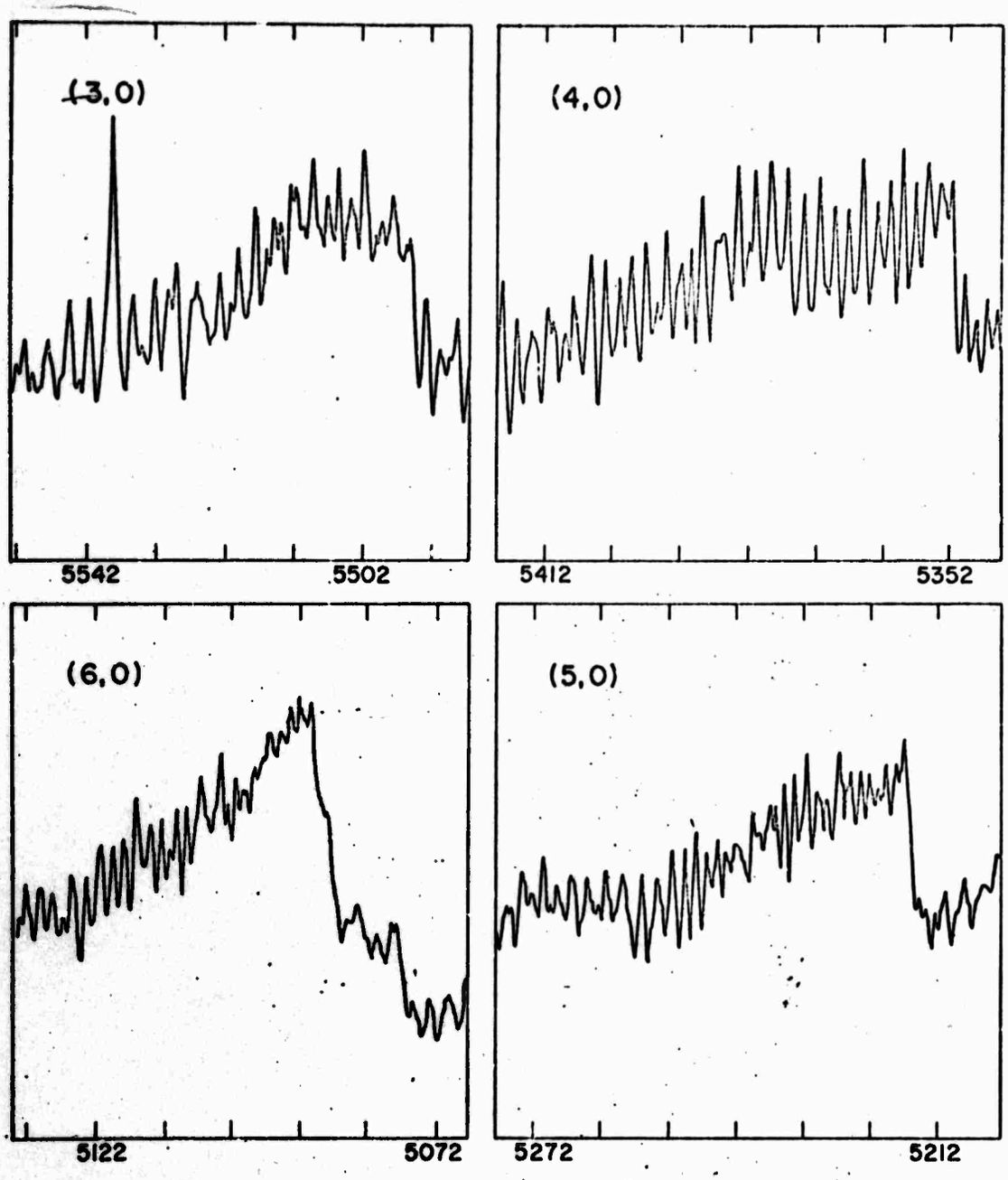

Figure 4.

19d