

Comparison of Ba + O₃ and Ba + N₂O chemiluminescence*

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The chemiluminescent reaction Ba + N₂O has been a topic of much recent research activity because of its possible use in the development of a visible chemical laser. At N₂O pressures on the order of 1 mtorr or less, this laboratory has found a headless, many-lined spectrum^{1,2}; with increasing N₂O pressure (3–100 mtorr), the spectrum shows features primarily attributable to the BaO A¹Σ–X¹Σ system³; at still higher pressures (0.4–40 torr), the BaO A–X band heads are clearly recognizable superimposed on an unresolved continuum that lies in the same spectral region as the low-pressure headless emission and that decreases in intensity with increasing pressure.⁴ Jones and Broida⁴ have investigated the quantum yield of BaO A–X photons per Ba atom consumed as a function of inert carrier gas pressure. They find that the BaO A–X emission increases with carrier pressure, reaching a maximum around 10 torr. Under the conditions, as much as 20% of the Ba atoms consumed result in BaO A–X emission. Confirmation of the large pressure-dependent yield of BaO A–X emission has been reported by Eckstrom, Edelstein, and

Benson⁵ and by Hsu, Krugh, and Palmer.⁶ These results clearly suggest that a major fraction of the Ba + N₂O reaction goes into one or more metastable states of BaO which are transferred by collisions into the radiating BaO A state with increasing foreign gas pressure.^{4–7} Further information on the nature of this precursor state has been provided by Field,⁸ who was able to assign perturbations in the BaO A–X high-resolution spectrum⁹ to a ¹Π state and to the three components of an inverted ³Π state which lies nearby to the ¹Π state.

The purpose of this Note is to report a comparison of the Ba + N₂O and Ba + O₃ chemiluminescent spectra taken in the low pressure regime (1 mtorr or less). The apparatus for studying the Ba + O₃ chemiluminescence is similar to that used previously to observe Ba + NO₂ and Ba + N₂O chemiluminescence.^{1,2} The ozone is generated by a Welsbach ozonator (Model T408) and trapped on silica gell at dry ice temperatures. The chemiluminescence is photoelectrically recorded using a 1-m scanning monochromator having a Centronic S-20 photomul-

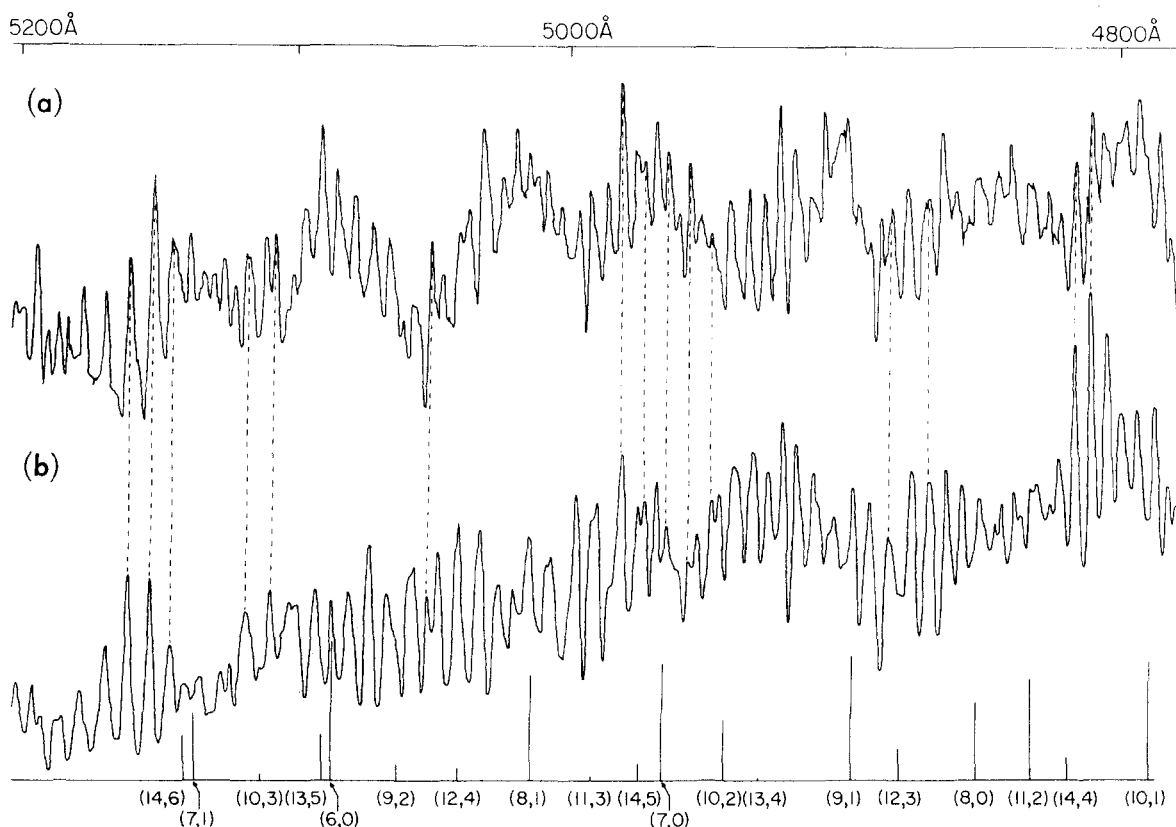


FIG. 1. Portion of the (a) Ba + O₃ chemiluminescent spectrum and (b) Ba + N₂O chemiluminescent spectrum, taken at 2 Å resolution. The gas pressure is 0.1–0.2 mtorr as measured by an uncalibrated ionization gauge 35 cm distant from the reaction zone. In the lower portion of this figure, the (v', v'') band origins of the BaO A–X systems are marked by vertical sticks whose heights are proportional to the emission intensity (see text).

tiplier in a (Products for Research, Inc.) cooled housing attached to its exit slit. Figure 1 shows (a) the Ba+O₃ and (b) the Ba+N₂O chemiluminescent spectra recorded under the same resolution (2 Å). Both spectra are remarkably similar; the linelike features are nearly coincident. The structure is found to be reproducible but not completely resolved. Even under a resolution of 0.5 Å, newly resolved and correspondent features continue to appear. The agreement between the peak positions of the Ba+N₂O and Ba+O₃ spectra permit the conclusion that in both cases an excited electronic state of BaO is the emitter.

Whereas in the case of Ba+NO₂, Jonah, Zare, and Ottinger clearly established that the chemiluminescence is the BaO A-X system, the spectrum of the corresponding Ba+N₂O chemiluminescent reaction proved puzzling to them. As in the case of the Ba+N₂O emission, the Ba+O₃ emission is found to be linear in the Ba flux and linear in the O₃ concentration. Hence, in both cases we conclude that the excited state of BaO is formed by a bimolecular reaction of barium atoms with oxidizer molecules.

The identity of the BaO excited state has not been conclusively established and two possibilities suggest themselves: (1) the BaO emission is from the BaO metastable ^{1,3}Π state; (2) the BaO emission is from high rotational and vibrational levels of the BaO A¹Σ state. These two possibilities are not mutually exclusive, but the linearity of the BaO emission with O₃ pressure over the range 0.03–0.5 mtorr rules out collisional transfer from the BaO ^{1,3}Π state to the BaO A state as primarily responsible for the observed low-pressure chemiluminescence. Recently Hsu, Krugh, and Palmer⁶ have reported that the many-line spectrum resulting from the reaction of Ba with N₂O is still collisionally unrelaxed at pressures as high as 80 mtorr where the average time between collisions is about 4×10⁻⁶ sec. They argue, therefore, that the emission must originate from an excited state of BaO with a radiative lifetime of 10⁻⁵ sec or shorter, thus ruling out long-lived levels of the BaO ^{1,3}Π state. In addition to the rapidly varying structure in Figs. 1(a)

and 1(b), there appears to be another slowly varying structure which matches rather well with the known BaO A-X bandhead positions. To bring out this comparison, the (v', v'') band origins are marked at the bottom of Fig. 1 by vertical sticks whose heights are proportional to $\nu^4(v', v'')q_{v', v''}$, where $\nu(v', v'')$ and $q_{v', v''}$ are the transition frequency and Franck-Condon factor of the (v', v'') band, respectively. Visual inspection of Fig. 1 shows that the band intensity increases with v'. While this observation tends to support the interpretation that the BaO emission originates from direct population of the A state, we cannot dismiss presently the possibility that the emission is from the shorter-lived levels of the BaO ^{1,3}Π state or is a combination of emission from both. In any case, the similarity of the Ba+O₃ and Ba+N₂O emission spectra suggests that quantum yield studies of the reaction Ba+O₃ should also be undertaken.

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