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Emission noise spectrum in a premixed H_2–O_2–N_2 flame

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Abstract—Experimental noise spectra in the frequency range of 15–10^5 Hz are reported for the thermal emission of the first resonance doublet of Na and K in a premixed H_2–O_2–N_2 flame, and for the flame background emission. Under certain conditions, low-frequency peaks arise in the noise spectrum below 100 Hz, while a minimum is found at about 3 kHz. This minimum is of interest with respect to the optimal modulation frequency in atomic fluorescence measurements. The possible sources of fluctuations are discussed, but definite conclusions cannot yet be drawn.

INTRODUCTION

IN THE STUDY of atomic fluorescence in flames, the optimal frequency of modulation of the primary light source depends on the noise spectrum of the flame emission with and without metal seed. The noise spectrum describes the distribution of noise components with frequency f over the frequency range [1, 2]. In our laboratory, fluorescence measurements were made in order to investigate the quenching of excited metal atoms by collisions with flame molecules [3, 4]. Here the signal-to-noise ratio is limited by the noise in the thermal emission of the metal vapour and/or of the flame background. This paper presents some preliminary results of our noise measurements, which will also be of interest in the analytical application of atomic fluoresence in flames.

EXPERIMENTAL

A premixed, laminar H_2–O_2–N_2 flame burning on a circular Méker grid was used. The central flame zone into which a NaCl- or KCl-solution could be sprayed by means of a pneumatic chamber-type nebulizer [1], was normally surrounded by a concentric sheath of hot flame gas with the same composition (H_2:O_2:N_2 = 2:1:6) [5]. The diameter of the central zone and of the whole flame was 1·8 and 3·0 cm, respectively. The total flow of $H_2 + O_2 + N_2$ gas-mixture to the central flame amounted to 7·4 l/min. The line-reversal temperature at a distance of 2 cm above the burner was 1875°K. The observed flame background was found to consist mainly of the OH-bands at 307 nm. The first resonance doublets of K and Na were selected by means of optical filters.

A vacuum phototube (Cintel VA 39) with a load resistor of about 10 MΩ was used to detect the radiation from the flame. The mean photocurrent i_{ph} was measured by means of an electrometer (Keithley) while the noise spectrum was analyzed in the frequency range of 10–5 × 10^4 Hz by a tuned linear a.c. voltmeter (PAR model 121).

[1] R. HERRMANN and C. TH. J. ALKEMADE, *Flame Photometry* (Transl. by P. T. GILBERT) Interscience, New York (1963).
[2] A. v.D. ZIEL, *Noise*. Prentice-Hall, New Jersey (1956).
[3] H. P. HOOYMAYERS, thesis, Utrecht, 1966.
[4] H. P. HOOYMAYERS and P. L. LIJNSE, *J. Quant. Spectrosc. Radiative Transfer*, **9**, 995 (1969).
[5] TJ. HOLLANDER, thesis, Utrecht, 1964.

The ratio of the frequency bandwidth Δf to the tunable central frequency f was constant and equal to 0·063. The frequency response of the whole system was calibrated.

The noise in the photocurrent was corrected for the amplifier noise observed with no illumination on the phototube. The characteristic flame emission noise was found by subtracting the noise power of the trivial shot and low-frequency noise components [6] in the photocurrent from the total noise power. These trivial components were determined by illuminating the phototube with an incandescent filament lamp fed by a stable current source, giving the same photocurrents as the flame emission. For $i_{ph} \leqslant 40$ nA, the lamp radiation was found to produce pure shot noise at $f \geqslant 10^3$ Hz, whereas at lower frequencies a flicker noise component became noticeable. The ratio of flame emission noise to pure shot noise was determined above 10^3 Hz by direct comparison with the noise produced by the lamp radiation at the same mean photocurrent. Below 10^3 Hz, this ratio was determined by making use of the calibrated frequency response of the whole measuring system. Using the theoretical expression for the spectral noise power of pure shot noise, $S_{sh}(f) = 2ei_{ph}$ (with e = elementary charge, [2]) the flame noise could be expressed in absolute units.

Observations

Figure 1 shows the ratio of Na-emission noise to pure shot noise (both expressed in RMS-values) as a function of frequency for two different Na-solution concentrations. The corresponding values of i_{ph} are stated in the figure. The higher concentration value lies on the square-root branch of the calibration curve (Na-emission vs. Na-concentration), which is bent by self-absorption [1]. The lower concentration value lies on the linear branch, where self-absorption is negligible. A flame section of 2×2 cm was viewed at a height of 2 cm above the burner. The general pattern of the noise spectrum did not change essentially, when other parts of the coloured flame were viewed.

A large peak at $f = 32$ Hz and a smaller one at about half this frequency are conspicuous. Apart from these peaks, a gradual decrease towards a minimum at about 3 kHz is noted, followed again by a slower rise at higher frequencies. The low-frequency peak was also observed, when the central flame was surrounded by a flow of cold N_2-gas. The peak frequency was shifted from about 20 to 30 Hz, when the N_2-flow velocity was increased by a factor of 3. Remarkably, these peaks were absent, when no (cold or hot) gas sheath was applied at all.

A quite similar noise spectrum was found for the K-emission. The ratio of K-emission noise to pure shot noise (again expressed in RMS-values) appeared to increase proportionally to $\sqrt{i_{ph}}$, when the K-concentration was raised from low values with negligible self-absorption to the range of strong self-absorption. Since the RMS shot noise increases proportionally to $\sqrt{i_{ph}}$, it follows that the RMS K-emission noise is a *constant* fraction of the K-emission intensity, independently of the occurrence of self-absorption. For given value of i_{ph}, the K-emission-noise appeared to be somewhat larger than the Na-emission noise.

[6] R. J. J. ZIJLSTRA and C. TH. J. ALKEMADE, *J. Appl. Phys.* **27**, 656 (1956).

The noise spectrum of the flame background emission measured for the flame as a whole, showed a similar pattern as in Fig. 1 apart from the low-frequency peaks. These peaks were absent, when the central flame was surrounded by a sheath of equally hot flame gas or when no gas sheath was present at all. With a sheath of cold N_2-gas, a small peak could be observed, if the N_2-flow velocity was relatively

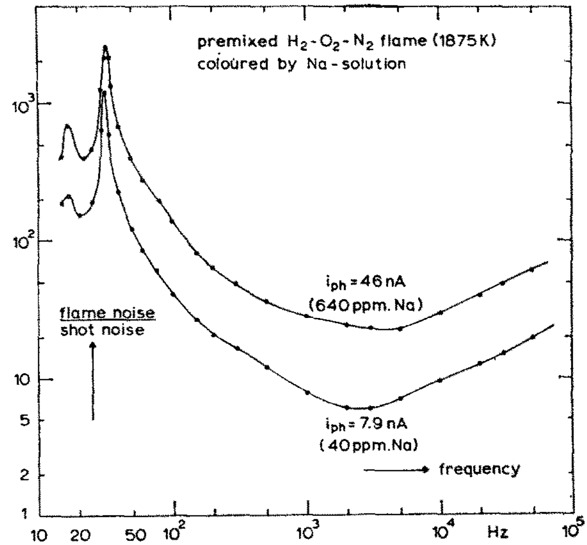

Fig. 1. The RMS noise, i.e. the noise in the Na-emission of a shielded, premixed H_2–O_2–N_2 flame, divided by the RMS shot noise of the photocurrent, i_{ph}, is plotted as a function of frequency.

high. The flame background noise showed a minimum at about the same frequency as the metal emission noise, followed by a gradual rise at higher frequencies. At this minimum, the background noise (expressed in RMS-value) was about 2–3 times smaller than the K-emission noise, if reduced to the same value of i_{ph}.

Discussion

When temperature fluctuations would be the major source of noise for the metal emission, the ratio of the K-emission noise to the Na-emission noise should be 0·76:1 for a given value of i_{ph}. This holds, because the variation in emission intensity as a consequence of a temperature variation is proportional to the excitation energy of the atomic line. Since the K-emission noise was found to be rather higher than the Na-emission noise, temperature fluctuations cannot be a major source of noise.

Fluctuations in the transport of metal salt to the flame must also be ruled out, as the K-emission noise relative to the mean emission intensity appeared not to be influenced by self-absorption. The square-root curvature of the calibration curve due to self-absorption would reduce the relative effect of any fluctuation in the K-concentration on the K-emission by a factor of 2 at high K-concentrations. In particular, the noise associated with the statistical nature of the discrete aerosol droplets introduced into the flame [1, 7], has thus not a dominant effect on the noise spectra observed.

The absence of low-frequency peaks in the alkali noise spectrum, when the flame is not surrounded by a sheath of hot or cold gas, as well as the shift in peak frequency with N_2-flow velocity point to the probable role of the boundary layer between the metal-seeded central flame and the metal-free gas sheath. Since with a sheath of hot flame gas, this (fluctuating) boundary layer forms no (marked) discontinuity for the background emission, it is not surprising that this boundary layer and its associated l.f. fluctuations have much less effect on the background noise. The observation that a peak appears in the background noise spectrum, when the flame is surrounded by a *cold* gas sheath, may also be understandable. For, in this case the (fluctuating) boundary layer forms a discontinuity for the background emission too.

CONCLUSION

In our case, the optimal modulation frequency for fluorescence measurements appears to lie at about 2–5 $\times$ 10^3 Hz where the noise spectrum of both the thermal alkali emission and the background emission attains a minimum.

The presence of a sheath of cold or hot gas flow entails the appearance of outstanding low-frequency peaks in the noise spectrum of the metal emission. In the background noise spectrum, these peaks are much less significant.

The major source of fluctuations in the metal and background emission has not yet been established. The similarity of the noise spectra above 10^2 Hz suggest a common source here. Fluctuations in the temperature or metal transport to the flame are probably not a dominant source. Further investigations are needed to explain the experimental results obtained so far, in particular the unexpected gradual rise in spectral noise power above 10^4 Hz.

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[7] C. TH. J. ALKEMADE, thesis, Utrecht, 1954.