Communications

Brief technical articles, comments on prior articles and book reviews

Note on "Metal Monochloride Emitters in Pyrotechnic Flames – Ions or Neutrals?"

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As pointed out in the subject paper,[1] several writers have erroneously attributed the molecular band spectra that produce the characteristic colours of flames containing various metals M, (M = Ca, Sr, Ba or Cu) and Cl to the singly-charged ions MCl^+.

A copy of a reference that the author had not seen at the time of writing was made available by the kind courtesy of Rutger Webb. This reference, mentioned by Shidlovskiy,[2] is a report on German signal flare compositions by H. J. Eppig[3] that describes research on colored signal lights at nine institutions involved with the research, testing and manufacture of military pyrotechnics in Germany during the Second World War. According to the report

> Very little fundamental research was done on the problem of the radiation emitted by pyrotechnic signal lights. Only small, direct-vision spectroscopes had been used in three of the pyrotechnic manufacturing plants… Nevertheless, it was known that blue lights were caused by radiation emitted by the bands in the molecular spectrum of copper chloride, green lights by the bands of the molecular spectrum of barium chloride and red lights by molecular bands due to strontium chloride.

This is the extent of the directly relevant information. The 29-page report contains some interesting information and formulas, and deserves to be more widely known. The title was slightly misquoted by Shidlovskiy (or his translator) as *The Chemical Composition of German Pyrotechnic Colored Signal Lights.*

The author has recently found a very early reference[4] by one of the founders of molecular orbital theory that is highly relevant to the "ions or neutrals?" issue.

As long ago as 1925, Robert S. Mulliken wrote:

> It is suggested that the absence of electronic band spectra for the hydrogen, silver and alkali halides may be associated with the non-occurrence of higher valence compounds of the type $NaCl_2$, and that the emission of any one of the CuX band spectra follows the transfer of a Cu^+ electron in the polar Cu^+X^- molecule from its normal state to one of a group of low-lying excited states, whose existence can be correlated with the occurrence of the compounds CuX_2, such easily excited electrons being absent in ions such as Na^+. The above relation may be accounted for by supposing that polar molecules cannot carry electronic energy in excess of their heat of dissociation into atoms. By analogy with the observed absence of electronic band spectra for compounds of the NaCl type, the band spectra of the alkaline earth halides should not be due to compounds MeX_2, since the Me^{++} ion contains no easily excited electron. The real emitter is probably MeX, which must contain a loosely bound valence electron like that in Me^+ or Na.

This is taken directly from the Abstract; more detail is provided in the text.

As pointed out previously,[1] a singly charged ion MCl^+ is "of the NaCl type" and does not have a loosely bound valence electron. Metal monochloride ions, therefore, cannot be the emitters of the band spectra responsible for the colours of pyrotechnic flames.

It is noteworthy that Mulliken's description of the origin of the CuX band spectra, written 80 years ago, is completely consistent with current

ideas on the subject as outlined by Parekunnel et al.[5] in 2001.

Mulliken (1896–1986) was awarded the Nobel Prize for chemistry in 1966 "for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular-orbital method". His Nobel Lecture[6] provides a brilliant introduction to molecular orbital theory and its history.

References:

1) B. T. Sturman, "Metal Monochloride Emitters in Pyrotechnic Flames – Ions or Neutrals?" *Journal of Pyrotechnics*, No. 19, 2004, pp 1–13.

2) A. A. Shidlovskiy, *Principles of Pyrotechnics*, 3rd ed., Mashinostoyeniye Press, Moscow, 1964, translated by Foreign Technology Division, Wright-Patterson Air Force Base, OH, 1974, pp 182–186.

3) H. J. Eppig, *The Chemical Composition of German Pyrotechnic Colored Signal Items*, Combined Intelligence Objectives Sub Committee, H. M. Stationery Office, London, 1945, p 5.

4) R. S. Mulliken, "The Isotope Effect in Band Spectra. III. The Spectrum of Copper Iodide as Excited by Active Nitrogen", *The Physical Review*, Vol. 26, 1925, pp 1–32.

5) T. Parekunnel, L. C. O'Brien, T. L. Kellerman, T. Hirao, M. Elahine and P. F. Bernath, "Fourier Transform Emission Spectroscopy of CuCl", *Journal of Molecular Spectroscopy*, Vol. 206, 2001, pp 27–32.

6) R. S. Mulliken, *Spectroscopy, Molecular Orbitals and Chemical bonding*, Nobel Lecture, December 12, 1966, in *Nobel Lectures, Chemistry 1963–1970*, Elsevier Publishing Company, Amsterdam, 1972. Available at http://nobelprize.org/chemistry/laureates/1966/mulliken-lecture.html