STUDIES OF VIBRATIONALLY EXCITED MOLECULES BY INFRARED CHEMI-
LUMINESCENCE

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I. INTRODUCTION

As the proceedings of this conference demonstrate, the subject
of chemiluminescence is primarily concerned with the observation of
radiation from electronically excited species in the visible region
of the spectrum or at shorter wavelengths. Chemiluminescence in
the infrared is generally associated with the formation of reaction
products which are in their ground electronic state but excited
vibrationally. Largely due to the later development of infrared
detectors which even approach the efficiency of those used for
shorter wavelengths, experimental studies of infrared chemi-
luminescence are all of quite recent origin, the first laboratory
observation of spontaneous emission in the instrumental infrared
from a chemically formed, vibrationally excited molecule being
reported by Cashion and Polanyi in 1958. 1

Since that time Polanyi and his coworkers have developed
their experimental technique to a high level of sophistication.
They 2, and other workers 3,4 have concentrated almost entirely on
discovering the initial quantum state distributions of diatomic
hydride molecules produced in simple atom-exchange reactions, such
as
\[ \text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}, \quad \Delta H_0^0 = -45.1 \text{ kcal mole}^{-1}. \]

Their more recent experiments have been carried out at very low
total pressures (\(\sim 10^{-4}\) Torr), thus effectively 'arresting' gas-
phase relaxation and making it possible to observe the product
distribution from the reaction directly. This technique has
proved so powerful that rotational, as well as vibrational, level
distributions have been determined for several reactions. 2a
The detailed state distributions which are obtained in experiments of this kind are particularly important in two ways. First, together with the results from crossed molecular beam experiments and from Monte Carlo trajectory calculations on reactive collisions, they have greatly increased our knowledge of the factors which affect how energy released in a chemical reaction is shared among the degrees of freedom of chemical reaction products. Secondly, reaction product distributions indicate which chemical reactions may be capable of sustaining laser action on the vibration-rotation transitions of the excited product and are essential information if these lasers are to be understood and systematically improved. An interest in both reaction dynamics and in the processes occurring in molecular gas lasers has stimulated the programme of research in infrared chemiluminescence which we have followed in Cambridge over the last four years. In this paper this work is reviewed in three sections: (i) the determination of the relative rates at which the related reactions

\[
O(^3P) + CS \rightarrow CO + S, \Delta H^0 = -85 \text{ kcal mole}^{-1}
\]

and

\[
O(^3P) + CSe \rightarrow CO + Se, \Delta H^0 = -117 \text{ kcal mole}^{-1},
\]

populate the energetically accessible vibrational levels of CO; (ii) the measurement of vibrational deactivation rates of CO, HCl, and HF and DF in high states of excitation; (iii) attempts to find a satisfactory system for producing a relatively simple OH chemical laser. Before discussing the results of these investigations, a brief description is given of the experimental apparatus and general method of interpretation.

II. METHOD

Observations of spontaneous infrared chemiluminescence have nearly all been carried out in discharge-flow systems of the type also commonly used to study electronic chemiluminescence from simple, gas-phase reactions. In our own experiments, which have been described fully elsewhere, atoms are generated by passing a diatomic gas, such as O₂, H₂, or Cl₂, highly diluted in Ar through a microwave discharge cavity. The diatomic parent species is partially dissociated and the atoms are subsequently mixed with the second reagent someway downstream from the discharge. This mixing occurs in a 1 liter spherical vessel which is internally coated in gold to collect as much as possible of the infrared emission. The radiation is viewed through a window on the side of the vessel with a spectrometer which can be fitted with a variety of infrared detectors--most usually cooled or uncooled PbS photoconductive cells.