

Absorption Spectra of Transient Species
in a Single-Pulse Microwave-Discharge

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ABSTRACT

An apparatus was described for production of an intense and short duration microwave pulse discharge in various gases. At power levels in the 50 kw range, the microwave energy was coupled to the gas with a high Q tuned cavity. For higher power levels up to 1 mw peak, a glass tube containing the gas was placed inside a wave guide, in the central region of maximum field. Thereby intense discharges were produced in metre long columns of gas, to provide ideal conditions for kinetic absorption spectroscopy. Some simple applications of the technique were described, including measurement of energy transfer from He(2^3S_1) to atomic neon, exchange of vibrational energy from nitric oxide to D₂S, and the production of diatomic free radicals in various gases.²

Flash photolysis is proving to be of considerable value in the study of structure and kinetics. Our first object in developing the microwave technique, in which the photolytic flash is replaced by a powerful microwave pulse, was to explore alternative means of achieving substantial electronic excitation of gases. It was believed that the method would complement flash photolysis and would also extend the direct techniques of flash spectroscopy to more diverse systems, for example gases which only absorb light in the extreme vacuum ultraviolet¹. Thus to mention a few as yet unattained and perhaps ambitious objects, we hope to follow dimer formation in pure helium and the other inert gases, to study N₂ A³Σ⁺ by absorption spectroscopy, to investigate CH formation² in CH₄ (which has now been achieved by vacuum ultraviolet flash photolysis²), and to detect both positive and negative ions by absorption spectroscopy.

A microwave field will couple only with free electrons, and direct change of translational energy of gases is unimportant (because of the mass restriction) compared to the energy appearing as electronic and vibrational excitation. Described here are results obtained with a microwave-pulse generator of peak power ~50 kw, and also the development of a more powerful apparatus with a capability to deliver power to a gas at just under 1 mw. Results from the second machine will be available by the early spring of 1967.

Experimental and Discussion

The first apparatus was constructed to establish the feasibility

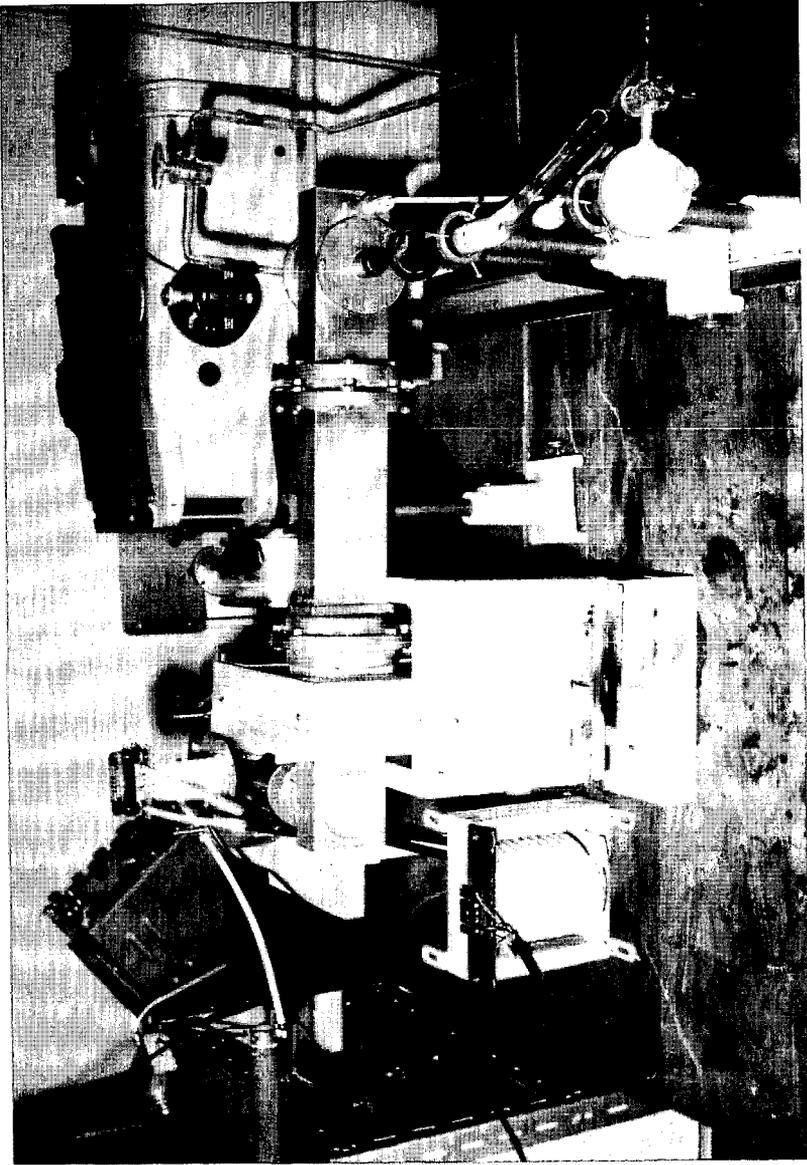


FIG. 1 Prototype equipment for microwave-pulse flash-spectroscopy.

of producing transients at concentrations detectable by absorption spectroscopy. An English Electric M561 Magnetron (3046 Mc/sec) was powered with a $1 \mu\text{F}$ capacitor charged to $\sim 15 \text{ kV}$, and the pulse duration could be varied in the range 2 - 50 μsec with English Electric FX290 thyratrons. Via a conventional 'door-knob' coupler and waveguide section (without an isolator), the power was transmitted to a cylindrical cavity with a Q of 380. This is illustrated by the photograph shown in figure 1, and the main details have already been described. Although a 10 μsec pulse corresponds to 0.8 joules, only a minute fraction of this was successfully delivered to the gas. However, a number of encouraging observations were made, and some energy transfer rate coefficients were measured, as described below.

More recently, R.E.M.Hedges, J.G.Guttridge and I have completed the construction of a powerful microwave generator, which incorporates the English Electric M578 magnetron, with a rated peak-power of 900 kw. Into a 'matched load', we have produced single pulses at 500 kw, duration 5 μsec ., which is close to the maximum power available per pulse. The H.T. arrangement is similar to that employed in the prototype equipment, with two thyratrons delivering a potential up to 30 kV. This particular magnetron turns out to be rather susceptible to arcing on single pulse operation, and in this respect is especially sensitive to reflected power. This has necessitated the inclusion of an isolator between the magnetron and the load; to obtain satisfactory functioning up to 25 kV (as evidenced by the profile of the current pulse), it is necessary to condition the magnetron cathode by somewhat laboriously pulsing with the applied potential increased by small increments from 20 kV upwards.

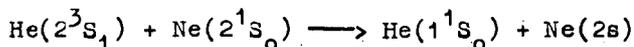
It was anticipated that the same cavity that had been employed in the early experiments would also be suitable for the high energy equipment. With the assistance of Mr. F.J.Weaver of the English Electric Valve Company, the size of the hole coupling the cavity to the waveguide was carefully optimised to give a standing-wave ratio of 1.2 and a Q of about 800. With such a tuned cavity, a discharge can be produced in helium at 1 atmos. pressure; however, the discharge was still quite feeble and it was obvious that only a minute fraction of the total energy was being coupled to the gas. Although the tuning and matching was near perfect under low power test conditions, for various reasons the cavity detunes as soon as the gas strikes.

Although a study of the cavity discharge may prove to be of some value, interest was directed at the problem of achieving ~~more~~ more efficient coupling of the microwave pulse to the experimental gas. In fact we have now achieved conditions under which it appears that practically the entire pulse may be absorbed by the gas. This innovation is a very simple one; a thin walled glass tube containing the gas is placed inside the waveguide in the region of

maximum field. In this manner, an intense discharge can be produced in metre long columns of gas, to provide ideal conditions for absorption spectroscopy. R.E.M.Hedges is presently assembling the optical components to carry out spectroscopic studies under these conditions. The beauty of this discovery lies in its inherent simplicity; power is coupled to the gas at low Q and matching problems are virtually eliminated.

Results

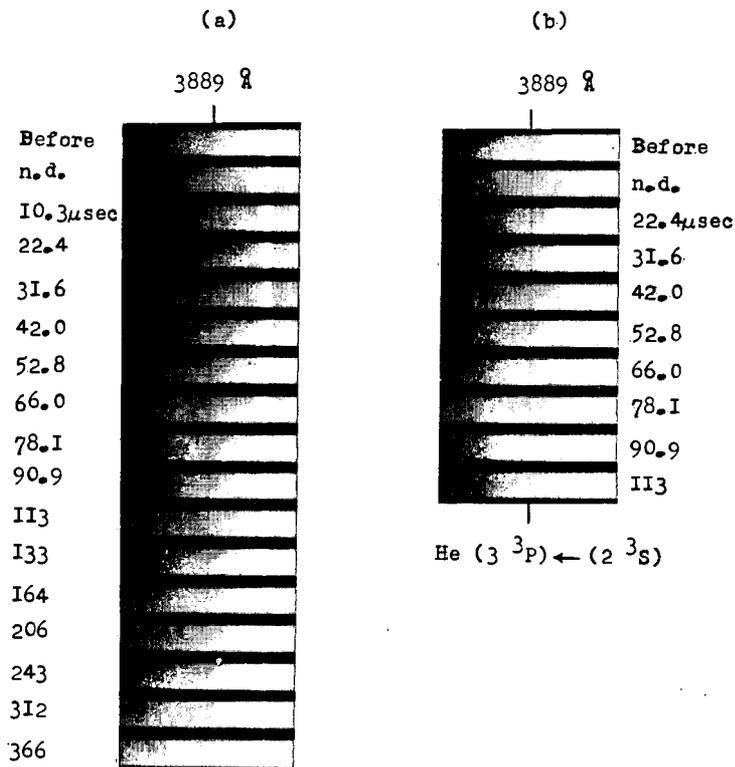
This section relates only to the low power equipment, with a tuned cavity discharge. Figure 2(a) shows the formation of $\text{He}(2^3\text{S}_1)$ in a single pulse of 10 μsec duration, and its decay following the pulse. Also observed in pulsed helium were the comparatively short lived 2^3P_1 and 2^1S_0 states. A simple quantitative application shown in figure 2(b), is the enhanced rate of decay of $\text{He}(2^3\text{S}_1)$ in the presence of a trace of neon. By means of photometry of plates similar to that illustrated in figure 2, the rate of the energy transfer process



was recorded as $0.35 \pm 0.02 \text{ \AA}^2$, in agreement with 0.37 \AA^2 reported by Javan, Bennett and Herriott³. The helium system is perhaps the simplest of all electric discharges and, as mentioned above, we hope to make more detailed observations of the formation of diatomic helium. All four of the 1s metastables were observed in pulsed neon¹.

Figure 3 illustrates vibrational excitation of nitric oxide, and its decay following the pulse. It was concluded that excitation occurs by direct collision of nitric oxide molecules with electrons, because of the extreme weakness of fluorescence from electronically excited molecules⁴. The total yield of vibrationally excited NO produced with a microwave pulse, is about 10 - 100 fold higher than the yield of electronically excited species or free radicals, in all the systems which have thus far been investigated. The technique may therefore prove to be generally applicable to the study of vibrational energy transfer. Figure 3(b) shows the catalysis of the NO relaxation, by a trace of D_2S , which has a vibrational frequency close to that of NO. A number of rate coefficients for V-V processes of this type have recently been published.

Finally we mention the formation of chemical intermediates, produced by microwave pulses in polyatomic gases. Thus far, these aspects of the chemistry of electric discharges have only been investigated in CS_2 , $(\text{CN})_2$, H_2O and H_2S . In each case, diatomic free radical intermediates were observed. Some of these are included in figure 4.



- (a) Formation and decay of He ($2\ ^3S$) in 5 mm of He.
- (b) Decay of He ($2\ ^3S$) in 5 mm He + 1.2×10^{-2} mm Ne.

Figure 2

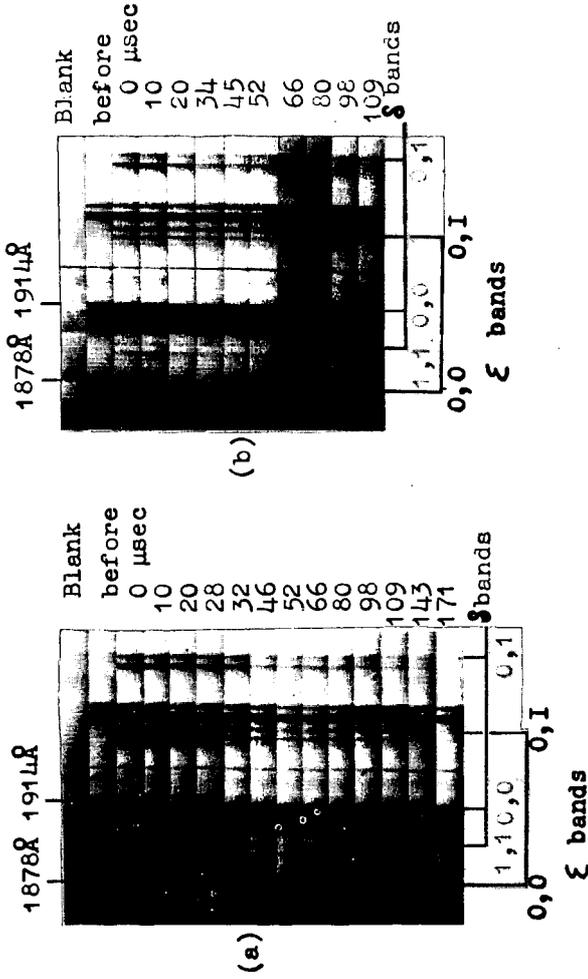


Fig. 3 Formation and decay of $\text{NO X } 2 \Pi(v=1)$ in pulsed He / NO mixtures.

(a) 6mm NO + 300mm He

(b) 3mm NO + 0.06mm D_2S + 300mm He

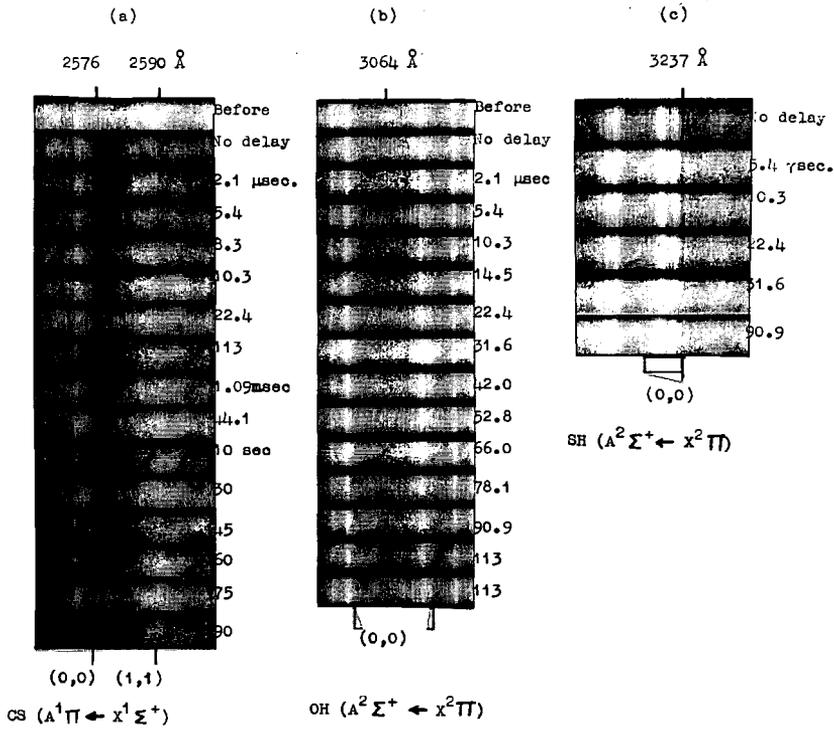


Fig 4 Formation and decay of (a) CS : 2mm CS₂ + 60 mm He;

(b) OH : 5 mm H₂O + 35 mm He; (c) SH : 20 mm H₂S + 100 mm He.

References

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