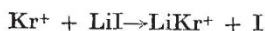


beam formation was observed, and it thus seems likely that the reactions are of the form



or possibly $\text{Kr}^* + \text{LiI} \rightarrow \text{LiKr}^+ + \text{I} + e$

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¹ Smith, D. F., *J. Amer. Chem. Soc.*, **85**, 816 (1963).

² Malm, J. G., Sheft, I., and Chernick, C. L., *J. Amer. Chem. Soc.*, **85**, 110 (1963).

³ Schissler, D. O., and Stevenson, D. P. J., *Chem. Phys.*, **24**, 926 (1956).

⁴ Henglein, A., and Muccini, G. A., *Angew. Chem.*, **72**, 630 (1960).

⁵ Field, F. H., and Franklin, J. L., *Symp. Mass Spectrometry* (Pergamon Press, 1961).

⁶ Freeman, J. H., *Nucl. Inst.*, **22**, 306 (1963).

Infra-red Microspectrometer using Molecular Beam to monitor Capillary Gas Chromatography Effluents

THE high resolution afforded by capillary columns in gas chromatography is often of no help in analysis since the samples which can be handled are too small to permit further thorough examination of the separated components. Only mass spectrometry has proved sensitive enough for the continuous identification of the eluted compounds¹; however, it yields little information about their molecular structures.

The single method which gives the most useful analysis of a substance is infra-red spectroscopy. However, even infra-red cells specially constructed for gas chromatography, with long optical paths obtained by multiple reflexion², require samples too large to be resolved by capillary columns.

Infra-red analysis with a sensitivity comparable with that of mass spectrometry could be achieved by measuring, not the absorption of radiation by molecules, but the capture cross-section of molecules for radiation. The infra-red microspectrometer delineated in Fig. 1 measures the concentration of each effluent compound as modulated by the spectrally resolved radiation from a fast-scan infra-red source. The infra-red microspectrometer utilizes the recent application of the electrostatic quadrupole mass spectrometer^{3,4} to molecular beams, as a rota-

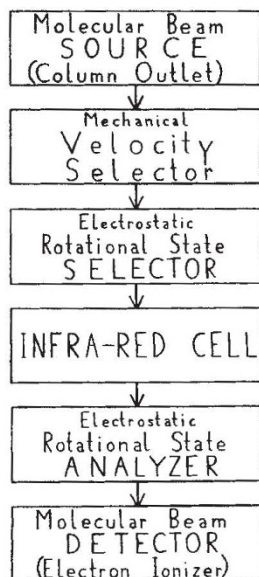


Fig. 1. Block diagram of the infra-red microspectrometer

tional state selector for molecules with a dipole moment⁵⁻⁷. Both rotational state selector and analyser, which preferably are parts of a single device, are thus tuned to the same appropriately selected rotational state; the analyser rejects those molecules which briefly experience transitions in the infra-red cell. It can be shown that thermal radiation from powerful radiant heaters, focused transversally on a node of the molecular beam, is intense enough for this purpose. The resulting plot of detected molecular-beam intensity against wave-length of the radiation is the infra-red spectrum of the compound.

The separate identification of compounds, eluted by extremely pure⁸ helium, makes the computation of their exact relative retention times superfluous. The efficiency of capillary columns can then be raised by temperature programming and by narrowing the vapour bands⁹ by the thermal conductivity method.

Particle detection is the normal observation method in molecular beam spectroscopy. At a future date some vibrational state selector for molecular beams may be invented, which would improve the apparatus of Fig. 1.

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¹ McFadden, W. H., and Teranishi, R., *Nature*, **200**, 329 (1963).

² Flett, M. S. C., and Hughes, J., *J. Chromatog.*, **11**, 434 (1963).

³ Paul, W., and Steinwedel, H., *Z. Naturforsch.*, **8**, a, 448 (1958).

⁴ Zahn, U. v., *Rev. Sci. Instr.*, **34**, 1 (1963).

⁵ Bennewitz, H. G., Paul, W., and Schlier, Ch., *Z. Physik*, **141**, 6 (1955).

⁶ Bennewitz, H. G., Kramer, K. H., and Toennies, J. P., *Second Intern. Conf. Phys. Electronic Atomic Collisions*, 113 (W. A. Benjamin, Inc., New York, 1961).

⁷ Toennies, J. P., Bennewitz, H. G., and Kramer, K. H., *Disc. Farad. Soc.* **33**, 96 (1962).

⁸ Kohman, G. T., and McAfee, jun., K. B., U.S. Patent 3,019,853 (Feb. 5 1962).

⁹ Behrendt, S., *Z. physik. Chem. Neue Folge*, **38**, 70 (1963).

Absorption Spectra of Transient Chemical Species produced in Gases by a Single-pulse Microwave-discharge

THE combination of flash photolysis with absorption spectroscopy has produced a powerful method of investigating transient chemical species and energy-transfer phenomena^{1,2}. In practice, application has generally been limited to substances which absorb at wave-lengths longer than 1900 Å, because of the suitability of quartz in the construction of the apparatus. Thus it has frequently been necessary to sensitize reactions by inclusion of substances which are opaque in the ultra-violet above 1900 Å, with consequent complications on the mechanism. In order to produce a high concentration of transient chemical species in any gas, we have recently constructed an apparatus which produces a short duration electric discharge by means of a single microwave-pulse, with a peak power of 8×10^4 W. It has been readily demonstrated that the absorption spectra of metastable atoms and free radicals present in the gas discharges can be photographed by absorption spectroscopy.

The detection of absorption spectra of transients produced by fast electrons in liquids has already been achieved, with a linear accelerator as electron source³. In the microwave-pulse method described here, a radioactive material produces electrons in a gas, which oscillate in the microwave field and give up energy to the gas molecules. The small mass of the electron compared with molecules limits translational energy transfer and results in a high electronic temperature. The chain reactions which produce additional electrons eventually cause the gas to break down and light is emitted. The energy-transfer processes which restore thermodynamic equilibrium can be followed by absorption spectroscopy. Rectangular microwave pulses can be produced with a duration of 1 μsec or