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INFRARED-LASER SPECTROSCOPY USING A LONG-PATHLENGTH ABSORPTION CELL

K. C. Kim and R. A. Briesmeister

The development of tunable infrared laser sources in recent years has played a major role in laser spectroscopy. The high-resolution capability greatly enhanced the study of rovibrational transitions in molecules. Diode lasers with the tunability and the narrow linewidth have been responsible for striking advances in infrared spectroscopy.

The absorption measurements in an ordinary cell may require typically a few torr pressure of sample gas. At these pressures the absorption lines are usually pressure-broadened and, therefore, closely spaced transitions are poorly resolved even at diode laser resolution. This situation is greatly improved in Doppler-limited spectroscopy at extremely low sample pressures.

We developed two very long pathlength absorption cells to be used in conjunction with diode lasers. They were designed to operate at controlled temperatures with the optical pathlength variable up to ~ 1.5 km. Not only very low sample pressures are used for studies with such cells but also the spectroscopic sensitivity is enhanced over conventional methods by a factor of 10^3 to 10^4 , improving the analytical capability of measuring particle densities to the order of 1×10^{11} molecules/cm³. In this paper we present some analytical aspects of the diode laser spectroscopy using the long pathlength absorption cells in the areas of absorption line widths, pressure broadening coefficients, isotope composition measurements and trace impurity analysis.

INTRODUCTION

The development of tunable ir laser sources in recent years has played a major role in laser spectroscopy.¹ The high resolution capability greatly enhanced the study of rovibrational transitions in molecules. Diode lasers with the tunability and the narrow linewidth have been responsible for striking advances in infrared spectroscopy.²

Several years ago we recognized the need for an absorption cell which utilizes fully the high resolution capability of diode lasers. The absorption measurements in an ordinary experimental cell may require typically a few torr pressure of sample gas. At these pressures the absorption lines are usually pressure-broadened and, therefore, closely spaced transitions are poorly resolved even at diode laser resolution. This situation is greatly improved if spectroscopic measurements can be made on molecules before they have time to collide at extremely low sample pressures.

We developed two very long pathlength absorption cells to be used in conjunction with diode lasers. The first cell had a physical length of 10.5 meters and the second of 4.5 meters.³ They were designed to operate at controlled temperatures in the range from ~100K to 300K with the optical pathlength variable from 16 m up to about 1.5 Km. Obviously, very low sample pressures are used for studies with such cells. The spectroscopic sensitivity is also enhanced over conventional methods by a factor of 10^3 to 10^4 , improving the analytical capability of measuring particle densities to the order of 1×10^{11} molecules/cm³.

Over the past few years, we used these two spectroscopic facilities for a variety of spectroscopic studies of fundamental molecular parameters,⁴ vibrational intensity measurements⁵ and laser photochemistry.⁶ In this paper, we present some other analytical aspects of the diode laser measurements using the long pathlength absorption cells. They are measurements of absorption line widths, pressure broadening coefficients, isotopic composition, and trace impurity analysis.

DIODE LASER SPECTROMETER WITH A LONG PATHLENGTH CELL

Figure 1 shows a schematic diagram of the long pathlength absorption cell. The cell employs conventional White cell optics. We found that White cell optics are most suitable for long pathlength optical transmission in terms of

operational ease and are relatively immune to vibrational interferences. The separation of the reflecting mirror surfaces is the same as the radius of the curvature. The laser beam enters the optical cavity as a point source and exits from the same side with very little distortion of the image. Thus it is relatively simple to sort out beams that have made different number of passes between the mirrors (Fig. 2).

Figure 3 shows an experimental set-up utilizing a diode laser spectrometer. The monochromator shown is used to select a longitudinal mode of the laser output and also serves as an approximate wavelength reference. The wavenumber calibration is done using a germanium etalon. For example, for a 1 in. germanium etalon the free spectral range at 16 μm is 0.048268 cm^{-1} . Accurate wavenumber markers are established by recording absorption lines of well known frequency standards (such as CO_2 , and NO_2 , etc.).⁷ The diode lasers are current- and temperature-tuned to cover approximately 0.5 cm^{-1} range. The details of diode laser operation were thoroughly reported previously¹ and will not be discussed here. Figure 4 shows a typical diode laser output tuned over a narrow spectral range, a few absorption lines and an etalon trace.

LINEWIDTH MEASUREMENTS

The amount of sample gas is typically a few mtorr, and at these low pressures it is possible to make Doppler-limited spectroscopic measurements. An example of pressure-broadened line shapes of N_2O in the 16 μm is shown in Fig. 5. Peak absorption of a pressure-broadened absorption line does not increase with increasing sample size. Frequently there are other adjacent interfering absorption lines which obscure the spectroscopic identification. Spectroscopic measurements of low pressure sample gases therefore enhance the analytical sensitivity and makes maximum use of the diode laser resolution.

Although the spectral range that can be covered is small and limited within a few wavenumbers because of the very nature of the diode laser, the Doppler widths of absorption lines provide information on the molecular weight of the sample gas. In Table I, we summarize experimentally measured linewidths of several gases compared to the room temperature Doppler widths evaluated at the particular transition wavenumbers $[\Delta\nu_D = 2\nu_0 (2kT \ln 2/MC^2)^{1/2}]$. Only those absorption lines that appear free of fine structures were used for the line width measurements. The measurement of Doppler widths alone seldom identifies a particular gas sample but approximate molecular weights combined

with accurate wavenumbers narrow down the list of possible compounds. Obviously, an FTIR spectrometer which can cover a wider spectral range with an intermediate resolution will be an ideal match with the long pathlength absorption cell for trace impurity analysis (Fig 6). For most polyatomic molecules, however, the Doppler widths are narrower than the resolution of commercially available FTIR spectrometers.

OTHER APPLICATIONS

Another important application of the diode laser spectrometer with the long pathlength absorption cell is measurements of lineshape and pressure-broadening coefficients by foreign gases. This has been demonstrated for UF_6 and CO_2 and the pressure-broadening coefficients by various gases have been obtained. Although somewhat insensitive to temperature variations, lifetimes of the existed states can be measured as a function of temperature.

Isotope shifts of some molecular species are rather small. High resolution measurements allow isotopic composition analysis. An example is shown in Fig. 7. In this figure, we analyze a mixture of ~5% $^{235}UF_6$ and 95% $^{238}UF_6$. Figure 8 shows absorption lines of a mixture of CO_2 isotopic species in the 16 μm region.⁸ Each species is identified by their isotopic composition. (The notation ijk at each peak corresponds to the $i_c j_o k_o$.) This method has the advantage of measuring isotopic composition in situ where there is a potential problem of isotopic scrambling.

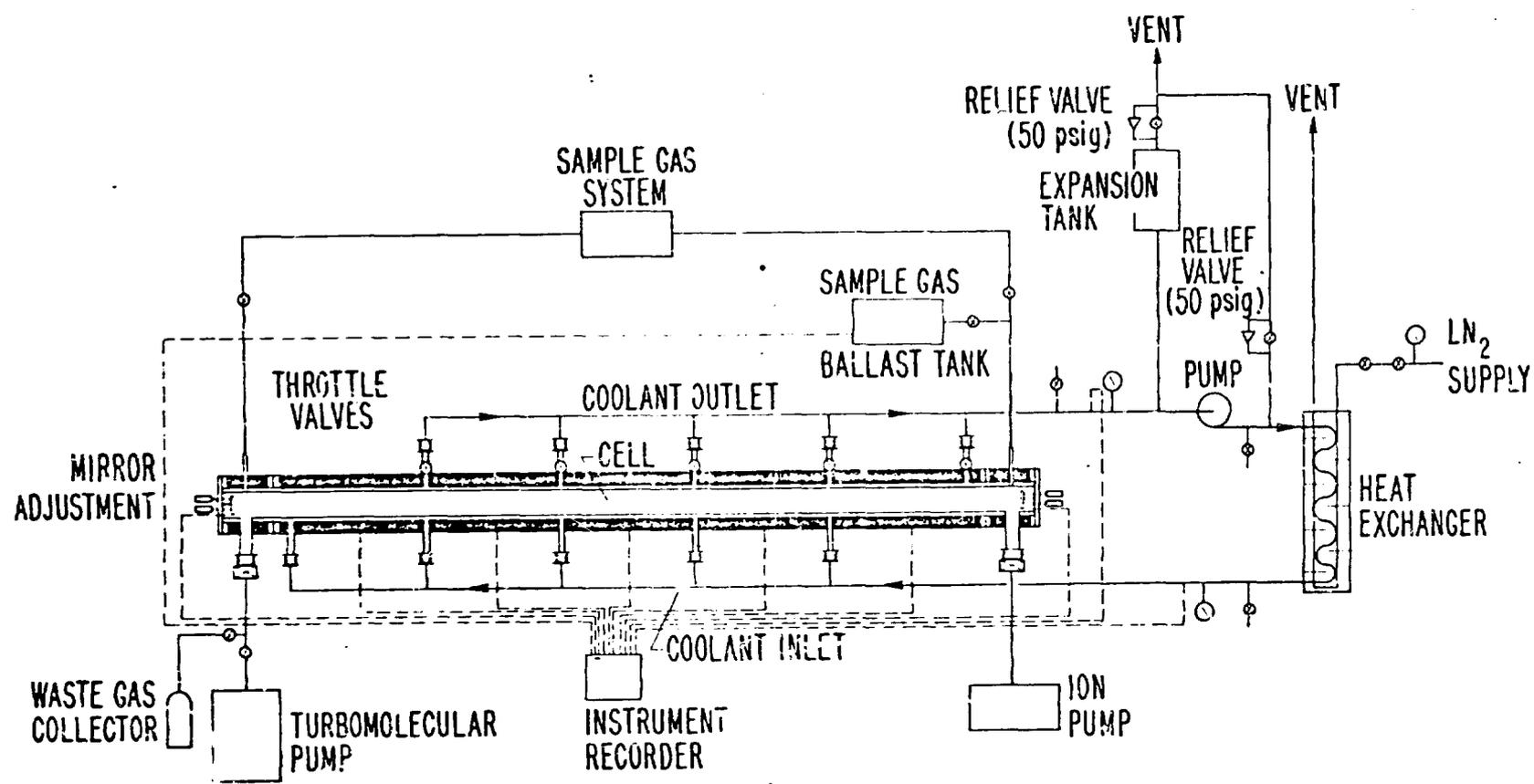
Finally, an important area of the laser spectroscopy in conjunction with the long pathlength absorption is the study of transient absorption measurements. Using powerful lasers one can generate significant concentrations of transient species. Because of the low pressures, these reactive species have relatively long lifetimes and they can be detected with the enhanced sensitivity of the long pathlength absorption technique. Figure 9 shows an example of the absorption by UF_6 generated from laser photolysis of UF_6 .

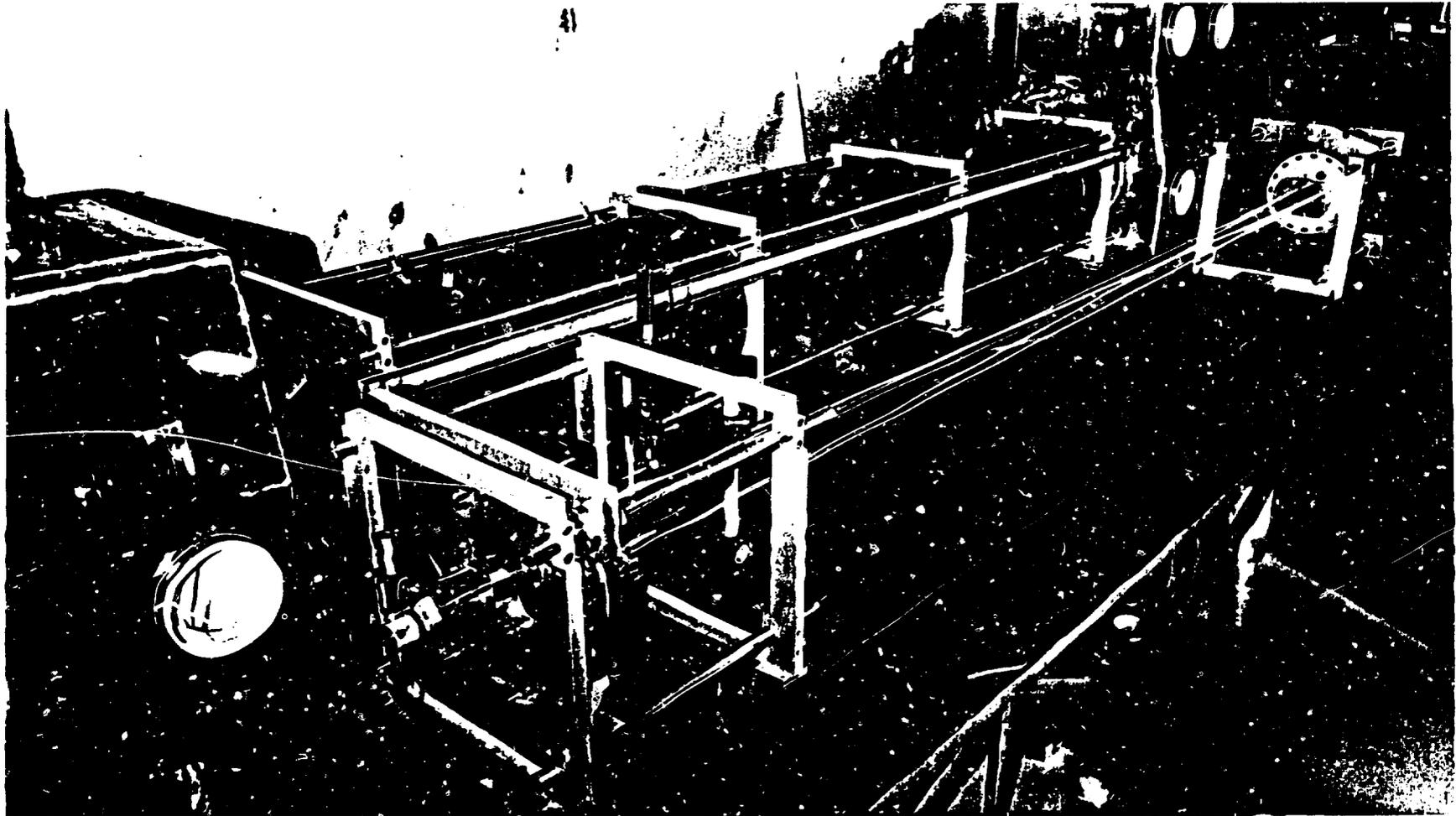
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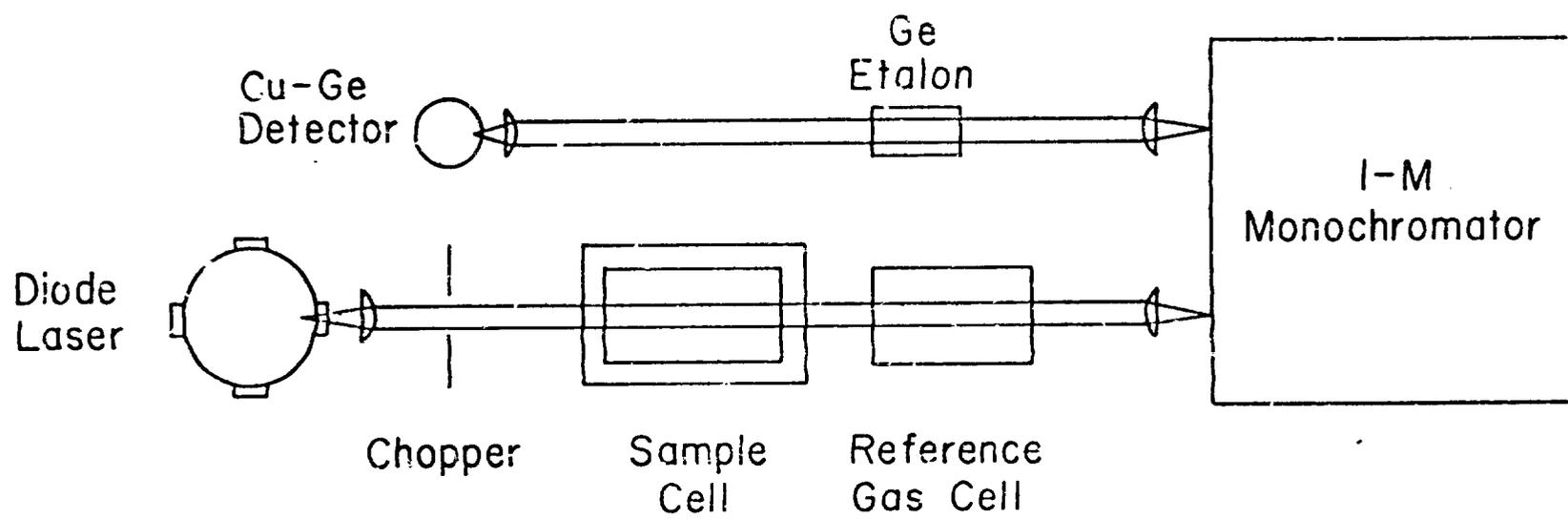
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TABLE I. SUMMARY OF LINEWIDTH MEASUREMENTS

<u>Compound</u>	<u>Molecular weight</u>	<u>Rcom Temp Linewidth ($\text{cm}^{-1} \times 10^3$)</u>	<u>Transition Wavenumber (cm^{-1})</u>	<u>Doppler Widths ($\text{cm}^{-1} \times 10^3$)</u>
NH ₃	17	3.70	628.444	1.89
CO ₂	44	1.50	617.2916	1.15
N ₂ O	44	1.30 1.35	535.2747 612.3516	1.09 1.14
CF ₄	88	1.18	617.2648	0.82
ClF ₃	92	1.25	627.701	0.81
UF ₆	352	0.57	627.5988	0.41

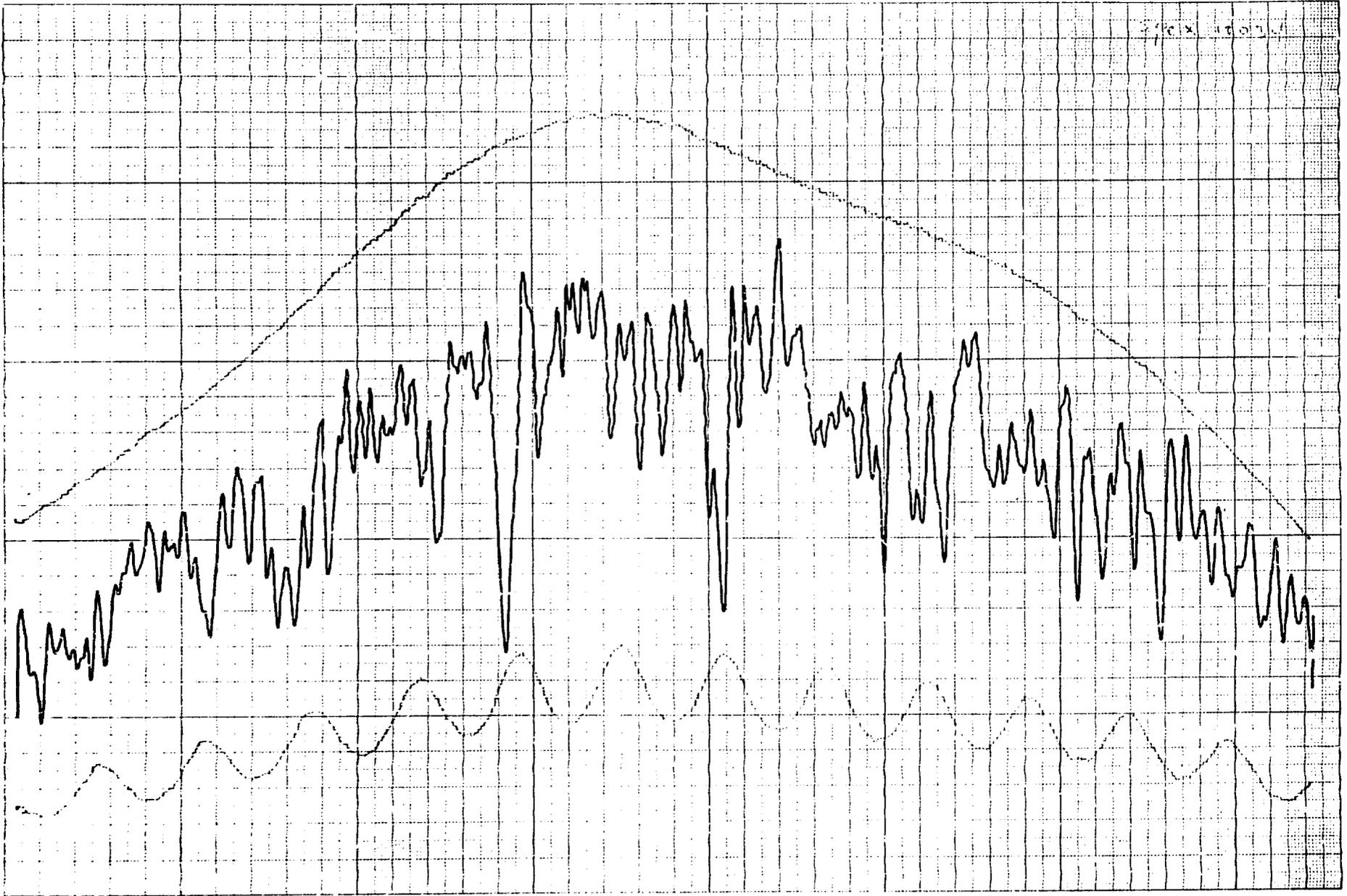


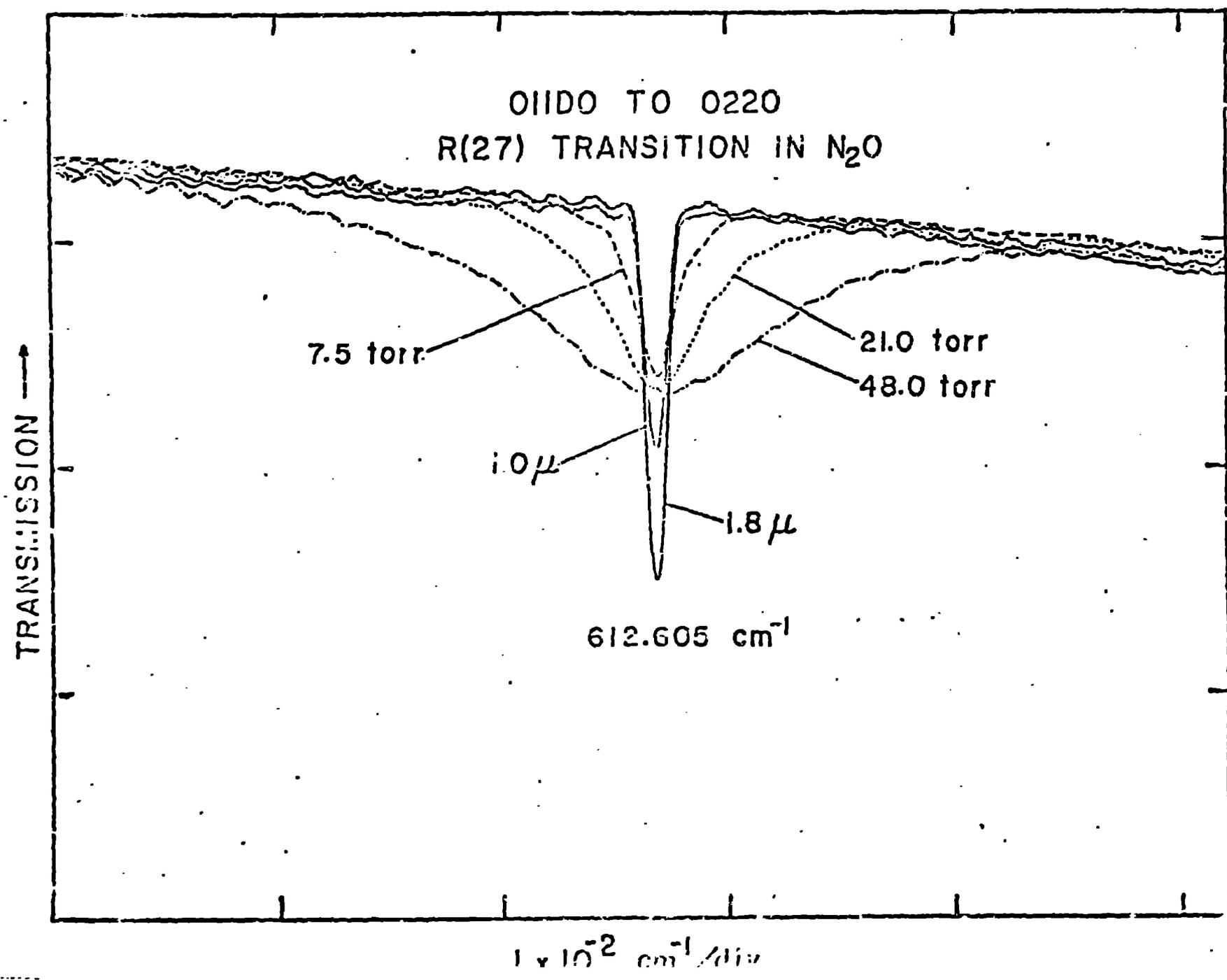


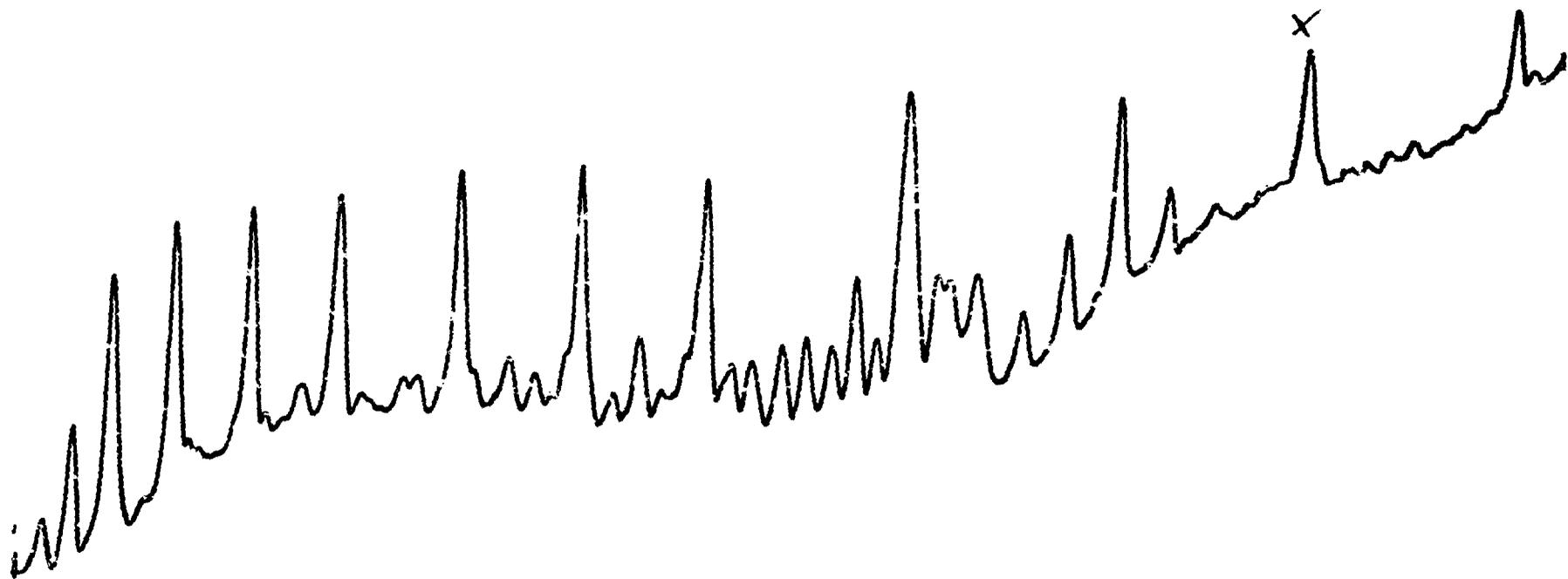


SYSTEMA EDMONDSONIUM

1921







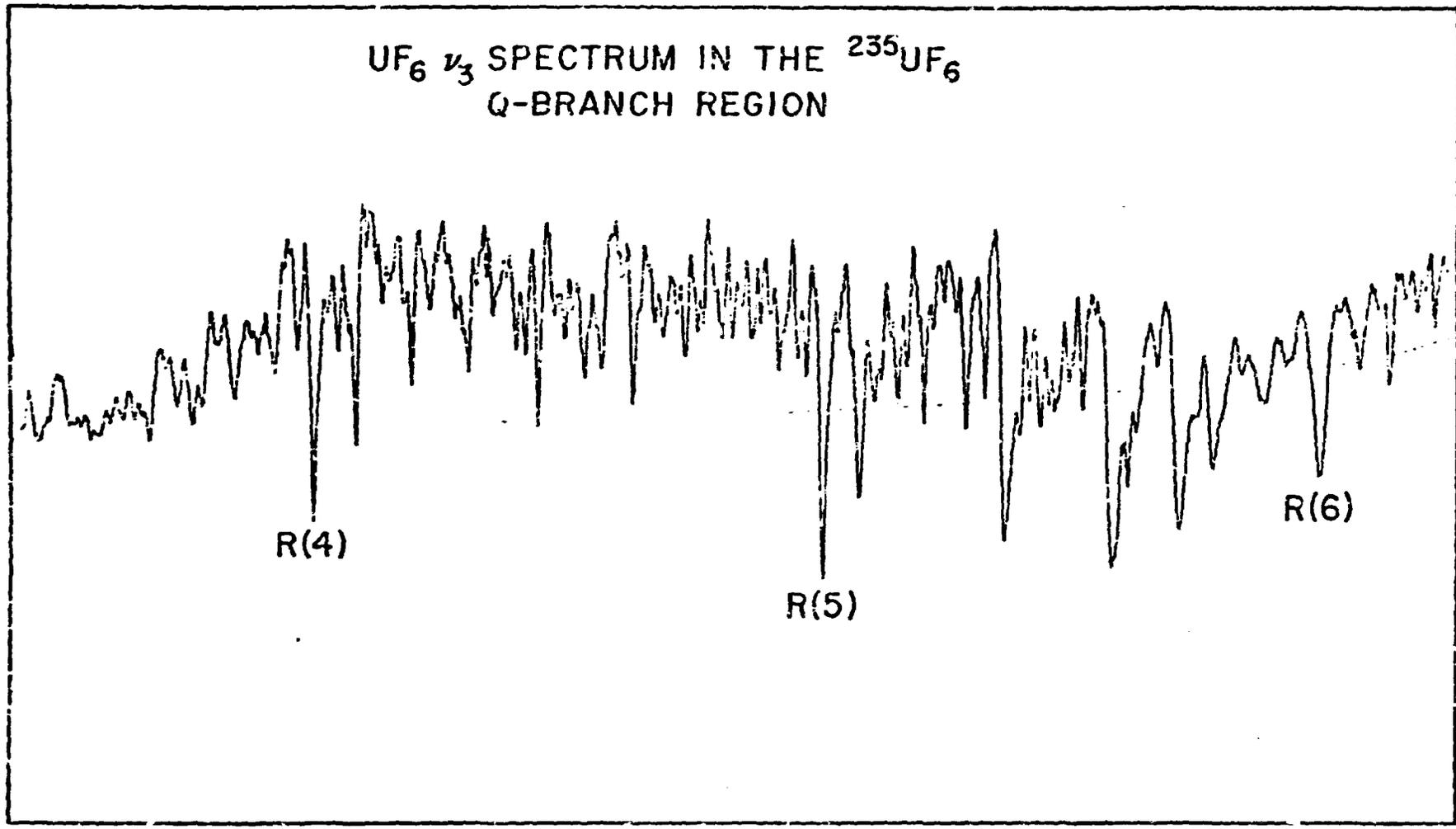
$f = 1.5$
 $\lambda = 1.32$

5/10/15 10/15

⑧ 4/3/34

UF₆ ν₃ SPECTRUM IN THE ²³⁵UF₆
Q-BRANCH REGION

— ABSORPTION



Laser Flash Photolysis - UF_5 Absorption

