

CH₃F absorption of the CO₂-laser emission measured by the photoacoustic technique

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Abstract. Spectra of coincidence of CH₃F IR absorption with CO₂-laser emission at pressures of 2, 10 and 60 Torr were recorded by the use of a photoacoustic detection method in the whole range of CO₂-laser emission. The spectra show that CH₃F absorbs many CO₂-laser lines in the range 1084–1071 cm⁻¹ with the strongest absorption at 1046.80 cm⁻¹, laser line P(20). Absorption is predominantly due to the fundamental of ν₃, which is well spread over the whole laser emission range. The intensities of all absorptions rise with increasing pressure, but some absorptions change their relative intensity with respect to one another. In addition, the fine structure of the line spectrum, characteristic of lower pressure samples, disappears as pressure is increased.

Keywords. Spectroscopy; CO₂-laser; photoacoustics; fluoromethane.

1. Introduction

Fluoromethane (CH₃F) and its absorption of the CO₂-laser draws much attention in a number of fields. The molecule itself and its deuterated forms, belong to the group of compounds which show high efficiency in laser isotope separation (LIS) of deuterium. It is also used as a far infrared laser medium. Fluoromethane could successfully be employed as a sensitizer in various CO₂-laser induced photochemical processes since it is a very strong absorber of CO₂-laser emission at several lines and a relatively stable compound. Due to that it is possible to pump great amounts of vibrational energy into the system. An illustrative example of how to excite another molecule (D₂S) by the CO₂-laser through CH₃F, to measure relaxation times by laser induced fluorescence, has been given in Miljanić *et al* (1982).

A CO₂-laser photoacoustic (PA) spectrum of CH₃F has been recorded before at pressures below 1 Torr (Walzer *et al* 1979). Considering that there are strong indications of absorption changes with pressure and expecting varying behaviour of coincidences with laser emission lines, appropriate spectra at higher pressures are needed. Actually, only those data are relevant for selection of laser lines suitable for stimulating desired photochemical reactions at certain pressures. Quite useful for laser photochemistry would also be similar spectra of CH₃F with mixtures.

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2. Experimental

A previously built CW CO₂-laser was used as a source around which a photoacoustic (PA) detection apparatus was set up (Radak *et al* 1989). The sample cell was designed to meet the conditions of high CH₃F absorption. It was basically a nonresonant cylindrical brass cell of 12 mm inner dia and 40 mm length, with a Knowless BT-1759 microphone mounted in the center of its sidewall. The sound signal from it was processed through phase sensitive electronics and the output divided by the laser power, the result being the true photoacoustic signal. The details of the apparatus are given in Petkovska *et al* (1991). In this way, laser photoacoustic spectra were obtained by scanning through about 60 laser lines.

The samples were three pressures of neat CH₃F in the range from 2 to 60 Torr. Fluoromethane was synthesized from Metosylate (methyl *p*-sulphonate) and KF at 140°C in Ar atmosphere, distilled *in vacuo* and kept in a pyrex bulb.

3. Results and discussion

Energy map of fluoromethane is well known (Weitz *et al* 1973). According to it, CH₃F absorption observed in this work predominantly belongs to the lowest fundamental stretching vibrational mode (ν_3). Comparison of the present PA results, figure 1–3, with spectroscopic data obtained in a spectrophotometer with classical light source (e.g. Smith *et al* 1963) shows a lot of resemblance, but also discrepancies associated with using the laser as a source, which provides direct data on coincidences of CO₂-laser emission with absorption of CH₃F. Only such data are actually relevant for using CH₃F in CO₂-laser applications. Pressure dependence of the spectra generally includes the same phenomena as observed with other molecules of similar size: the fine structure of line spectra disappears with increasing pressure.

The strongest absorption, as expected, was observed with laser line P(20) at 1046.80 cm⁻¹ at all pressures (figure 1–3). Absorption of R(24) at 978.47 and R(32) at 983.25 cm⁻¹ lines are relatively strong if compared to many others that appear at lower pressures (figure 1). Some absorptions, however, change their relative intensity

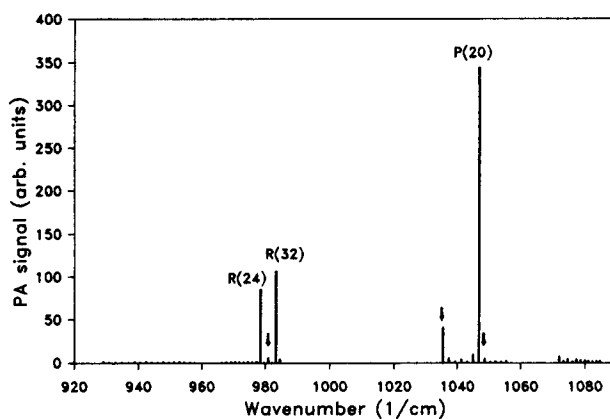


Figure 1. Photoacoustic spectrum of CH₃F at 2 Torr.

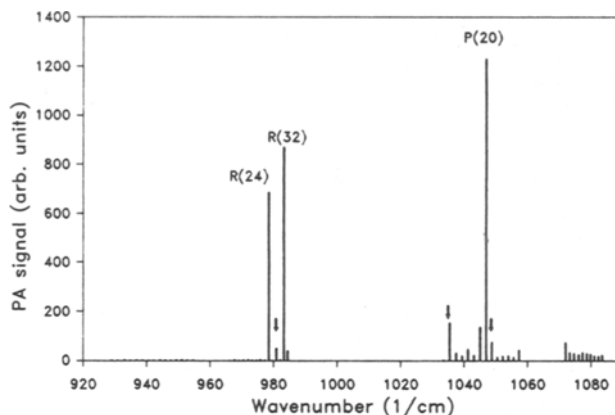


Figure 2. Photoacoustic spectrum of CH₃F at 10 Torr.

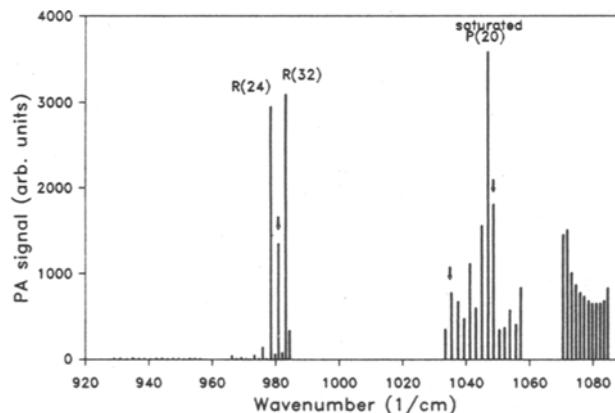


Figure 3. Photoacoustic spectrum of CH₃F at 60 Torr.

with respect to one another if gas pressure is changed. Even if this can partly result from nonlinearities possible with stronger signals, there are absorptions which, when observed in pairs, qualitatively exchange their relative intensity with one another, so that the absorption which was lower than the other at one pressure is higher at another pressure. For example, the intensity of absorption of *R*(28) at 980.91 rises dramatically, as well as that of *P*(18) at 1048.66 cm⁻¹, while *P*(32) at 1035.43 cm⁻¹ remains almost constant over the pressure range (2 to 60 Torr). The intensity ratios of absorptions of *R*(32)/*P*(18) and *R*(32)/*R*(28) decrease from about 23 to 2. At the same time the ratio *R*(32)/*P*(32) increases from 2 to only about 5. In addition to this, other experiments have indicated that if a foreign gas, even a noble monoatomic one like argon, is added instead of neat CH₃F, the behaviour is different from that in the present case when only neat gas is added.

Similar pressure effects have been observed with other molecules as well (Petkovska *et al* 1991; Radak *et al* 1991), and attempts are made to discuss them in the context of pressure broadening and, possibly, shifting of absorption lines. An important fact to take into account here is that a laser emission line usually overlaps more than one (or part of one) absorption line of a molecule like this.

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