

Buffer gas effect on laser photoacoustic spectra of methyl chloride

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Abstract. Spectra of coincidence of CH₃Cl IR absorption with CO₂-laser emission were recorded by a photoacoustic detection method in the whole range of CO₂-laser emission. The samples were neat gas and mixtures with argon, at several pressures (10 to 600 Torr) so that pressure effects could be observed. The results show that argon affects absorption of CO₂-laser emission quite differently from neat chloromethane, both regarding the most prominent coincidences and background absorption.

Keywords. Spectroscopy; CO₂-laser; photoacoustic; chloromethane.

1. Introduction

Gaseous methyl chloride, or chloromethane (CH₃Cl), is the most abundant of all halomethanes in the earth's atmosphere and a very frequent pollutant from modern industries. It thus draws much attention in laser spectroscopy and photochemistry. Its vibrational energy transfer mechanism, especially in mixtures, is of interest both to laser chemistry and gas-laser development.

Vibrational energy transfer of this molecule has been studied to some extent by laser induced fluorescence (LIF) (Knutson and Flynn 1973; Grabiner and Flynn 1974), but with difficulties due to poor *S/N* ratio. Very little energy transfer research (Grabiner and Flynn 1972) up to recently (R T Bailey, F R Cruickshank, D Pugh and B B Radak 1990, unpublished results) has been done by the thermal lensing technique. All results obtained so far indicate that a study of pressure effects on absorption of the CO₂-laser by chloromethane should be helpful.

Some of the work using photoacoustic detection (PA) was done previously on neat CH₃Cl (Petkovska 1989), but different behaviour of the gas can be expected when a buffer gas is added.

2. Experimental

A previously built (Radak *et al* 1989) CW CO₂-laser was used as a source around which a photoacoustic (PA) detection apparatus was set up, which is described in

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more detail elsewhere (Petkovska *et al* 1990). Laser photoacoustic spectra were obtained by scanning through about 60 laser lines. These spectra actually represent the coincidences of CO₂-laser emission with the absorption of the samples. Argon was taken as a typical monoatomic buffer gas commonly used in laser energy transfer and photochemical investigations. The samples were 10 and 200 Torr of neat CH₃Cl and mixtures of 10 Torr of CH₃Cl with argon added up to 200 and 600 Torr total pressure.

3. Results and discussion

The results obtained are presented in figure 1 (neat gas) and figure 2 (mixture).

Besides a number of pronounced coincidences of the laser with CH₃Cl absorption, identifiable with features in its absorption spectrum, intensive background absorption was detected. This has also been observed in some thermal lens experiments (R T Bailey, F R Cruickshank, D Pugh and B B Radak 1990, unpublished results). Present results show that argon affects absorption of CO₂-laser emission quite differently from neat chloromethane. For example, much more argon than neat gas is needed for background absorption to be lifted to a level comparable with the strongest absorptions detected.

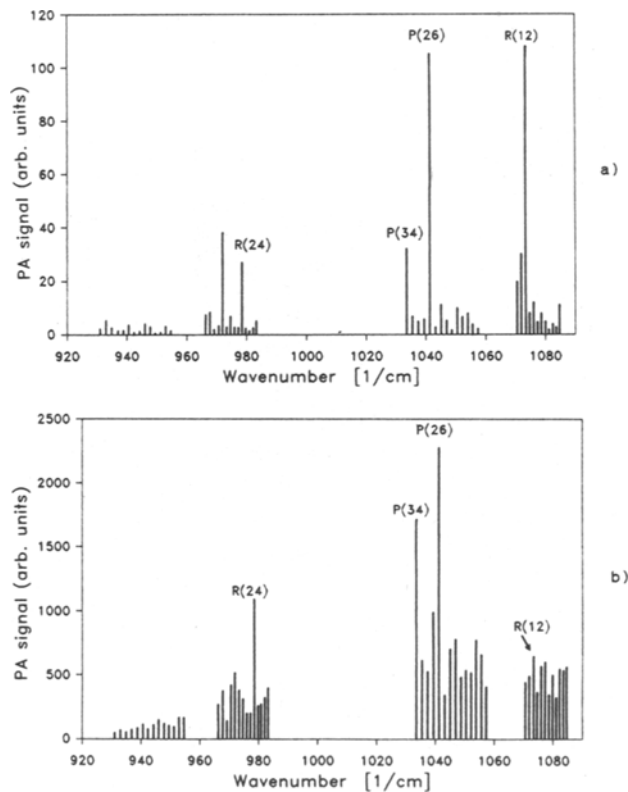


Figure 1. Photoacoustic spectra of neat CH₃Cl at: (a) 10 Torr and (b) 200 Torr.

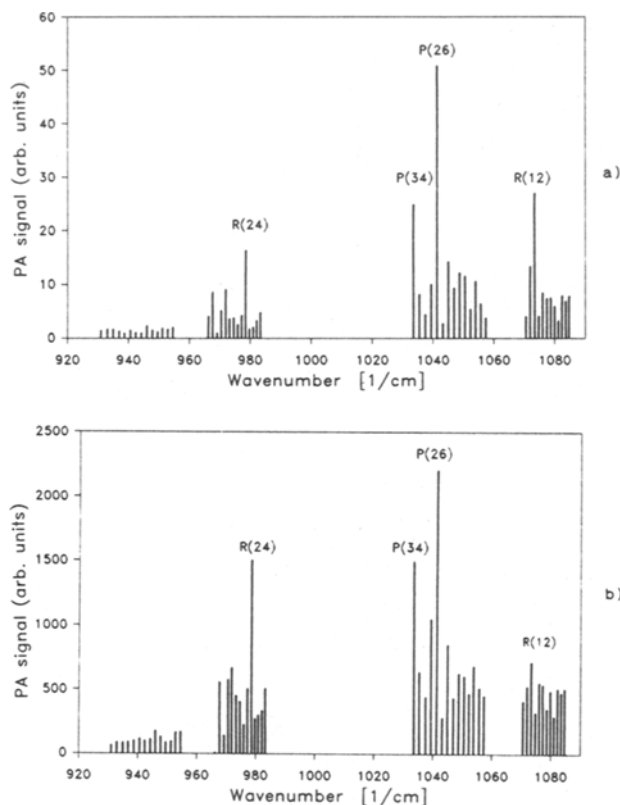


Figure 2. Photoacoustic spectra of 10 Torr of CH_3Cl in mixture with argon added up to the pressure of: (a) 200 Torr and (b) 600 Torr.

Looking at the most prominent absorptions, it is evident that their relative intensities in mixtures with argon can drastically differ from those in neat gas samples of the same total pressure. Comparing figures 1b and 2a this is quite evident e.g. absorption of laser lines $R(24)$ at 978.47 cm^{-1} , $P(34)$ at 1033.49 cm^{-1} and $R(12)$ at 1073.28 cm^{-1} . As in cases with some other molecules (Miljanić *et al* 1991; Petkovska *et al* 1991) 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.

On the whole, the results indicate the significance of the nature of the gas added to a system, associated with its pressure effects on IR absorption. This is especially important in laser chemistry and photochemistry, where energy transfer and even reaction paths may depend on the nature of the absorption.

References

- Grabner F R and Flynn G W 1974 *J. Chem. Phys.* **60** 398
 Grabner F R, Siebert D R and Flynn G W 1972 *Chem. Phys. Lett.* **17** 189

Knudtson J T and Flynn G W 1973 *J. Chem. Phys.* **58** 2684

Miljanić S S, Radak B B and Petkovska Lj T 1991 *Proc. Indian Acad. Sci. (Chem. Sci.)* **103** 405

Petkovska Lj T, Radak B B and Miljanić S S 1990 *Bull. Chem. Technol. Macedonia* **8** 213

Petkovska Lj T, Radak B B, Miljanić S S, Bailey R T, Cruickshank F R and Pugh D 1991 *Proc. Indian Acad. Sci. (Chem. Sci.)* **103** 401

Radak B B, Petkovska Lj T and Miljanić S S 1989 *J. Radional. Nucl. Chem.* **129** 351