Determination of Dynamic Properties of the System $N_2O_4 = 2NO_2$
by Photoacoustic Resonance Spectroscopy

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Chemical relaxation in the system $N_2O_4 = 2NO_2$ has been included in
the theory of acoustical resonances in a cylindrical cavity. The
acoustic resonance profiles of the first radial mode were measured
employing a computer controlled photoacoustic resonance
spectrometer. For optical excitation of the acoustic modes we used
a waveguide $CO_2$ laser and $SF_6$ as sensitizer with $SF_6$
concentrations of 50 to 250 Pa and total pressures in the region
of 100 - 10000 Pa. The theory has been fitted to the data and
values for the rate constant of dissociation $k_2$, the dissociation
energy $D$ and the mean relaxation time for vibrational and
rotational relaxation ($\tau$) were obtained.

The fit yields $k_2 = (1.47 \pm 0.07) \cdot 10^5$ s$^{-1}$ at 1 bar,
$D = (53.0 \pm 1.0)$ kJ/mol and $\tau = (1.71 \pm 0.07) \cdot 10^{-8}$ bar·sec at
300 K. No evidence for vibrational relaxation was found in the
$p_f/p$ region of chemical relaxation.

1. INTRODUCTION

The effect of chemical relaxation, i.e. the influence of the
chemical reaction on the sound velocity in a reacting gas
mixture, has been known for a long time [1] and a theoretical
model has been developed [2][3][4] for a simple type of reaction,
namely the dissociation of a molecule into two identical parts
$A_2 = 2A$. Later, the theory has been extended to a larger number of
different types of reactions [5].

Early attempts to measure the predicted effect in the
$N_2O_4 = 2NO_2$ system failed [1][6]. Ultrasonic methods using
electrostatic transducers could detect the effect of chemical
relaxation and determine the rate constant [7]. Recently the
$N_2O_4 = 2NO_2$ system was investigated using the temperature jump
relaxation method employing a pulsed laser [8].

In this work photoacoustic resonance spectroscopy was used as a
powerful tool to determine precisely the sound velocity and sound
absorption via resonance frequency and halfwidth of the resonance
profile in the $N_2O_4 = 2NO_2$ mixture in the pressure range of
100 - 10000 Pa at frequencies of about 3 kHz. So far acoustical
resonators have been applied to such different problems as
precision measurement of sound velocity [9], measurement of
vibrational relaxation times [10] and detection of gaseous air
pollution in small concentrations [11]. A quantitative theory of
acoustical resonators has been developed that describes the
photoacoustic signal [12], the dispersion of resonance frequencies
and the broadening of the resonance profile [10]. The photo-
acoustic resonance spectroscopy method has now been extended to
the investigation of binary reacting gaseous mixtures giving
information about the kinetics on time scales of about $10^4$ gas
kinetic collisions.

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2. EXPERIMENTAL

Figure 1 shows the setup of a photoacoustic resonance spectrometer. The cylindrical resonator cavity in which standing pressure waves are excited is machined from stainless steel with an inside radius of 0.05 m and an inside length of 0.1 m. Into the front and back plate of the resonator NaCl windows are glued to allow the laser beam to traverse the cylinder along the axis. An Edinburgh Inst. waveguide CO₂ laser with an output power of about 3 W tuned to the 10⁴ P20 transition served as the light source. The 1/e² beam diameter was 1.3 mm and the divergence was 10 mrad. The beam was modulated by a Pockels cell supplied by II-VI Inc., Pennsylvania, USA, with a modulation depth of 80 % driven by a computer controlled Philips frequency synthesizer model PM 5190 via a linear high voltage amplifier.

A standard electret microphone mounted flat with the interior resonator wall at half the length of the cell transformed the pressure waves into an electronic signal recorded by a computer controlled Ithaco lock-in amplifier model 3961 with a sampling time of 1 sec. A Hewlett Packard Vectra personal computer was used for data processing. More details on the photoacoustic resonance technique can be found elsewhere [13].

The temperature was measured by the piezo quartz oscillation method described in [14]. Pressure measurements were performed by MKS baratron capacitance manometers.

The N₂O₄ gas was produced by mixing oxygen and nitrogen oxide both supplied by Messer Griesheim with stated purities of 99.995 % (O₂) and 99.8 % (NO). The contamination of the gases were stated to be < 5 vpm H₂O in O₂ and < 200 vpm N₂O in NO. The N₂O₄ was frozen at 77 K with a surplus of oxygen present. Allowing slow melting of the crystals the middle fraction was kept and refrozen. This procedure was repeated until the crystals showed a white colour. The whole vacuum system was evacuated to about 1 Pa and became inert against the aggressive gases after filling with N₂O₄ for some time.

Since neither N₂O₄ nor NO₂ possess any absorption in the 10 μm region SF₆ was added in concentrations of 50 to 250 Pa as a sensitizer. The 10 P20 transition of the CO₂ laser was used for excitation.

3. RESULTS

3.1 Experimental data

The resonance curves for the first radial mode were recorded point by point for various total pressures and nine different SF₆