H_2-LASER PHOTOLYSIS STUDY OF THE TEMPERATURE DEPENDENCE OF THE QUENCHING OF $O_2(b^1\Sigma_g^+)$

K. Kohse-Höinghaus and F. Stuhl*

Physikalische Chemie I, Ruhr Universität, D-4630 Bochum (F.R.G.)

We wish to report on the application of an H_2-laser system to a photochemical study. The H_2-laser consists of a Blumlein discharge according to the design by Goujon et al.[1] The laser channel is 20 cm long and the stored energy is about 3 J. The laser is operated at a repetition frequency of 1 Hz. The energy of the laser pulse was measured to be roughly 1 μJ. This energy of the laser radiation is 500 times smaller than that reported by Goujon et al.[1] The half-width time of the pulse is estimated to be approximately 1 ns. The spectrum of the laser was investigated in the wavelength region from 155 to 170 nm. It was found to consist of several P-branch lines originating from different vibrational levels of the $H_2(B^1\Sigma_u^+)$ state. Further experimental details are given elsewhere.[2]

Since we have been interested for some time in the quenching of diatomic molecules in metastable ($^1\Sigma$) states[3] we have used the H_2-laser pulse in this study to generate small concentrations of $O_2(^1\Sigma)$ by photolysing O_2. Since the laser emissions coincide well with the strong absorption region of the Schumann-Runge continuum of O_2, $O_2(^1\Sigma)$ can be produced by the fast process

$$O_2 + h\nu\ (\lambda \approx 160\ \text{nm}) \rightarrow O(^1D) + O(^3P)$$

$$O(^1D) + O_2 \rightarrow O_2(b^1\Sigma_g^+) + O(^3P)$$

The concentration of $O_2(^1\Sigma)$ thus generated is estimated to be smaller than 10^{10} cm^{-3}. Metastable O_2 are detected at right angles to the laser beam by their emission

$$O_2(b^1\Sigma_g^+) \rightarrow O_2(X^3\Sigma_g^-) + h\nu\ (\lambda \approx 762\ \text{nm})$$

The decay of $O_2(^1\Sigma)$ was always observed to be exponential. Thus, in the presence of an excess of quenching gas over the concentration of $O_2(^1\Sigma)$, the observed decay rates allow the determination of the quenching rate constants of $O_2(^1\Sigma)$. As an example, Fig. 1 shows data on the quenching of H_2 and D_2 at different temperatures. In this figure the quenching rate constants are displayed in an Arrhenius plot. Each of the data points represents 15 to 30 decay time measurements and the error limits indicate three times the standard deviation. The rate constants for the quenching by H_2 and D_2 obtained from this figure are

$$k(H_2) = (7.3\ {}^{+2.7}_{-2.0}) \times 10^{-12} \exp - \left(\frac{1.32 \pm 0.14\ \text{kcal mol}^{-1}}{RT}\right)$$

$$k(D_2) = (2.3\ {}^{+0.8}_{-0.6}) \times 10^{-13} \exp - \left(\frac{1.63 \pm 0.14\ \text{kcal mol}^{-1}}{RT}\right)$$

---

*on sabbatical leave at NOAA, Aeronomy Laboratory, and CIRES, University of Colorado, Boulder, Colorado 80303

This data and further results will be discussed.

References

1) P. Goujon, A. Petit and M. Clerc, B.I.S.T., Commisariat à l'Energie Atomique, 205, 31 (1975).

2) K. Kohse-Höinghaus and F. Stuhl, Ber. Bunsenges. Phys. Chem. (to be published).

3) C. Zetzsch and F. Stuhl, J. Chem. Phys., 66, 3107,(1977).

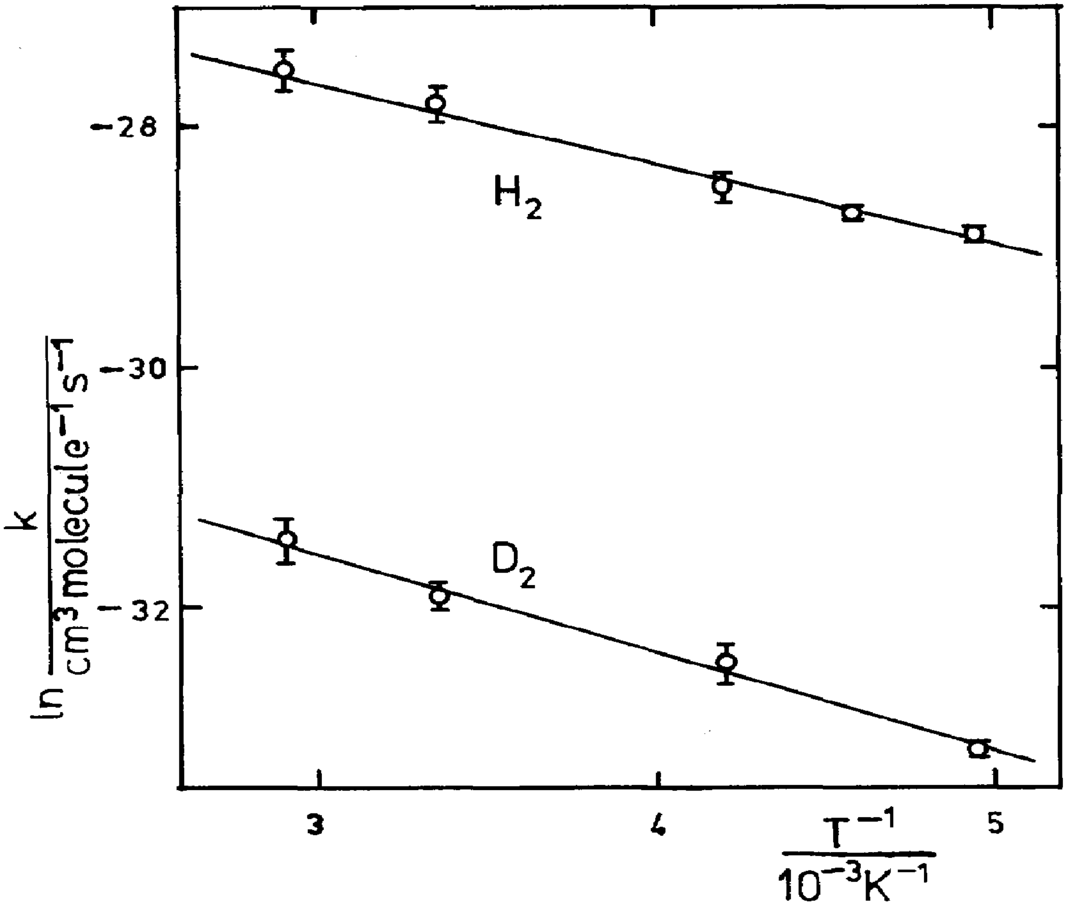

Fig. 1. Arrhenius plot of the quenching of $O_2(^1\Sigma)$ by H_2 and D_2 (see text).