H₂-laser photochemical study of the temperature dependent quenching of $O_2(b\,^1\Sigma_g^+)$

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An H₂–VUV-laser was used to generate metastable $O_2(b\,^1\Sigma_g^+)$ molecules in the photolysis of O_2. The metastable molecules were monitored using the emission of their forbidden transition $O_2(b\,^1\Sigma_g^+ \rightarrow X\,^3\Sigma_g^-)$. From the decays of this emission rate constants for the quenching of $O_2(b\,^1\Sigma_g^+)$ by H_2, D_2, N_2, HCl, DCl, CH_4, CD_4, NH_3, and ND_3 were determined as a function of temperature. Significant isotope effects were observed for the activation energies.

INTRODUCTION

The kinetics of the quenching of metastable $O_2(b\,^1\Sigma_g^+)$ molecules has been investigated in a number of studies[1-5] which have been summarized by Davidson and Ogryzlo[1] for most of the work performed before 1973. Several interesting features have been noticed in previous studies. For example, marked isotope effects have been observed for the rates of the quenching by deuterated and by hydrogenated compounds.[5-7] Furthermore, for the kinetics of the quenching of O_2, NH, and ND in their metastable $(b\,^1\Sigma^+)$ states, similar trends have been recently observed implying the possibility that similar quenching processes occur for these three molecules.[8,9] Also, the previous suggestion that the energy of $O_2(^1\Sigma)$ is released to form vibrational excitation of the quencher[1] and of the metastable $O_2(a\,^1\Delta)$ molecules has been substantiated in recent studies[10,11] for a number of molecules.

Previously, Davidson and Ogryzlo[1] have reported an empirical correlation between the logarithm of the rate constant and the highest fundamental frequency of the quenching molecule. Thereafter, several theoretical investigations have been performed. Kear and Abrahamson[2] have calculated rate constants for the quenching of $O_2(^1\Sigma)$ by some diatomic molecules assuming short range repulsive interactions for the energy transfer process. Their calculated values are generally smaller than the experimental ones. Braithwaite *et al.*[12] have calculated quenching rate constants for several diatomic molecules taking long range forces into account. With this method the values of the rate constants for the quenching by H_2, HD, D_2, CO, and N_2 were found to be close to those determined experimentally while those for the quenching by NO, HCl, and O_2 differed from the experimental values.[12]

The only experiments and the only calculations so far reported on the temperature dependence of the rate constants deal with the quenching of $O_2(^1\Sigma)$ by H_2 and HBr.[3,13] For their calculations Braithwaite *et al.*[3,13] took both short range (exchange) and long range (multipolar) interactions into account. The authors were able to confirm the results of their calculations by their experiments.

These previous theoretical investigations favor processes in which the released electronic energy is in near resonance with the vibrational energy gained by the quenching molecules. On the other hand, using the statistical theory, Thomas and Thrush[14] have recently shown that 20% to 25% of the energy released goes into translation and rotation. Of all the quenching processes investigated by these authors, only the excitation of HCl $(v = 2)$ requires more energy than that released in the quenching of $O_2(b\,^1\Sigma_g^+; v = 0)$ to $O_2(a\,^1\Delta; v = 0)$. It can hence be expected that this process exhibits an activation energy.

The present study was undertaken to provide experimental data on the temperature dependence of the kinetic isotope effects in the quenching of $O_2(^1\Sigma)$. It was observed that the kinetics of the quenching by all molecules studied (with the exception of NH_3 and N_2) exhibits a marked temperature dependence. Furthermore, significant isotope effects were found for the temperature dependences of the quenching processes.

EXPERIMENTAL

The experimental setup consists of an H₂-VUV-laser, a reaction chamber, and a detection system for light emission. A schematic diagram of the apparatus which will be described in the following part is shown in Fig. 1.

The laser was built according to the design given by Goujon *et al.*[15-17] The laser essentially consists of a Blumlein discharge[18] with a discharge channel of 200 mm length and electrodes 8 mm apart. The discharge is triggered by a separate spark gap in air or nitrogen at 1 atm pressure. The laser was usually operated at 25 kV. At this voltage 3 J are stored in the capacitor. The flash time of the laser pulse was determined by a multiplier (RCA 1P28) which viewed a quartz plate coated with sodium salicylate at right angles to the laser beam. The light pulse was found to be shorter than 10 ns, the upper limit being given by the frequency response of the oscilloscope (Tektronix 7623 and 7A16A plug in) used. Usually, the laser was operated at a repetition frequency of 1 Hz.

The laser channel consists of plexiglass and has a volume of approximately 120 cm³. It is closed at one end by a LiF window to allow transmission of the laser emission. The channel can be evacuated to better than

3×10^{-2} mbar by a mechanical pump (Leybold, type D4A).
Care was taken to minimize the partial pressure of
oxygen, since oxygen effectively absorbs the H_2-laser
radiation. The intensity of the laser pulse varied with
the pressure of H_2 in the discharge channel. Figure 2
displays the relative intensity measured at 160.9 ± 0.1
nm by a photomultiplier (EMI Gencom G26H315) as a
function of pressure of H_2. Below a pressure of 50
mbar H_2 in the laser channel, the discharge extended
into the connected vacuum lines. Therefore, 67 mbar
N_2 were added at these low pressures. The maximum
intensity was found for 65 mbar H_2. This pressure
was used in the subsequent experiments. The absolute
intensity of the laser pulse was determined by CO_2
actinometry[19] and was found to be $\approx 1.5 \times 10^{12}$ quanta
per flash. This value corresponds to a pulse energy
of ≈ 2 μJ. This energy is about three orders of mag-
nitude smaller than that given by Goujon et al.[15-17]
for a somewhat larger discharge setup but it is similar
to the energy reported by Hodgson,[20] Waynant et al.[21]
and Andreyev et al.[22] for comparable discharge arrange-
ments. During the last part of the present work the in-
tensity could be enhanced by a factor of 4 by properly
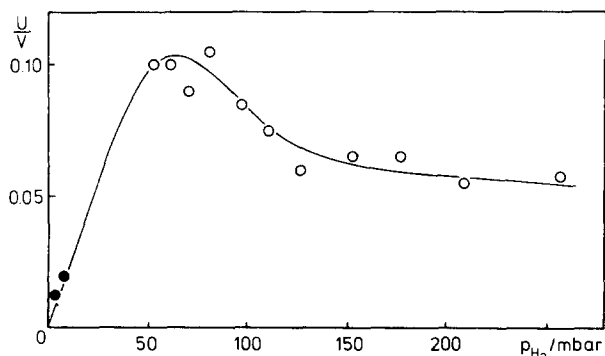placing a mirror at the rear end of the laser channel.

FIG. 2. Dependence of the intensity of the H_2-laser emission
at 160.9 nm on the pressure of H_2. The intensity is repre-
sented by the maximum photomultiplier signal U. The capaci-
tor was charged using 25 kV. o: H_2, •: $H_2 + 67$ mbar N_2.
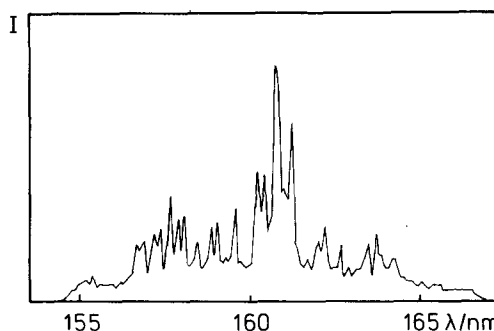

FIG. 3. The spectrum of the H_2-laser emission at 80 mbar
H_2 and 28 kV. The spectral resolution is 0.1 nm.

Since the intensity of the laser radiation is rather
small, the divergence of the laser beam was estimated
by an indirect method. For this purpose the discharge
was first operated in N_2 or air in order to generate
N_2-laser emission at 337 nm. The divergence of this
emission was determined visually on a fluorescence
screen to be 6×20 mrad. Then the ratios of the inten-
sities of both laser emissions were compared at a
distance of 80 and 230 cm from the laser. From
this comparison we conclude that both laser emissions
have approximately the same divergence.

The spectrum of the H_2-laser emission was investi-
gated in the wavelength region from 120 to 220 nm.
Figure 3 shows the spectrum between 154 and 168 nm.
No emission was observed below 154 nm and above 168
nm. The spectrum in Fig. 3 was taken with a 0.5 m
VUV monochromator (Minuteman type 305 M) using a
spectral resolution of 0.1 nm. For this purpose the
intensities of the individual laser pulses were monitored
on an oscilloscope at intervals of 0.1 nm. The spec-
trum of Fig. 3 is found to be similar to that reported
by Antonov et al.[23] Mainly $P(1)$, $P(2)$, and $P(3)$ lines
of the $H_2 \left[(B\,^1\Sigma_u^+; v' = 2 \text{ to } 11) \rightarrow (X\,^1\Sigma_g^+; v'' = 9 \text{ to } 14) \right]$
transitions are observed in these spectra.

The laser including the trigger pulse generator is
placed in an housing ($170 \times 75 \times 93$ cm) made of copper
sheets which are 0.1 mm thick. This housing effec-
tively minimizes electric interferences from the dis-
charge.

The laser is connected with the reaction chamber by
a tube (15 cm long) which is flushed with N_2 at atmo-
spheric pressure to avoid absorption of the laser light
by O_2. The reaction chamber ($\approx 4.5\,\ell$) is made of
stainless steel which is coated with black teflon on the
inside. The distance window–effective reaction volume
is 9.5 cm. The chamber can be evacuated to less than
10^{-6} mbar. Its leak rate is less than 5×10^{-7} mbar ℓ s^{-1}.
The pressure in the chamber was measured using
capacitance manometers (MKS Baratron types
220-3-A-4, 210 and 221 HSD). The reaction chamber
is surrounded by a temperature bath (water or methan-
ol), the temperature of which is controlled by a thermo-
stat (Haake NBS, regulator F 20) and a cryostat (Lauda
UK 80 DW). The temperature was varied from 200 to
350 K and was kept constant during an experiment to
within ± 1 K.

The gases were introduced into the reaction chamber trough valves and lines made of stainless steel. The gas mixtures in the chamber were irradiated under static conditions.

The gases used had the following minimum purities stated by the manufacturers: O_2, 99.995% or 99.998%; He, 99.996%; H_2, 99.999%; HCl, 99.8%; CH_4, 99.995%; D_2, 99.7% (two samples our mass spectrometric analyses of which resulted in 99.2% D_2, 0.64% HD, ≤0.16% H_2 and 99.4% D_2, 0.4% HD, ≤0.2% H_2); N_2, 99.995% (all samples from Messer Griesheim); DCl, 99% (Merck Sharp &Dohme); CD_4, 99% C–D (Merck Sharp & Dohme) or (95.1±0.3)% C–D (79.4% CD_4, 18.0% CD_3H, 2.6% CD_2H_2) (Isotopen- und Strahlenforschung, Akademie der Wissenschaften der DDR) [our mass spectrometric analysis: (94.2±1)% C–D]; NH_3, 99.99% (Baker). ND_3, >90% N–D, was produced in our laboratory by the reaction of D_2O with a large excess of Mg_3N_2 and contained traces of D_2O. O_2, He, H_2, D_2, N_2, CH_4, and CD_4 were additionally purified by feeding these gases through a trap at 77 K. HCl, DCl, NH_3, and ND_3 were fed through a trap at 195 K. It should be noted that the two different samples of O_2, D_2, and CD_4 were used with no difference in the results.

It was found that NH_3, ND_3, HCl, and DCl were strongly adsorbed at the walls of the reaction chamber. Therefore, O_2 and He were not added until the pressure of these gases became constant. Since marked isotope effects were observed for the quenching by NH_3/ND_3 and by HCl/DCl, care was taken to minimize isotope exchange of the deuterated compounds with hydrogenated impurities in the chamber such as H_2O. For this reason the chamber was filled a large number of times with the deuterated compound until reproducible results were obtained.

Metastable oxygen molecules in the $(b\,^1\Sigma_g^+)$ state were detected by the emission of their forbidden transition $(b\,^1\Sigma_g^+; v' = 0 \rightarrow X\,^3\Sigma_g^-; v'' = 0)$ at about 762 nm. This emission was observed at right angles to the incident laser beam through either an optical filter (Corion, 761 nm peak wavelength, 0.4 nm bandwidth, and 40% transmission) or a cutoff glass (Schott, transmission for $\lambda > 715$ nm). The emission was detected by a cooled photomultiplier (EMI, type 9658 R). The signal from the photomultiplier was amplified, discriminated (Ortec, models 9301, 454, and 436) and then stored in a multichannel analyzer (Tracor Northern NS 570 A). The analyzer was triggered by a diode which received light from the trigger gap of the laser. The signals from 32 to 512 laser shots were accumulated to obtain a decay curve of $O_2(^1\Sigma)$ of the desired precision.

RESULTS

Metastable $O_2(b\,^1\Sigma_g^+)$ molecules were produced in the H_2-laser photolysis of O_2. The emission from $O_2(^1\Sigma)$ was found to be generated in a rise time much shorter than the time resolution of the multichannel analyzer (10 μs). The emission intensity of the transition $O_2(b\,^1\Sigma_g^+ - ^3\Sigma_g^-)$ always decayed exponentially. This decay of the metastable $O_2(^1\Sigma)$ was always observed for more than one and a half orders of magnitude in concentra-
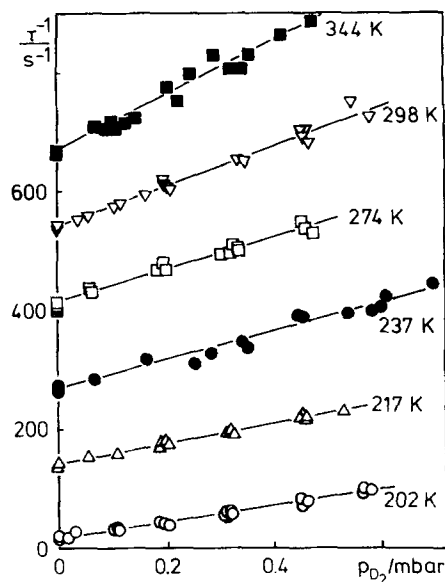

FIG. 4. The decay rate of O_2 $(b\,^1\Sigma_g^+)$ as a function of the pressure of D_2. The decays determined at different temperatures are displaced by 125 s^{-1} for 217 K; by 250 s^{-1} for 237 K; by 375 s^{-1} for 274 K; by 500 s^{-1} for 298 K; and by 625 s^{-1} for 344 K.

tion. The maximum emission intensity was found for the addition of 0.9 mbar O_2. Using this pressure, the known absorption coefficient of O_2 at 160 nm, the laser intensity, and the geometry of the reaction chamber, the maximum concentration of $O_2(^1\Sigma)$ is estimated to be about 10^{10} cm^{-3}. This concentration is at least four orders of magnitude smaller than that of the added quenching gas.

Upon the addition of a quenching gas Q the decay rate of $O_2(^1\Sigma)$ increased. As described previously[5] the decay rate of $O_2(^1\Sigma)$, i.e., τ^{-1}, can be represented by the equation

$$\tau^{-1} = \tau_0^{-1} + k_Q(T)[Q] \,, \tag{I}$$

where τ and τ_0 are the lifetimes in the presence and in the absence of the quenching gas, respectively. [Q] is the concentration of the quenching gas and $k_Q(T)$ is the temperature dependent rate constant for the quenching process. The slope of a plot of τ^{-1} vs. the pressure of Q thus determines $k_Q(T)$ while the intercept gives τ_0^{-1}. Typical plots of τ^{-1} vs. the pressure of D_2 are displayed in Fig. 4 for different temperatures. For the purpose of clarity the curves in Fig. 4 are displaced by constant values added to the value of τ_0^{-1}.

Table I summarizes the values of the rate constants $k_Q(T)$ for diatomic quenching molecules and Table II those for polyatomic molecules. Some relevant experimental conditions such as the pressure ranges of the added quenching gases (Δp), the pressures of $O_2(p_{O_2})$ and He (p_{He}) in this system, and the number of experiments Z are also displayed in these tables. For each quenching gas the rate constant was determined at four to six different temperatures ranging from 200 to 350 K, and at each temperature 10 to 47 experiments were performed. At each temperature the pressure of the

TABLE I. Experimental data for the quenching of $O_2(b\,^1\Sigma_g^+)$ by diatomic molecules.

	T (K)	$(k \pm 3\sigma)$ (cm³ molecule⁻¹ s⁻¹)	Δp (mbar)	$(p_{O_2} \pm \sigma)$ (mbar)	$(p_{He} \pm \sigma)$ (mbar)	Z
H_2	202	$2.80 \pm 0.22\ (-13)^a$	$0.004 - 0.053$	1.53 ± 0.44	93.2 ± 0.8	17
	218	$3.36 \pm 0.23\ (-13)$	$0.004 - 0.039$	1.37 ± 0.07	94.4 ± 3.1	20
	237	$4.17 \pm 0.71\ (-13)$	$0.009 - 0.046$	1.07 ± 0.23	101.2 ± 7.2	10
	298	$8.24 \pm 1.03\ (-13)$	$0.003 - 0.031$	0.93 ± 0.15	93.0 ± 0.5	10
	344	$1.12 \pm 0.20\ (-12)$	$0.005 - 0.035$	1.15 ± 0.35	101.7 ± 6.3	11
D_2	202	$3.87 \pm 0.32\ (-15)$	$0.015 - 0.583$	2.03 ± 0.37	93.3 ± 0.8	23
	217	$4.97 \pm 0.42\ (-15)$	$0.056 - 0.533$	2.03 ± 0.23	93.8 ± 2.0	17
	237	$7.84 \pm 1.19\ (-15)$	$0.068 - 0.702$	2.93 ± 1.28	99.6 ± 4.3	17
	274	$1.05 \pm 0.12\ (-14)$	$0.061 - 0.479$	1.81 ± 0.23	93.4 ± 1.5	18
	298	$1.39 \pm 0.15\ (-14)$	$0.040 - 0.584$	3.1 ± 1.6	98.0 ± 3.2	19
	344	$2.19 \pm 0.34\ (-14)$	$0.071 - 0.479$	1.5 ± 0.03	99.6 ± 2.9	18
N_2	203	$2.38 \pm 0.27\ (-15)$	$0.171 - 1.249$	1.41 ± 0.13	40.1 ± 0.8	18
	243	$2.04 \pm 0.35\ (-15)$	$0.111 - 1.330$	1.37 ± 0.16	40.1 ± 0.5	26
	296	$2.06 \pm 0.60\ (-15)$	$0.127 - 1.693$	1.33 ± 0.04	40.4 ± 1.6	21
	349	$2.34 \pm 0.58\ (-15)$	$0.297 - 1.333$	1.33 ± 0.04	40.0 ± 0.5	29
HCl	205	$4.78 \pm 0.61\ (-14)$	$0.009 - 0.065$	1.33 ± 0.11	40.3 ± 0.9	14
	221	$5.63 \pm 0.16\ (-14)$	$0.007 - 0.067$	1.50 ± 0.20	40.3 ± 0.6	10
	238	$6.30 \pm 1.33\ (-14)$	$0.027 - 0.138$	1.30 ± 0.10	40.3 ± 1.1	17
	264	$8.45 \pm 2.17\ (-14)$	$0.010 - 0.081$	1.39 ± 0.17	40.4 ± 0.8	16
	295	$1.32 \pm 0.42\ (-13)$	$0.011 - 0.073$	1.36 ± 0.09	40.3 ± 1.2	15
	311	$1.32 \pm 0.35\ (-13)$	$0.010 - 0.057$	1.51 ± 0.31	40.4 ± 1.0	12
DCl	199	$1.77 \pm 0.43\ (-14)$	$0.045 - 0.400$	1.40 ± 0.18	33.6 ± 0.4	15
	218	$1.90 \pm 0.21\ (-14)$	$0.060 - 0.533$	1.34 ± 0.04	34.4 ± 1.7	16
	254	$1.90 \pm 0.49\ (-14)$	$0.047 - 0.468$	1.46 ± 0.23	35.6 ± 5.2	16
	294	$2.22 \pm 0.85\ (-14)$	$0.039 - 0.432$	1.34 ± 0.02	34.7 ± 2.0	14
	295	$2.45 \pm 0.42\ (-14)$	$0.245 - 0.940$	1.54 ± 0.39	34.4 ± 1.5	17
	337	$3.91 \pm 0.74\ (-14)$	$0.040 - 0.436$	1.39 ± 0.06	34.2 ± 1.0	14

[a] The numbers in parenthesis represent exponents to the basis 10.

TABLE II. Experimental data for the quenching of $O_2(b\,^1\Sigma_g^+)$ by polyatomic molecules.

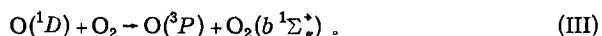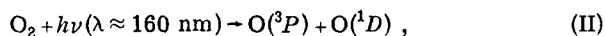|	T (K)	$(k \pm 3\sigma)$ (cm³ molecule⁻¹ s⁻¹)	Δp (mbar)	$(p_{O_2} \pm \sigma)$ (mbar)	$(p_{He} \pm \sigma)$ (mbar)	Z
CH_4	198	$3.26 \pm 0.46\ (-14)^a$	$0.004 - 0.051$	1.24 ± 0.12	93.7 ± 1.2	24
	220	$4.31 \pm 0.23\ (-14)$	$0.007 - 0.075$	1.41 ± 0.13	94.4 ± 2.1	20
	245	$5.38 \pm 0.76\ (-14)$	$0.005 - 0.052$	1.43 ± 0.15	93.8 ± 0.8	23
	269	$7.40 \pm 0.46\ (-14)$	$0.013 - 0.129$	1.60 ± 0.09	94.4 ± 0.8	25
	295	$9.62 \pm 0.91\ (-14)$	$0.014 - 0.106$	2.75 ± 0.11	40.1 ± 1.1	$19(+9)^b$
	352	$1.32 \pm 0.10\ (-13)$	$0.008 - 0.050$	1.64 ± 0.16	93.7 ± 1.3	20
CD_4	202	$3.21 \pm 0.91\ (-14)$	$0.004 - 0.040$	1.35 ± 0.15	94.0 ± 1.9	$30(+16)^b$
	234	$4.56 \pm 0.41\ (-14)$	$0.004 - 0.072$	1.56 ± 0.25	93.7 ± 1.3	47
	266	$5.56 \pm 0.52\ (-14)$	$0.012 - 0.066$	1.79 ± 0.21	93.3 ± 1.2	26
	297	$6.65 \pm 0.51\ (-14)$	$0.005 - 0.126$	1.37 ± 0.21	93.7 ± 0.9	$33(+17+16)^b$
	351	$9.31 \pm 1.24\ (-14)$	$0.006 - 0.071$	1.96 ± 0.40	93.1 ± 1.9	25
NH_3	207	$1.62 \pm 0.25\ (-12)$	$0.003 - 0.031$	1.43 ± 0.23	34.0 ± 0.8	13
	218	$1.83 \pm 0.26\ (-12)$	$0.003 - 0.027$	1.45 ± 0.19	34.4 ± 3.7	14
	261	$1.86 \pm 0.18\ (-12)$	$0.003 - 0.034$	1.56 ± 0.35	34.5 ± 2.7	21
	297	$1.68 \pm 0.24\ (-12)$	$0.003 - 0.032$	1.49 ± 0.31	37.5 ± 4.8	23
	353	$2.21 \pm 0.39\ (-12)$	$0.003 - 0.027$	1.45 ± 0.33	35.2 ± 6.7	14
ND_3	198	$5.48 \pm 1.28\ (-14)$	$0.019 - 0.340$	1.44 ± 0.40	34.4 ± 3.0	16
	217	$6.05 \pm 1.31\ (-14)$	$0.024 - 0.264$	1.39 ± 0.25	33.7 ± 0.5	24
	253	$1.06 \pm 0.16\ (-13)$	$0.040 - 0.288$	1.41 ± 0.18	34.4 ± 1.8	18
	296	$1.42 \pm 0.21\ (-13)$	$0.020 - 0.332$	1.35 ± 0.05	34.0 ± 0.9	$18(+11)^b$
	354	$1.73 \pm 0.28\ (-13)$	$0.036 - 0.331$	1.33 ± 0.03	34.2 ± 1.1	17

[a] The numbers in parenthesis represent exponents to the basis 10.
[b] These numbers in parenthesis state the numbers of control measurements which are not included in the statistical evaluation for the value of the rate constant.

quenching gas was varied by about an order of magnitude. Also shown in these tables are the standard deviations of the pressures of O_2 and He. Both these gases are very inefficient quenchers[24,25] and in the pressure ranges of these gases the value of τ_0 is mainly determined by impurities such as residual H_2O in the reaction chamber. Helium was always added to minimize diffusion from the effective reaction volume in the middle of the reaction chamber.

The precision of the rate constants listed in Tables I and II is given by three times the standard deviation (3σ). The resulting relative errors range from 5% to 30%.

DISCUSSION

Metastable $O_2(b\,^1\Sigma_g^+)$ molecules are produced in the present system by photolyzing O_2:

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

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2(b\,^1\Sigma_g^+)\ . \tag{III}$$

Metastable $O(^1D)$ atoms are generated in Reaction (II) with an excess energy of about 0.33 eV. The efficient energy transfer reaction (III) excites the $v=0$ and $v=1$ levels of $O_2(^1\Sigma)$.[26] Under the present experimental conditions $(p_{O_2} \approx 1\ \text{mbar})$ the lifetime of $O(^1D)$ is $\tau \approx 1\ \mu s$.[26,27] Vibrationally excited $O_2(b\,^1\Sigma_g^+;\ v'=1)$ are relaxed within about 2 μs in this system.[26] Hence, even for the fastest decay time $(\tau = 550\ \mu s)$ measured the decay of metastable O_2 only in the $v'=0$ level is monitored.

The temperature dependent rate constants of Tables I and II are plotted in Figs. 5 and 6 for diatomic and for polyatomic quenchers, respectively. According to previous presentations[3,13] the Arrhenius form has been chosen for these figures. For the quenching by H_2 the experimental and the theoretical data obtained by Braithwaite et al.[3] are included in Fig. 5. For all the other quenching gases, data on the temperature dependence of the rate constants does not seem to be available in the literature. As can be seen in Figs. 5 and 6, the data
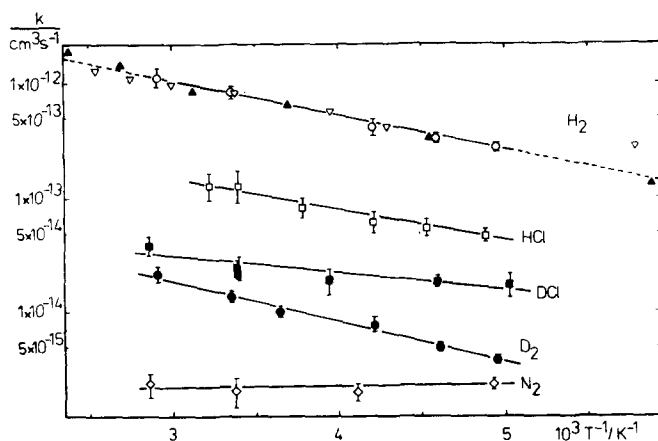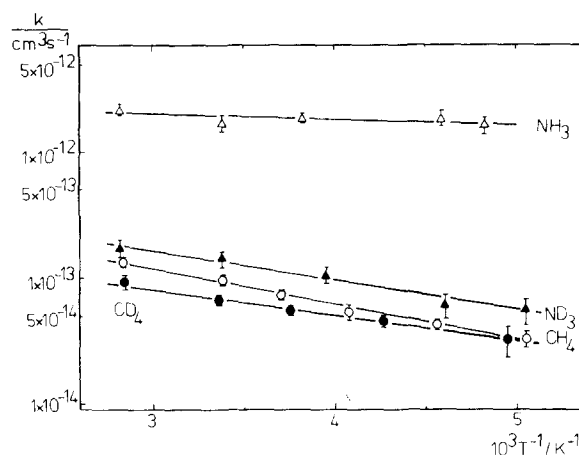

FIG. 6. Arrhenius plot of the rate constants for the quenching of O_2 $(b\,^1\Sigma_g^+)$ by polyatomic molecules. The error bars represent three times the standard deviation.

can be well approximated by straight lines in the limited temperature range of the present study. The resulting activation energies E_a together with the corresponding collision factors A are summarized in Table III. Furthermore, the rate constants measured at room temperature are listed in Table III together with values previously reported in the literature. It should be noted in this table that the errors given for the present values represent three times the standard deviation.

The comparison with literature values in Fig. 5 shows for the quenching by H_2 that almost all experimental and the theoretical values reported by Braithwaite et al.[3] are in excellent agreement with those of the present investigation. An extensive discussion of the literature values of the room temperature data for the quenching by H_2 and by D_2 has been given previously[5] and will not be repeated here. As has also been mentioned in our previous discussion,[5] the present value of the rate constant for the quenching by D_2 can be too large by about 10% to 20% because of isotopic impurities.

It is evident from Table III that the present rate constant for N_2 determined at room temperature is in excellent agreement with the literature data. From the data listed in this table the value reported by O'Brien and Myers[6] appears to be slightly too large and that calculated by Braithwaite et al.[12] to be slightly too small.

The room temperature values previously reported for the quenching by CH_4 are in good agreement with that of the present investigation. The only exception is the value reported by Arnold et al.,[28] which seems to be too low by a factor of 6 to 7. For the quenching by CD_4 no comparison is possible since literature data are not available. The rate constants measured for the quenching by CH_4 and by CD_4 are not very different and hence the isotopic impurities as given above are not expected to influence the rate data for CD_4 significantly.

The room temperature values determined in the present study for the quenching by HCl and by DCl are about two and about four times larger than the experimental values given in the literature; however, it should be noted for HCl that all experimental values agree within

FIG. 5. Arrhenius plot of the rate constants for the quenching of O_2 $(b\,^1\Sigma_g^+)$ by diatomic molecules. For the quenching by H_2 the calculated (▲) and measured (▽) rate constants of Ref. 3 are included. The error bars represent three times the standard deviation.

TABLE III. A comparison of the present rate data with those reported in the literature.

Quenching molecule	Rate constant at room temperature $(k \pm 3\sigma)$ (cm^3 molecule^{-1} s^{-1})	Activation energy E_a (kJ mol^{-1})	Frequency factor A (cm^3 molecule^{-1} s^{-1})	References
H$_2$[a]	8.2 ± 1.0 (−13)[b]	5.7 ± 0.6	$8.0^{+3.1}_{-2.3}$ (−12)	This work
	8.2 ± 0.5 (−13)	4.6	5.2 (−12)	Braithwaite et al.[3]
D$_2$[a]	1.4 ± 0.2 (−14)	6.7 ± 0.5	$2.1^{+0.6}_{-0.4}$ (−13)	This work
N$_2$	2.1 ± 0.6 (−15)	$-(0.4 \pm 1.0)$	$1.7^{+1.3}_{-0.8}$ (−15)	This work
	2.5 (−15)			Arnold et al.[28]
	2.3 (−15)			Izod and Wayne[29]
	2.2 (−15)			Stuhl and Welge[30]
	1.8 (−15)			Filseth et al.[31]
	2.0 (−15)			Noxon[32]
	2.2 (−15)			Becker et al.[24,33]
	3 ± 1 (−15)			O'Brien and Myers[6]
	2.22 (−15)			Kear and Abrahamson[2]
	1.5 (−15)			Braithwaite et al.[12]
HCl	1.3 ± 0.4 (−13)	5.0 ± 1.1	$8.6^{+6.8}_{-3.8}$ (−13)	This work
	6.6 ± 3.3 (−14)			Gauthier and Snelling[34]
	7.3 ± 1.7 (−14)			Thomas and Thrush[4]
	8.8 (−15)			Braithwaite et al.[12]
DCl	2.5 ± 0.4 (−14)	2.7 ± 0.9	$8.1^{+4.4}_{-2.9}$ (−14)	This work
	5.8 ± 1.7 (−15)			Thomas and Thrush[4]
CH$_4$	9.6 ± 0.9 (−14)	5.5 ± 0.4	$8.6^{+1.8}_{-1.5}$ (−13)	This work
	1.3 (−14)			Arnold et al.[28]
	1.1 (−13)			Filseth et al.[31]
	7.5 (−14)			Becker et al.[24]
	7.3 (−14)			Davidson and Ogryzlo[1]
	8.4 (−14)			Kear and Abrahamson[2]
CD$_4$	6.7 ± 0.5 (−14)	3.9 ± 0.8	$3.4^{+1.4}_{-1.0}$ (−13)	This work
NH$_3$	1.7 ± 0.2 (−12)	0.7 ± 0.8	$2.6^{+1.1}_{-0.8}$ (−12)	This work
	2.7 (−13)			Arnold et al.[28]
	8.6 (−14)			Filseth et al.[31]
	3.0 (−12)			O'Brien and Myers[6]
	1.8 ± 0.5 (−12)			Becker et al.[24,33]
	2.2 (−12)			Davidson and Ogryzlo[1]
	2.2 ± 0.5 (−12)			Thomas and Thrush[4]
ND$_3$	1.4 ± 0.2 (−13)	4.6 ± 0.9	$8.8^{+4.5}_{-3.0}$ (−13)	This work

[a]A comparison with room temperature values has been given in Ref. 5.
[b]The numbers in parenthesis represent exponents to the basis 10.

their combined error limits. On the other hand, the value calculated by Braithwaite et al.[12] is a factor of about 10 smaller than the experimental values for HCl. According to the minimum isotopic purity stated for the DCl sample, the rate constant for the quenching by DCl is expected to be about 10% lower than the value given in Table III. In order to minimize isotope exchange with residual hydrogenated compounds in the reaction vessel, the experiments with DCl were performed after the vessel was flushed with DCl for two weeks before the measurements began. The discrepancy found for the quenching by DCl hence is not evident.

A comparison of the values listed in Table III for the room temperature rate constants of the quenching of O$_2$($^1\Sigma$) by NH$_3$ shows that the present value is in agreement with those values determined previously by Becker et al.,[24,33] by Davidson and Ogryzlo,[1] and by Thomas and 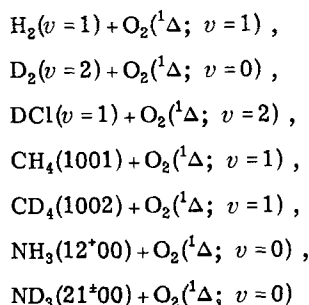Thrush.[4] The values reported by O'Brien and Myers[6] and by Arnold et al.[28] are somewhat larger than the present value. The value determined by Filseth et al.[31] is about 20 times smaller than the present value. In a flash photolysis system similar to that used by Filseth et al.,[31] the production of metastable NH($b\,^1\Sigma^+$) has been recently observed.[8] NH($^1\Sigma$) is quenched by O$_2$ and there is the possibility that O$_2$($^1\Sigma$) is formed in this process. This would lengthen the decay time of O$_2$($^1\Sigma$) in the NH$_3$/O$_2$ flash photolysis system. In the present H$_2$-laser photolysis system metastable NH($^1\Sigma$) can not be generated at the wavelength of irradiation ($\lambda \approx 160$ nm).[8] For the quenching of O$_2$($^1\Sigma$) by ND$_3$ no earlier result is available for comparison. It should be noted that the isotopic impurities mentioned before infer that the rate constants determined in this study for the quenching by ND$_3$ can only be taken as upper limits. Since the quenching by NH$_3$ however exhibits only a weak temperature dependence, the value of the activation energy determined for the quenching by ND$_3$ is likely to be

close to the true value.

Table III shows that the activation energies which were obtained in this investigation range from -0.4 kJ mol^{-1} for N_2 to 6.7 kJ mol^{-1} for D_2. It should be noted that the temperature dependence of the present rate constants can be represented by an expression of the form $k = A \times T^n$ as well. The following values were determined for n: (2.70 ± 0.29) for H_2; (3.22 ± 0.23) for D_2; (-0.15 ± 0.47) for N_2; (2.13 ± 0.55) for HCl; (1.27 ± 0.40) for DCl; (2.45 ± 0.18) for CH_4; (1.75 ± 0.34) for CD_4; (0.35 ± 0.35) for NH_3; and (2.05 ± 0.41) for ND_3. The given error limits represent three times the standard deviation.

In all cases the activation energy for the quenching by the deuterated compound was found to be different from that for the quenching by the corresponding hydrogenated compound. The smallest difference is observed for the quenching by H_2 and by D_2, the activation energies of which lie within their combined error limits.

Thomas and Thrush[11] have recently shown by IR emission spectroscopy that HCl $(v = 2)$ is excited in the quenching of $O_2(^1\Sigma)$. This process is endothermic by 427 cm^{-1} (5.1 kJ mol^{-1}) if $O_2(^1\Delta;~v = 0)$ is formed. The present activation energy of (5.0 ± 1.1) kJ mol^{-1} is consistent with the endothermicity of this process. For the quenching by N_2, Braithwaite et al.[12] have postulated the generation of $O_2(^1\Delta;~v = 2)$ and of N_2 $(v = 1)$ in their calculation. The near resonance of this process also agrees well with the small activation energy observed $[-(0.4 \pm 1.0)$ kJ mol$^{-1}]$. Similarly, for the other quenching processes one can easily find vibrational states of the products which result in endothermicities very close to the activation energies measured in this work. These vibrational product states are

$$H_2(v = 1) + O_2(^1\Delta;~v = 1)~,$$

$$D_2(v = 2) + O_2(^1\Delta;~v = 0)~,$$

$$DCl(v = 1) + O_2(^1\Delta;~v = 2)~,$$

$$CH_4(1001) + O_2(^1\Delta;~v = 1)~,$$

$$CD_4(1002) + O_2(^1\Delta;~v = 1)~,$$

$$NH_3(12^+00) + O_2(^1\Delta;~v = 0)~,$$

$$ND_3(21^\pm00) + O_2(^1\Delta;~v = 0)$$

for the respective reaction.

This tempting approach of correlating the observed activation energies with endothermic processes, however, is not in agreement with the formation of the vibrationally excited product states previously adopted for the quenching by H_2, D_2, DCl, and NH_3.[11,12,14] In particular, it does not seem to confirm the rule that 20% to 25% of the energy released goes into translation and rotation.[14] Further work appears to be necessary to fully explain the isotope effects and the marked enhancement of the rate for the quenching by several molecules upon increasing temperature.

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