

QUENCHING OF TWO-PHOTON-EXCITED H(3s, 3d) AND O(3p $^3P_{2,1,0}$) ATOMS BY RARE GASES AND SMALL MOLECULES

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Measurements of the quenching rate coefficients for hydrogen atoms in the 3s 2S and 3d 2D states and of oxygen atoms in the 3p 3P state by rare gases and several combustion-relevant collision partners are presented. The excited atomic states are prepared by two-photon laser excitation. Quenching cross sections for most collision partners are found to be larger than classical collision cross sections; H atoms are mostly quenched faster than O atoms. For the quenching of H and O atoms by the rare gases, the rate coefficients increase significantly with the mass of the rare gas atom.

1. Introduction

Collisional energy transfer processes, for example quenching, are the subject of continuous interest both from the theoretical and experimental points of view. In particular, electronic quenching of various specific states of light atoms has been investigated for a variety of different collision partners [1-7]. Until recently, the available experimental data were scarce because of experimental limitations in selectively populating well-defined states of light atoms. However, with the development of multiphoton techniques, these constraints have been considerably relaxed.

Measurements of atomic quenching rate coefficients are of interest in two respects. First, there is a need for quenching data for the interpretation of experiments in fields like atmospheric chemistry or optical diagnostics of plasmas and combustion processes; secondly, the development of theoretical models for the description of quenching processes must be based on experimental data.

Theoretical approaches to the understanding of the collision dynamics underlying quenching processes have been discussed in the literature [1,2,7,8]. De-

spite considerable efforts, however, there is no generally applicable formalism available for the theoretical treatment of quenching processes. This is partly due to the fact that the physical nature of the interaction responsible for the energy transfer changes with different collision partners. For example, potential curve crossing mechanisms have been proposed to treat quenching of O(1D) by rare gases [2] or of Na(2P) by nitrogen [8]. On the other hand, quenching of metastable states of the heavier rare gases by small molecules [1] or of N(4D) atoms by heavier rare gases can be treated in terms of long range attractive interactions [7].

To achieve a physical understanding of electronic quenching, it is reasonable to use a comparatively simple and well-defined system as a starting point. In this respect, experiments on the quenching of excited atoms by the rare gases are of interest for several reasons. There are no complications due to vibrational or rotational structure of the collision partners; this implies that measured quenching rate coefficients do not have to be interpreted as a thermal average over the state distribution of the quenching molecule at a given temperature. Furthermore, due to the 1S character of the ground state wavefunction of the rare gases, no fine structure components or orientation effects except for those

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arising from the excited atom itself have to be considered.

We have measured rate coefficients for the quenching of H(3s,3d) and O(3p³P) atoms by rare gases and several small molecules. We are pursuing two objectives: First, quenching data are required for quantitative measurements of atom concentrations by fluorescence techniques in combustion environments. In such systems, fluorescence is subject to quenching by a variety of molecular species, e.g. H₂, O₂, H₂O, N₂, CH₄, CO₂ or CO [9,10]. We have measured individual quenching rate coefficients of H and O atoms for these molecules. Secondly, we have determined rate coefficients for the quenching of H and O atoms by rare gases; these measurements are intended to provide additional data for the development and testing of theoretical models for the description of energy transfer processes.

2. Experimental

The detailed experimental arrangement has been described previously [9]. Here only a brief summary is given.

Quenching rate coefficients were determined from measurements of the radiative lifetimes of the excited states of hydrogen and oxygen atoms, which were produced in a discharge flow reactor by dissociation of H₂ and O₂, respectively, via a microwave discharge. The reactor was usually operated at a total flow rate up to 4 slm and pressures between 1.5 and 4 mbar, except for the measurements with He, Ne and Ar where quenching was so slow that the pressure had to be increased up to 35 mbar until a significant lifetime change could be measured. To minimize the influence of background quenching of H and O atoms by H₂ or O₂, the test gases were strongly diluted with helium. The fraction of H₂ and O₂ was usually less than 2%. Helium was found to be a very inefficient quencher for the excited states under investigation; this was verified by increasing the pressure in the reactor without any additional quencher present. Concentrations of quencher gases were calculated from pressure and flow rates with an estimated uncertainty of $\pm 5\%$. All gases had a purity of better than 99.99% as stated by the manufacturer (Messer-Griesheim) and were used without further

purification, except for CO. When the latter was added to the flow, the H atom fluorescence signal disappeared almost completely and did not reappear when the CO flow was turned off. It was concluded that the activity of the reactor walls was increased considerably by impurities in the CO, leading to very high wall recombination rates for H atoms. Consequently, CO was passed through a cold trap at about -65°C before entering the flow reactor. The same problem was experienced in the quenching of oxygen atoms by acetylene. Hence the corresponding rate coefficient could not be measured (see table 1 below). The excited states of H and O atoms were populated by two-photon laser absorption at 205 and 226 nm, respectively [11,12]. Tunable laser radiation for the excitation of oxygen atoms was produced by a Nd:YAG-pumped dye laser, the output of which was frequency doubled and mixed with the residual IR radiation of the YAG laser, resulting in approximately 3 mJ/pulse at 226 nm. For excitation of hydrogen atoms, additional Raman shifting in H₂ was employed. The first anti-Stokes order yielded about 50 μJ /pulse at 205 nm. Quenching rate coefficients were determined from measurements of the temporal decay of the fluorescence from the excited states at 656 nm for H atoms and 845 nm for O atoms. Fluorescence was controlled via $f/3.75$ optics, passed through interference filters and observed by a R298 or R636 photomultiplier (Hamamatsu). Time-resolved fluorescence signals were recorded by a transient digitizer. The intensity and temporal shape of the laser pulses were monitored by a fast calibrated vacuum photodiode.

3. Results and discussion

The excitation/detection mechanism is illustrated schematically in fig. 1. According to two-photon selection rules, for H atoms both the 3s and 3p states are populated. For O atoms, the energy spacing of the three fine-structure components of the 2p³P_{2,1,0} state is large compared to the laser bandwidth so that absorption occurs only from one single component. Because of the signal intensity, we generally employed excitation from the $J''=2$ state, resulting in the population of all three fine-structure components of the excited 3p³P_{2,1,0} state [6,13]. In both cases,

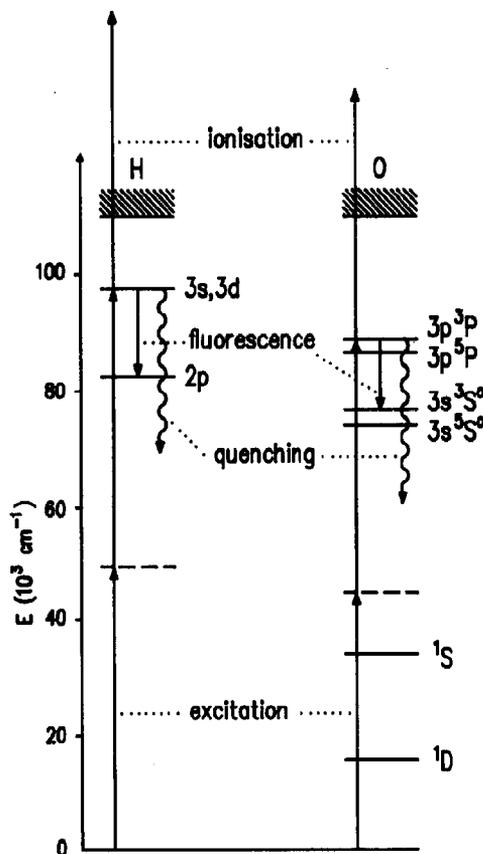


Fig. 1. Excitation and detection mechanism for the quenching of H($n=3$) and O($3p^3P$) atoms after two-photon excitation.

fluorescence from different fine-structure components of the excited state could not be resolved. Thus, the reported quenching rate coefficients must be regarded as total removal rate coefficients from the excited states; correspondingly, quoted lifetimes are average values over different fine-structure components.

Quenching rate coefficients were determined from radiative lifetime measurements as a function of the concentration of different collision partners. The measured removal rate A from the laser-excited state is given by the relation

$$A = 1/\tau_0 + k_{\text{He}}[\text{He}] + k_{\text{Q}}[\text{Q}],$$

where τ_0 is the radiative lifetime, k_{Q} the quenching rate coefficient and $[\text{Q}]$ the concentration of collision partner Q. The second term in the sum accounts for the (usually negligible) contribution of quenching by helium. A typical temporal decay of the flu-

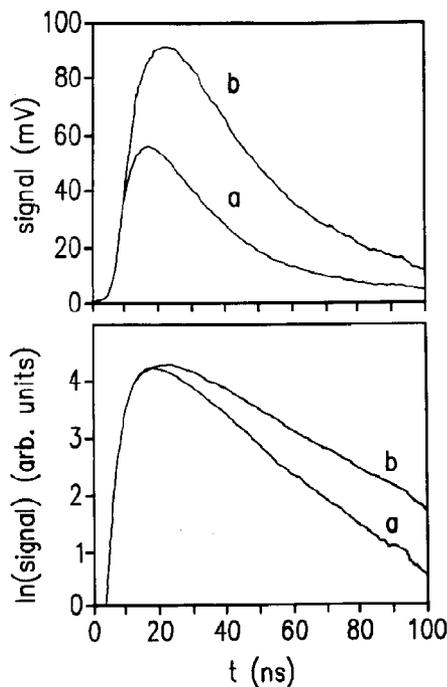


Fig. 2. Time decays for O atom fluorescence in linear (upper half) and logarithmic (lower half) representations. Curves (b) correspond to signals without additional quencher, curves (a) to quenching by CH_4 . The logarithmic plots are scaled to a common maximum.

orescence signal is shown in fig. 2. The logarithmic curves were fitted by straight lines using an unweighted least-squares procedure. The evaluation started about 10 ns after termination of the laser pulse as determined by the photodiode. Usually the temporal profiles were fitted over a time interval corresponding to 3 to 4 lifetimes.

Fig. 3 shows measured removal rates as a function of quencher concentration for quenching of H and O atoms by rare gases. From the ordinate intercepts, radiative lifetimes can be determined, if negligible quenching by He, O_2 or H_2 is assumed. This requirement can be verified by calculating the removal rates by these gases from measured quenching rate coefficients and mole fractions, and comparing them to the measured decay rate. From a total of 26 measurements for O and 55 measurements for H atoms, we derived radiative lifetimes of 36.2 ± 0.69 ns for O($3p^3P$) and 20.9 ± 0.80 ns for H($n=3$). The value for O atoms is in good agreement with the results of former in-

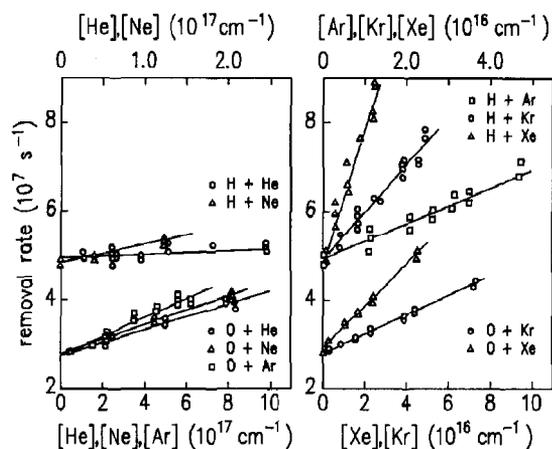


Fig. 3. Quenching rates of H and O atoms versus concentrations of rare gases. Left half, "slow" quenchers; right half, "fast" quenchers. The removal rate is given by $1/\tau_0 + k_{He}[He] + k_Q[Q]$, where τ_0 is the radiative lifetime, k_Q the quenching rate coefficient and $[Q]$ the concentration of collision partner Q.

vestigations, where values between 34.6 and 39 ns have been reported [6,14–17]. For H atoms, the measured lifetime is in accord with a predominant excitation of the 3d over the 3s state, as predicted by theory [11,18]. Furthermore, this result supports the assumption that mixing of the 3s, 3p and 3d fine structure components is a relatively slow process. In the case of fast mixing, a shorter lifetime would be observed, mainly due to the very fast 3p–1s transi-

tion [14], which would then be dominant.

Table 1 summarizes the results of our measurements on H and O quenching. Most data are averaged values from several experiments. The quoted errors correspond to statistical errors (one standard deviation). For completeness, data from an earlier investigation in our laboratory are included [9]. In several experiments where we reinvestigated quenching rate coefficients, the results agreed with those in ref. [9] within the stated error limits except for O atom quenching by He, Ar, and O_2 . The new values for quenching of O atoms by He and Ar should be considered as more reliable since the corresponding experiments were performed over a larger pressure range; this leads to a higher accuracy since the rate coefficients for quenching of O atoms by the lighter rare gases are particularly small. In the case of quenching of O by O_2 , the value of $6.3 \times 10^{-10} \text{ cm}^3/\text{s}$ quoted here is almost a factor of 2 higher than that in ref. [9]; we do not know the reason for this discrepancy. Our new value is in much better agreement with recent experiments by Bamford et al. [6], who report a value of $(8.64 \pm 0.16) \times 10^{-10} \text{ cm}^3/\text{s}$.

For oxygen atoms, different population distributions in the excited state can be prepared by using different fine structure components of the ground state as initial levels. We found no variation, either of the radiative lifetime or the measured quenching

Table 1

Quenching rate coefficients k_Q and cross sections σ_Q for H($n=3$) and O($3p^3P$) atoms

Quencher	H($n=3$)		O($3p^3P$)	
	k_Q ($10^{-10} \text{ cm}^3/\text{s}$)	σ_Q (\AA^2)	k_Q ($10^{-10} \text{ cm}^3/\text{s}$)	σ_Q (\AA^2)
He	0.099 ± 0.05	0.35 ± 0.2	0.15 ± 0.05	1.1 ± 0.4
Ne	0.44 ± 0.05	1.7 ± 0.2	0.16 ± 0.06	1.9 ± 0.7
Ar	4.6 ± 0.5	18 ± 2.0	0.21 ± 0.07	2.8 ± 0.9
Kr	11.0 ± 1	44 ± 4.0	2.3 ± 0.06	34 ± 0.9
Xe	31.0 ± 2	124 ± 8.0	5.2 ± 0.18	79 ± 2.7
N_2	27.7 ± 1.1	109 ± 4.3	4.3 ± 0.74	55 ± 9.5
H_2	19.9 ± 3	65 ± 10	6.5 ± 0.25	35 ± 1.3
O_2	26.0 ± 1	102 ± 3.9	6.3 ± 0.12	82 ± 1.6
H_2O	110 ± 10	428 ± 39	49 ± 3	57 ± 3.5
CO	29.7 ± 1.7	117 ± 6.7	4.9 ± 0.15	63 ± 1.9
CO_2	39.4 ± 1.5	156 ± 6.0	6.6 ± 0.17	90 ± 2.3
CH_4	35 ± 2	136 ± 8.0	5.5 ± 0.15	62 ± 1.7
C_2H_2	56 ± 4	220 ± 16	a)	–

^{a)} Not measurable, see text.

rate coefficients, within our experimental accuracy on excitation from states with different J' in the case of quenching of O atoms by N_2 . This indicates that at least for this system, quenching is probably not very sensitive to the total angular momentum of the excited atom, although it should be noted that a weak dependence on J' will be obscured by population of more than one fine-structure component following two-photon excitation [6].

Only limited data are available on $H(n=3)$ and $O(^3P)$ quenching. Quickenden et al. [5] measured quenching of $H(n=3)$ atoms by water vapour in a pulse radiolysis experiment. Whereas their value of $91 \times 10^{-10} \text{ cm}^3/\text{s}$ for $H+H_2O$ is in good agreement with our own value of $110 \times 10^{-10} \text{ cm}^3/\text{s}$, for $O+H_2O$ they obtained a rate coefficient of $9.4 \times 10^{-10} \text{ cm}^3/\text{s}$, which disagrees with our result ($49 \times 10^{-10} \text{ cm}^3/\text{s}$) by a factor of 5. For the experiment in ref. [5], however, the fluorescence decay rate data versus H_2O pressure show considerable scatter, and the extrapolation to zero pressure leads to an incorrect natural radiative lifetime, which casts some doubt upon this measurement. For quenching of O atoms by N_2 , Bischel et al. [17] report a value of $2.5 \times 10^{-10} \text{ cm}^3/\text{s}$, which is a factor of 1.8 lower than the value in this study. We have no explanation for this discrepancy. In a recent study from the same laboratory [7], however, the authors found the quenching rate coefficient for quenching of N atoms by N_2 to be a factor of 1.9 higher than in the earlier work of Bischel et al. [17], though this does not necessarily mean that the reason for the discrepancies is the same.

It can be seen from table I that, with the exception of helium, quenching rate coefficients for H atoms are generally larger than for O atoms. All rate coefficients lead to quenching cross sections of the order of gas kinetic collision cross sections or larger, except those for the lighter rare gases.

Within the rare gas series, a significant increase in the quenching rate coefficient is observed with increasing mass of the collision partner for both H and O atoms; this increase is much larger than would be expected considering only the effect of the reduced mass, particularly for H atoms. The increase of k_Q is not continuous; the values "jump" by one order of magnitude on going from Ne to Ar for H atoms and between Ar and Kr in the case of O atoms. This result can be qualitatively interpreted in terms of en-

ergetically accessible states of the collision partners that can accept at least part of the large excitation energy (97492 cm^{-1} for H atoms, 88630 cm^{-1} for O atoms). For H atoms, the lowest excited states of He and Ne lie 62360 and 36550 cm^{-1} , respectively, above the excited $H(n=3)$ state, whereas Ar possesses four excited states below the excited H level which facilitate transfer of excitation energy from hydrogen atoms. Krypton has several, xenon many excited levels below the $H(n=3)$ state which can accept excitation energy. For oxygen atoms, the lowest excited states of He, Ne and Ar lie at 71220 , 45414 and 4513 cm^{-1} , respectively, above the excited $O(^3P)$ state; consequently, fast energy transfer to excited levels of the rare gases is energetically possible only for Kr and Xe.

Copeland et al. [7] measured quenching rate coefficients for $N(3p^4D^o)$ with rare gases. In their work a strong increase of the rate coefficients with heavier collision partners was also noted; however, in the case of N atoms the sudden increase of k_Q when excited levels of the rare gas atoms become energetically accessible is less pronounced than for H and O atoms. In particular, within the scope of the qualitative picture outlined above, the difference between the quenching rate for nitrogen atoms by Ne and Ar would be expected to be very large since Ar has excited states closely spaced with the excited N atom state. In fact these two rate coefficients differ only by a factor of 7. This shows that energy considerations alone may give only a very crude idea about relations between individual quenching rate coefficients.

Copeland et al. [7] proposed a model based on long-range attractive interactions to describe the quenching of $N(3p^4D^o)$ by rare gases; this formalism is suggested by the generally high values of the rate coefficients and a correlation between the quenching cross sections and the square of the polarizability α . The calculations yield satisfactory agreement with measured data in view of the simplifying assumptions; the most severe probably being the neglect of orientation effects due to the anisotropy of the p orbital on N. It would be interesting to perform similar calculations for comparison with our data on H and O atom quenching, especially since these atoms behave differently with regard to the correlation with α^2 : Whereas the cross sections for H atom quenching follow this empirical relation quite

satisfactorily, O atoms are quenched by He significantly faster and by Ar considerably slower than predicted.

In summary, we have measured rate coefficients for quenching of H($n=3$) and O($3p\ ^3P$) atoms by rare gases and several small molecules. The rate coefficients are found in general to be large; for quenching by rare gases, they exhibit a strong increase when going from light to heavy collision partners. A relation between the quenching rate coefficients and available excited states of the collider capable of accepting the excitation energy is observed. These data can be used for the development of theoretical descriptions of collisional energy transfer processes. The most instructive approach to these processes would probably be an *ab initio* quantum mechanical treatment, provided that reliable potential energy surfaces are available.

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