

QUENCHING OF $\text{Ar}(^3\text{P}_1)$: RATE CONSTANTS FOR DEACTIVATION AND "ESCAPE FACTORS" FOR TRAPPED RADIATION

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Summary

Fluorescence lifetimes in the presence of quencher were used to derive rate constants for quenching of $\text{Ar}(^3\text{P}_1)$. The values obtained were:

Quencher	Rate constant $\times 10^{11}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
N_2	0.8 ± 0.2
O_2	23 ± 6
NO	26 ± 2
CO	4.6 ± 0.8
H_2	19 ± 5

Possible mechanisms for quenching are considered in the light of the kinetic data.

The quenching rate constants were combined with steady or pseudo-steady state intensity measurements (of the Stern-Volmer type) to yield effective rate constants for radiative decay. These latter rate constants are related to the "escape factors" for the imprisoned radiation. Escape factors for excitation by pulsed radiation were essentially identical when derived either directly from the lifetime studies or from the intensity measurements; they were also statistically indistinguishable from the escape factors for excitation by steady radiation. The similarity of the escape factors in the two cases confirmed our earlier conclusion that most of the detected fluorescence originates from that part of the system illuminated by the exciting radiation, even where there is very extensive radiation trapping.

Introduction

We suggested in an earlier paper [1] that deliberate use of a system with strong radiation trapping could be an attractive method for the study of the quenching of resonance fluorescence. However, the spatial distribution

of emitters can be altered by quenching so that erroneous results could be obtained. In this connection, Van Volkenburgh and Carrington [2] point out that the changes in emitter distributions in the presence of quencher lead to differences in behaviour for (a) pulsed and (b) steady state illumination. "Escape factors" g and h may be defined for the two cases (a) and (b) as the ratio of trapped to natural radiative rate constants: for pulsed radiation, g refers to the *lowest* decay mode [1]. The two factors may not be identical; both, but especially h , may be dependent on the geometry of the apparatus.

Our studies of the imprisonment and absorption of argon resonance radiation [1] indicate that, for our experimental system, the bulk of the *detected* fluorescence came from the central, illuminated, region, both for steady (absorption studies) and pulsed (lifetime measurements) irradiation. Thus g and h should be similar in our case. In order to test this hypothesis, we have studied the quenching of Ar(3P_1) (monitored by the $^3P_1-^1S_0$ fluorescence at $\lambda = 106.7$ nm) by a number of gases.

Three types of experiment were performed. First, the fluorescence lifetimes in the presence of quencher, M, were directly determined. Here the intensity, $I(t)$ is related to t by the proportionality:

$$I(t) \propto \exp - (k_q[M] + gA)t \quad (1)$$

where A is the natural spontaneous Einstein coefficient and k_q the rate constant for quenching. Secondly, pseudo-steady state intensities were measured with pulsed illumination, so that:

$$I \propto gA / (k_q[M] + gA) \quad (2)$$

Finally, steady illumination was used: the intensities are given by:

$$I \propto hA / (k_q[M] + hA) \quad (3)$$

(It should be noted that eqns. (2) and (3) may be invalidated if the quencher fluoresces or absorbs strongly.) The results of the first experiment are used to give independent values of k_q , gA , and hence g . Then the values of k_q were used to derive h and a new value of g from the results of third and second types of experiment, respectively.

We shall show that, in accordance with our earlier conclusion [1], h and the two values of g , are identical within experimental error. The data obtained also, of course, give results for the quenching rate constants.

Experimental

Materials

Argon, helium, nitrogen (oxygen-free), oxygen, hydrogen, carbon monoxide and nitric oxide were obtained from cylinders; the first four gases were dried over phosphorus pentoxide. All gases except nitric oxide were passed at low pressure through cold-traps (78 K) immediately before they were admitted to the reaction system. Nitric oxide was purified by repeated trap-to-trap distillation. "X"-grade argon was used for the excitation lamp.

Apparatus

Fluorescence experiments were carried out in a flow system, with Ar pressures of around 1 Torr, the flow (~ 30 cm/s) being used to prevent the build-up of any photolysis products. Any quencher used was added to the argon at the upstream end of the tube. A sealed Ar resonance lamp, containing ~ 1 Torr of "X"-grade argon, was employed in this work. The lamp was excited at microwave frequencies, the source being either unmodulated, or modulated by relatively large pulses (repetition frequency ~ 15 kHz) superimposed on a low energy background. Full details of the flow apparatus, the source lamp and excitation, the detection system and the associated electronics appear in our earlier paper [1].

Lifetime measurements

The intensity of fluorescence was measured as a function of time, following illumination by a pulse of exciting radiation. An effective first-order decay rate constant, $k_{\text{obs}} (= k_{\text{q}}[M] + gA)$, was extracted from the decay data by imposing an exponential decay on the lamp intensity-time profile, as discussed previously [1]. Values of k_{obs} were measured as a function of $[M]$ to give individual values for k_{q} and gA .

Where the quencher itself fluoresced significantly (H_2, CO) attempts were made, in separate experiments, to determine the fluorescence lifetime of the "quencher" on its own. In each case the lifetime was less than $0.1 \mu\text{s}$, so that no correction to the lifetime measurements is necessitated by fluorescence of the quencher.

Stern-Volmer experiments

Equations (2) or (3) are, of course, the basis of the ordinary Stern-Volmer quenching relationship:

$$I^0/I^M = 1 + k_{\text{q}}[M]/\beta \quad (4)$$

where β is the effective radiative rate constant ($=gA$ or hA), and I^0 , I^M are the intensities of fluorescence in the absence and presence of quencher. Stern-Volmer measurements were made for each quenching gas using the excitation source in both continuous and pulsed modes. In each case, the fluorescence intensity was monitored, for a fixed argon pressure, as a function of quencher pressure in the flow tube.

Any fluorescence of the quenching gas obviously invalidates the simple Stern-Volmer relationship. Fluorescence intensities of the quenching gases alone were measured in independent experiments. In principle, a correction for the fluorescence of the quenching gas can now be applied to the raw quenching data. This correction is discussed in detail later.

Results

Lifetime measurements

The rate constants for the quenching of $\text{Ar}(^3\text{P}_1)$ by N_2 , NO , O_2 , CO and H_2 were determined from the lifetime measurements as described above.

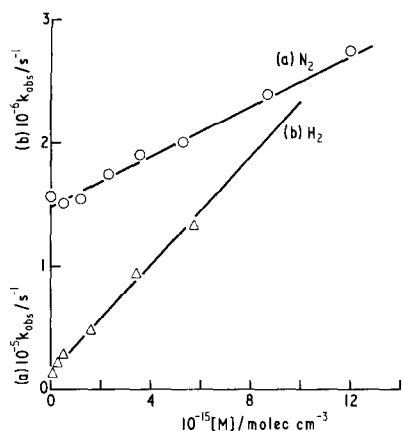


Fig. 1. Observed first order decay rate constant, k_{obs} , as a function of quencher concentration. (a) \circ , $M = \text{N}_2$; (b) \triangle , $M = \text{H}_2$. $[\text{Ar}] = 3.2 \times 10^{17}$ atom/cm³. (Values from lifetime measurements.)

TABLE 1

Rate constants for quenching (k_q) and radiation (gA) obtained from lifetime measurements

Quencher	$[\text{Ar}] \times 10^{-17}$ (atom/cm ³)	$k_q \times 10^{11}$ (cm ³ mole- cule ⁻¹ s ⁻¹)	$gA \times 10^{-5}$ (s ⁻¹)	$k_q \times 10^{11}$ ^a (cm ³ mole- cule ⁻¹ s ⁻¹)
N ₂	2.5	0.4 ± 0.2	1.6 ± 0.3	
	3.2	1.0 ± 0.1	1.5 ± 0.1	0.8 ± 0.2
O ₂	3.2	23 ± 6	2.8 ± 0.8	23 ± 6
NO	2.5	24 ± 2	2.0 ± 0.6	
	3.2	31 ± 6	2.1 ± 0.4	26 ± 2
CO	2.0	5.6 ± 1.4	2.5 ± 0.2	
	2.5	3.0 ± 2.0	2.7 ± 0.2	
	3.2	5.4 ± 0.8	1.1 ± 0.1	4.6 ± 0.8
H ₂	2.5	14 ± 4	2.8 ± 1.2	
	3.2	23 ± 3	1.5 ± 0.4	19 ± 5

Weighted mean = 1.8. SD of mean = 0.4.

^a Suggested values for k_q . Where there is more than one determination, a value is chosen which, together with its quoted error, is consistent with the several determinations.

Figure 1 shows typical results for the variation of $k_{\text{obs}} (= k_q[M] + gA)$ with $[M]$. Table 1 gives values for k_q and gA for each of the quenchers. Errors quoted are twice the standard deviations of a linear least squares analysis. The actual errors for the χ^2 fitting procedure may be somewhat greater [1].

Intensity measurements

Nitrogen was a model quencher in that it neither fluoresced nor absorbed the exciting radiation. While both O₂ and NO absorb Ar resonance

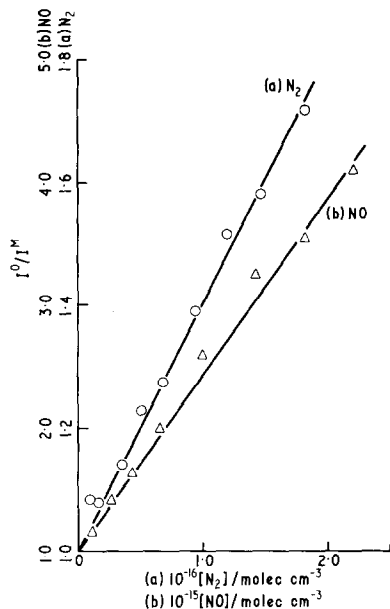


Fig. 2. Stern-Volmer plots for the quenching of fluorescence by (a) \circ , N_2 ; (b) \triangle , NO . $[\text{Ar}] = 2.5 \times 10^{17}$ atom/cm $^{-3}$, pulsed lamp.

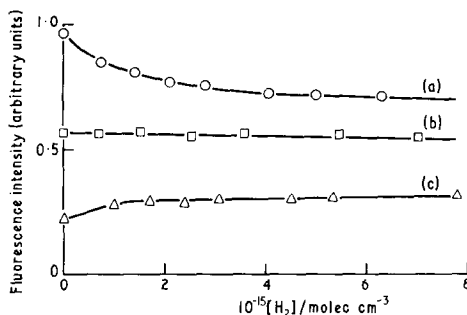


Fig. 3. Total fluorescence (*i.e.* argon + hydrogen) intensity as a function of $[\text{H}_2]$ for three values of $[\text{Ar}]$. (a) \circ , $[\text{Ar}] = 3.0 \times 10^{17}$; (b) \square , $[\text{Ar}] = 2.5 \times 10^{17}$; (c) \triangle , $[\text{Ar}] = 1.3 \times 10^{17}$ atom/cm 3 .

radiation to some extent, the concentrations needed to give good quenching were small enough (less than about 0.1 Torr) that the linearity of the Stern-Volmer plots was not affected. Figure 2 shows typical data for N_2 and NO as quenching gases.

Both H_2 and CO fluoresce when irradiated by our source lamp. Indeed, the fluorescence of H_2 is so strong that the detected intensity is comparable with that of the Ar fluorescence. The argon obviously itself absorbs the exciting radiation, so that increasing $[\text{Ar}]$ decreases the fluorescence from H_2 . Thus the total observed intensity can either increase or decrease with increasing $[\text{H}_2]$ according to whether H_2 fluorescence, or Ar fluorescence quenching, dominates. Figure 3 shows the behaviour at different argon concentrations. In view of the difficulty of assessing accurately the intensity of H_2 fluorescence in the presence of Ar , we decided not to attempt any correction of the intensity measurements for H_2 as quencher, and hence no Stern-Volmer plots are given.

For CO as quencher, the problems are less severe. The CO fluorescence was less (and often much less) than the Ar fluorescence intensity. A correction was therefore applied to the raw intensity data by subtraction of a contribution from CO fluorescence. This contribution was determined by measurement of the CO fluorescence intensity using a helium, rather than

argon, carrier under conditions otherwise identical to those obtaining in the Ar fluorescence quenching experiments. The procedure could overestimate the correction needed, since no allowance is made for the absorption of the exciting Ar resonance radiation in the quenching experiments. However, two factors made us decide to make no second-order correction. First, the absorption by Ar is in any case relatively weak in our system [1, 3]. Secondly, the CO is very probably excited not by the Ar, or even the H, lines, at which wavelengths absorption by CO is quite weak [4]. Rather, resonant excitation by CO fourth positive ($A^1\Pi-X^1\Sigma^+$) system contamination present in the lamp outputs is likely. Weak fourth positive emission is known to be present in the output even of gettered rare gas lamps, and is capable of exciting strong resonance fluorescence in CO [5].

The CO fluorescence intensity increases rapidly with [CO] at first; and then reaches a plateau. This behaviour cannot be a result of self-quenching by CO at the concentrations employed, and is therefore probably a result of self-absorption of the fluorescence by CO in the paths between the lamp, the irradiated region and the detector. Since the intensity distribution of the various vibrational bands in the lamp emission is unknown, it is not possible to assess the relative contributions of absorption (a) between the lamp and sample, and (b) between the sample and detector. However, a "mean" absorption cross-section, $\bar{\sigma}_{CO}$, applicable to either the lamp or fluorescent emission, can be estimated for the two cases. The intensity of CO fluorescence, I^{CO} , will be given very approximately by

$$I^{CO} = [\text{CO}] \exp(-[\text{CO}]\bar{\sigma}_{CO}x) \quad (5)$$

where x is the effective optical path (1 or 10 cm in the cases (a) and (b)).

Figure 4 shows $\ln(I^{CO}/[\text{CO}])$ as a function of [CO] for modulated and unmodulated light sources. The slopes are almost identical for the two sources, and suggest an effective value for $\bar{\sigma}_{CO}$ of about $4.5 \times 10^{-16} \text{ cm}^2$ for case (a), or $4.5 \times 10^{-17} \text{ cm}^2$ for case (b); these results are consistent with other data [5, 6]. The intercepts for the two sources suggest that the mean intensity of exciting radiation is about 6.5 times greater in the modulated, than in the unmodulated, lamp for lamp powers that give roughly the same count rate of argon resonance fluorescence, probably because the higher average power used for the unmodulated experiments results in higher CO concentrations in the lamp.

Figure 5 shows the effect of the CO fluorescence correction on Stern-Volmer plots for quenching of Ar fluorescence by CO using an unmodulated source. As pointed out in the last paragraph the corrections needed are relatively much smaller when the source is modulated.

Table 2 lists the slopes ($\equiv k_q/\beta$) of the Stern-Volmer plots for the various quenchers.

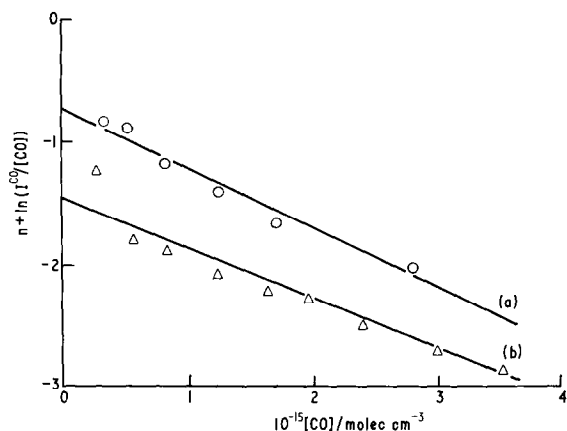


Fig. 4. Variation of $\ln(I^{\text{CO}}/[\text{CO}])$ with $[\text{CO}]$. (a) \circ , unpulsed lamp; $n = 27$. Slope = $-0.49 \pm 0.05 \text{ molecule}^{-1} \text{ cm}^3$; intercept = -27.73 ± 0.07 . (b) \triangle , pulsed lamp; $n = 29$. Slope = $-0.43 \pm 0.05 \text{ molecule}^{-1} \text{ cm}^3$; intercept = -30.45 ± 0.09 .

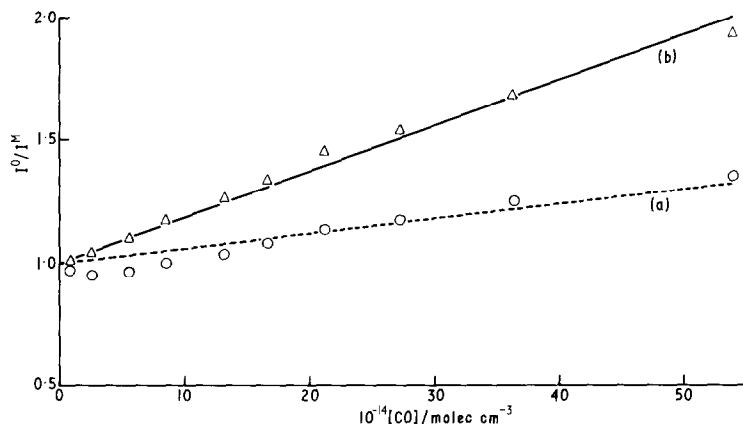


Fig. 5. Stern-Volmer plots for quenching of Ar fluorescence by CO. (a) \circ , uncorrected for CO fluorescence; (b) \triangle , corrected. Unpulsed lamp; $[\text{Ar}] = 3.2 \times 10^{17} \text{ molecule/cm}^3$.

Discussion

Quenching

Sensitized fluorescence

The quenching process can involve electronic energy transfer to M, followed by radiation of sensitized fluorescence by the primary quencher. So long as excited $M(M^*)$ radiates in a spectral region to which our detector is insensitive ($\lambda > 170 \text{ nm}$) (or M^* itself is quenched) our results for Ar($^3\text{P}_1$) quenching will be unaffected. If, however, radiation from M^* is detected, the Stern-Volmer plots could give erroneous values for k_q/fA . Indeed, if M^* were not itself quenched, and the detector responded equally to Ar($^3\text{P}_1$)

TABLE 2
Data from the Stern-Volmer quenching experiments

Quencher	[Ar] × 10 ⁻¹⁷ (molecule/cm ³)	Modulated source		Unmodulated source		Student's <i>t</i> (comparison between <i>h_A</i> and <i>g_A</i> of Table 1 - see text)
		$k_q/gA \times 10^{16}$ (cm ³ /molecule)	$gA \times 10^{-5}$ (s ⁻¹)	$k_q/hA \times 10^{16}$ (cm ³ /molecule)	$hA \times 10^{-5}$ (s ⁻¹)	
N ₂	2.5	0.38 ± 0.04	2.1 ± 0.7	0.61 ± 0.06	1.3 ± 0.5	2.304
	3.2	0.56 ± 0.04	1.4 ± 0.5	0.52 ± 0.01	1.5 ± 0.4	0.000
O ₂	3.2	13.7 ± 2.2	1.7 ± 0.7	9.6 ± 0.8	2.4 ± 0.8	1.732
	1.25	9.9 ± 1.6	2.6 ± 0.6	9.5 ± 2.0	2.7 ± 0.8	—
NO	1.7	11.2 ± 1.6	2.3 ± 0.5	9.9 ± 1.2	2.6 ± 0.5	—
	2.5	13.5 ± 1.8	1.9 ± 0.4	12.7 ± 0.8	2.1 ± 0.3	0.730
CO	3.2	17.6 ± 0.6	1.5 ± 0.2	11.3 ± 0.8	2.3 ± 0.3	1.959
	3.2	uncorrected corrected	(3.2 ± 0.2) (3.2 ± 0.2)	(1.5 ± 0.4) (1.5 ± 0.4)	(0.61 ± 0.12) (1.9 ± 0.10)	(7.5 ± 2.8) (2.5 ± 0.6)
		Weighted mean = 1.8 SD of mean = 0.3		Weighted mean = 2.1 SD of mean = 0.3		

and M^* fluorescence, then the observed intensity would be independent of $[M]$. For intermediate cases, the Stern–Volmer plots would show some curvature, the extent depending on the fraction of M^* formed that gives rise to detectable emission. Within the precision of our data, no curvature was seen in the Stern–Volmer plots. Thus the contribution from sensitized fluorescence is probably small or non-existent.

Lifetime measurements are not affected by sensitized fluorescence in quite the same way. If M^* produces a significant fluorescence intensity, its lifetime must be correspondingly small. Under these conditions, the total intensity faithfully follows relative $\text{Ar}(^3\text{P}_1)$ concentrations, and the measured lifetimes still yield correct values for k_q .

Nature of the quenching process

Two possibilities exist for the quenching of $\text{Ar}(^3\text{P}_1)$: either spin-orbit relaxation to the metastable $^3\text{P}_2$ state (followed by quenching of $\text{Ar}(^3\text{P}_2)$ [3]) or direct quenching to the ground, $^1\text{S}_0$, state. Our data do not allow us to distinguish between these alternatives.

It is generally accepted [7] that electronic quenching is more efficient, other factors being equal, the smaller the energy which must be converted to translation. Near-resonant energy transfer to M is therefore favoured. For the $^3\text{P}_1$ – $^1\text{S}_0$ excitation energy in Ar , this thesis necessarily means that an electronically excited state of M should be produced in rapid quenching of $\text{Ar}(^3\text{P}_1)$. We shall examine later the availability of suitable electronic states in the individual quenchers. For the present, we shall confine ourselves to some remarks on spin conservation in $\text{Ar}(^3\text{P}_1)$ quenching. Conservation of spin is believed to be important in collisional electronic energy transfer from even the heavier rare gases [8]. This means that a singlet acceptor must be excited to a triplet, and so on. The result is surprising since, for Ar , $^3\text{P}_1$ is essentially a resonance level ($f \sim 0.02 - 0.06$ [1]); that is, Russell–Saunders coupling provides an inadequate description even for the isolated atom, let alone for the situation in a collision.

“Long range” dipole–dipole interaction would require the electric dipole optical selection rules to be obeyed jointly by donor and acceptor.

Individual quenchers

Nitrogen: $k_q = 0.8 \pm 0.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

The rate constant for this quenching reaction is in reasonable agreement with our earlier estimate of $0.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [3]. The value is smaller by a factor of about four than the equivalent quenching reactions of the metastable, $^3\text{P}_2$, state [9]. It would be tempting to ascribe these differences in rate constant to the closeness of energy match of $\text{Ar}(^3\text{P}_1)$ ($93,751 \text{ cm}^{-1}$) and $\text{Ar}(^3\text{P}_2)$ ($93,144 \text{ cm}^{-1}$) with the $\text{C } ^3\Pi_u$ state of N_2 which is known to be excited ($\text{C } ^3\Pi_u, v' = 2 - \text{X } ^1\Sigma_g^+, v'' = 0 \equiv 92,952 \text{ cm}^{-1}$). However, Setser *et al.* [10] make it clear, on the basis of spectroscopic evidence, that the excitation of the C state of N_2 by $\text{Ar}(^3\text{P}_2)$ is not governed by reso-

nant transfer. There is an overpopulation in odd rotational levels of N_2 ($C\ ^3\Pi_u$) which suggests a two step electron exchange mechanism. Further the kinetic data indicate that both B and C states of N_2 are formed from a common precursor $Ar-N_2^*$, so that there is an "intimate and long duration collision" [11] and the efficiency of energy transfer is not determined by the Franck-Condon principle. Stedman and Setser [11] suggest that this slow interaction might not be appropriate for the $Ar(^3P_1)$ resonance level, and that the quenching of the 3P_1 state might be consequently more rapid than that of $Ar(^3P_2)$. The present data are in conflict with this view.

Oxygen: $k_q = 2.3 \pm 0.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

This quenching proceeds at approximately the gas kinetic collision rate. In contrast, earlier results [12] on the suppression of Penning ionization (ionization of NO by $Ar(^3P_1)$) showed that O_2 was only about 1.5 times more efficient a quencher than N_2 : *i.e.*, $k_q^{O_2} \sim 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The gross discrepancy between the two values could be reconciled if the quenching of $Ar(^3P_1)$ by O_2 were to excite some state of O_2 which can itself ionize NO ($IP = 9.25 \text{ eV}$ [13]). There is spectroscopic evidence [14] for three states lying just below the $Ar(^3P_1)$ excitation energy: $^1\Pi_u$, $^1\Delta_u$ and $^3\Sigma_u^+$ ($T_{00} = 89,245, 88,278$ and $87,369 \text{ cm}^{-1}$ respectively). However, optical transitions from the singlet levels to $^1\Delta_u$ are strong, and the believed absence of sensitized fluorescence tends to preclude the formation of these states. The $\alpha^1\Sigma_u^+$ and $\beta^3\Sigma_u^+$ states, as well as several unidentified levels, also lie above the 9.25 eV ionization potential of NO [14]. Many predicted high lying levels of O_2 have not been observed experimentally, since the strong Schumann-Runge continuum dominates in absorption at wavelengths shorter than about 120 nm [14].

Nitric oxide: $k_q = 2.6 \pm 0.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

The Penning ionization data [12] give $k_q^{N_2}/k_q^{NO} = 3 \pm 1 \times 10^{-2}$, so that k_q^{NO} would be about $2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in agreement with the present fluorescence quenching result. Our earlier estimate [3] of k_q from resonance fluorescence quenching was approximately $4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

It is interesting that the very large quenching rate constant is associated with a species possessing an ionization potential below the $Ar(^3P_1)$ excitation energy, and for which Penning ionization is known to occur [12]. The absorption at wavelengths near the Ar resonance line is strong, and the direct photo-ionization cross-section approaches the absorption cross-section [15]. The absorbing states do not appear to have been identified, although it has been suggested [15] that the A and E states of NO are the first two terms of a Rydberg series. (The closest vibrational levels of the $E\ ^2\Sigma^+$ state itself is $v' = 15$, which lies at 92,554, 92,663 cm^{-1} above the $J = 3/2, 1/2$ levels of $X^2\Pi$, $v'' = 0$ [16].) If a bound electronic state of neutral NO is actually excited in the initial step, the efficiency of Penning ionization by $Ar(^3P_1)$ — about 20% of the quenching collisions — presumably reflects the relative rates of auto-ionization and energy degradation.

The data suggest a rate constant for quenching equal to, or possibly even in excess of, the gas kinetic frequency factor ($\sim 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for NO and *ground state* Ar [12]).

Carbon monoxide: $k_q = 4.6 \pm 0.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

The closest levels to which there could be near-resonant energy exchange are $v' = 1$ of $j^3\Sigma^+$ ($93,154 \text{ cm}^{-1}$); $v' = 0$ of $E^1\Pi$ ($92,929 \text{ cm}^{-1}$); $v' = 0$ of $c^3\Pi$ ($92,076 \text{ cm}^{-1}$); $v' = 0$ of $C^1\Sigma^+$ ($91,919 \text{ cm}^{-1}$) (spectroscopic data from Krupenie [17] as modified by Tilford and Simmons [4]).

Hydrogen: $k_q = 1.9 \pm 0.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Only the $B^1\Sigma_u^+$ state is energetically accessible. The origin of the 3,0 band in the B-X systems lies at $94,064 \text{ cm}^{-1}$, just above the $\text{Ar}(^3P_1)$ excitation energy [21]. Specific resonance excitation of $\text{H}_2(B, v' = 3)$ is well known [22, 23].

Correlation of quenching rate with other data

There are three obvious parameters with which the observed quenching efficiencies might correlate.

(1). The closeness of resonance of the $\text{Ar}(^3P_1 \leftarrow ^1S_0)$ excitation energy with an electronically excited level of the quencher; the possible states of the quencher were discussed in the last section for the individual cases.

(2). The closeness of energy match of the 3P_1 - 3P_2 splitting with vibrational ($v = 1 \leftarrow 0$) energy in the quencher.

(3). The ionization potential of the quencher [7].

Table 3 summarizes the data. There is no apparent connection between quenching efficiency and energy match with available electronic states. Decreasing ionization potentials, and to a lesser extent decreasing $1 \leftarrow 0$ vibrational energies of the ground states of the quenchers, generally follow at least the order of the quenching efficiencies. However, H_2 is in both cases anomalous. It is possible that the anomaly results from some direct chemical interaction between H_2 and $\text{Ar}(^3P_1)$, in the same way as between H_2 and $\text{Hg}(^3P_1)$ [7]. While the analogy with $\text{Hg}(^3P_1)$ should not be carried too far, it is nevertheless interesting that the relative rates of quenching of $\text{Ar}(^3P_1)$ and $\text{Hg}(^3P_1)$ by the various quenchers show a marked correlation (next-to-last column of Table 3). The two species (N_2 , CO) known to be effective in $^3P_1 \rightarrow ^3P_0$ spin-orbit relaxation in Hg are the least efficient overall quenchers of both $\text{Ar}(^3P_1)$ and $\text{Hg}(^3P_1)$. Finally, we may compare the quenching of $\text{Ar}(^3P_1)$ with that of $\text{Ar}(^3P_2)$. The last column of Table 3 gives quenching rate constants for $\text{Ar}(^3P_2)$ [24] relative to that for N_2 as quencher. There are no clear correlations, although the most efficient quenchers of $\text{Ar}(^3P_1)$ are also most efficient in quenching $\text{Ar}(^3P_2)$; these quenchers are the paramagnetic species NO and O_2 . For both NO and O_2 , the absolute rates of quenching are similar for $\text{Ar}(^3P_1)$ and $\text{Ar}(^3P_2)$.

TABLE 3
Kinetic and spectroscopic data for the several quenchers

Quencher	Relative efficiency (k_q , $N_2 = 1.0$)	Nearest electronic state (energy below $\text{Ar}(^3P_1)$) given in cm^{-1} measured from X, $V = 0$ of the quencher	$v'' = 1 \leftarrow 0$ energy (cm^{-1})	Ionization potential (eV) [13]	Relative k_q for $\text{Hg}(^3P_1)$ [7]	Relative k_q for $\text{Ar}(^3P_2)$ [24]
N_2	1.0	$\text{C } ^3\Pi_u, v = 2$ 798	2331	15.6	1.0	1.0
O_2	28.7	$^1\Delta_u, v = 3$ (†) 369	$^3\Sigma_u^+, v = 3$ (†) 1556	12.1	33.1	5.8
CO	5.8	$\text{E } ^1\Pi, v = 0$ 821	$\text{c } ^3\Pi, v = 1$ 2143	14.0	9.7	0.4
NO	32.5	(Doublet $\text{E } ^2\Sigma^+, v = 15$) 1087	1876	9.25	58.8	5.5
H_2	23.7	$\text{B } ^1\Sigma_u^+, v = 3$ -314	4159	15.4	14.3	1.8

† Vibrational constants unknown for these $^1\Delta_u$ and $^3\Sigma_u^+$ states of O_2 ; the spacings are taken to be the same as for ground state O_2 .

Radiation trapping

The lifetime measurements for each quencher yield an “effective radiative rate constant”, gA , at the extrapolated $[M] = 0$ limit. These are the values of gA listed in Table 1. No dependence of gA on the nature of the quencher is expected; nor, for $[Ar] > 2 \times 10^{17}$ atom/cm³ should $[Ar]$ affect gA [1]. All measurements lie within about 2.5 standard deviations of the weighted mean; the corresponding reliability coefficient is approximately 0.96 (Student’s t , $\nu = 9$). Even the extreme values in the range, for CO at $[Ar] = 3.2 \times 10^{17}$ atom/cm³ and for O₂, have a statistically insignificant probability (<90%) of differing from the mean according to the ‘T’ criterion [18]. Thus there is, indeed, no significant change of gA with change of quencher. Taking the weighted mean of $gA = 1.8 \times 10^5$ s⁻¹, and $A = 1.2 \times 10^8$ s⁻¹ [19] we conclude that $g = 1.5 \times 10^{-3}$, a value very similar to that obtained in our earlier trapping studies [1].

Table 2 lists the values of hA (unmodulated source) and gA (modulated source) derived from the slopes of the Stern–Volmer quenching experiments. Similar arguments to those used above indicate that there is no statistically significant dependence of either hA or gA on the nature of the quencher. (In fact, for gA the variability within the results for a given quencher (N₂, NO) is as great as the deviations from the mean.) Weighted means can therefore be quoted for hA and gA .

The object of the present discussion is to determine whether the radiation is imprisoned to a similar extent in both steady and pulsed systems. The mean values of gA determined by lifetimes and by Stern–Volmer methods are identical (at 1.8×10^5 s⁻¹) to two significant figures, as expected. With the unmodulated lamp, the mean effective radiative rate constant is 2.1×10^5 s⁻¹, but a Student’s t comparison of gA and hA gives $t = 1.173$ for $\nu = 16$, so that the probability that gA and hA differ is small. Individual values, for each quencher, of hA and gA (from lifetime measurements) shows an even closer correlation. The last column of Table 2 gives t for each pair of results; in every case ν is near 10. With the exception of CO, for which the lifetime measurement of gA is suspect, the values of t indicate that the differences between gA and hA are statistically insignificant.

The inference to be drawn from the similarity of g and h is that the imprisonment of radiation is governed by essentially the same factors with both pulsed or steady excitation. As we suggested in the introduction, this situation might be expected if most of the detected fluorescence comes from that part of the gas sample which is directly illuminated. Our experiments on unquenched fluorescence had already forced us to the same conclusion on the basis of a model for the magnitudes of the effective radiative lifetimes. The present results therefore provide further circumstantial confirmatory evidence for the validity of the model. Direct numerical simulation [20] of trapping also shows that the observed radiation will originate mainly in the central illuminated zone of a system such as ours.

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References

- 1 M. J. Boxall, C. J. Chapman and R. P. Wayne, *J. Photochem.*, 4 (1975/76) 281.
- 2 G. van Volkenburgh and T. Carrington, *J. Quant. Spectrosc. Radiat. Transfer*, 11 (1971) 1181.
- 3 C. J. Chapman, A. J. Masson and R. P. Wayne, *Mol. Phys.*, 23 (1972) 979.
- 4 S. G. Tilford and J. D. Simmons, *J. Phys. Chem. Ref. Data*, 1 (1972) 147.
- 5 T. G. Slanger and G. Black, *J. Chem. Phys.*, 51 (1969) 4534.
- 6 R. D. Hudson, *Critical Review of Ultraviolet Photoabsorption Cross Sections for Molecules of Astrophysical and Aeronomic Interest*, NSRDS-NBS 38 (1971).
- 7 A. B. Callear in P. G. Ashmore, F. S. Dainton and T. M. Sugden (ed.), *Photochemistry and Reaction Kinetics*, Cambridge University Press, Cambridge, 1967.
- 8 D. H. Stedman and D. W. Setser, *J. Chem. Phys.*, 52 (1970) 3957.
- 9 J. M. Calo and R. C. Axtmann, *J. Chem. Phys.*, 54 (1971) 4961.
- 10 D. W. Setser, D. H. Stedman and J. A. Coxon, *J. Chem. Phys.*, 53 (1970) 1004.
- 11 D. H. Stedman and D. W. Setser, *Progr. React. Kinet.*, 6 (1971) 193.
- 12 I. D. Clark, A. J. Masson and R. P. Wayne, *Mol. Phys.*, 23 (1972) 995.
- 13 J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl and F. H. Field, *Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions*, NSRDS-NBS 26 (1969).
- 14 P. H. Krupenie, *J. Phys. Chem. Ref. Data*, 1 (1972) 423.
- 15 K. Watanabe, *J. Chem. Phys.*, 22 (1954) 1564.
- 16 G. Herzberg, *Spectra of Diatomic Molecules*, van Nostrand, New York, 1950.
- 17 P. H. Krupenie, *The Band Spectrum of Carbon Monoxide*, NSRDS-NBS 5 (1966).
- 18 K. Eckschlager, *Errors, Measurement and Results in Chemical Analysis*, van Nostrand-Reinhold, London, 1969.
- 19 G. M. Lawrence, *Phys. Rev.*, 175 (1968) 40.
- 20 L. F. Phillips, *J. Photochem.*, 4 (1975) 407.
- 21 B. Rosen (ed.), *Spectroscopic data relative to diatomic molecules*, Pergamon Press, Oxford, 1970.
- 22 S. Takezawa, F. R. Innes and Y. Tanaka, *J. Chem. Phys.*, 45 (1966) 2000.
- 23 E. H. Fink, D. L. Akins and C. Bradley Moore, *J. Chem. Phys.*, 56 (1972) 900.
- 24 L. G. Piper, W. C. Richardson, G. W. Taylor and D. W. Setser, *Faraday Discuss. Chem. Soc.*, 53 (1972) 100.

Appendix

Average fluorescence intensity in a system with modulated excitation

It is not immediately obvious that the simple Stern-Volmer quenching relationship will apply to the average fluorescence intensity in a system where the incident radiation is fluctuating. This Appendix tests the validity of the relationship for the specific intensity-time profile of our source.

The "modulated" source emits a pulse of radiation superposed on a steady background. The pulse has a very sharp rise time and a near-exponential decay [1]. We may therefore represent the intensity at time t , I_t , by:

$$I_t = I_b + I_p \exp(-\alpha t) \quad (\text{A1})$$

where I_b , I_p are the intensities of the background and peak of the pulse respectively, and α is a decay constant characteristic of the lamp.

Let n be the concentration of electronically excited species at any time t , ϕ be the fraction of incident light leading to excitation (in the case of atomic fluorescence, essentially the fraction of light absorbed), and γ be the decay constant ($= k_{\text{obs}} = \beta + k_q[M]$). Then:

$$\frac{dn}{dt} = \phi I_t - \gamma n \quad (\text{A2})$$

After substitution of eqn. (A1) for I_t , the eqn. (A2) may be solved to yield:

$$n = n_0 \exp(-\gamma t) + \frac{\phi I_b}{\gamma} [1 - \exp(-\gamma t)] + \frac{\phi I_p}{\gamma - \alpha} [\exp(-\alpha t) - \exp(-\gamma t)] \quad (\text{A3})$$

where n_0 is the concentration of excited species at the initiation of the pulse ($t = 0$). In the repetitive situation, n_0 reaches a steady state such that $n_0 = n_{t_1}$, where t_1 is the period between pulses. Substitution of this equality in eqn. (A3) gives the result:

$$n_0 = \frac{\phi I_b}{\gamma} + \frac{\phi I_p}{\gamma - \alpha} \left[\frac{\exp(-\alpha t_1) - \exp(-\gamma t_1)}{1 - \exp(-\gamma t_1)} \right] \quad (\text{A4})$$

so that:

$$n = \frac{\phi I_b}{\gamma} + \frac{\phi I_p}{\gamma - \alpha} \left[\exp(-\alpha t) - \frac{1 - \exp(-\alpha t_1)}{1 - \exp(-\gamma t_1)} \exp(-\gamma t) \right] \quad (\text{A5})$$

The average intensity of fluorescence, \bar{I}_f , is given by:

$$\bar{I}_f = \frac{1}{t_1} \int_0^{t_1} fA n dt \quad (\text{A6})$$

Integration of eqn. (A5) with respect to t gives:

$$\bar{I}_f = \frac{\phi f A}{\gamma} \left[I_b + \frac{I_p}{\alpha t_1} \{1 - \exp(-\alpha t_1)\} \right] \quad (\text{A7})$$

The terms within the square brackets are dependent only on the lamp characteristics and not on the fluorescer. Thus if all the constants are lumped together as C :

$$\bar{I}_f = C\beta/\gamma = C\beta/(\beta + k_q[M]) \quad (\text{A8})$$

and the Stern-Volmer relationship is seen to hold.