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On departures from the Stern–Volmer law for fluorescence quenching in liquids^{a)}

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With solutions of fluorophores and quenchers in inert solvents, one commonly finds that the fluorescence emitted can be expressed by $I_0/I_Q = 1 + K_{SV}[Q]$, where $[Q]$ is the quencher concentration, K_{SV} is the Stern–Volmer coefficient, and I_0 and I_Q are the fluorescence intensities in the presence and absence, respectively, of the quencher.¹ If k is the rate constant for bimolecular collisions between fluorophores and quenchers, and τ is the lifetime of the emitting state of the fluorophore, then $K_{SV} = k\tau$.

In some solutions, however, K_{SV} is not constant, but increases by as much as 50%–80% as $[Q]$ runs from 0 to ~ 0.1 M.^{2–7} A number of theoretical models involving various combinations of static quenching with dynamic quenching (with and without diffusion control) have been invoked to explain these observations.^{7–14} No matter whether the static quenching arises from a chemical⁹ or physical⁸ interaction, it has been found that

$$I_0/I_Q = 1 + a_1[Q] + a_2[Q]^2, \quad (1)$$

where a_1 and a_2 are coefficients specific to the interaction. For the chemical interaction, Eq. (1) is the complete result⁹; for the physical interaction, it represents the first three terms of a convergent series.⁸

In this note, we introduce and evaluate an alternative to Eq. (1) which is based upon the theory of diffusion-controlled reactions developed by Felderhof and Deutch

(FD).^{15,16} They considered a random array of stationary sinks embedded in a medium through which a swarm of mobile particles diffused. Whenever a mobile particle came within an effective radius γ of a sink, it was quenched. The rate of quenching depended upon the mobile particle concentration gradient at a given sink. As the sink concentration increased, mobile particle concentration gradients evaluated at neighboring sinks tended to overlap. The result of the overlap could be expressed in the form of a bimolecular rate constant $k = 4\pi Da(\rho)$, where D was the mobile particle diffusion coefficient, and $a(\rho)$ was a length which was an increasing function of the sink concentration ρ . Incorporating this result into the Stern–Volmer mechanism, we obtain

$$I_0/I_Q = 1 + 4\pi D\gamma\tau N[Q] + 4\pi D\gamma\tau(4\pi\gamma^3)^{1/2} N^{3/2}[Q]^{3/2}, \quad (2)$$

which is asymptotic as $[Q] \rightarrow 0$. The next higher term is $4\pi D\gamma\tau(2\pi\gamma^3)N^2[Q]^2 \ln(4\pi\gamma^3 N[Q])$, where $N = 6.023 \times 10^{20} \text{ M}^{-1} \text{ cm}^{-3}$.

Using linear regression, we fitted existing data to Eq. (2) with the coefficients of $[Q]$ and $[Q]^{3/2}$ taken as free parameters. Expecting Eq. (2) to apply with increasing accuracy as $[Q]$ went to zero, we made n iterations of the regression with the data points represented by the $n-1$ highest values of $[Q]$ removed. This process was terminated when the Gauss gauge¹⁷ was minimized.

TABLE I. Quenched fluorescence of fused ring compounds.

Fluorophore	Quencher	Solvent	T (°C)	n	τ (ns)	γ (Å)	D (cm ² /s) $\times 10^6$	Reference
1,2-Benzanthracene	CBr ₄	1,2-Propanediol	15	3(9)	39.2	22 ± 3	0.098 ± 0.026	7
1,2-Benzanthracene	CBr ₄	1,2-Propanediol	25	4(10)	38.5	19 ± 3	0.20 ± 0.05	7
1,2-Benzanthracene	CBr ₄	1,2-Propanediol	35	2(6)	37.7	12.2 ± 0.4	0.70 ± 0.04	7
1,2-Benzanthracene	CBr ₄	Mineral oil	25	2(10)	42.8	32 ± 6	0.045 ± 0.014	7
1,2-Benzanthracene	CBr ₄	Mineral oil	35	2(10)	42.4	30 ± 6	0.084 ± 0.030	7
1,2-Benzanthracene	CBr ₄	Mineral oil	45	2(10)	41.9	27 ± 6	0.16 ± 0.06	7
Perylene	Oxygen	Dodecane	25	1(11)	5.4	6.6 ± 0.2	36 ± 1	6

TABLE II. Quenching of chlorophyll *a* fluorescence.²

Quencher	Solvent	<i>T</i> (°C)	<i>n</i>	τ (ns) ¹⁸	γ (Å)	<i>D</i> (cm ² /s) × 10 ⁶
<i>p</i> -Aminophenol	MeOH	28	0(5)	14.3	4.1 ± 0.8	1.2 ± 0.3
Chloranil	Me ₂ CO	25	0(10)		16 ± 2	
<i>m</i> -Dinitrobenzene	MeOH	24	1(7)	14.3	15 ± 1	3.1 ± 0.4
Duroquinone	MeOH	22	0(11)	14.3	6.8 ± 1.4	11 ± 2
Nitric oxide	EtOH	23	0(5)	6.22 ^a	22 ± 5	2.9 ± 0.9
Nitrobenzene	MeOH	22	2(10)	14.3	5.5 ± 1.4	4.5 ± 1.3
Nitrobenzene	EtOH	20	2(8)	6.22	6.3 ± 0.9	8.1 ± 1.3
2-Nitro-2-hexene	MeOH	27	0(7)	14.3	12 ± 2	0.54 ± 0.12
β -Nitro- β -methylstyrene	MeOH	29	0(5)	14.3	8.4 ± 1.5	3.9 ± 0.8
2-Nitroso-1-naphthol	MeOH	24	0(9)	14.3	12 ± 2	3.6 ± 0.6
β -Nitrostyrene	MeOH	27	2(7)	14.3	5.0 ± 2.1	10 ± 4
Oxygen	EtOH	27	0(4)	6.22 ^a	18 ± 1	2.9 ± 0.2
Phenylhydrazine	MeOH	22	0(6)	14.3	7.2 ± 3.8	0.23 ± 0.17
Quinone	MeOH	24	0(11)	14.3	7.1 ± 1.2	13 ± 2
Trinitrotoulene	MeOH	24	3(15)	14.3	10.9 ± 1.0	6.6 ± 0.7

^aReference 3.TABLE III. Quenching of porphyrin fluorescence in benzene.⁴

Fluorophore	Quencher	<i>n</i>	τ (ns) ¹⁹	γ (Å)	<i>D</i> (cm ² /s) × 10 ⁶
Meso	Chloranil	0(5)	19	16 ± 4	9.2 ± 3.0
Meso	<i>m</i> -Dinitrobenzene	0(8)	19	12 ± 3	3.8 ± 1.2
Meso	Trinitrotoulene	1(7)	19	18 ± 3	4.2 ± 0.8
Proto	Trinitrotoulene	1(7)	18	21.6 ± 0.7	2.5 ± 0.1

Using known values of τ , we determined γ and *D* from the regression coefficients. The results are summarized in the tables. In the columns labeled *n*, we give the number of iterations required to minimize the Gauss gauge, and, in parentheses, the total number of data points initially in the set.

In Table I, the 1,2-benzanthracene results show a monotonic increase in *D* with increasing temperature, as to be expected. We suggest that the corresponding decrease in γ is due to its implicit dependence upon *D* through the equation $\gamma = R(1 + 4\pi DR/\kappa)^{-1}$, where *R* is the geometric radius of a sink, and κ is the specific collision rate in the absence of diffusion.²⁰⁻²² Apparently, the ratio *D*/ κ increases with increasing temperature.

In the experiments on chlorophyll² and porphyrin⁴ fluorescence, (Tables II and III), it was customary to define $[Q]_{1/2}$ as the concentration where $I_Q/I_0 = 1/2$. We found generally that $[Q]_{1/2}$ decreased with increasing γ .

Employing a linear regression with Eq. (1), we noted that in most cases Eq. (1) fitted the data with a lower Gauss gauge than Eq. (2). The situation was not significantly changed when the term in $[Q]^2 \ln[Q]$ was included in Eq. (2). This may be due to the fact that strict application of the FD model requires the fixed sinks to be identified with the quenchers and the mobile particles with the fluorophores. On the basis of molecular radii and the Stokes-Einstein relation, this is hardly satisfied by the available data. Although we obtained reasonable values of γ and *D*, we conclude that to perform a completely conclusive comparison of Eqs. (1) and (2), measurements should be performed on systems

where the quencher molecules are larger than the fluorophores.

Even with this proviso, we have shown that the FD model is capable of explaining qualitatively the curvature in the Stern-Volmer plot. We regard this to be preferable to the vague active sphere concept used alone⁸ or in combination¹⁴ with models involving diffusion. Furthermore, the FD model provides an alternative to the assumption of a fluorophore-quencher complex^{5,9} in those cases where the chemical evidence for its existence is weak.⁷

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Scattering of Na $3^2P_{3/2}$ from Ar

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Many experimental¹⁻⁶ and theoretical⁷ investigations of the scattering process of Na $3^2P_{3/2}$ with Ar have been performed in recent years. From the experiments, a quite consistent set of data may be constructed. The results may be summarized with the equilibrium point of the $A^2\Pi_{1/2}$ potential, the well depth ϵ , and the equilibrium distance R_m . With respect to these two quantities the various experiments quoted above differ by their sensitivity. The line shape measurements¹ and the measurement of a rainbow angle in differential cross sections⁶ will have a small error for the well depth and the spectroscopy of the van der Waals²⁻⁴ molecule for the equilibrium distance. From all these experiments combined, the equilibrium point is established by $\epsilon = 2.55$ (10^{-3} a.u.) and $R_m = 5.50$ (a.u.) with an upper error limit of approximately 1%.

In this note we want to report another determination of R_m from a differential scattering experiment. It will be seen that in our experiment the accuracy of the spectroscopic determination²⁻⁴ is not achieved. But our result may serve as an independent confirmation of the value obtained there.

We have measured the total differential cross section with a laser excited Na beam of thermal energy scattered from a secondary beam of Ar. The experimental apparatus and techniques are similar to those used in previous experiments from our laboratory.⁸ By a refinement of our previous experiment with Na-Ar² in the present work, the "rapid oscillations" in the differential cross section⁹ have been resolved. This quantity is especially sensitive to the equilibrium distance.

Figure 1 shows one of our experimental results together with a calculated one. It is a measurement where the range of the main rainbow maximum is investigated with high resolution. In the calculation, the close coupling system of the fine structure states has been numerically integrated and a potential has been used which had been determined previously in our laboratory.² Comparing these results, the discrepancies, both with respect to the spacing and the position of the rapid os-

cillations, are visible. The discrepancy in the spacing $\Delta\vartheta$ is a consequence of the error in the equilibrium distance of the potential used in the calculation.² Our aim is to remove this error by evaluating the energy dependence of $\Delta\vartheta$ —similar measurements have been performed with other collision energies—to yield the correct value from the experimental data.

In the elastic scattering for spherically symmetric potentials the rapid oscillations follow the relation¹⁰

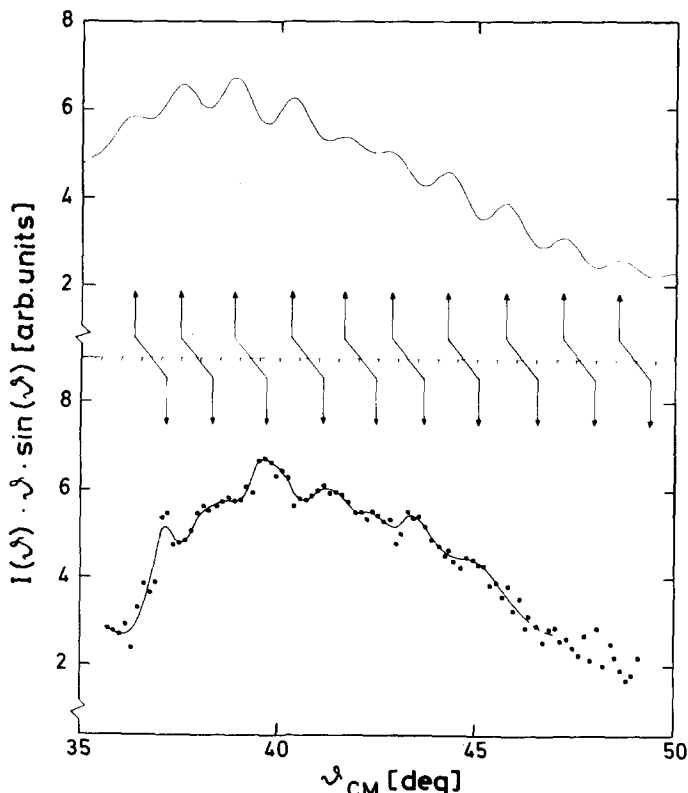


FIG. 1. Calculated (upper panel) and experimental (lower panel) differential cross section for Na ($3^2P_{3/2}$)-Ar. Presented as $I(\vartheta)\vartheta \sin \vartheta$ as a function of the center of mass angle ϑ . The collision energy is 24.16×10^{-14} erg.