Quenching of Fluorescence in Small Molecules

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The optical fluorescence of small molecules in a low-density gas was first observed by Lommel[2] in 1883. Soon after that (in terms of the leisurely time scale of those early days), Wood[3] noticed that the fluorescence was diminished by admixture of gases, and the study of fluorescence quenching was under way. In the ensuing years, a great deal of phenomenological information on quenching was collected, much of which can be found in Pringsheim's text.[4]

Typically the fluorescing species was irradiated in a "T" cell and the fluorescent emission was observed at right angles to the exciting light. A foreign gas was then admitted to the cell and the diminution of fluorescence was observed as a function of the pressure of the added gas. In photochemists' jargon, the reduction in intensity of the emitted light is called "quenching."

The standard kinetic treatment of quenching and related processes is by means of a graphical method devised by Stern and Volmer[5] over 50 years ago and now named in their honor. If one assumes a simple mechanism

$$A + h\nu \xrightarrow{I} A^* \qquad \text{absorption}$$

$$A^* + X \xrightarrow{Q} A + X \qquad \text{quenching}$$

$$A^* \xrightarrow{k_f} A + h\nu' \qquad \text{fluorescence, } k_f = 1/\tau_{rad}$$

then, by means of a steady-state treatment, one may readily derive

$$\frac{I_0}{I} - 1 = Q\tau_{rad}X$$

In the above expression, I_0 is the intensity of fluorescence in the absence of a quencher, and I is the intensity of the fluorescence with a pressure (X) of the quenching species. Thus, if one knows the radiative lifetime of species A*, one may deduce the quenching constant Q and, hence, in a collision theory model, the quenching cross section σ_Q^2.

Many studies have been undertaken to correlate the structure and the cross section of various quenching species. Other studies have dealt with the fate of the excited quenching species. As a result of obtaining the additional energy, the excited quenching species could undergo chemical reaction (a "sensitized" reaction), or themselves fluoresce or, more commonly, simply degrade the excess energy into heat.

It is only recently, however, that measurements have become accurate enough to provide data which demonstrate meaningful variations among different molecular systems and which can be interpreted to yield information about repulsive potential curves inaccessible to ordinary spectroscopy. In this Account, we shall first present the kinetics of the process, discuss some of the techniques for measuring quenching efficiencies (with their associated problems), and give a summary of data for some selected, well-studied systems. We shall then discuss a recently published model for electronic quenching by gas collisions, and the phenomena of quenching by external electromagnetic fields and by intramolecular coupling effects. Finally, a complete set of potential curves for the very well-studied diatomic iodine system is presented, combining results of both spectroscopic and quenching studies.

Stochastic Model for Quenching

The classic approach to the kinetics of fluorescence quenching is *via* the photostationary equations introduced by Stern and Volmer.[5] It may be instructive, however, to reach this point *via* the currently more fashionable stochastic formulation of rate equations.[6] To proceed with this formulation, we first note that the population of excited molecules at a time t after excitation is given by

$$N(t) = N_0 e^{-k_{rad}t}$$

where N_0 is the population at $t = 0$ and $k_{rad} = (\tau_{rad})^{-1}$. Thus, the rate of photon emission by excited molecules that have lasted a time τ following excitation is given by

$$N'(\tau) = \left(\frac{dN(t)}{dt}\right)_{t=\tau} = N_0 k_{rad} e^{-k_{rad}\tau}$$

We now ask for the probability that, in this time τ, a quenching collision will *not* have taken place; this is just

$$\{1 - P_{quench}(t \leq \tau)\} = e^{-Z_Q\tau}$$

where

$$Z_Q = \sqrt{2}N_{gas}\sigma_Q^2\bar{v} \qquad (1)$$

defining an effective quenching cross section σ_Q^2, with N_{gas} as the density (molecules cm^{-3}) and $\bar{v}$ as the mean thermal velocity of the collision pair. We can also write

$$Z_Q = QX$$

with X the gas concentration or pressure (moles liter^{-1}, Torr, etc.), thus defining the quenching constant Q.

The total fluorescence intensity I is proportional to the net emission rate, which is the resultant of molecules emitting over a complete distribution of lifetimes, reduced by the probability that quenching has occurred. Thus

$$I \propto k_{emission} = \int_0^\infty N_0 k_{rad} e^{-k_{rad}\tau} e^{-Z_Q\tau} d\tau$$

(1) Alfred P. Sloan Foundation Fellow.
(2) E. Lommel, *Ann. Phys. Chem.*, **19**, 356 (1883).
(3) R. W. Wood, *Phil. Mag.*, **21**, 309 (1911).
(4) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience, New York, N. Y., 1965.
(5) O. Stern and M. Volmer, *Phys. Z.*, **20**, 183 (1919).
(6) I. Oppenheim, K. E. Shuler, and G. H. Weiss, *J. Chem. Phys.*, **50**, 460 (1969).

$$= N_0 k_{\text{rad}} \int_0^\infty e^{-(k_{\text{rad}}+Z_Q)\tau} d\tau$$

$$= \frac{N_0 k_{\text{rad}}}{k_{\text{rad}} + Z_Q}$$

In the absence of quenching, when $Z_Q = 0$, all the excited molecules emit; thus

$$I_0 = I\ (X = 0) \propto N_0$$

so that

$$\frac{I_0}{I} = \frac{k_{\text{rad}} + Z_Q}{k_{\text{rad}}} = 1 + Z_Q \tau_{\text{rad}} = 1 + Q'X$$

where $Q' = Q\tau_{\text{rad}}$; or

$$\frac{I_0}{I} - 1 = Q'X \qquad (2)$$

which is just the Stern–Volmer quenching law previously obtained.

Methods of Measuring Quenching Constants

The form of eq 2 suggests a direct, obvious way of measuring Q'. This is: measure a fluorescence intensity under a given set of conditions, and then admit a foreign gas at various pressures; the resulting intensities are then plotted according to eq 2, yielding Q' directly. Although this seems straightforward, this method is fraught with many difficulties, arising mainly from failure of Beer's law for absorption.[7] Essentially, the foreign gas pressure can affect the widths of the narrow absorption lines in the spectrum of the fluorescing gas. This can change not only the effective absorption coefficient, and thus the amount of energy being absorbed by the sample (*i.e.*, N_0 is not a constant as X is varied), but also the intensity of light that reaches the volume of fluorescing sample in the interior of the cell. These effects can reinforce or cancel each other and thus provide a very erratic dependence of I upon X.

There is an alternative method of measurement which avoids the above-mentioned difficulties but introduces new ones; this is based on lifetime measurements. The relation employed is that of the additivity of parallel first-order processes, so that eq 3 obtains. The lifetimes themselves can in principle be measured by

$$\tau_{\text{measured}}^{-1} = \tau_{\text{rad}}^{-1} + QX \qquad (3)$$

applying either pulsed exciting radiation, and observing the decay of the luminescence, or modulated exciting radiation, and observing the phase shift $\delta\phi$ of the fluorescence.[8,9] This phase shift can be related to the lifetime by use of the expression $\tan \delta\phi = 2\pi f\tau$, where f is the modulation frequency of the light. The difficulty with the former method is the low signal resulting from the small number of photons available in a sufficiently narrow, monochromatic pulse from most light sources, although dye solution lasers now offer some hope of overcoming this limitation. Typically, photon counting techniques must be applied to the fluorescence signal. The phase shift technique suffers from interference by scattered light having zero phase shift, which yields an artificially short measured lifetime.

Quenching by Collision-Induced Predissociation

Quenching by Cross Sections. Although a large number of molecules have been observed to luminesce and to be quenched by foreign gas collisions, only a relatively small number have been sufficiently well characterized to provide quantitative data on the efficiencies of quenching collisions. In addition to having good values for Q', corrected for all the absorption nonlinearities mentioned above, we need to know the radiative lifetime, τ_{rad}, in order to be able to convert to absolute collision efficiencies. These data are available for those systems summarized in Table I.

In Table I, quenching efficiencies are given as effective cross sections in units of ångströms squared (10^{-16} cm^2). These are derived from the measured Q' using eq 1, *i.e.*

$$\sigma_Q^2 = 1000Q'/(\sqrt{2}\mathfrak{N}_0 \tau_{\text{rad}} \bar{v})$$

where Q' is expressed in liters mole^{-1} and $\mathfrak{N}_0$ is Avogadro's number.

One point which may be noted from Table I is the variety of methods which have been used to excite the fluorescing species. These include optical excitation by a resonance lamp or a laser, excitation by white light, radiofrequency or microwave discharge, photodissociation yielding an excited fragment, or photosensitization with metastable excited atoms. Only the first method can produce a pure vibration–rotation state of the excited molecule; the others produce a wide distribution of states over which the measured quenching constant is averaged.

The most extensively studied systems thus far are NO and I_2. For the former system, cross sections for the $A^2\Sigma^+$ state obtained independently in Soviet, American, and British laboratories (Table I, columns a–c) seem to agree within a factor of ten or better; this is considered a reasonably good level of agreement for many of these measurements. A similar consistency is found for the Japanese, American, and Dutch work on the $A^2\Sigma^+$ state of OH (Table I, columns l–n). It is clear from columns d and e, though, that the magnitudes of the quenching constants appropriate to one excited state of a particular molecule need bear no relation to those for some other excited state.

The $B^3\Pi_{0u^+}$ state of iodine has had the longest history of investigation,[2,3] but quantitative quenching cross sections for a succession of vibrational levels in this state were first obtained in Klemperer's laboratory at Harvard, and this work has been continued in our laboratory at M.I.T. (Table I, columns f–i). The variation in cross section between the different vibration levels appears to be due primarily to a Franck–Condon effect (see following section).

(7) R. H. Kummler and M. McCarty, *J. Phys. Chem.*, **71**, 2456 (1967).
(8) L. Brewer, R. A. Berg, and G. M. Rosenblatt, *J. Chem. Phys.*, **38**, 1381 (1963).
(9) A. Chutjian, J. K. Link, and L. Brewer, *ibid.*, **46**, 2666 (1967).

Table I

Molecule	NO			NO	NO	I_2				N_2	N_2	HD	OH			CO	NO_2		SO_2	CH_3OH
State	$A^2\Sigma^+$			$B^2\Pi$	$D^2\Sigma^+$	$B^3\Pi_{0u}^+$				$A^3\Sigma_u^+$	$B^3\Pi_g$	$B^1\Sigma_u^+$	$A^2\Sigma^+$			$d^3\Delta$, $e^3\Sigma$, $a^3\Sigma$	$^2\Sigma_g(^2B_1)$		$^1\tilde{A}(^1B_1)$	$^1E(n,3s)$
v'	1	1	0–3	0	0	15	25	43	51	0–12	0–8	3	0	Thermal	0	4, 6, 7, 9				
Rotation	$K' =$ 13	$K' =$ 13	Thermal	Thermal	Thermal	$J' =$ 37, 44	$J' =$ 34	$J' =$ 11, 15	$J' =$ 29	Thermal	Thermal	$J' = 2$	$K' = 0$–21	Thermal	$K' =$ 10, 11	Thermal				
Method of excitation	Cd 2144 Å	Cd 2144 Å	Xe arc	rf discharge	Xe arc	Na 5895 Å	Hg 5461 Å	Ar laser 5145 Å	Cd 5086 Å	Photodissocn of N_2O at 1470 Å	Photodissocn of N_2O at 1236 Å	Ar 1066 Å	Photodissocn of H_2O at 1236 Å	OH lamp (unfiltered)	Bi 3067.7 Å	Xe^+ (8.43 eV) sensitized	Hg 4358 Å	Ar–Kr laser 4579–5028 Å	Hg–Xe arc	Hg 1849 Å
Quenching gas																				
^3He							0.94					6.4								
^4He	0.03	0.002			14	0.19	1.8	1.3	24	<0.002	1.1	7.2	0.63			0.024	1.6		0.66	
Ne						0.59	5.8	5.2	25			2.5							1.3	
Ar	0.04	0.005	0.0032		24	2.5	10	5.1	47	<0.0004	0.41		7.8	<2		0.31	3.8		2.6	2.2
Kr						5.7	17	7.4	58										3.7	7.8
Xe						14	35	10.6	74											19.5
H_2	0.03	0.003		1.1		0.60	1.4			<0.004	24		2.4			1.05	2.5		1.2	
HD												57								
D_2						0.78							2.4						1.3	
N_2	0.04	0.03			41	2.9				<0.0005	6.4		3.9		7	2.6	5.0		3.7	2.4
O_2						3.4	17			0.95	28		6.3	7	10		1.6		3.4	
NO	4	18	5.1		530	9.0				17	58					24	9.7		7.6	
NO_2																	13.5	0.9		
N_2O				9.5						1.7	42									
CO										0.059	20		25			5.7			4.2	
CO_2	9	21	18	2	180		45			<0.0007	39		15	35			3.8		11	18
H_2O				~67									45	16	37		23.8			
D_2O																			22	
SO_2							27												15	
I_2						78	97	65	120											
SF_6																	25.7		14	
NH_3										37										
CH_4							17			<0.0007							7.9		4.9	3.3
CH_3Cl							31													
CF_4																	4.5		8.5	
C_2H_2										37										
C_2H_4										35										
C_2N_2										15										
CH_3OH																				20.5
C_2H_6																				8.0
C_3H_8																				16
C_4H_{10}																				19
References	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*j*	*k*	*l*	*m*	*n*	*o*	*p*	*q*	*r*	*s*

[a] A. V. Kleinberg, *Opt. Spektrosk.*, **1**, 469 (1956). [b] H. P. Broida and T. Carrington, *J. Chem. Phys.*, **38**, 136 (1963). [c] A. B. Callear and I. W. M. Smith, *Trans. Faraday Soc.*, **59**, 1720 (1963). [d] I. M. Campbell and B. A. Thrush, *J. Quant. Spectrosc. Radiat. Transfer*, **8**, 1571 (1968). [e] A. B. Callear, M. J. Pilling, and I. W. M. Smith, *Trans. Faraday Soc.*, **64**, 2296 (1968). [f] R. L. Brown and W. Klemperer, *J. Chem. Phys.*, **41**, 3072 (1964). [g] J. I. Steinfeld and W. Klemperer, *ibid.*, **42**, 3475 (1965). [h] R. B. Kurzel and J. I. Steinfeld, *ibid.*, in press. [i] A. N. Schweid and J. I. Steinfeld, *ibid.*, in press. [j] R. A. Young, G. Black, and T. G. Slanger, *ibid.*, **50**, 303 (1969). [k] E. Fink and C. B. Moore, private communications. Preliminary data, estimated accuracy ±20%. [l] M. Kaneko, Y. Mori, and I. Tanaka, *J. Chem. Phys.*, **48**, 4468 (1968). [m] T. Carrington, *ibid.*, **30**, 1087 (1959). [n] H. P. Hooymayers and C. Th. J. Alkemade, *J. Quant. Spectrosc. Radiat. Transfer*, **7**, 495 (1967). [o] T. G. Slanger, *J. Chem. Phys.*, **48**, 586 (1968). [p] G. H. Myers, D. M. Silver, and F. Kaufman, *ibid.*, **44**, 718 (1966). [q] K. Sakurai and H. P. Broida, *ibid.*, **50**, 2404 (1969). [r] H. D. Mettee, *J. Phys. Chem.*, **73**, 1071 (1969). [s] J. Hagege, P. C. Roberge, and C. Vermeil, *Trans. Faraday Soc.*, **64**, 3288 (1968); the cross sections are normalized to an assumed unit quenching efficiency for CH_3OH^*–CH_3OH collisions.

A comment may be made on the two measurements of the self-quenching cross section for NO_2. The smaller value of 0.9 Å^2 appears to be the more nearly correct one; the larger value found by Myers, *et al.* (Table I, column p), may be a result of vibrational relaxation in the NO_2*, increasing the mean wavelength of the fluorescence to a point at which the photomultiplier used in the experiment was unable to respond.

Quenching Model. The earliest attempt at a theoretical correlation of the quenching efficiencies for different gases was that of Rössler,[10] who asserted that the efficiency would be directly proportional to the polarizability α of the gas molecule and to the duration of the collision, *i.e.*, to $\alpha\mu^{1/2}$, where μ is the reduced mass of the collision; this sort of correlation was displayed by the rare gases in quenching excited I_2. No firmer theoretical interpretation was forthcoming until quite recently, when Selwyn[11] derived an expression for the quenching cross section based on a van der Waals interaction between the excited molecule and the quencher.

Essentially, quenching is conceived as taking place as a result of a transition, induced by the collision, from the excited state of the molecule to a repulsive state degenerate with it but of different symmetry. One reason for postulating such a mechanism, in the particular case of iodine, is that free ground-state atoms have been observed following irradiation of the molecule with light having an energy below the excited-state dissociation limit.[12] The effect of the collision is to destroy the symmetry element which prevents the bound and repulsive states from being coupled. This is accomplished by an asymmetric interaction between the excited molecule and the quencher; for uncharged, nonpolar species, the potential of interaction is taken to be the same as that giving rise to the London or van der Waals dispersion energy, namely

$$V_{12} = \frac{e^2}{R_1^3}(X_1X_2 + Y_1Y_2 - 2Z_1Z_2)$$

where R_1 is the distance between the two molecules and (X,Y,Z) represent sums over the coordinates of the electrons in each system. Using this potential in the "Fermi golden rule" result of first-order time-dependent perturbation theory and averaging over phase space give the effective quenching cross section

$$\sigma_Q^2 = \left(\frac{\pi\mu}{8kT}\right)^{1/2}\left(\frac{12\pi^3}{15h}\right)\rho(f)\,\frac{e^2I\alpha}{R_c^3}\,|\langle\chi_E|\chi_{v'}\rangle|^2 \times$$
$$(|\langle\psi_b|X|\psi_f\rangle|^2 + |\langle\psi_b|Y|\psi_f\rangle|^2 + 4|\langle\psi_b|Z|\psi_f\rangle|^2) \quad (4)$$

The previously undefined notation in eq 4 is: $\rho(f)$ = density of states for the dissociated atoms; I = ionization potential of the quenching molecule; R_c = mean distance of closest approach of the collision pair, taken to be the hard-sphere distance $(\sigma_Q + \sigma_{M^*})/2$; $\langle\chi_E|\chi_{v'}\rangle$ = Franck–Condon overlap integral between the wave function for vibrational state v' of the excited molecule and the free-particle wave function for dissociated atoms with kinetic energy E; $|\psi_b\rangle$ = electronic wave function of excited molecule; and $|\psi_f\rangle$ = electronic wave function appropriate to the repulsive state reached in the collision-induced predissociation.

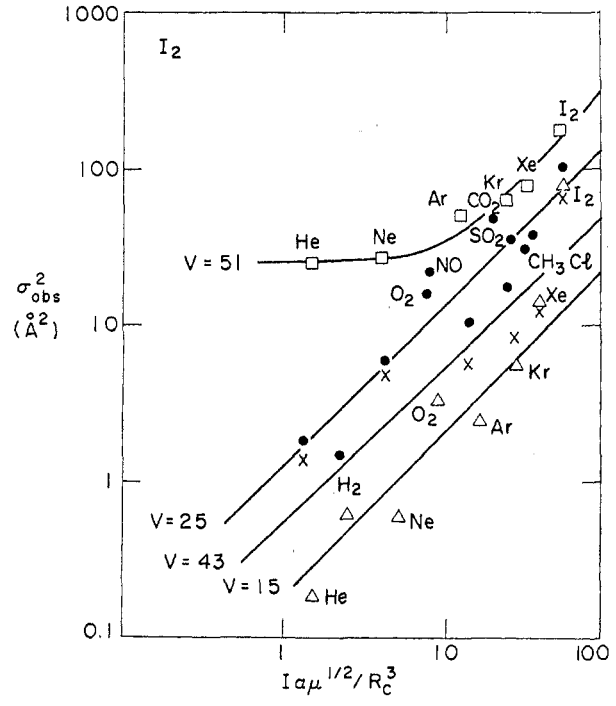

Figure 1. Quenching correlation for I_2 ($B^3\pi_{ou}^+$). Data: △, v' = 15 (Table I, footnote *f*); ○, v' = 25 (Table I, footnote *g*); ×, v' = 43 (Table I, footnote *h*); □, v' = 51 (Table I, footnote *i*).

The important consequences of eq 4 may be summarized as follows: (i) quenching efficiencies for different gases should obey the parametric dependence

$$\sigma_Q^2 \propto \mu^{1/2}I\alpha/R_c^3$$

(ii) a repulsive state coupled to the bound state by an electric-dipole transition is required, which sets requirements on the symmetry of the repulsive state; (iii) for a given electronic state of a molecule, quenching cross sections for different vibration levels should differ by a constant factor representing the relative Franck–Condon overlap; (iv) the quenching rate constant, k_Q, should be nearly independent of temperature, since $k_Q = \sigma_Q^2\bar{v}$ and $\bar{v} \propto T^{1/2}$ while $\sigma_Q^2 \propto T^{-1/2}$.

The test of the predicted parametric dependence is shown in Figures 1–8. The correlation works quite well for I_2, the system for which it was originally designed (Figure 1); the data for v' = 15, 25, and 43 cluster around parallel 45°-slope lines on the log–log plot. The data for v' = 51 show a deviation from these lines; this is taken to indicate the presence of a new mechanism, in this case a "collisional release" process, *viz.*

$$I_2^* + M \longrightarrow I(^2P_{3/2}) + I^*(^2P_{1/2}) + M$$

which probably acts in addition to the canonical mechanism

(10) F. Rössler, *Z. Phys.*, **96**, 251 (1935).
(11) J. E. Selwyn and J. I. Steinfeld, *Chem. Phys. Lett.*, **4**, 217 (1969).
(12) L. A. Turner and E. W. Samson, *Phys. Rev.*, **37**, 1684 (1931).

$$I_2^* + M \longrightarrow 2I(^2P_{3/2}) + M$$

Evidence for the former process has been furnished independently by Callear, *et al.*,[13] who have observed the excited atoms being produced.

A clear example of the possibility for different excited electronic states of the same molecule to possess widely differing quenching cross sections is afforded by NO (Figure 2). Three separate correlation lines can be drawn for the $A^2\Sigma^+$, $B^2\Pi$, and $D^2\Sigma^+$ states, although the data are relatively sparse. However, NO and CO_2 deviate markedly from the $A^2\Sigma^+$ line, as they also do in quenching I_2 ($B^3\Pi_{0u^+}$, $v' = 25$) (Figure 1) and CO (Figure 4). Fairly good correlations are also obtained for OH (Figure 3), NO_2 (Figure 6), and SO_2 (Figure 7), but not for N_2 ($B^3\Pi_g$) (Figure 5) and CH_3OH (Figure 8). In the cases of NO_2 and SO_2, quenching is presumed to occur by a collision-induced internal conversion to high vibrational levels of the ground state, since the excitation energy is less than the N–O or S–O bond energy, as the case may be. The quenching model based on symmetry breaking through van der Waals forces would thus be expected to apply to these cases too, as it seems to do.

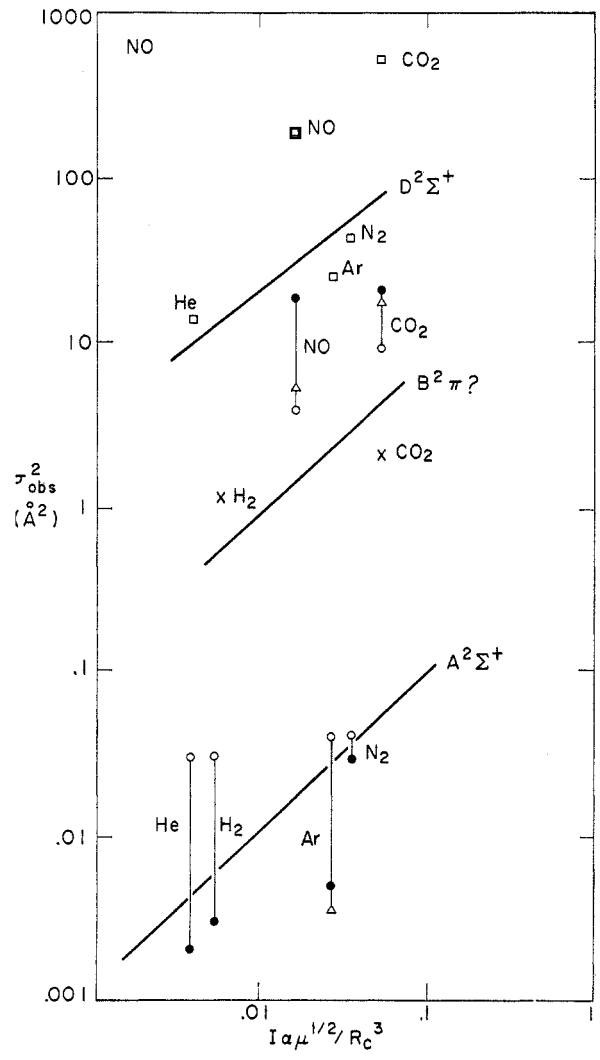

Figure 2. Quenching correlation for NO. Data: ○, ●, △, $A^2\Sigma^+$ state (Table I, footnotes *a–c*); ×, $B^2\Pi$ (Table I, footnote *d*); □, $D^2\Sigma^+$ (Table I, footnote *e*).

(13) A. B. Callear and J. F. Wilson, *Trans. Faraday Soc.*, **63**, 1358 (1967); T. W. Broadbent, A. B. Callear, and H. K. Lee, *ibid.*, **64**, 2320 (1968).

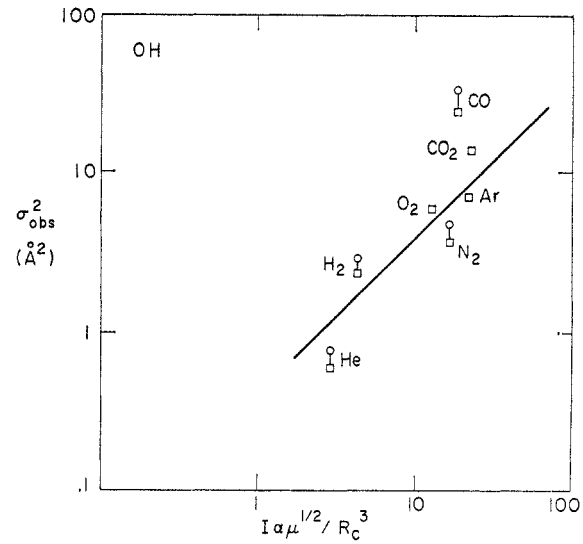

Figure 3. Quenching correlation for OH ($A^2\Sigma^+$); data of table I, footnotes *l–n*.

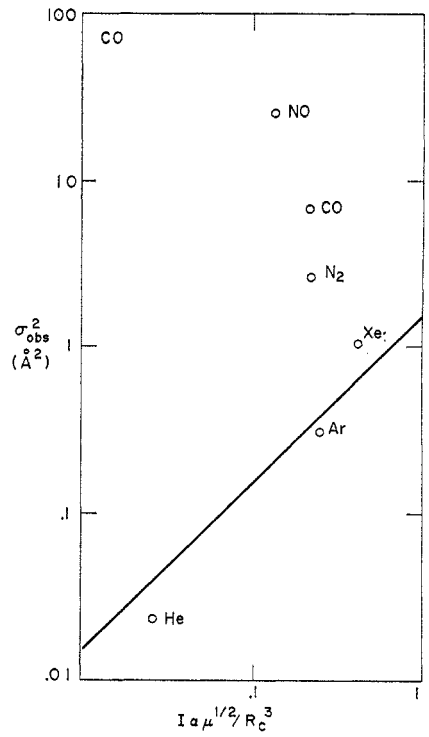

Figure 4. Quenching correlation for CO triplet states; data of Table I, footnote *c*.

Interestingly enough, this model, which is based on a molecular Hamiltonian, also seems to be a good predictor of relative quenching efficiencies for some excited atoms, such as $Hg^*(^1P_1)$ (Figure 9). The correlation is less good for $Na^*(^2P)$ (Figure 10), presumably because of specific chemical interactions; further data on rare-gas quenching of this atom would be helpful.

A further test of this model is the temperature dependence of the quenching rate, which is predicted to be temperature independent by eq 4. Edwards[14] has measured the self-quenching constant for I_2 ($B^3\Pi_{0u^+}$, v'

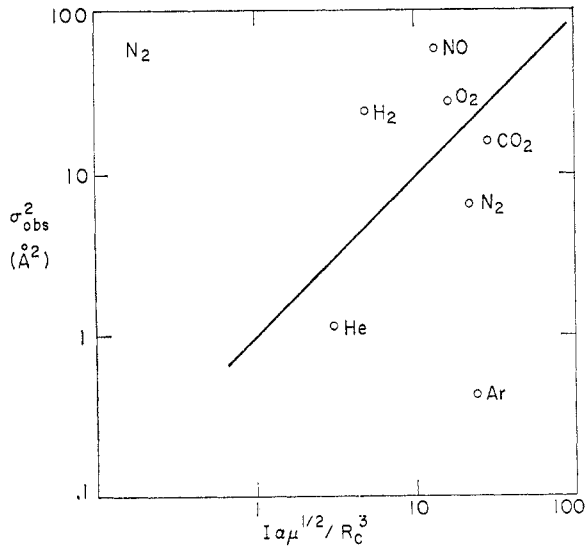

Figure 5. Quenching correlation for N_2 ($B^3\Pi g$); data of Table I, footnote *j*.

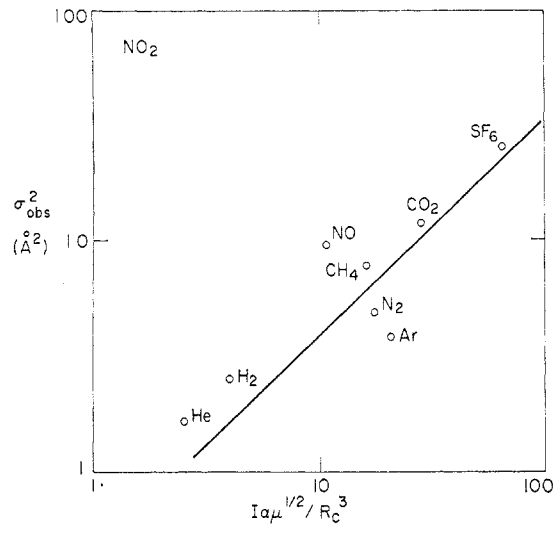

Figure 6. Quenching correlation for NO_2 [$^2\Sigma g(^2B_1)$]; data of Table I, footnote *p*.

= 25) over the range 300 to 600°K and finds a slight increase of k_{quench} over this range, so that $\sigma_Q{}^2$ falls off less rapidly than $T^{-1/2}$. He proposes an alternative model, based on the Zener theory of predissociation,[15] to explain his results.

A more direct test is the measurement of the velocity dependence of the unaveraged quenching cross section. Such an experiment has been carried out by Sheridan and Peterson[16] on a beam of metastable nitrogen ($A^3\Sigma_u{}^+$) molecules colliding with argon. They fit the cross section to a form

$$(\sigma_Q{}^2)^{1/2} = -a \ln v + b$$

predicted from a spin-exchange model,[17] although they concede that a $\sigma_Q{}^2 \propto 1/v$ dependence, as implied by

(14) R. V. Edwards, Ph.D. Thesis, Johns Hopkins University, 1968.
(15) C. Zener, *Proc. Roy. Soc., London*, **140**, 660 (1933).
(16) J. R. Sheridan and J. R. Peterson, *J. Chem. Phys.*, **51**, 3574 (1969).
(17) D. R. Bates, *Discuss. Faraday Soc.*, **33**, 7 (1962).

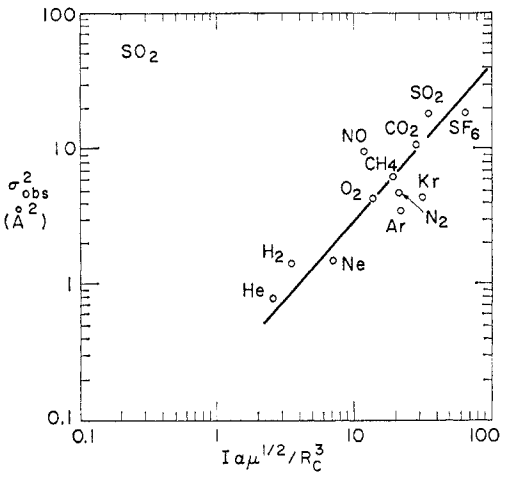

Figure 7. Quenching correlation for SO_2 ($\tilde{A}^1B_1$); data of Table I, footnote *r*.

Selwyn's model,[11] gives a nearly equally satisfactory fit. In summary, quenching of excited molecules by collisions appears to be a complex process, characterized by many open channels, and no one simple model may be able to account in detail for all the systems that have been studied.

Quenching by Noncollision Processes

Magnetically Induced Predissociation. Although the fact that the visible iodine fluorescence is quenched by an external magnetic field had been known for a long time,[18] it was not until quite recently that accurate values for the quenching rate constant as a function of vibrational level became available.[19] This rate depends on the square of the magnetic field strength, $k_{nQ} = bH^2$. The rate is obtained from the data by using a modification of the Stern–Volmer plot (eq 1)

$$\frac{I_0}{I} - 1 = \gamma H^2$$

where

$$\gamma^{-1} = (1 + Q'[I_2])/b'$$

with $b' = b\tau_{\text{rad}}$. If the measured γ^{-1} values are plotted against I_2 pressure, straight lines are obtained, with the intercept at $[I_2] = 0$ equal to b' and the slope equal to Q'/b'. Thus, the pressure dependence of the magnetic quenching efficiency gives an independent determination of self-quenching constants.

The magnetic quenching rates have a Gaussian-shaped dependence on v', with a maximum at $v' \simeq 25$. Huo[20] has carried out an *ab initio* calculation of this rate and obtains excellent agreement with our experimental results. This calculation also yields the slope of the repulsive potential curve responsible for the magnetically induced predissociation and the location of its intersection with the B-state potential, which appears to be near $v' = 18$.

(18) W. Steubing, *Verh. Deut. Phys. Ges.*, **15**, 1181 (1913).
(19) E. O. Degenkolb, J. I. Steinfeld, E. Wasserman, and W. Klemperer, *J. Chem. Phys.*, **51**, 615 (1969).
(20) W. Huo, *ibid.*, **52**, 3110 (1970).

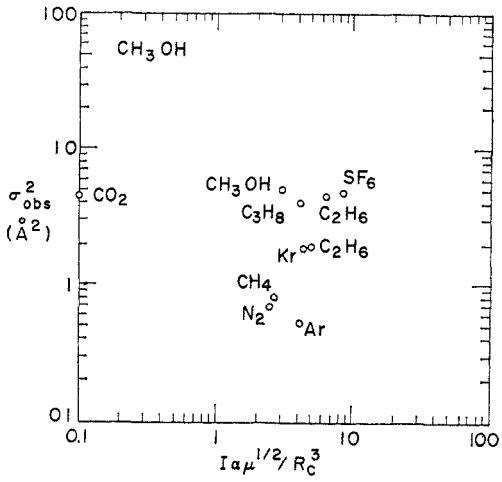

Figure 8. Quenching correlation for CH_3OH (^1E); data of Table I, footnote *s*.

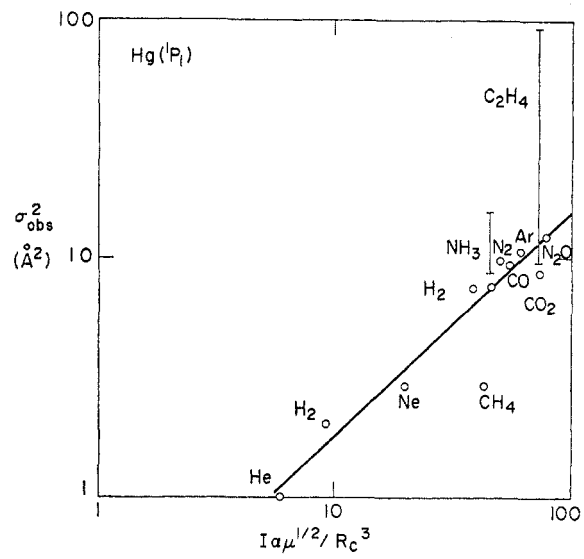

Figure 9. Quenching correlation for $Hg^*(^1P_1)$; data of A. Granzow, M. Z. Hoffman, and N. N. Litchtin, submitted for publication.

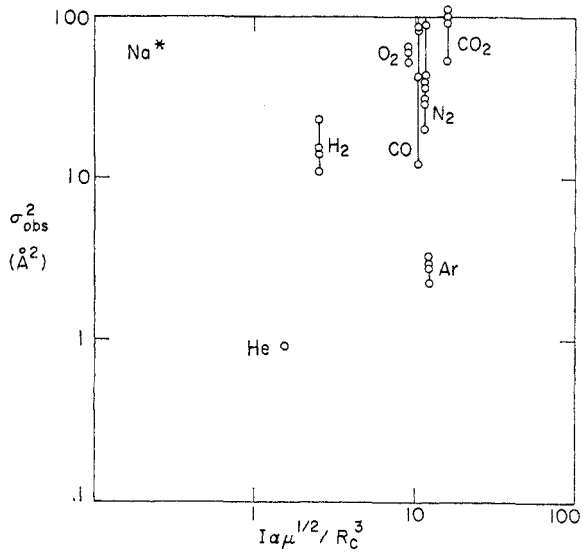

Figure 10. Quenching correlation for $Na^*(^2P)$; data of H. P. Hooymayers and C. T. J. Alkemade, *J. Quant. Spectrosc. Radiat. Transfer*, **6**, 847 (1966).

Thus far, the B state of iodine is the only system for which magnetic quenching of the fluorescence has been observed. This would seem to be a rewarding area for further investigation, since the phenomenon, where it exists, is a fruitful source of detailed molecular information.

Spontaneous Predissociation. The phenomenon of predissociation is well known to occur in both diatomic and polyatomic molecules. It is usually manifested as the complete absence or breaking off of fluorescence; thus, when fluorescence is observed at all, it is generally presumed that no spontaneous dissociation is occurring. This presumption has recently been shown to be untrue in the case of excited iodine.

The first clear evidence for this was the measurement of the concentration of $I(^2P_{3/2})$ atoms by epr, extrapolated to conditions of zero pressure and magnetic field.[21] These results indicated that at least 30% of the excited molecules dissociated spontaneously. Chutjian and James[22] made a careful comparison of absorption line strengths with radiative lifetimes measured by both pulse and phase-shift methods and found that the measured lifetimes were always shorter than would be calculated from the line strength. This is simply a manifestation of the relationship, analogous to eq 3.

$$\tau_{\text{eff}}^{-1} = \tau_0^{-1} + k_{\text{nr}} \qquad (5)$$

where

$$\tau_0^{-1} = \frac{64\pi^4}{3hc^3} |R_e|^2 \sum_{v''} \nu_{v'v''}^3 q_{v'v''}$$

in which $\nu_{v'v''}$ and $q_{v'v''}$ are the frequency and Franck–Condon factor, respectively, for each fluorescence band, and R_e is the electronic transition moment determined from an absorption measurement. The values of k_{nr} derived from eq 5 indicated that about two-thirds of the excited molecules dissociated spontaneously. Finally, Wilson's photodissociation experiments,[23,24] which are run under collision-free and magnetic-field-free conditions, show unambiguously that atoms are produced by irradiating iodine below the dissociation limit of the B ← X transition.

The reason that spontaneous predissociation was never suspected in this system is that most predissociation due to curve-crossing has a k_{nr} of the order of 10^{10} sec^{-1}, and thus completely quenches fluorescence. The potentials in I_2 are such that k_{nr} has a value of the order of 10^6 sec^{-1}, similar to $k_{\text{rad}} = \tau_0^{-1}$, and furthermore produces no discernible line broadening in absorption. Chutjian[25] has calculated k_{nr} on the basis of a

(21) E. Wasserman, W. E. Falconer, and W. A. Yager, *J. Chem. Phys.*, **49**, 1971 (1968).
(22) A. Chutjian and T. C. James, *ibid.*, **51**, 1242 (1969).
(23) G. E. Busch, R. T. Mahoney, R. I. Morse, and K. R. Wilson, *ibid.*, **51**, 837 (1969).
(24) K. R. Wilson, private communication.
(25) A. Chutjian, submitted for publication.

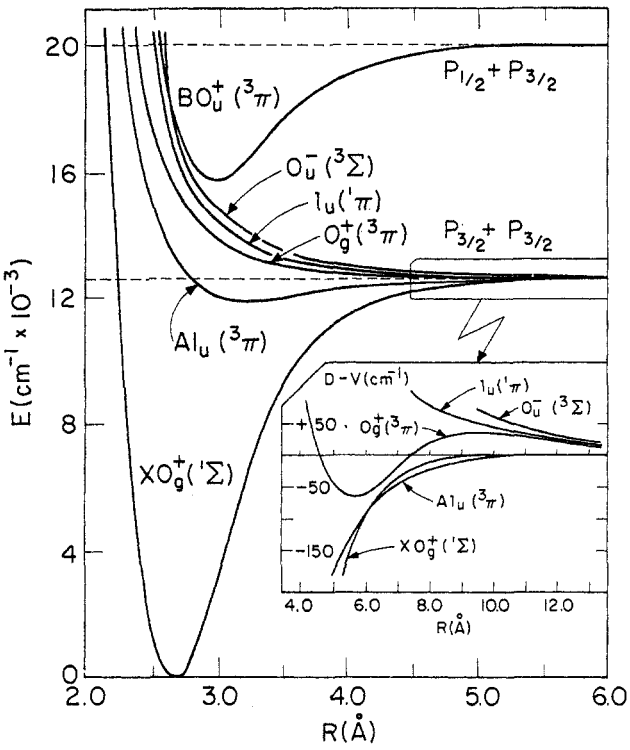

Figure 11. Potential curves for I_2, adapted from Figure 3 of ref 26.

$^1\Pi_{1u}$ potential curve approaching but not crossing the left-hand side of the $B^3\Pi_{0u}^+$ potential, and obtains good agreement with experiment.

(26) R. J. LeRoy, WIS-TCI-331-Rev, University of Wisconsin Theoretical Chemistry Institute, Madison, Wis., Aug 13, 1969.

Potential Curves for Iodine

The many spectroscopic and quenching studies on iodine now furnish enough data to provide a fairly complete picture of the potential curves in iodine, including many of the repulsive states. The $X^1\Sigma_{0g}^+$, $A^2\Pi_{1u}$, and $B^3\Pi_{0u}^+$ curves are established from absorption and emission spectroscopy. The $^3\Sigma_{0u}^-$ curve is established from magnetic quenching.[19,20] A $^3\Pi_{0g}^+$ state is required for the collision-induced predissociation and its curve cannot lie too close to the B-state curve; otherwise, the quenching rate would be higher than is actually observed.[27] Fortunately, LeRoy's recent careful reexamination[26] of the ultraviolet fluorescence in iodine locates a $^3\Pi_{0g}^+$ state in just the right position to be effective in quenching. Finally, Chutjian's calculation[25] indicates that a $^1\Pi_{1u}$ state, lying very close to the $^3\Pi_{0u}^+$ curve, is responsible for spontaneous predissociation, rather than the $A^3\Pi_{1u}$ state. The set of curves so derived is shown in Figure 11. These now account for nearly all the molecular states arising from the $^2P_{3/2} + {}^2P_{3/2}$ atomic states, except for some $^3\Delta$ levels, and furthermore are in just the relative order of energy predicted by Mulliken over 30 years ago.

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(27) J. E. Selwyn, M.S. Thesis, Massachusetts Institute of Technology, June 1969.