

Short Communication

Electronic energy transfer in the gas phase: the quenching of $O_2(^1\Sigma_g^+)$ *

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Several years ago we demonstrated that the formation of $O_2(^1\Sigma_g^+)$ could be sensitized by a variety of triplet sensitizers including $SO_2(^3B_1)$ [1 - 3]. The time-resolved flash photolysis technique employed for this study proved to be a most convenient method of studying the physical quenching of $O_2(^1\Sigma_g^+)$ by small quenching molecules. As the quenching constants obtained by this method were generally of higher precision and accuracy than those obtained by other methods we accordingly made a systematic study of a number of diatomic and triatomic quenching molecules as well as methane and ethane and their derivatives.

As we could detect dimole emission of $O_2(^1\Delta_g)$ developing during the quenching process we concluded that $O_2(^1\Delta_g)$ was formed directly and that the electronic energy difference between $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ was converted into vibrational, rotational and translational energy of the quencher molecule. Attempts have been made to relate the quenching rate constants to the dipole moment, polarizability and ionization potential of the quencher [4]. However, on examination of our results and those of others we found [5, 14] that for a whole series of molecules which quench $O_2(^1\Sigma_g^+)$, the quenching efficiency q , here defined as the quenching rate divided by the collision number, was related to the vibrational frequency of the quencher molecule according to an empirical equation where K and C are constants characteristic of a given molecular type:

$$\log q = K \frac{\Delta E'}{\nu_{\text{vib}}(\text{max})} + C \quad (1)$$

i.e. diatomic, triatomic, methane derivative, etc., $\Delta E'$ is the energy difference between the 0-0 vibronic levels of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$, and $\nu_{\text{vib}}(\text{max})$ is the maximum normal mode vibrational frequency of the quencher. Data illustrating this are shown in Table 1 and Fig. 1.

It was quite clear from eqn. (1) that the closer in energy $\Delta E'$ and $\nu_{\text{vib}}(\text{max})$ were, the more efficient was the quencher, a conclusion reached also by

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TABLE 1

$O_2(^1\Sigma_g^+)$ quenching efficiency, q , as calculated from the quenching rate constants. The formula for the conversion is obtained from collision theory: $q = (2\mu_{1\Sigma-Q}/\pi RT)^{1/2} \times (\sigma_{1\Sigma} + \sigma_Q)^{-2} k_q$. The assumption is made that $\sigma_{1\Sigma} \cong \sigma_{O_2} = 3.46 \text{ \AA}$.

Q	$\sigma(\text{\AA})$	$k_q(M^{-1}s^{-1})$	q	$\log q$	$\nu_{\text{vib}}(\text{max})$
H ₂	2.90	6.55×10^8	1.88×10^{-3}	-2.736	4395
HD†	2.90	1.9×10^8	6.44×10^{-4}	-3.191	3817
D ₂	2.90	1.02×10^7	4.00×10^{-5}	-4.398	3118
N ₂	3.70	1.34×10^6	8.49×10^{-6}	-5.071	2359
CO	3.60	3.4×10^6	2.22×10^{-5}	-4.654	2170
O ₂	3.46	2.76×10^4	1.94×10^{-7}	-6.710	1580
H ₂ O	2.82	1.22×10^9	8.86×10^{-3}	-2.053	3756
D ₂ O†	2.82	2.3×10^9	1.71×10^{-2}	-1.767	2784
H ₂ S	3.73	3.85×10^8	2.55×10^{-3}	-2.594	2627
CO ₂	4.00	2.5×10^8	1.62×10^{-3}	-2.790	2349
N ₂ O	3.88	8.10×10^7	5.44×10^{-4}	-3.264	2224
CS ₂	4.44	1.7×10^6	1.09×10^{-5}	-4.963	1532
SO ₂	4.29	4.0×10^5	2.56×10^{-6}	-5.592	1361
CH ₄	3.88	5.03×10^7	2.57×10^{-4}	-3.590	3020
CF ₄	4.70	1.59×10^6	9.73×10^{-6}	-5.012	1265
CCl ₄	5.88	2.7×10^5	1.34×10^{-6}	-5.873	776
C ₂ H ₆	4.42	2.75×10^8	1.47×10^{-3}	-2.833	2996
C ₂ D ₆	4.42	1.03×10^8	5.39×10^{-4}	-3.268	2236
C ₂ F ₆	5.31*	1.90×10^6	1.06×10^{-5}	-4.975	1250**
C ₂ H ₄	4.23	2.34×10^8	1.29×10^{-3}	-2.891	3103

*Calculated from atomic sizes. † Ref. 13.

**Obtained from the i.r. spectrum.

Davidson and Ogryzlo [6]. Thus the conversion of electronic energy into vibration appeared logically to be the most probable process. But naturally the question arose as to how the energy difference between $\Delta E'$ and $\nu_{\text{vib}}(\text{max})$ was partitioned between rotational and translational modes and the factors governing the partitioning. Since an answer to this question was not forthcoming without resort to much more elaborate and sophisticated experiments, we have attempted to gain some insight into the problem through a theoretical treatment along the lines previously pursued by Dickens *et al.* [7] in their treatment of the physical quenching of electronically excited atoms.

To simplify the problem we decided to treat only diatomic quenching molecules, Q_2 . In this initial treatment we have neglected the effect of rotation and have considered that the vibronic energy of the excited diatomic oxygen molecule is partitioned between ground state vibrational levels of the quencher and the relative translation of the collision partners. Further, in these inefficient physical quenching processes, the potential

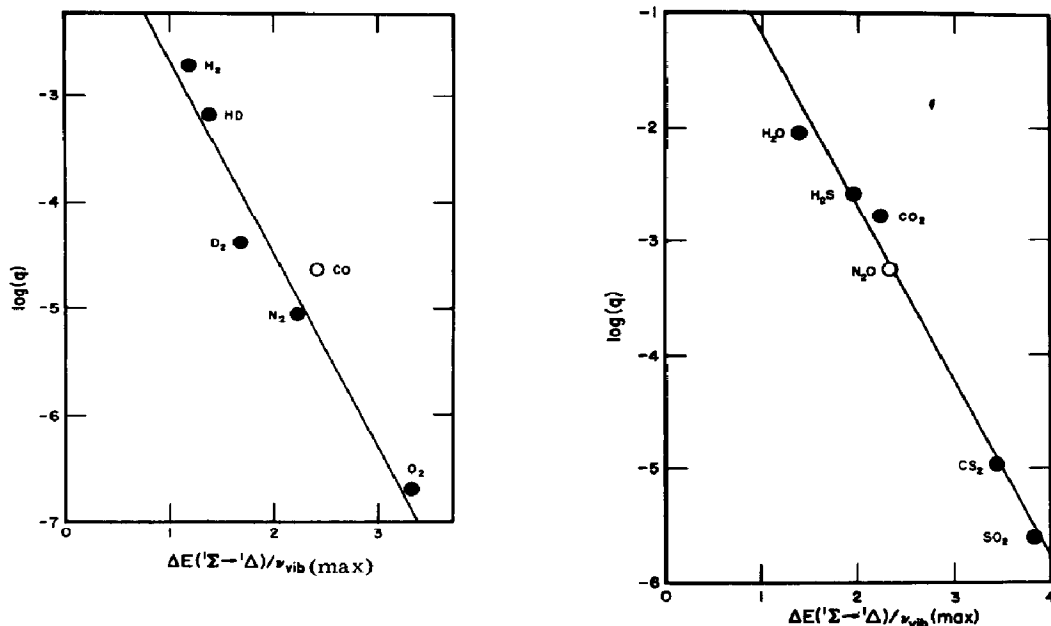
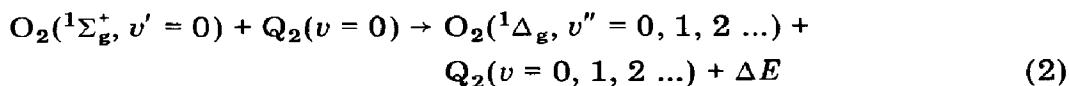


Fig. 1.

energy surfaces of the initial and final states are assumed to be well separated with no regions of crossing or strong interaction. This permits the use of the "distorted wave" approximation [8] in treating the collision process.

Equation (2) describes the collision process:



where ΔE is the change in the relative kinetic energy of translation of the colliding molecules.

The wave equation for the collision process (2) is given by:

$$\left[\frac{\hbar^2}{2\mu} \nabla^2 - H_1(r_1, q_1) - H_2(r_2, q_2) + \frac{\mu v_0^2}{2} + E - V(r, r_1, q_1, r_2, q_2) \right] \Psi = 0 \quad (3)$$

H_1 and H_2 are the normal free space hamiltonians of the oxygen and quencher molecules, respectively, V is the interaction potential, $\frac{1}{2}\mu v_0^2$ is the kinetic energy of the colliding molecules, μ is their reduced mass, and r is the center of mass separation coordinate. E is the sum of the normal internal energies of the free space molecules. The coordinates r_1 and r_2 are the electronic coordinates of O_2 and Q_2 , respectively, while q_1 and q_2 are their vibrational coordinates.

A solution to eqn. (3) is sought of the form:

$$\Psi = \sum_n R_n(r) \psi_n(r_1, q_1, r_2, q_2) \quad (4)$$

where $\psi_n(r_1, q_1, r_2, q_2)$ is the wave function for the electronic and vibrational motions of O_2 and Q_2 . These in turn are approximated in Born–Oppenheimer fashion by:

$$\psi_n(r_1, q_1, r_2, q_2) = \phi_n^{\text{el}}(r_1)\phi_n^{\text{vib}}(q_1)\chi_n^{\text{el}}(r_2)\chi_n^{\text{vib}}(q_2) \quad (5)$$

$R_n(r)$ is the translational wave function which is treated in terms of scattering theory [8]. The asymptotic form of these wave functions is given by:

$$R_0(r \rightarrow \infty) \rightarrow \exp(ik_0 r \cos \theta) + f_0(\theta, \phi) \frac{1}{r} \exp(ik_0 r) \quad (6)$$

and

$$R_n(r \rightarrow \infty) \rightarrow f_n(\theta, \phi) \frac{1}{r} \exp(ik_n r) \quad (7)$$

The “elastic” scattering process (6) is represented by two terms: the first, an incoming plane wave and the second, an elastically scattered spherical wave. The “inelastically” scattered translational wave function, $R_n(r)$ is a spherical wave whose amplitude, $f_n(\theta, \phi)$ is a function of the normal spherical coordinate angles, θ and ϕ and the wave number term, k_n of the exponential is given as $k_n = \mu V_n / \hbar$.

If eqn. (4) is substituted into (3) the set of equations (8) is obtained:

$$(v_r^2 + k_i^2)R_i(r) = \frac{2\mu}{\hbar^2} \sum_n R_n V_{in}(r) \quad (8)$$

where

$$V_{in} = \int \dots \int V(r, r_1, q_1, r_2, q_2) \psi_i \psi_n dr_1 dq_1 dr_2 dq_2 \quad (9)$$

Now the exact interaction potential has a complicated dependence upon the various variables but a reasonable approximation similar to that used by Dickens *et al.* [7] can be made by separating the variables as in:

$$V(r, r_1, q_1, r_2, q_2) = V(r)V(r_1)V(q_1)V(r_2)V(q_2) \quad (10)$$

This permits (9) to be written as:

$$V_{in} = U_{in} \cdot V(r) \quad (11)$$

$$\text{where } U_{in} = \int \dots \int V(r_1)V(q_1)V(r_2)V(q_2) \psi_i \psi_n dr_1 dq_1 dr_2 dq_2 \quad (12)$$

It is convenient to express the interaction potential of eqn. (10) in terms of exponentials in which a characteristic length, α^{-1} , that defines the region where V varies markedly with r , appears as a coefficient in the exponent [9]. This is assumed to be large compared to the vibrational amplitudes, $A_1 q_1$ and $A_2 q_2$ of the colliding molecules (Fig. 2). Generally α^{-1} can be estimated from a Lennard–Jones potential fit of gas viscosity data [9, 10], assuming equilibrium (or average) values for the internal coordinates.

For the quenching process described in eqn. (2) a tractable form of the interaction potential (10) can be derived from considerations similar to those used by Dickens *et al.* [7]. For simplicity we considered the collision to be

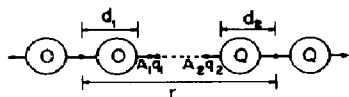


Fig. 2.

collinear as in Fig. 2. In the repulsive portion V_{00} of eqn. (9) should have the form [7, 10]:

$$V_{00} = V_0 \exp(-\alpha r) \quad (13)$$

To obtain a tractable form for the interaction potential consistent with eqn. (10) the following was used:

$$V = V'_0 (1 + \beta r_1 + \gamma r_1^2)(1 + \beta' r_2 + \gamma' r_2^2) \exp(-\alpha d) \quad (14)$$

where from Fig. 2, d is the distance between the closest O and Q atoms. $V_{(r_1)}$ and $V_{(r_2)}$ of eqn. (10) appear in eqn. (14) as truncated series expansions of exponentials. Their form assumes spherically symmetric shells of electron density about O_2 and Q_2 whose radii are r_1 and r_2 respectively.

Since from Fig. 2:

$$d = r - d_1 - d_2 - A_1 q_1 - A_2 q_2 \quad (15)$$

one can rewrite eqn. (10) as:

$$V(r, r_1, q_1, r_2, q_2) = V_0 (1 + \beta r_1 + \gamma r_1^2)(1 + \beta' r_2 + \gamma' r_2^2) \exp(\alpha A_1 q_1) \exp(\alpha A_2 q_2) \exp(-\alpha r) \quad (16)$$

Under the gas kinetic conditions employed in our experiments one would expect:

$$V_{0n} = V_0 U_{0n} \exp(-\alpha r) < V_{00}, V_{nn} \quad (17)$$

where $V_{00} \cong V_{nn} \cong V_0 \exp(-\alpha r)$

Therefore the use of distorted wave approximation [7, 8] appeared to be justifiable in the calculation of the quenching efficiency for the system of eqn. (2). For this purpose we first calculated the differential inelastic cross-section for the collision [8] which is:

$$\sigma_n(\theta, v_0) \sin \theta \, d\theta d\phi = \frac{k_n}{k_0} |f_n(\theta, \phi)|^2 \sin \theta d\theta d\phi \quad (18)$$

Integration over the unit sphere yields the total, velocity dependent, inelastic cross-section, $\sigma_n(v_0)$. Further integration over a Maxwellian velocity distribution of the incident relative velocity of collision, V_0 , yields the deactivation cross-section, σ_n , for the n th transition. This is given by:

$$\sigma_n = \frac{1}{2} \left(\frac{\mu}{k_b} \right)^2 \int_0^\infty \sigma_n(v_0) v_0^3 \exp(-\mu v_0^2 / 2k_b T) dv_0 \quad (19)$$

where k_b is the Boltzmann constant. An analytical expression approximating

the value for σ_n has been obtained by Wittenman [11] for the case of vibrational energy transfer which is given in:

$$\sigma_n = \left[\frac{\frac{128}{9} \pi^{7/2} (3)^{1/2} \alpha^{-6} \hbar^{-4} \mu^2 (\Delta E)^2 \exp(-3b^2)}{\frac{2\mu k_b T}{4\alpha^2 \hbar^2} \left(\frac{\hbar^2 \alpha^2}{2\mu k_b T} + \frac{\Delta E}{k_b T} \right)^2 + b^2} \right] U_{0n}^2 \times \left[b \left\{ \frac{5}{12} + \frac{\Delta E}{2k_b T} + \frac{3}{16} \left(\frac{\Delta E}{k_b T} \right)^2 \right\} + \left\{ \left(\frac{5}{3} + \frac{\Delta E}{k_b T} \right) b^3 + b^5 \right\} \right] \quad (20)$$

where

$$b = \left[\frac{\pi \mu \Delta E}{\alpha \hbar (2\mu k_b T)^{1/2}} \right]^{1/3} \quad (21)$$

and ΔE is the translational energy assumed to appear or disappear in the process. This is given by:

$$\Delta E = |\Delta E_{\text{vib}} - \Delta E_{\text{elec}}| = \left| \frac{\hbar^2 (k_0^2 - k_n^2)}{2\mu} \right| \quad (22)$$

For net activation eqn. (20) is multiplied by a factor $\exp(-\Delta E/k_b T)$.

The matrix elements, U_{0n} in eqn. (20) are given by:

$$U_{0n} = (U_1^{\text{el}})_{0n} \cdot (U_1^{\text{vib}})_{0n} \cdot (U_2^{\text{el}})_{0n} (U_2^{\text{vib}})_{0n} \quad (23)$$

As there is no electronic transition in the quencher molecule, $(U_2^{\text{el}})_{0n}$ can be taken as unity. The electronic matrix element $(U_1^{\text{el}})_{0n}$ for the ${}^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ process in O_2 is rather difficult to evaluate as the transition is formally forbidden. Of course, in the collision there will be a strong perturbation which may give it a value approaching unity and for the present purposes this is what we will assume it to be.

The two vibrational matrix elements, $(U_1^{\text{vib}})_{0n}$ and $(U_2^{\text{vib}})_{0n}$ were calculated by numerical integration of Morse oscillator wave functions [12] (24) and (25). In the case of eqn. (25) an exponential perturbation potential was included.

$$(U_1^{\text{vib}})_{0n} = \int \psi_{10}^* \psi_{1n} dq_1 \quad (24)$$

$$(U_2^{\text{vib}})_{0n} = \int \psi_{20}^* \psi_{2n} \exp(\alpha A_2 q_2) dq_2 \quad (25)$$

The quenching efficiency was calculated using eqn. (26) by summing over all the inelastic cross-section terms, σ_n , for the various vibronic transitions in O_2 and vibrational transitions in Q_2 quenching molecules.

$$q = \sum_n \sigma_n / \sigma_{\text{total}} \quad (26)$$

In Table 2 the calculated and experimental values of the quenching constants are compared. The former are less than the latter by roughly an order of magnitude except for the ground state O_2 and here the quenching

TABLE 2

The q_{theory} vs. q_{exp} comparison for diatomic quenchers

Q	Δv_Q	Δv_{O_2}	ΔE (cm ⁻¹)*	σ'_n (Å ²)**	q_{theory}	q_{exp}
H ₂	1	0	-844	5.82×10^{-2}	1.23×10^{-4}	1.88×10^{-3}
HD	1	1	87	2.17×10^{-1}	1.03×10^{-5}	6.44×10^{-4}
D ₂	1	1	-612	1.02×10^{-1}	3.59×10^{-6}	4.00×10^{-5}
N ₂	1	2	138	1.51	6.35×10^{-8}	8.49×10^{-6}
CO	1	2	-51	3.98	2.04×10^{-7}	2.22×10^{-5}
	0	3	-712	1.16×10^{-3}		
O ₂	1	2	-641	2.99×10^{-3}	2.38×10^{-10}	1.94×10^{-7}
	2	1	-570	7.80×10^{-3}		

* ΔE is negative when $\Delta E_{\text{vib}} > \Delta E_{\text{elec}}$ in eqn. (22).** $\sigma'_n = \sigma_n/U_{0n}^2$ (eqn. 20).

process is no doubt complicated by collisions in which complete exchange of electronic excitation energy occurs, *i.e.* no net quenching. Thus the trend and relative ratios of quenching efficiencies are correctly predicted by the theory. Furthermore the empirical formula for q in eqn. (1), derived from experimental data, is essentially compatible with the theory.

The calculated efficiencies have assumed a value of unity for the electronic matrix element for the O₂(¹Σ_g⁺ → ¹Δ_g) transition which, of course, may be too high. If one calculates q for inert gas quenching and compares it with experimental data the value for this matrix element, assuming the vibronic transition O₂(¹Σ_g⁺, $v = 0 \rightarrow$ ¹Δ_g, $v \neq 3$) as the predominant transition coupling with translation, lies between 0.1 and 0.5. But this neglects any possible change in rotational level of the O₂ in the transition. Furthermore rotational transitions in the quenching molecule, Q₂, have also been neglected. These factors undoubtedly play a significant role in the quenching process and our current efforts are directed toward evaluating them.

Details of the calculations and experimental techniques will appear elsewhere.

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