Erratum: Role of Singlet Excited States of Molecular Oxygen in the Quenching of Organic Triplet States

Kenji Kawaoka, A. U. Khan, and David R. Kearns

Erratum: Interaction of Thermal Electrons with Polarizable and Polar Molecules

[J. Chem. Phys. **44**, 3506 (1966)]

L. G. Christophorou, G. S. Hurst, and A. Hadjiantoniou

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There is an error in Fig. 6 concerning the plotting of the prediction of the Mittleman–von Holdt calculation.[1] The ratio A_I'/A_E as predicted by Mittleman and von Holdt shows a much stronger dependence on μ^2 than that shown in Fig. 6. This makes the overall experimental results favor the calculation by Altshuler[2] rather than that by Mittleman–von Holdt. A corrected and more complete version of Fig. 6 will appear in a paper by Christophorou and Compton.[3]

[1] M. H. Mittleman and R. E. von Holdt, Phys. Rev. **140**, A726 (1965).

[2] S. Altshuler, Phys. Rev. **107**, 114 (1957).

[3] L. G. Christophorou and R. N. Compton, "Interaction of Low-Energy Electrons with Polyatomic Molecules," Health Phys. (to be published).

Erratum: Cavity Concept in Dielectric Theory

[J. Chem. Phys. **46**, 784 (1967)]

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The left-hand side of Eq. (41) should read $\frac{4}{3}\pi Na^3{}_{B-O}$. On page 790, left column, top line, change $\frac{4}{3}\pi Na^3{}_{B-O}$ to $\frac{4}{3}\pi Na^3{}_{B-O}$.

Erratum: Detection of $O(^1D)$ in Photolysis of O_2 at 1470 Å and Its Quenching by Several Gases

[J. Chem. Phys. **45**, 2702 (1966)]

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The emission reported in this letter as being the 6300-Å line from $O(^1D)$ is, in fact, due to the (0, 0) O_2 atmospheric band at 7618 from $O_2(b\ ^1\Sigma_g{}^+)$. The combination of an unsuspected transmission of the 6300-Å interference filter beyond 7000 Å, the high sensitivity of the tri-alkali photomultiplier at 7618 Å, and the occurrence of the extremely rapid reaction

$$O(^1D) + O_2 \rightarrow O_2(b\ ^1\Sigma) + O(^3P) \qquad (1)$$
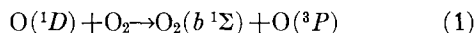
combined to induce the misinterpretation of the radiation being measured. An extensive study of O_2 photolysis at 1470 Å and Reaction (1) will soon be published.

Erratum: Role of Singlet Excited States of Molecular Oxygen in the Quenching of Organic Triplet States

[J. Chem. Phys. **46**, 1842 (1967)]

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In a recent paper with the above title, we examined the mechanisms by which molecular oxygen quenches triplet state molecules. We now find that several of the wavefunctions used to describe the states of a complex formed between a ground-state donor molecule and oxygen in an excited state were incorrectly labeled. The proper labeling of these functions is given below:

$$^1\psi_3(^1D,\ ^1\Delta_g) = (1/\sqrt{2})[\ |\ \phi_1(1)\bar\phi_1(2)\pi_x{}^*(3)\bar\pi_y{}^*(4)\ |$$
$$-\ |\ \phi_1(1)\bar\phi_1(2)\bar\pi_x{}^*(3)\pi_y{}^*(4)\ |\ ],$$

$$^1\psi_3(^1D,\ ^1\Delta_g{}') = (1/\sqrt{2})[\ |\ \phi_1(1)\bar\phi_1(2)\pi_x{}^*(3)\bar\pi_x{}^*(4)\ |$$
$$-\ |\ \phi_1(1)\bar\phi_1(2)\pi_y{}^*(3)\bar\pi_y{}^*(4)\ |\ ],$$

$$^1\psi_2(^1D,\ ^1\Sigma_g{}^+) = (1/\sqrt{2})[\ |\ \phi_1(1)\bar\phi_1(2)\pi_x{}^*(3)\bar\pi_x{}^*(4)\ |$$
$$+\ |\ \phi_1(1)\bar\phi_1(2)\pi_y{}^*(3)\bar\pi_y{}^*(4)\ |\ ].$$

The major consequence of this relabeling is that the function which was given in Eq. (16a) and identified with the $^1\Sigma_g{}^+$ state of molecular oxygen is in fact one of the $^1\Delta_g$ components, whereas the minus component given in Eq. (16b) is to be associated with the $^1\Sigma_g{}^+$ state. The calculation of the quenching rates, however, proceeds exactly as before. The only difference is that certain of the matrix elements need to be appropriately relabeled. With these changes, we now find that there is no direct mixing of the initial state (complex between a triplet-state donor molecule and a ground-state oxygen molecule) with the final state, where a ground-state donor molecule is weakly complexed with molecular oxygen in its excited $^1\Sigma_g{}^+$ state. There is still significant direct mixing of the other three final states with the initial state by an exchange interaction.

When charge-transfer virtual states were included in the calculation, we found that all of the final states, including the one in which molecular oxygen is left in its $^1\Sigma_g{}^+$ state, were about equally mixed with the initial state. Since charge-transfer interactions were calculated to be larger than exchange interactions, none of the important conclusions presented in our original paper are altered. The new result regarding exchange mixing of states does, however, suggest a possible experimental test of the importance of charge transfer interactions. If, contrary to our calculations, charge-transfer interactions were negligible compared to exchange interactions, we predict that only $^1\Delta_g$ molecular oxygen would be generated in the quenching process. On the other hand, if charge-transfer interactions are as important as our calculations indicate, then significant amounts

of $^1\Sigma_g^+$ oxygen should be generated by the quenching of high-energy triplet-state sensitizers $(E_T > 17\,000\ cm^{-1})$. Experimental evidence for the production of significant amounts of $^1\Sigma_g^+$ oxygen is discussed elsewhere.[1]

Subscript errors appeared in Eqs. (18b), (22b), and (22d). In Eq. (18b), change Π_y^* to Π_x^*, and in Eqs. (22b) and (22d), change $\phi_i(j)$ to $\phi_1(j)$.

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[1] D. R. Kearns, R. A. Hollins, A. U. Khan, R. W. Chambers and P. Radlick (unpublished).

Erratum: Theoretical Investigations of Translation–Rotation Energy Transfer: (H₂, He) and (D₂, He) Systems

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An error in the digital computer program used to numerically evaluate the integral appearing in Eq. (13) has been found. Correction of this error indicates that the following modifications must be made in the data reported: relaxation times listed in Figs. 6, 8, 9, and 10 should be decreased by a factor of $2^{5/2}$. Collision numbers reported in Fig. 7 should be decreased by a factor of 4. The labeling of the abscissa of Figs. 6, 7, 8, and 10 should be $2 \times T/°K$ rather than $T/°K$. The corrected Table II is shown here.

TABLE II. Comparison of calculated and predicted $0 \rightarrow 2$ rotational relaxation times for the (H₂, He) System at 150°K.

Well depth $\times 10^3$ (eV)	τ_{02} (Parker) (sec)	τ_{02} (this work) (sec)
0.1953	0.60×10^{-8}	0.71×10^{-8}
0.68203	0.44×10^{-8}	0.54×10^{-8}
2.7986	0.25×10^{-8}	0.34×10^{-8}
7.3415	0.14×10^{-8}	0.26×10^{-8}

With regard to the conclusions listed in Sec. V of the paper, Nos 1–5, and 7–9 are unaltered. The numerical values listed in Conclusion 6 must be modified according to the above scheme, and the extent of agreement of the model with experiment implied in this conclusion and in Footnote 24(a) is greatly reduced. With the approximations discussed in Footnote 24(a), one now calculates τ_{exptl} values of 2.65×10^{-9} and 2.35×10^{-9} sec at 90.5° and 170°K, respectively, as compared with 1.61×10^{-8} and 1.24×10^{-8} sec obtained experimentally by Jonkman and Ertas. Thus, while the ratios of τ_{exptl} at 90.5° and 170°K are still in satisfactory agreement, the magnitudes are too small by a factor of 5.

The author wishes to express his thanks to Dr. G. C. Berend for calling his attention to the above numerical error.

Erratum: Iterative Method for Solution of the One-Dimensional Wave Equation: Eigenvalues and Eigenfunctions for the L–J (12, 6) and Exponential (α, 6) Interatomic Potentials

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Certain systematic errors in Tables Va–Vd (the WKBJ integrals) have been kindly pointed out by J. K. Cashion: all entries are too small by varying amounts. However, the only ones seriously in error are those in the first row $(K=0)$ of each table; they are low by amounts ranging from 0.038 to 0.028 for θ ranging from 0 to 2×10^{-2}. Entries for $K \leq -0.1$, $\theta \leq 10^{-3}$ are correct to the fourth decimal place. The error increases toward the "upper-right" corners of the tables.

The integrals have now been recomputed[1] taking as the limits Z_a and Z_b, the zeros of the integrand in Eq. (4) (not identical to the classical turning points) and using a sufficient number of cuts in the Simpson's rule quadrature to assure accuracy better than 10^{-4}. Samples of the results were checked using a Gaussian 100-point quadrature. The value for $K=\theta=0$ in Table Va now agrees with that of Stogryn and Hirschfelder.[2]

The WKBJ entries in Table IV had been separately computed; they have now been rechecked satisfactorily. Linear interpolation of Table V is not sufficiently accurate to determine the uppermost levels $(K \gtrsim -0.1)$.

An additional discrepancy was pointed out by L. W. Bruch and I. J. McGee, who have independently checked a number of values of B_z-crit in Table I. For $\alpha = 12$, $v=0$, they obtain 6.19 (versus 6.34 in Table I). Their value for $n=12$, $v=0$ is 7.043, to be compared with a recently published calculation[3] which yields 7.052; both of these are in essential agreement with the value of 7.07 ± 0.1 listed in Table I.

[1] The recomputed tables and other supplementary material have been deposited as Document number 9499 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the Document number and by remitting $2.50 for photoprints, or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.
[2] D. A. Stogryn and J. O. Hirschfelder, J. Chem. Phys. 31, 1531 (1959).
[3] A. Goldberg, H. M. Schey, and J. L. Schwartz, Phys. Rev. 146, 176 (1966).