New electron-energy transfer rates for vibrational excitation of $\text{O}_2$

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Abstract. We report on our computation of electron-energy transfer rates for vibrational excitation of $\text{O}_2$. This work was necessitated by inadequacies in the electron-impact cross section databases employed in previous studies and, in one case, an inaccurate approximate formulation to the rate equation. Both these inadequacies led to incorrect energy transfer rates being published in the literature. We also demonstrate the importance of using cross sections that encompass an energy range that is extended enough to appropriately describe the environment under investigation.

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1. Introduction

The physical chemistry that occurs in the Earth’s ionosphere is significantly influenced by the electron temperature ($T_e$) [1], which in turn is affected by the interaction between electrons and neutral molecules. This interaction between electrons and neutral molecules plays an important role in the cooling of electrons in the ionosphere, and as molecular oxygen ($O_2$) makes up $\approx 5\%$ (at 160 km) of our ionosphere its role in this cooling process is crucial. The electron cooling process involves excitation of molecules into their vibrational and electronic-vibrational states. As the number density of vibrationally unexcited $O_2$, i.e. $[O_2\{X^3\Sigma_g^-(v = 0)\}]$, is much larger than the number density of vibrationally excited $O_2$, i.e. $[O_2\{X^3\Sigma_g^-(v \geq 1)\}]$, including for geomagnetic storm periods at middle latitudes [2], it is reasonable to consider only excitation from the ground vibrational state of $O_2$. The probability for excitation of a particular transition in $O_2$ via electron impact is, in fact, the electron impact integral cross section for that transition.

The role of molecular oxygen in electron cooling has been examined previously by Lane and Dalgarno [3], Stubbe and Varnum [4], Prasad and Furman [5] and Pavlov [2]. In most of these earlier studies the electron energy transfer rates were calculated for vibrational excitation of the $X^3\Sigma_g^-$ ground state, and as a consequence we restrict our study to these same processes. All these earlier calculations required the relevant electron impact vibrational excitation integral cross sections, with the values taken from the experimental measurements of Hake and Phelps [6], Spence and Shultz [7], Linder and Schmidt [8] or Allan [9]. Recent advances in experimental techniques have resulted in improved and/or extended cross section measurements [10], so that some of the earlier cross section data [6]–[8] are now obsolete. Consequently, we use the recommended $O_2$ electron impact vibrational integral cross sections from Brunger et al [11], extended to threshold with the data of Allan [9], to calculate new electron energy transfer rates.

In section 2 we provide details of our calculations, including the cross section database we employed. Results and discussion are presented in section 3 and conclusions are drawn in section 4.

2. Computational details

The electron cooling rate ($L$) for electron impact excitation of the ground vibrational quantum is calculated from [2]

$$ L(v = 0) = N_e \sum_{v=1}^{N} Q_{0v} \left( [O_2(0)] - [O_2(v)] \exp \left( \frac{E_v}{k_B T_e} \right) \right) , $$

where

$$ Q_{0v} = E_v \left( \frac{8 k_B T_e}{\pi m_e} \right)^\frac{1}{2} \int_0^\infty \sigma_{0v}(x) x \exp(-x) \, dx $$

and

$$ x = \frac{E}{k_B T_e} . $$

In equations (1)–(3), $N_e$ is the number density of electrons, $[O_2(v)]$ is the number density of oxygen molecules in vibrational level $v$, $k_B$ is Boltzmann’s constant, $E$ is the energy of the electrons, $T_e$ is the electron temperature, $m_e$ is the mass of an electron, $N$ is the number of
vibrational levels, \( E_v \) is the energy of state \( v \), and \( \sigma_{0v} \) is the integral vibrational cross section for electron impact from state \( v = 0 \) to state \( v \) in the ground electronic state.

As noted above, the integral cross sections employed in this study were taken from Brunger et al [11] and extended to threshold with the data of Allan [9]. These cross sections have been interpolated, linearly in this case, which is a prerequisite in evaluating the integral in equation (2), and are shown in figure 1. The magnitudes of the integral cross sections were found to decrease systematically for excitations to the higher vibrational levels (figure 1). Furthermore, figure 1 shows that the interaction between the electrons and ground-state molecular oxygen involves the temporary capture of the electron [12]. This creates the molecular ion \( \text{O}_2^- (2\Sigma_u^+ (v' > 4), 4\Sigma_u^- (v' \geq 0), 2\Sigma_u^- (v' \geq 0)) \leftrightarrow \text{O}_2 (v > 0) + e \) (4)

and it plays an important role in the scattering dynamics of this system. Noble et al [12] showed that direct (non-resonant) excitation is also non-negligible.

It is of practical interest to determine \( Q \) rather than \( L \), as the respective molecular oxygen and electron number densities are altitude dependent. Hence we calculated the energy transfer rate for excitation to the \( v \)th vibrational level, \( Q_{0v} \), as a function of \( T_e \), as defined in equation (2). The total electron energy transfer rate for vibrational excitation \( (Q_T) \) was determined by summing the energy transfer rate over all vibrational levels:

\[
Q_T = \sum_{v=1}^{N} Q_{0v},
\]

Figure 1. Recommended [9, 11] integral cross sections for ground-state vibrational transitions in \( \text{O}_2 \).
Figure 2. $Q$ as a function of $T_e$ for the 0–1 process in $O_2$. ——, Pavlov’s result [2]; ·–·, our results using equation (6) and Pavlov’s cross section database [9]; ——, our results using equation (2) and Pavlov’s cross section database [9].

Figure 3. $Q_{0v}$ and $Q_T$ as a function of $T_e$ as calculated in the present study using equation (2) and the cross sections of figure 1.
Figure 4. Ratio of the rate determined using our recommended [9, 11] cross sections to that of previous workers, as labelled, for the 0–1 transition.

Numerical integration is required to evaluate the integral in equation (2). Reliable integral cross sections [10, 11] only exist up to energies $\sim$25 eV, which thus sets the upper limit for the integration. Three different numerical procedures were employed to evaluate the integral in equation (2). The first followed the step-integral technique of Campbell et al [13], the second was based on the trapezoidal/midpoint rule and the third was Simpson’s rule. In each case, for a given cross section database, the results from our three integration techniques were found to be consistent across the range of $T_e$ investigated. We are therefore confident in the accuracy of our numerical integration in equation (2).

An alternative (approximate) formulation for computing $Q_{0v}$ was recently proposed by Pavlov [2]. In this approach he assumed that the vibrational integral cross sections (for $0 \rightarrow 1, 2, \ldots$) consisted solely of a series of sharp spikes, so that the integration in equation (2) is approximated by the sum over the spikes:

$$Q_{0v} = E_v \left( \frac{8k_BT_e}{\pi m_e} \right)^\frac{1}{2} \sum_j S_{jv} X_j \exp(-X),$$

where $S_{jv}$ is the height of the ‘spike’ in the 0–$v$ integral vibrational cross section at energy $E^*_v$ [9], $X_j = E^*_j/(k_BT_e)$ and $E^*_j$ are the energies of the electrons. Considering specifically the 0–1 transition (although what follows is also true for 0–2, 3, 4), in figure 2 we plot the $Q_{01}$ results from Pavlov [2] for this process, the $Q_{01}$ result we obtain using equation (6) and the cross section database Pavlov employed [9] and the $Q_{01}$ results we obtain using equation (2) and the same cross section database of Pavlov [9]. It is clear from figure 2 that we can reproduce the data reported by Pavlov [2], for $Q_{01}$. It is also clear from this figure that the $Q_{01}$ calculated using the approximate formulation (equation (6)) overestimates the energy transfer rate by as
Figure 5. Ratio of the rate determined using our recommended [9, 11] cross sections to that of previous workers, as labelled, for the 0–2 transition.

much as an order of magnitude for $T_e \geq 1000$ K. This is no moot observation as Pavlov has used the incorrect rates in later studies that attempt to interpret ionospheric behaviour [14]. We believe the error in using equation (6), instead of (2), comes from the fact that there are important non-resonant contributions [12] to the cross section in the region of the $^2\Pi_g$ resonance, so that the summation in equation (6) is an invalid approximation to the integral.

3. Results and discussion

In figure 3 we plot the present electron energy transfer rates as a function of electron temperature for the 0–1, 2, 3, 4 and $\sum_{v'=1}^{4} 0 \rightarrow v'$ vibrational excitation processes in O$_2$. It is apparent from this figure that energy transfer rates for the 0–1 and 0–2 transitions are dominant over the electron temperature range considered here. This observation is intuitively reasonable as the cross sections for the 0–1 and 0–2 excitations (see figure 1) are significantly bigger in magnitude than those of the higher order vibrational quanta. Note that all the $Q_{0v}$ shown in figure 3 were calculated using equations (2), (3) and (5), the step integral technique of Campbell et al [13] and the recommended cross section matrix of figure 1.

In the appendix, analytic expressions for each of our calculated energy transfer rates are provided. These analytic forms were derived using a standard least squares fit analysis and are given to make our calculated rates easily accessible to workers in the field. We note that several different analytic forms were used to represent the data in figure 3, including that suggested by Pavlov [2], before that chosen in the appendix was finalized. These other analytic functions did not provide as good a fit as did equation (A.1) and were discarded. When making use of equation (A.1) and the coefficients in table A.1 it is important to realize that they are only accurate for the respective $T_e$ ranges specified in table A.1.

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Figure 6. Ratio of the rate determined using our recommended [9, 11] cross sections to that of previous workers, as labelled, for the 0–3 transition.

Our results are compared to those of other researchers [2, 4, 5] for each vibrational quantum (figures 4–7). To aid this comparison we plot on the y-axis in each case the ratio of the present calculated energy transfer rate to that determined earlier by either Stubbe and Varnum [4], Prasad and Furman [5] or Pavlov [2]. In the case of Pavlov, we compare to the rate he would have calculated using the cross sections of Allan [9] and equation (2), rather than the incorrect values he reported in his paper using equation (6). Further note that, by doing this, we ensure that the present and earlier work all use equivalent formulations to calculate the energy transfer rates, the only difference in each case being the vibrational cross section matrix employed.

Considering figure 4, for the 0–1 vibrational quantum, in more detail we find poor agreement between the present results and those of Prasad and Furman [5], for a neutral temperature ($T_n$) of 500 K, effectively over the entire range of $T_e$. This result was not entirely unexpected as Prasad and Furman used the O$_2$ 0–1, 0–2 and 0–3 cross sections of Linder and Schmidt [8], which, as noted by Brunger and Buckman [10], are no longer considered to be accurate. However, the severity of the disagreement (see also figure 5 for 0–2 and figure 6 for 0–3) was something of a surprise and indicated the sensitivity of the electron energy transfer rate to the magnitude and shape of the integral cross section used. For $T_e \leq 2000$ K, the present $Q_{01}$ (this is also true for $Q_{02}$, $Q_{03}$ and $Q_{04}$—see figures 5–7) and that of Pavlov [2] are in total agreement. This was expected as both Pavlov and the present recommended cross section matrix used the data of Allan [9] for electrons with energies in the 0–3 eV range. At $T_e > 2000$ K, however, where the effect of the higher energy electrons become more important, the agreement between the present $Q_{0e}$ and those of Pavlov [2] becomes progressively worse as $T_e$ increases (see figures 4–7). This illustrates the importance of not only having an accurate cross section for the process under consideration, but also having an accurate cross section over a large enough energy range to model the physical phenomena under study. For instance, it is well known [15] that during the
day and for altitudes greater than about 240 km (i.e. the thermosphere) the electron temperature easily exceeds 2000 K.

Finally, in figure 8, we compare the present total energy transfer rate to that from Stubbe and Varnum [4] (again for a neutral temperature of 500 K), as well as those from Prasad and Furman [5] and Pavlov [2]. Note that in their formulations Stubbe and Varnum and Prasad and Furman allowed for the dependence of $Q_{0v}$ upon the neutral species temperature as well as $T_e$. However, as Pavlov [16], and we as a part of this study (not shown), demonstrated, the formulations of Stubbe and Varnum [4] and Prasad and Furman [5] and equation (2) are identical when $T_n = 500$ K. Recall that Stubbe and Varnum [4] used the swarm-derived cross sections of Hake and Phelps [6] for $v' = 0–1, 2, \ldots, 7$. Hence the $Q_T$ of Stubbe and Varnum incorporates processes ($v' = 0–5, 6, 7$) not considered in this study. However, from figure 3 it was previously seen that the rates for the higher quanta ($v' > 2$) made only small contributions to the total rate in the $T_e$ range considered. As a consequence a valid comparison can be made between the present $Q_T$ and the $Q_T$ of Stubbe and Varnum [4]. Unfortunately, the level of agreement in making this comparison is very poor for all $T_e$, the energy transfer rates of Stubbe and Varnum being much larger than the present. This lack of agreement is attributed to the inaccurate cross sections used by Stubbe and Varnum in their analysis. As expected, the $Q_T$ of Prasad and Furman [5] is also in poor agreement with the present, while that of Pavlov [2] becomes in progressively worse agreement with ours as $T_e$ increases past 2000 K.

4. Conclusions

We have reported new electron energy transfer rates for vibrational excitation in O$_2$. A comparison of these new $Q$ values to those calculated earlier [4, 5] indicated significant
Figure 8. Ratio of the total energy transfer as calculated using our recommended [9, 11] cross sections and equation (5) to that of previous workers as labelled.

discrepancies, which are likely to have important ramifications for conclusions drawn, on ionospheric behaviour, by those earlier studies. We attribute these discrepancies to the respective use by Stubbe and Varnum and Prasad and Furman of superseded cross sections. In addition, an approximate formulation to equation (2), as employed by Pavlov [2], was found to lead to severe errors in the computed electron energy transfer rates.

The present study highlights the sensitivity of electron energy transfer rates to the shape and magnitude of the integral cross sections employed in their calculations. Our work also indicates the need to use integral cross sections that cover an energy range compatible with the electron temperatures of the physical phenomena under study.

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Appendix. Analytic expression for energy transfer rates

We obtain analytic forms for the present calculated electron energy transfer rates. Least squares analytic expressions of the form

$$\log(Q_{0v}) = A_v + B_v T_e + C_v T_e^2 + D_v T_e^3 + E_v T_e^4 + F_v T_e^5 + G_v T_e^6 + H_v T_e^7 + I_v T_e^8 + J_v T_e^9$$  \hspace{1cm} (A.1)
Table A.1. Coefficients for $Q_{\nu v}$ (eV cm$^3$ s$^{-1}$).

| $v$ | $A_v$ | $B_v$ | $C_v$ | $D_v$ | $E_v$ | $F_v$ |
|-----|-------|-------|-------|-------|-------|-------|
| 1   | $4.9863 \times 10^{-31}$ | $-1.5263 \times 10^{-26}$ | $2.0026 \times 10^{-22}$ | $-1.4726 \times 10^{-18}$ | $6.6626 \times 10^{-15}$ | $-1.9183 \times 10^{-11}$ |
| 2   | $3.3506 \times 10^{-31}$ | $-1.0640 \times 10^{-26}$ | $1.4583 \times 10^{-22}$ | $-1.1299 \times 10^{-18}$ | $5.4490 \times 10^{-15}$ | $-1.6973 \times 10^{-11}$ |
| 3   | $1.4630 \times 10^{-31}$ | $-4.8912 \times 10^{-27}$ | $7.1173 \times 10^{-23}$ | $-5.9164 \times 10^{-19}$ | $3.1004 \times 10^{-15}$ | $-1.0664 \times 10^{-11}$ |
| 4   | $5.5675 \times 10^{-32}$ | $-1.9493 \times 10^{-27}$ | $2.9883 \times 10^{-23}$ | $-2.6366 \times 10^{-19}$ | $1.4810 \times 10^{-15}$ | $-5.5352 \times 10^{-12}$ |
| Total | $5.0148 \times 10^{-31}$ | $-1.5346 \times 10^{-26}$ | $2.0127 \times 10^{-22}$ | $-1.4791 \times 10^{-18}$ | $6.6865 \times 10^{-15}$ | $-1.9228 \times 10^{-11}$ |

| $v$ | $G_v$ | $H_v$ | $I_v$ | $J_v$ | $\delta_v$ (10$^{-3}$) |
|-----|-------|-------|-------|-------|----------------|
| 1   | $3.5171 \times 10^{-8}$ | $-4.0044 \times 10^{-5}$ | $0.0268$ | $-19.9282$ | $4.00$ (300 K $\leq T_e \leq 6000$ K) |
| 2   | $3.4334 \times 10^{-8}$ | $-4.4224 \times 10^{-5}$ | $0.0345$ | $-25.1660$ | $1.30$ (500 K $\leq T_e \leq 6000$ K) |
| 3   | $2.4300 \times 10^{-8}$ | $-3.6130 \times 10^{-5}$ | $0.0334$ | $-28.2785$ | $0.29$ (800 K $\leq T_e \leq 6000$ K) |
| 4   | $1.3970 \times 10^{-8}$ | $-2.3583 \times 10^{-5}$ | $0.0256$ | $-27.9360$ | $0.04$ (1100 K $\leq T_e \leq 6000$ K) |
| Total | $3.5187 \times 10^{-8}$ | $-3.9960 \times 10^{-5}$ | $0.0267$ | $-19.9171$ | $4.00$ (300 K $\leq T_e \leq 6000$ K) |
114.11

were fitted to the calculated energy transfer rates. This type of polynomial was chosen so that the fitted curve accurately represented the calculated results. The determined coefficients and maximum relative error ($\delta_v$) for each vibrational level and total $Q$ are shown in table A.1. The relative error is calculated by

$$\delta_v = \left| \frac{Q_{0v}(T_e) - f(T_e)}{Q_{0v}(T_e)} \right|, \quad (A.2)$$

where $Q_{0v}(T_e)$ is the calculated energy transfer rate at $T_e$ and $f(T_e)$ is the analytically determined energy transfer rate at $T_e$. Clearly, our fits to the calculated $Q_{0v}$ are very good (see $\delta_v$) over the specified electron temperature range.

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