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H Kawahara[1], H Kato[1], M Hoshino[1], H Tanaka[1], L Campbell[2] and M J Brunger[2]

[1] Physics Department, Sophia University, Chiyoda-ku, Tokyo 102-8554, Japan
[2] ARC Center for Antimatter-Matter Studies, SoCPES, Flinders University, GPO Box 2100, Adelaide SA 5001, Australia

Abstract
We apply the method of Kim (2007 *J. Chem. Phys.* **126** 064305) in order to derive integral cross sections for the $^1\Sigma_u^+$ and $^1\Pi_u$ states of CO$_2$, from our corresponding earlier differential cross section measurements (Green *et al* 2002 *J. Phys. B: At. Mol. Opt. Phys.* **35** 567). The energy range of this work is 20–200 eV. In addition, the BEf-scaling approach is used to calculate integral cross sections for these same states, from their respective thresholds to 5000 eV. In general, good agreement is found between the experimental integral cross sections and those calculated within the BEf-scaling paradigm, over the entire common energy range. Finally, we employ our calculated integral cross sections to determine the electron energy transfer rates for these states, for a thermal electron energy distribution. Such transfer rates are in principle important for understanding the phenomena in atmospheres where CO$_2$ is a dominant constituent, such as on Mars and Venus.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

We have been undertaking a systematic study into the utility of the BEf-scaling approach [1] to predict integral cross sections (ICSs), for electron impact excitation of dipole-allowed electronic states in molecules. Our previous studies have included electronic states in H$_2$ [1], CO [2, 3] and H$_2$O [4], with the results from that work indicating in each case that the BEf-scaling methodology is quite successful in reproducing the available experimental ICSs. Here we further extend those studies to the important $^1\Sigma_u^+$ and $^1\Pi_u$ electronic states in CO$_2$. Note that said work is important because it is the ICSs that are crucial to people attempting to model the behaviour of atmospheric and/or technological phenomena, in which such species are constituents. In particular, excitation of electronic states in molecules gives rise to the plethora of emission lines seen when, for example, observing atmospheric auroral behaviour.

To achieve our goal experimentally in CO$_2$, we have used the method of Kim [1] to derive ICSs from our previous differential cross section (DCS) measurements [5] for the $^1\Sigma_u^+$ and $^1\Pi_u$ electronic states. Further details for this approach are given later. In each case we now report the corresponding ICSs for incident electrons of 20 eV, 30 eV, 60 eV, 100 eV and 200 eV energy. From a theoretical perspective we have derived Born ICSs from the work of Buenker *et al* [6], and then applied the optical oscillator strengths from Chan *et al* [7] in order to perform the f-scaling operation [1] in the BEf-scaling methodology. Again, more details of this procedure will be given in the following section. Finally we note that as extensive details of the spectroscopy of the electronic states of CO$_2$ were given in Green *et al* [5], we do not repeat them again here.

Morrison and Greene [8] identified electron cooling by electron impact excitation of CO$_2$ as an important energy transfer process in the atmospheres of Venus and Mars. They presented electron energy loss rates (i.e. cooling rates per unit electron and molecule density) as a function of electron temperature. Their rates [8] were calculated at each temperature for relevant excitation processes by averaging

over an electron energy distribution which was assumed to be Maxwellian in form. These rates can then be multiplied by the electron and CO_2 densities to give cooling rates in an actual atmosphere, as was undertaken by Strangeway [9] in his modelling of the ionosphere of Venus. We therefore here calculate the corresponding electron energy transfer rates for the $^1\Sigma_u^+$ and $^1\Pi_u$ electronic states of CO_2.

In the following section of this paper we describe the BEf-scaling approach to calculate ICSs, as well as how the present experimental ICSs were derived from the respective $^1\Sigma_u^+$ and $^1\Pi_u$ DCSs of Green *et al* [5]. In this section, we also briefly describe how the corresponding electron energy transfer rates for these states are calculated. Thereafter, in section 3, our results and a discussion of these results are presented. Finally, some conclusions pertaining to the present study are drawn.

2. Theory and analysis details

A full description of the BEf-scaling approach for calculating integral cross sections with molecules can be found in Kim [1], so that only a cursory discussion of the more important details is given here. Note that the scaled (plane-wave) Born cross sections used in this technique are not only subject to the approximations in the collision theory part, but also depend on the accuracy of the wavefunctions used for the initial and final states of the target molecule.

The f-scaled Born cross section (σ_f) is given by

$$\sigma_f(E_0) = \frac{f_{\text{accur}}}{f_{\text{Born}}} \sigma_{\text{Born}}(E_0), \quad (1)$$

where E_0 is the incident electron energy, f_{accur} is an accurate dipole oscillator strength (f) value from accurate wavefunctions or experiments and f_{Born} is the dipole f value from the same wavefunctions used to calculate the unscaled Born cross section σ_{Born}. The f-scaling process has the effect of replacing the wavefunction used for σ_{Born} with accurate wavefunctions. We note that in the present application the accurate $^1\Sigma_u^+$ and $^1\Pi_u$ oscillator strengths from Chan *et al* [7] were used in this process.

The BE-scaled Born cross section (σ_{BE}) is given by

$$\sigma_{\text{BE}}(E_0) = \frac{E_0}{E_0 + B + E} \sigma_{\text{Born}}(E_0), \quad (2)$$

where E is the excitation energy for each electronic state and B is the binding energy of the target electron being emitted. The BE-scaling corrects the deficiency of the Born approximation at low E_0, without losing its well-known validity at high E_0.

If an unscaled σ_{Born} is obtained from poor or marginal wavefunctions while an accurate f value is known, then both f-scaling and BE-scaling can be applied to obtain a BEf-scaled Born cross section ($\sigma_{\text{BE}f}$),

$$\sigma_{\text{BE}f}(E_0) = \frac{f_{\text{accur}} E_0}{f_{\text{Born}}(E_0 + B + E)} \sigma_{\text{Born}}(E_0). \quad (3)$$

We note that it is the $\sigma_{\text{BE}f}(E_0)$ integral cross sections that we later compare against the corresponding experimental values

Table 1. A comparison between the present optical oscillator strengths and a selection of those from previous workers [6, 7, 10–13]. The error on the present OOSs is ∼30%.

	$^1\Sigma_u^+$	$^1\Pi_u$
Experiment		
Present work	0.147	0.057
Chan *et al* [7]	0.171	0.060
Klump and Lassettre [10]	0.119	0.045
Inn *et al* [11]	0.120	–
Theory		
Buenker *et al* [6]	0.085	0.048
McCurdy and McKoy [12]	0.116	0.168
Padial *et al* [13]	0.046	0.030

derived from the DCS measurements of Green *et al* [5] and also from Klump and Lassettre [10].

The numerical uncertainty in the plane-wave Born cross sections would be <1%, however the final uncertainty on our BEf-scaled results will be largely determined by the accuracy of the optical oscillator strength used in the f-scaling process. Such an uncertainty would typically be in the range 5–10% [7].

Finally, we note that in the present calculations we chose the theoretical work of Buenker *et al* [6] to generate the unscaled Born cross sections. While their optical oscillator strength values do not agree with those from the accurate dipole (e, e′) experiment of Chan *et al* [7] (see table 1), the BEf-scaled Born cross sections [$\sigma_{\text{BE}f}(E_0)$] in principle correct for this.

The values of [θ, DCS(θ)] from Green *et al* [5], for each electronic state at each incident electron energy of their study, are transformed to (K^2, G_{expt}) using the standard formula [1]

$$G_{\text{expt}}(K^2) = \frac{(E/R)k_i a_0}{4a_0^2 k_f a_0} K^2 \text{DCS}(E_0, \theta), \quad (4)$$

where k_i and k_f are the initial and final momenta of the incident electron, a_0 is the Bohr radius (0.529 Å), R is the Rydberg energy (13.6 eV), θ is the electron scattering angle, $G_{\text{expt}}(K^2)$ is the experimental generalized oscillator strength and K^2 is the momentum transfer squared defined by

$$K^2 = (k_i a_0)^2 + (k_f a_0)^2 - 2(k_i a_0)(k_f a_0)\cos\theta. \quad (5)$$

Vriens [14] proposed the following formula to represent the generalized oscillator strength for a dipole-allowed excitation, based on the analytic properties identified by Lassettre [15] and Rau and Fano [16]:

$$G(x) = \frac{1}{(1+x)^6}\left[\sum_{m=0}^{\infty} \frac{f_m x^m}{(1+x)^m}\right], \quad (6)$$

where,

$$x = \frac{K^2}{\alpha^2} \quad (7)$$

and

$$\alpha = \sqrt{B/R} + \sqrt{(B-E)/R}. \quad (8)$$

In equation (6), f_m are fitting constants to be determined in a least-squares fit analysis of the experimental generalized oscillator strengths, which we reiterate are determined from

the DCSs of Green *et al* [5] in this study. The beauty of Vriens' [14] formalism is that at the $x = 0$ optical limit, the value of $G(0) \equiv f_0$ is the optical oscillator strength (OOS). The present OOSs, as derived from an analysis of the 100 eV and 200 eV data of Green *et al* [5], are given in table 1. Also listed in table 1 are the OOSs for the $^1\Sigma_u^+$ and $^1\Pi_u$ electronic states from previous measurements [7, 10, 11] and calculations [6, 12, 13].

Finally, estimates of the ICS(σ) at each energy can be obtained from equations (6)–(8) using the standard formulae [17]

$$\sigma(E_0) = \frac{4\pi a_0^2}{E_0/R} \int_{K_{min}^2}^{K_{max}^2} \frac{G(K^2)}{E/R} \, d\ln(K^2), \qquad (9)$$

with

$$K_{min}^2 = 2\frac{E_0}{R}[1 - E/2E_0 - \sqrt{1 - E/E_0}] \qquad (10)$$

and

$$K_{max}^2 = 2\frac{E_0}{R}[1 - E/2E_0 + \sqrt{1 - E/E_0}]. \qquad (11)$$

Electron energy transfer rates ($Q_{0\times}$), these being the energy transferred in one second per unit electron and molecule density, for electronic excitations of $CO_2(0 \rightarrow \times)$ for $\times = ^1\Sigma_u^+$ and $^1\Pi_u$ were calculated using the formulation of Pavlov [18],

$$Q_{0\times} = E_\times \{8kT_e(\pi m_e)^{-1}\}^{1/2} \int_0^\infty \sigma_{0\times}(y)y \exp(-y) \, dy, \quad (12)$$

where $E_\times$ is the energy of the electronic state being excited, $y = E/kT_e$, E is the energy of the electron, k is Boltzmann's constant, T_e is the electron temperature, $\sigma_{0\times}$ is the integral cross section for electronic-state excitation of the relevant neutral species and m_e is the mass of the electron. Full details of how $Q_{0\times}$ is evaluated, including our numerical procedure for evaluating the integral in equation (12), can be found in Campbell *et al* [19] and Jones *et al* [20]. Here we simply note that the values of $\sigma_{0\times}$ used for the $^1\Sigma_u^+$ and $^1\Pi_u$ electronic states' transfer rates were taken from the respective results of our BEf-scaling calculation.

3. Results and discussion

In table 1 we compare the present OOSs against those from other measurements and calculations. It is apparent from this table that the current $^1\Sigma_u^+$ and $^1\Pi_u$ OOSs are in very good agreement with the corresponding values from Chan *et al* [7]. This is particularly the case when the experimental uncertainties ($\sim$30%) on our respective OOSs are taken into account. We therefore believe that the current results confirm the earlier values of Chan *et al*, which were made to a higher precision than the present. Agreement between the present OOSs, and therefore also those from Chan *et al*, with the available theoretical determinations is not as satisfactory, indicating that none of those calculations used $^1\Sigma_u^+$, $^1\Pi_u$ and ground electronic state wavefunctions that provided an adequate physical representation for those states.

The present $^1\Sigma_u^+$ and $^1\Pi_u$ integral cross sections, both experimental and from our BEf-scaling calculations, are respectively plotted in figures 1 and 2 and listed in tables 2
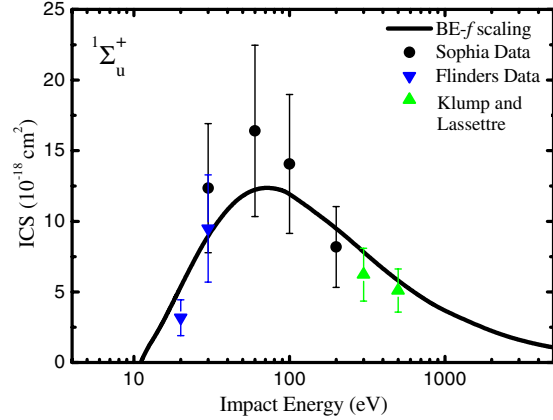

Figure 1. Integral cross sections for electron impact on the $^1\Sigma_u^+$ state of CO_2 by BEf-scaling (——), present Sophia measurements (●), present Flinders measurements (▼) and measurements of Klump and Lassettre [10] (▲).

Figure 2. Integral cross sections for electron impact on the $^1\Pi_u$ state of CO_2 by BEf-scaling (——), present Sophia measurements (●), present Flinders measurements (▼) and measurements of Klump and Lassettre [10] (▲).
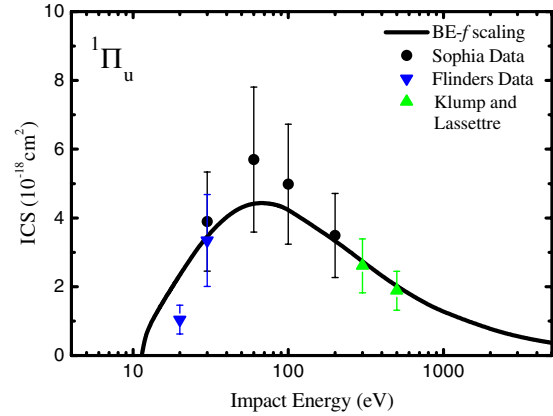
and 3. Also plotted on figures 1 and 2 are the ICSs derived by us from the measurements of Klump and Lassettre [10]. As the DCS data in Green *et al* [5] were compiled from independent measurements made at Sophia University and Flinders University, our $^1\Sigma_u^+$ and $^1\Pi_u$ ICSs are also tabulated and plotted in this way to reflect their independent determinations. Note that the estimated uncertainties on the present Sophia University ICSs are 35% at 100 eV and 200 eV and 37% at 30 eV and 60 eV, while the corresponding uncertainties on the current 20 eV and 30 eV ICSs from Flinders University are $\sim$40%. Further note that we estimate the uncertainties on the ICSs we have derived from the generalized oscillator strength data of Klump and Lassettre are of the order of 30%. All these uncertainties apply for both the $^1\Sigma_u^+$ and $^1\Pi_u$ electronic states. It is clear from figures 1 and 2 that for both these states the present experimental ICSs, and those from Klump and Lassettre [10], are largely consistent (except at 20 eV for the $^1\Pi_u$ state which is a little lower in magnitude) to within their stated uncertainties with our

Table 2. Present integral cross sections (10^{-18} cm^2) for electron impact excitation of the $^1\Sigma_u^+$ state in CO$_2$. Data from Sophia (S) and Flinders (F) Universities are shown. Also given are the present BEf-scaling results and ICSs derived from the measurements of Klump and Lassettre [10]. Numbers in parentheses are the absolute uncertainties on the ICSs.

	Present ICS (10^{-18} cm^2)			
E_0 (eV)	BEf	S	F	Klump and Lassettre [10]
11.048	0	–	–	–
12	0.877	–	–	–
13	1.484	–	–	–
14	2.081	–	–	–
15	2.673	–	–	–
16	3.254	–	–	–
17	3.818	–	–	–
18	4.362	–	–	–
19	4.883	–	–	–
20	5.379	–	3.175 (1.270)	–
25	7.483	–	–	–
30	9.026	12.352 (4.570)	9.490 (3.796)	–
40	10.926	–	–	–
50	11.863	–	–	–
60	12.275	16.398 (6.067)	–	–
70	12.393	–	–	–
80	12.342	–	–	–
90	12.193	–	–	–
100	11.977	14.058 (4.920)	–	–
200	9.555	8.177 (2.862)	–	–
300	7.824	–	–	6.221 (1.866)
400	6.647	–	–	–
500	5.800	–	–	5.097 (1.529)
600	5.161	–	–	–
700	4.660	–	–	–
800	4.256	–	–	–
1000	3.643	–	–	–
2000	2.186	–	–	–
3000	1.598	–	–	–
4000	1.273	–	–	–
5000	1.064	–	–	–

BEf-scaling result. In addition, the independent Flinders and Sophia $^1\Sigma_u^+$ and $^1\Pi_u$ ICSs, at 30 eV incident electron energy, are seen to be in very good agreement. This latter result gives us added confidence in the validity of the experiments, and hence the theory, presented in figures 1 and 2. As a consequence we believe, at least to first order, the BEf-scaling results listed in tables 2 and 3, from threshold to 5000 eV, provide the modelling community with ICSs that they can reliably use in their simulations of relevant phenomena.

To illustrate the efficacy of the BEf-scaling ICSs for modelling purposes, in figure 3 we plot our calculated electron energy transfer rates, as a function of electron temperature, for both the $^1\Sigma_u^+$ and $^1\Pi_u$ electronic states. Also plotted in figure 3 are the transfer rates from Morrison and Greene [8] for the sum of all the vibrational channels, and the sum of all the electronic states. It is clear from figure 3 that the present $^1\Sigma_u^+$ and $^1\Pi_u$ energy transfer rates are consistent with the major conclusion of Morrison and Greene. Namely, that for a Maxwellian distribution of electron energies it is vibrational excitation that will dominate the energy cooling processes in CO$_2$. Note that this does not mean the electronic-state ICSs can be ignored in predicting atmospheric behaviour in general. This follows as there are many environments in which the electron energy distribution is very non-Maxwellian
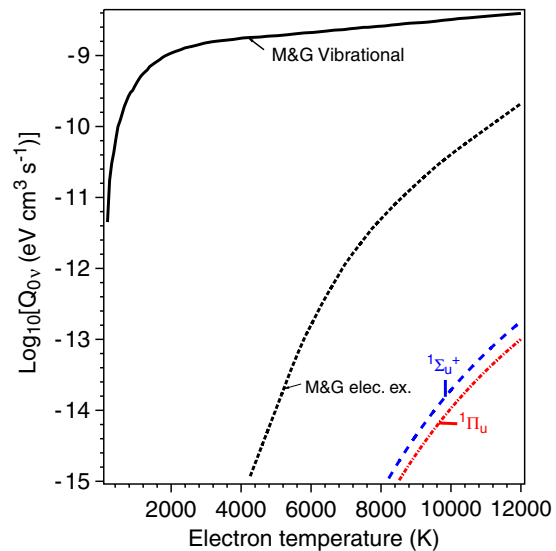

Figure 3. Electron energy transfer rates for electron impact on CO$_2$ calculated by Morrison and Greene [8] for the sums of vibrational modes (——) and electronic states (- - -) and as calculated using the BEf-scaling ICSs for the $^1\Sigma_u^+$ (– – –) and $^1\Pi_u$ (- · - · -) states.

Table 3. Present integral cross sections (10^{-18} cm^2) for electron impact excitation of the $^1\Pi_u$ state in CO_2. Data from Sophia (S) and Flinders (F) Universities are shown. Also given are the present BEf-scaling results and ICSs derived from the measurements of Klump and Lassettre [10]. Numbers in parentheses are the absolute uncertainties on the ICSs.

	Present ICS (10^{-18} cm^2)			
E_0 (eV)	BEf	S	F	Klump and Lassettre [10]
11.385	0	–	–	–
12	0.580	–	–	–
13	0.939	–	–	–
14	1.204	–	–	–
15	1.432	–	–	–
16	1.640	–	–	–
17	1.834	–	–	–
18	2.014	–	–	–
19	2.184	–	–	–
20	2.344	–	1.043 (0.417)	–
25	3.007	–	–	–
30	3.483	3.892 (1.440)	3.345 (1.338)	–
40	4.056	–	–	–
50	4.324	–	–	–
60	4.428	5.696 (2.107)	–	–
70	4.440	–	–	–
80	4.401	–	–	–
90	4.333	–	–	–
100	4.245	4.982 (1.744)	–	–
200	3.349	3.493 (1.223)	–	–
300	2.732	–	–	2.608 (0.522)
400	2.317	–	–	–
500	2.019	–	–	1.883 (0.377)
600	1.795	–	–	–
700	1.619	–	–	–
800	1.478	–	–	–
1000	1.264	–	–	–
2000	0.757	–	–	–
3000	0.553	–	–	–
4000	0.440	–	–	–
5000	0.368	–	–	–

[21], such as with aurora, so that a quantitative prediction of the observed emission spectra fundamentally requires a knowledge of the electronic state ICSs. Hence on Venus and Mars, where CO_2 is the predominant species, predicting the observed emission spectra requires the availability of ICSs such as we have reported here.

Unfortunately, Morrison and Greene [8] did not report individual electronic state transfer rates. Hence a direct comparison between our results and theirs (which represents a summed rate over all the open electronic channels) is not possible. Nonetheless the present transfer rates (see figure 3) are not inconsistent with the results from Morrison and Greene.

4. Conclusions

We have reported experimental and BEf-scaling calculated integral cross sections, for electron impact excitation of the $^1\Sigma_u^+$ and $^1\Pi_u$ electronic states in CO_2. In general, good agreement was found between the measured and calculated ICSs for both states. Electron energy transfer rates using BEf-scaling results were also calculated as a function of electron temperature. The present energy transfer rates support the view of Morrison and Greene [8] that for a thermal energy

distribution it is vibrational excitation processes that will most efficiently cool electrons in a CO_2 atmosphere.

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