Electron Collisions with Small Molecules

B. M. McLaughlin, C. P. Ballance, D. G. Thompson, K. A. Berrington, and P. G. Burke

Department of Applied Mathematics & Theoretical Physics

The Queen's University of Belfast, Belfast BT7 1NN, UK

1 Introduction

Ab initio methods in electron collisions with molecules provide accurate data for use in the modelling of many astrophysical phenomena. Molecules are found in shock waves, dense interstellar clouds, circumstellar outflows, supernova remnants and accretion disks. Molecular species such a water, hydrogen, oxygen, and carbon monoxide and triatomic hydrogen ions are of interest at temperatures below 4000 K. Developments in techniques using R-matrix methodology [1] by the UK group over many years, based around the ALCHEMY [2] and more recently the SWEDEN-MOLECULE [3] quantum chemistry programs are providing information on a variety of systems [4]. Species such as molecular oxygen and nitrogen and their ions are of great interest in understanding the ionospheric and auroral phenomena and in many gaseous discharges. A vast amount of R-matrix work has been done on the molecular oxygen complex, providing electronic and vibrational excitation cross sections together with dissociation [4]. Hydrocarbons and many impurities such as water and carbon monoxide are of interest in tokamak plasmas. Many of the sought after observables, cross sections and rates, for electronic and vibrationally elastic and inelastic processes are of great importance for applications.

2 Diatomics

Electron and photon collisions with nitrogen molecules are of fundamental interest in understanding ionospheric and auroral phenomena in the Earth's upper atmosphere, in the modelling of re-entry flow fields around high velocity projectiles and in many gaseous discharge processes. Quite a number of calculations have been reported on electronically elastic, low energy, electron collisions with N_2 molecules but there are relatively fewer studies in which the target is itself excited [5, 6, 8]. Although, experiments exist they are frequently limited in scope, in energy range and in the range of angles for which differential cross sections are reported. Recently, R-matrix theoretical studies on e$^-$ - N_2 collisions [7] have been extended to study electronic excitation of the target, with a comparison of the integrated and differential cross sections being made with the available experimental data [8]. Extensive calculations of angular distributions in e$^-$ - N_2 collisions were then performed to provide a comprehensive set of differential cross section data on several low lying optically forbidden transitions, from each of their thresholds to 17 eV [9].

The applications of cross sections and rates obtained from ab initio studies on electron impact excitation of CH molecules are multi-fold. CH molecules are of particular interest due to recent speculation of their presence in the Red Rectangle nebula at wavelengths longer than 3000 Å[10]. The use of carbon fibre composites as a plasma facing material give rise to a range of C_nH_n ($n \geq 1$) hydrocarbon impurities in tokamak plasmas and molecular constituents such as BeD, CD, H_2O and CO are additional species of interest. Therefore electronic and vibronic excitation

of the CH molecule by electrons are of fundamental importance in fusion plasmas edges and for astrophysical applications. Furthermore, the excited Rydberg states of the CH molecule are thought to play a vital role in the dissociative recombination process, that occurs in interstellar shocks and diffuse molecular clouds. The chemistry of the interstellar medium is influenced by hydrocarbon molecules and their cyclic partners which are important constituents that play an active role in the astrochemistry. Cross section calculations for electronic excitation were performed on the e^- - CH complex, for a range of low electron impact energies, using the R-matrix technique. The X $^2\Pi$ ground state and the lowest four valence excited states (A $^2\Delta$, B $^2\Sigma^-$, C $^2\Sigma^+$ and a $^4\Sigma^-$), of CH are included in the close coupling expansion with each state being represented by a multi-configuration interaction wave function. Cross section calculations for electronic excitation of the CH molecule by electron impact were then made for the, A $^2\Delta$ - X $^2\Pi$, B $^2\Sigma^-$ - X $^2\Pi$ and C $^2\Sigma^+$ - X $^2\Pi$ transitions. A Morse potential was fitted to the ab initio values and the adiabatic approximation invoked to determine the vibronic excitation cross sections for the X-A transition in both the CH and CD molecules [11, 12].
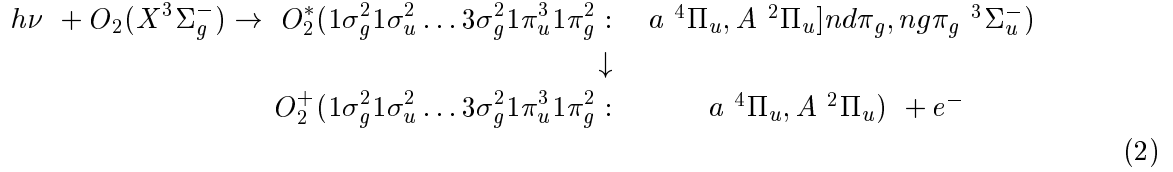
For R-matrix studies on the molecular nitrogen cation the lowest three electronic target states; $X\ ^2\Sigma_g^+$: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g 1\pi_u^4$, $A\ ^2\Pi_u$: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3$ and the $B\ ^2\Sigma_u^+$: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u 3\sigma_g^2 1\pi_u^4$, were included in the close coupling expansion of the inner region wave-function with each state represented by the valence CI model. The N_2^+ molecular cation belongs to the $D_{\infty h}$ Abelian point group, so the Slater basis from the work of Ermler and co-workers [13] is a natural choice to use to represent the target states. Initially an SCF calculation was performed on the ground state of N_2^+. In order to provide a suitable representation of the excited states of the molecular cation at the equilibrium separation, this was extended to a valence CI and an elaborate CI model. Closed channel bound state calculations were performed for several symmetries of the neutral nitrogen molecule within both approximations. In Table 2, the Rydberg bound state results for the N_2 molecule close to equilibrium separation for the $^{1,3}\Sigma_g^+$ symmetries in both approximations are given. Electronic excitation cross sections for the X-A and X-B states of the N_2^+ cation were investigated and vibronic excitation calculated for the same transitions in both the adiabatic and non-adiabatic approximations [14].

In our R-matrix work on the molecular oxygen cation, the lowest five electronic target states; $X\ ^2\Pi_g$, $a\ ^4\Pi_u$, $A\ ^2\Pi_u$, $b\ ^4\Sigma_u^-$ and the $B\ ^2\Sigma_u^-$ were included in the close coupling expansion with each target state represented by the valence CI model. There has been recent photon impact experimental studies on the oxygen molecule [15] and many of the resonant characteristics evident in the corresponding photoabsorption cross sections may be identified from electron scattering by the molecular oxygen cation. The possible channels open within our five-state valence CI model would therefore feature the following;

$$h\nu + O_2 \quad \rightarrow \quad O_2^{**} \quad \rightarrow \quad O_2^+(X\ ^2\Pi_g, a\ ^4\Pi_u, A\ ^2\Pi_u, b\ ^4\Sigma_g^-, B\ ^2\Sigma_g^-) + e^-. \tag{1}$$
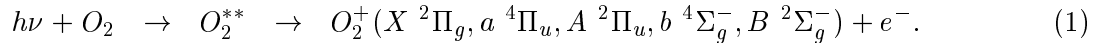
We note that the lowest five states of the molecular cation are denoted by; $X\ ^2\Pi_g$, $A\ ^4\Pi_u$, $a\ ^2\Pi_u$, $b\ ^4\Sigma_g^-$ and $B\ ^2\Sigma_g^-$. In the SCF representation these are; $X\ ^2\Pi_g$: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g$, $a\ ^4\Pi_u$ and $A\ ^2\Pi_u$: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 1\pi_g^2$, $b\ ^4\Sigma_g^-$ and $B\ ^2\Sigma_g^-$: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 1\pi_u^4 1\pi_g^2$. In order to improve upon the SCF representation of the target states one has either to use, the valence CI, an elaborate CI, the MCSCF approach or a combination of them. In order to highlight the resonant features we have chosen the $^3\Sigma_u^-$ scattering symmetry. Table 3 gives a comparison of our 5-state VCI results for the $nd\pi_g$ resonances in the $^3\Sigma_u^-$ scattering symmetry with recent 3-state VCI work [17]. The $nd\pi_g$ resonances in this scattering symmetry represent a transitory state of a Rydberg electron interacting with the O_2^+ core on the fringes of the molecular charge cloud. This activity manifests itself in the form of Rydberg resonance series in the $^3\Sigma_u^-$ symmetry denoted by $nd\pi_g$ and

$ng\pi_g$ which approach the a $^4\Pi_u$ and A $^2\Pi_u$ thresholds of the molecular oxygen cation. In this half collision process for the $^3\Sigma_u^-$ scattering symmetry, we note that the following resonant processes may occur;

$$h\nu + O_2(X^3\Sigma_g^-) \rightarrow O_2^*(1\sigma_g^2 1\sigma_u^2 \ldots 3\sigma_g^2 1\pi_u^3 1\pi_g^2 : \quad a\ ^4\Pi_u, A\ ^2\Pi_u]nd\pi_g, ng\pi_g\ ^3\Sigma_u^-)$$
$$\downarrow$$
$$O_2^+(1\sigma_g^2 1\sigma_u^2 \ldots 3\sigma_g^2 1\pi_u^3 1\pi_g^2 : \qquad a\ ^4\Pi_u, A\ ^2\Pi_u)\ + e^-$$

$$(2)$$

As noted by Noble [17] the $ng\pi_g$ resonances are three orders of magnitude narrower than those of the corresponding $nd\pi_g$ series. The lower members of the $nd\pi_g$ series are sufficiently broad and isolated that the resonance parameters may be obtained by fitting the eigenphase sum. Higher members of the $nd\pi_g$ series become narrow and so reliable results require the use of the complex energy technique or variant theories that calculate the parameters directly. For the $^3\Pi_u$ scattering symmetry there is more elaborate resonance structure, due to the target states being able to couple to both σ and δ continuum. Rydberg series of the form $ns\sigma$, $nd\sigma$, $ns\delta$ and $nd\delta$ will therefore be associated with the respective $a^4\Pi_u$ and $A^2\Pi_u$ thresholds of the molecular oxygen cation.

3   Polyatomics

Electron collisions with polyatomic systems within the R-matrix methodology [4] is currently being undertaken as a part of a UK wide collaborative project based around the SWEDEN-MOLECULE Gaussian code [3]. Integral and differential cross sections results have been performed on N_2O [18] at the static-exchange plus polarization (SEP) level and compared with experiment and previous theoretical work [19]. Presently the UK group are working on several systems such as; H_2O, O_3, CO_2, CH_4 and CH_2. Table 1 gives the SCF energies of the lowest $^1A_1$ state for the three polyatomic systems; CH_2, CH_4 and H_2O obtained using the SWEDEN-MOLECULE code with their respective contracted Gaussian type orbital (CGTO) basis. Detailed scattering results for these and several other systems will be forthcoming in the near future.

Table 1: Electronic energies of the polyatomic molecular systems; CH_2, CH_4 and H_2O at the SCF level in the Abelian point group C_{2v} from the SWEDEN-MOLECULE Gaussian code. The bond angle Θ and the bond distance r are given in their appropriate units.

CGTO Basis	Species	E_{SCF} (a_0)	r (a_0)	r ($\mathring{A}$)	Θ (Deg)	Molecular State
$[4s\ 2p\ 1d/2s\ 1p]$	CH_2	-38.8677980686	2.110	1.11656	102.4^o	$1a_1^2 2a_1^2 1b_2^2 3a_1^2\ ^1A_1$
$[8s\ 5p\ 2d/5s\ 2p]$	CH_4	-40.2148093594	2.066	1.09328	109.47^o	$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2\ ^1A_1$
$[5s\ 3p\ 2d/2s\ 1p]$	H_2O	-76.0440308704	1.800	0.95252	105.0^o	$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_2^2\ ^1A_1$

4   Acknowledgments

Table 2: The lowest ten $^1\Sigma_g^+$ states of the N_2 molecule at the fixed internuclear distance of 2.1 a_0 from the basic valence and the extended CI scattering models. All energies are given in Hartrees. The effective quantum numbers and defects, respectively ν and μ of these states are presented for both scattering approximations.

	VALENCE – CI (VCI)			EXTENDED – CI (EX-CI)		
State	Energy (Ry)	ν	μ	Energy (Ry)	ν	μ
X $^1\Sigma_g^+$	-109.083784	0.950793	0.049207	-109.087911	0.949250	0.050750
2	-108.644130	2.099451	-0.099451	-108.648555	2.080286	-0.080286
3	-108.589836	2.907556	0.092444	-108.592441	2.900719	0.099281
4	-108.582016	3.121228	-0.121228	-108.584833	3.106394	-0.106394
5	-108.570430	3.547164	0.452836	-108.570982	3.629105	0.370895
6	-108.563275	3.917315	0.082685	-108.565722	3.910057	0.089943
7	-108.559335	4.178071	-0.178071	-108.561758	4.170959	-0.170959
8	-108.551443	4.908630	0.091370	-108.553849	4.899187	0.100813
9	-108.550750	4.992768	0.007232	-108.553073	4.993064	0.006936
10	-108.549396	5.170251	-0.170251	-108.551823	5.156397	-0.156397

Table 3: The $nd\pi_g$ resonance positions (ϵ_r) and autoionization widths (,) for $e^- - O_2^+$ scattering in the $^3\Sigma_u^-$ symmetry at the fixed bond length of 2.30 a_0. The effective quantum number ν, the real and imaginary parts, α and β respectively of the complex quantum defect $\mu = \alpha + i\beta$ for several members of the $nd\pi_g$ series are included for completeness. The $nd\pi_g$ resonance parameters from our work for the $^3\Sigma_u^-$ symmetry were obtained by fitting the eigenphase sum of the 5-state valence configuration interaction (VCI) scattering model to a Breit-Wigner form. The 3-state valence CI results obtained using a similar approach for the molecular oxygen Rydberg resonance states; O_2 $(1\sigma_g^2 1\sigma_u^2 \ldots (a^4\Pi_u) nd\pi_g\ ^3\Sigma_u^-)$ are included for comparison purposes.

Resonance	ϵ_r^a (Ry)	ϵ_r^b (Ry)	Γ^a (Ry)	Γ^b (Ry)	ν	$Re(\mu)$	β	$\Gamma^b\nu^3$
$3d\pi_g$	0.2151	0.2103	0.1060(-2)	0.1085(-2)	3.0088	0.0088	0.7390(-2)	0.029
$4d\pi_g$	0.2610	0.2583	0.4270(-3)	0.2102(-3)	4.0019	0.0019	0.3367(-2)	0.048
$5d\pi_g$	0.2822	0.2796	0.1990(-3)	0.2185(-3)	4.9264	0.0736	0.6531(-2)	0.026
$6d\pi_g$	0.2937	0.2918	0.0822(-3)	0.1172(-3)	5.8724	0.1736	0.3811(-2)	0.015
$7d\pi_g$	–	0.2998	–	0.1414(-3)	6.9176	0.0824	0.1170(-1)	0.039
$8d\pi_g$	–	0.3047	–	0.7934(-4)	7.8934	0.1066	0.9756(-2)	0.037
$9d\pi_g$	–	0.3081	–	0.5237(-4)	8.8840	0.1160	0.9182(-2)	0.036
$10d\pi_g$	–	0.3105	–	0.3688(-4)	9.8778	0.1222	0.8883(-2)	0.035
$11d\pi_g$	–	0.3123	–	0.2704(-4)	10.8744	0.1256	0.8667(-2)	0.034
$12d\pi_g$	–	0.3137	–	0.2044(-4)	11.8717	0.1283	0.8551(-2)	0.034

[a] 3-state valence CI
[b] 5-state valence CI

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