R-matrix calculations of electron molecule collision data

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Abstract

Results for R-matrix calculations performed during the Coordinated Research Project (CRP) on Atomic and Molecular Data for Plasma Modelling are discussed. Electron collision problems studied include collisions with various carbon containing molecules including C_2, HCCH, CH_4, C_2H_6 and C_3H_8.

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1. Introduction

The R-matrix method provides a powerful and flexible method of calculating cross-sections and rates for a variety of electron collision processes. Although there are a number of numerical implementations of the method for electron- molecule collisions, the UK molecular R-matrix codes [1, 2] provide the most general and flexible implementation available, particularly in the polyatomic version of the code which is designed to work with Gaussian Type Orbitals (GTOs) [3]. An expert system, Quantemol-N, has recently been developed for running which greatly simplifies the running of the polyatomic version of the codes [4].

2. The R-matrix Method

The basic step in the R-matrix method is the division of configuration space into two regions [5]. A sphere centred at the molecular centre of mass is used define the inner region. For the method to be successful this sphere must contain the electronic wave function of the entire N-electron target; for small molecules sphere of radius of about 10 a_0 is usually sufficient although radii significantly larger than this have been used on occasion [6, 7].

In this inner region, the wave function of the $(N + 1)$-electron system (target plus scattering electron) is given by:

$$\Psi_k = \mathcal{A}\sum_{i,j} a_{i,j,k}\Phi_i(1,\ldots,N)F_{i,j}(N+1) + \sum_i b_{i,k}\chi_i(1,\ldots,N+1) \quad (1)$$

where $\mathcal{A}$ is the antisymmetrization operator, $F_{i,j}$ are continuum orbitals and χ_ι are two centre L^2 functions constructed from N-electron target orbitals.

In Eq. (1), Φ_i is the wave function of the i^{th} target state. Electron-correlation effects can be included efficiently in these target wave functions via configuration interaction (CI) expansions [8]. It is the choice of this CI expansion which largely determines which L^2 functions are included in the wave function; the standard choice is to use a complete active space valence CI ie to freeze the core electrons and to allow the valence electrons to move freely within both the occupied and valence orbitals [9].

The inclusion of polarization effects in low energy electron-molecule collision calculations, even when close-coupling expansions such as Eq. (1) are employed, presents a difficult problem [10]. Recently Gorfinkiel and Tennyson developed a molecular R-matrix with pseudostates (MRMPS) method [11, 12] which uses large numbers of states in the close-coupling expansion, many of which are not true physical states of the system. This procedure was originally designed to treat electron impact ionization, a process surprisingly well described by cruder semi-empirical methods [13]. The MRMPS method is indeed successful at giving near threshold ionization cross-sections [14], but is probably of greater use in fully converging polarization potentials [7, 15].

3. Results

3.1. *Carbon dimer*

Carbon dimers, the C_2 molecule, can easily form in fusion plasmas that use graphite walls. Indeed C_2 electronic emission spectra have been monitored as part of the ASDEX experiments [16, 17] using the Swan band. The Swan band involves emissions from the d $^3\Pi_u$ state to the a $^3\Pi_u$ state, which is a very low lying excited state of the system. Given that these are triplet states and the ground state of C_2 is of $^1\Sigma^+$ symmetry the most likely excitation route is via electron collisions.

Halmova et al. [18] used the R-matrix method to study a variety of processes involving low energy collisions with C_2. As part of their study, Halmova et al. calculated a comprehensive set of potential energy curves for C_2 which not only formed important input to their R-matrix electron scattering calculations but also can be used for interpreting or simulating electron spectra of C_2. I therefore note that subsequent to this work a comprehensive set of potential energy curves C_2 have been computed as part of detailed new studies of the electronic spectrum of C_2 [19, 20].

Halmova et al.'s electron impact excitation cross-sections are summarized in Fig. 1 which, in particular, details separately excitation to the d $^3\Pi_u$ state from both the ground state and the low lying metastable state. Neither of these cross-sections are particularly big although excitation from the metastable state actually gives a significantly larger cross-section. The reader is referred to the original paper for further details.

It is worth noting that Halmova et al. used their study on electron collisions with C_2 as the starting point for a series of calculations on electron collisions with C_2^- with special emphasis on the electron impact electron detachment cross-section [14, 15]. These studies, which used the MRMPS method discussed above, successfully reproduced the rather unexpected resonance structure observed in this process [21] and the total cross-section. They demonstrated that, while the resonances were essentially short range in nature, the remainder of the cross-section could be calculated using a Born model which considered simply the dipole coupling between the target anion and the continuum (or their case the pseudo-continuum).

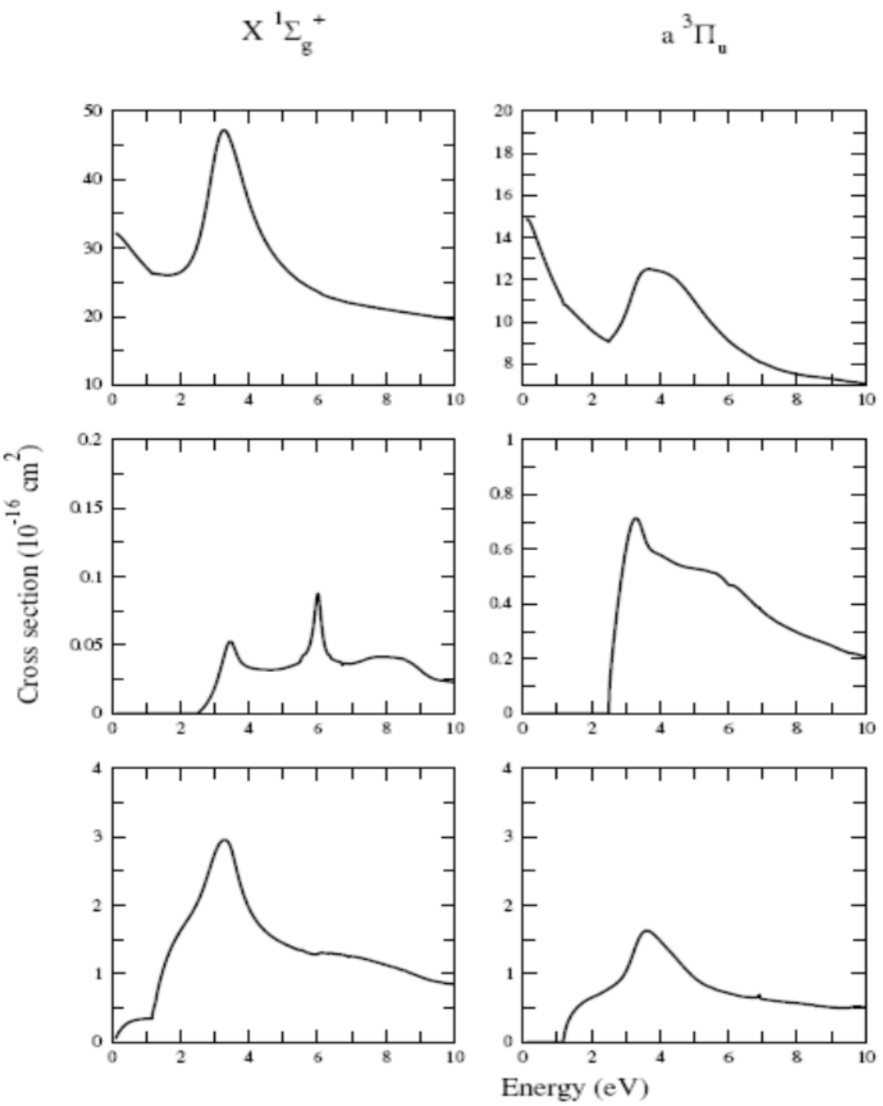

FIG. 1. Electron impact cross-sections for the C_2 molecule at its equilibrium geometry as calculated by Halmova et al. [18]. The left hand panels are for molecules starting in the $X^1\Sigma_g^+$ ground state and the right hand panels are for molecules starting in the low lying $a^3\Pi_u$ metastable state. The top row is the total cross-section as a function of energy. The second row is for excitation to the $d^3\Pi_u$ state and the lower panels are for excitation to all other states.

3.2. Hydrocarbons

Hydrocarbons are considered to be an important contaminant in fusion plasmas [25, 26]. Electron collisions with hydrocarbons have been extensively studied experimentally by Tanaka and co-workers [23, 27], as discussed elsewhere in this volume, and others [10, 24, 28, 29].

My group has undertaken a number of electron collision studies with hydrocarbon species including acetylene [30] and the alkanes methane, ethane and propane [22]. Cross-sections for electron collisions with these systems are given in the cited papers where comparisons with measurements and other theoretical studies can also be found.

Figure 2 gives differential cross-sections for electron collisions with methane at 5 eV. This figure compares the R-matrix calculations of Varambhia et al. [22] with measurements due to Tanaka et al. [23] and Sohn et al. [24]; the agreement is good. I note that there are other experimental [29] and theoretical [28, 29] studies of this process and comparisons with these generally give a similar level of agreement.

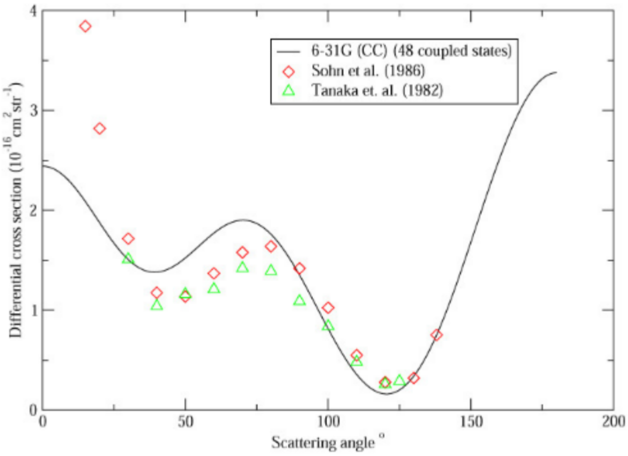

FIG. 2. Differential cross-sections for electron collisions with methane at 5 eV: results of an R-matrix study with 48 coupled states [22] are compared with the measurements of Tanaka et al. [23] and Sohn et al. [24].

Varambhia et al. [22] found that by including a significant number of coupled states in their CC expansion they were able to get good results for electron–methane cross-section, including correctly reproducing the Ramsauer minimum in the elastic scattering channel. However, their results are less satisfactory for the higher alkanes as it proved harder to completely include polarization effects in these systems. It would seem likely that it will be necessary to use the MRMPS method to get completely satisfactory results for these systems. However, MRMPS calculations are very computationally demanding; at the moment, the largest MRMPS calculation is the one for C_2 discussed above. New MRMPS calculations for small hydrocarbons are now underway in my group; such calculations should be extendable to the alkanes in the near future.

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