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LETTER TO THE EDITOR

Rotational and polarisation effects in low-energy positron–CO collisions using the *R*-matrix method

Jonathan Tennyson† and Lesley Morgan‡

† Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK
‡ Computer Centre, Royal Holloway and Bedford New College, Egham, Surrey TW20 0EX, UK

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Abstract. *R*-matrix calculations are presented for elastic and rotationally inelastic scattering of positrons from CO at energies below the positronium formation threshold. The calculations are performed within a number of models that represent charge polarisation effects, the rotational motion of the target and the asymptotic potential. The computed total and momentum transfer cross sections are found to vary widely between the different models employed. A comparison is made between the experimental results for this system and the recent calculations of Jain.

In a recent paper (Tennyson 1986, hereafter referred to as I) *ab initio* calculations were reported on the scattering of low-energy positrons from H_2 and N_2 targets. These calculations employed an adaptation of the molecular *R*-matrix method which has been successfully applied to a number of electron scattering problems (e.g., see Salvini *et al* 1984, Morgan 1986, Burke and Noble 1986, Gillan *et al* 1987). In I the calculations on e^+–H_2 collisions were compared with those of Armour (1985) and good agreement was found at a number of levels of approximation. Furthermore, the computed e^+–N_2 cross sections were found to be in agreement with the experimental results below the positronium formation threshold, except at the lowest energies. This latter failing can be attributed to the lack of long-range polarisation in the calculations reported in I. Subsequent work (Tennyson and Danby 1988) has shown how this effect can, at least partially, be accounted for.

Carbon monoxide is isoelectronic with N_2 but has a permanent dipole which thus introduces new features into a scattering calculation. The dipole contributes the leading term to the asymptotic potential but its effect is reduced at long range by the rotational motion of the CO target. One would thus expect that an accurate representation of e^+–CO collisions would require not only account to be taken of polarisation effects, as for N_2, but also of the rotational motion of the target. In this letter we report the results of a number of calculations on e^+–CO collisions using the *R*-matrix method outlined in I, but augmented by the inclusion of rotational motion by use of the multipole-extracted adiabatic-nuclei (MEAN) approximation of Norcross and Padial (1982).

Positron impact on CO has been studied in a number of experiments. In particular, results below the positronium formation threshold (≤ 7.2 eV) are available from the experiments of Kwan *et al* (1983) and Sueoka and Mori (1984). To our knowledge

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only Jain (1986a, b) has previously attempted to study this system *ab initio*. He used a single-centre expansion method and reported results for both a static CO target and with polarisation introduced via a parameter-free polarisation potential. We note that this potential took no account of 'third-order' effects which depend on the sign of the charged projectile (see Morrison *et al* 1984) and that his results with and without polarisation effects are very similar.

The present calculations initially paralleled the e^--CO scattering calculations of Salvini *et al* (1984). The target was represented by the SCF target wavefunction of Nesbet (1964) augmented by suitable δ STO giving 7σ, 3π and 1δ STO on each nucleus. The CO separation was fixed at its equilibrium value of 2.132 a_0. Inside the R matrix, for which a radius of 10 a_0 was employed, the continuum was represented by a numerical function with partial waves up to $l=6$. These numerical functions were Schmidt orthogonalised to the target molecular orbitals. For further details see I and Salvini *et al* (1984); Gillan *et al* (1987) provide a discussion of the theory.

The scattering calculations were performed using two basic models. The first was the static approximation in which the target wavefunction was frozen during the collision. In this model the only L^2 terms in the wavefunction are the so called correlation terms which allow for high angular momentum effects near the nuclei. These were generated by allowing the e^+ to occupy target orbitals of the same symmetry as the continuum. In the static plus polarisation (SP) model allowance was made for the polarisation of the target by the charged projectile by including two-particle-one-hole configurations in the wavefunction. These were generated by considering single excitations of all the target electrons into the 6σ, 7σ, 8σ, 2π, 3π, 4π, 5π, 1δ and 2δ virtual orbitals. This model corresponds to the SP4 approximation of I. As discussed below, long-range polarisation effects were accounted for in some of our calculations by including the target polarisabilities in the asymptotic potential.

Both static and SP calculations were performed for Σ, Π and Δ total scattering symmetries. One feature of the SP calculations was the occurrence of broad pseudoresonances in the calculations with Π and Δ symmetries. These resonances occurred at scattering energies of about twice the positronium formation threshold, but were found to have an effect on the elastic cross sections below this threshold. Although this effect was small because of the dominance of the Σ symmetry in the low-energy region, it was thought best to follow Tennyson and Danby (1988) and remove the terms which caused the resonances from the wavefunction.

The effects of symmetries higher than Δ and of rotational motion of the target were allowed for using the MEAN approximation of Norcross and Padial (1982). This method uses the properties of the static, space-fixed, first Born approximation to compensate for effects not included in the more accurate calculation. Table 1 compares results for e^+-CO scattering for two energies and a range of approximations. The total cross sections presented in this table were obtained using a Boltzmann distribution of target rotational levels for a temperature of 300 K.

Table 1 shows that at both the energies considered the cross sections obtained are sensitive to the model used. Not surprisingly, the first Born approximation gave poor results for the cross sections $\langle\sigma_\text{I}\rangle$, $\langle\sigma_\text{m}\rangle$ and $\sigma(0\text{–}0)$ which are dominated by the Σ symmetry. Because of the penetrating nature of the s wave this symmetry is the most sensitive to short-range effects. Our calculations with a frozen (static) CO target gave poor results, overestimating all the cross sections, except $\sigma(0\text{–}2)$, by anything up to a factor of two. This appears to be a common feature of positron scattering calculations in the static approximation (see I), but one not found in Jain's (1986a) calculations.

Table 1. Comparison of various approximations for e^+-CO scattering at two scattering energies. The total, $\langle\sigma_l\rangle$, and momentum transfer, $\langle\sigma_m\rangle$, cross sections are rotational averages (in Å^2) for a 300 K Boltzmann distribution of the target states. Rotationally resolved cross sections (in a_0^2) $\sigma(J\text{-}J')$, are for excitation of the target from J to J'.

(*a*) $E = 2$ eV

Approximation	Symmetries	$\langle\sigma_l\rangle$	$\langle\sigma_m\rangle$	$\sigma(0\text{-}0)$	$\sigma(0\text{-}1)$	$\sigma(0\text{-}2)$
Born	All	3.57	0.94	0.00	13.48	1.98
Static+MEAN	$\Sigma+\Pi+\Delta$	10.18	6.21	23.76	14.76	0.41
SP	Σ	3.45	3.59	11.32	0.44	0.30
SP	$\Sigma+\Pi$	3.76	3.34	11.29	1.13	0.59
SP	$\Sigma+\Pi+\Delta$	3.86	3.32	11.29	1.60	0.60
SP+MEAN	Σ	6.16	4.27	11.32	12.10	1.17
SP+MEAN	$\Sigma+\Pi$	6.07	3.94	11.29	12.07	0.89
SP+MEAN	$\Sigma+\Pi+\Delta$	6.02	3.94	11.29	12.07	0.73
SP+MEAN†	$\Sigma+\Pi+\Delta$	6.04	3.89	10.93	12.07	1.10
Jain (1986a)	$\Sigma+\Pi+\Delta+\Phi+\Gamma$	3.4	3.5	9.5	3.0	$\ll 0.1$
Experiment‡		4.2 ± 0.2				

(*b*) $E = 6$ eV

Approximation	Symmetries	$\langle\sigma_l\rangle$	$\langle\sigma_m\rangle$	$\sigma(0\text{-}0)$	$\sigma(0\text{-}1)$	$\sigma(0\text{-}2)$
Born	All	1.69	0.68	0.00	5.00	1.98
Static+MEAN	$\Sigma+\Pi+\Delta$	7.77	5.12	21.35	6.00	1.00
SP	Σ	3.98	3.54	13.40	0.39	0.35
SP	$\Sigma+\Pi$	4.18	3.28	14.12	0.48	0.17
SP	$\Sigma+\Pi+\Delta$	4.52	3.74	14.89	0.56	0.51
SP+MEAN	Σ	4.96	3.95	13.40	4.73	0.42
SP+MEAN	$\Sigma+\Pi$	5.14	3.76	14.12	4.57	0.48
SP+MEAN	$\Sigma+\Pi+\Delta$	5.40	4.23	14.89	4.55	0.65
SP+MEAN†	$\Sigma+\Pi+\Delta$	5.38	4.23	14.81	4.55	0.65
Jain (1986a)	$\Sigma+\Pi+\Delta+\Phi+\Gamma$	4.0	3.8	10.2	1.9	0.1
Experiment‡		4.1 ± 0.2				

† Including polarisabilities in the asymptotic potential.
‡ Kwan *et al* (1983).

The SP calculations show greatly reduced cross sections illustrating the importance of polarisation effects. Comparison of cross sections calculated with and without the MEAN approximation suggests that, particularly for $\sigma(0\text{-}1)$, it is necessary to include many symmetries to obtain converged results when the MEAN or some similar approximation is employed. At 2 eV the results calculated using the MEAN approximation agreed closely with those calculated including Σ, $\Sigma+\Pi$ and $\Sigma+\Pi+\Delta$ symmetries explicitly, suggesting that the MEAN approximation is working well. The convergence is not quite so good at 6 eV, suggesting that near the positronium formation threshold the Born approximation is less adequate for the higher symmetries which might need to be explicitly included to obtain complete convergence.

In all the calculations presented the charge distribution of the CO target was represented by a dipole of 0.156 au and a quadrupole of -1.332 au in the asymptotic region. These multipole moments are responsible for the 0–1 and 0–2 rotational excitation cross sections, respectively, in the static Born approximation. We find little difference in our results if this asymptotic potential is augmented by the CO polarisabilities $\alpha_0 = 13.31$ au and $\alpha_2 = 2.61$ au (Bogaard *et al* 1978), these are the same values as those used by Jain (1986a, b). It is clear that polarisation effects are small in the region where the positron is more than 10 a_0 from the target. It is primarily these effects which are represented by Jain's polarisation effects.

Table 1 and figure 1 show that even our best calculations, which are the most sophisticated *ab initio* results for e^+-CO, still overestimate the total cross section. This problem is almost certainly due to the fact that none of our models account completely for charge polarisation effects. The most important part is probably in the intermediate region between the immediate vicinity of the target and the *R*-matrix boundary (Tennyson and Danby 1987). Polarisation effects are probably best represented in this region by polarised pseudostates. However, our predicted rise in the total cross section below 1 eV is consistent with the behaviour found at low energy in other positron scattering systems (Charlton 1985).

Figure 2 presents our results for the momentum transfer cross section. Like Jain we find that this property only varies slightly with scattering energy in the range in which our calculations are valid. Again our cross sections are larger than his.

Figure 3 gives rotationally resolved cross sections for CO in its ground rotational state. The variation of our elastic cross section $\sigma(0\text{-}0)$ with energy parallels that of Jain and is fairly close in magnitude. Conversely, our inelastic cross sections $\sigma(0\text{-}1)$ and $\sigma(0\text{-}2)$ are considerably larger. It is the difference between the inelastic cross sections that is responsible for the different magnitude and shape of our total cross section. Jain's lower value for $\sigma(0\text{-}1)$ may be caused by the use of an SCF wavefunction which gave a smaller CO dipole moment than ours. No such explanation can be given for his anomalous $\sigma(0\text{-}2)$ values as his CO target gave a quadrupole moment 14% larger than ours.

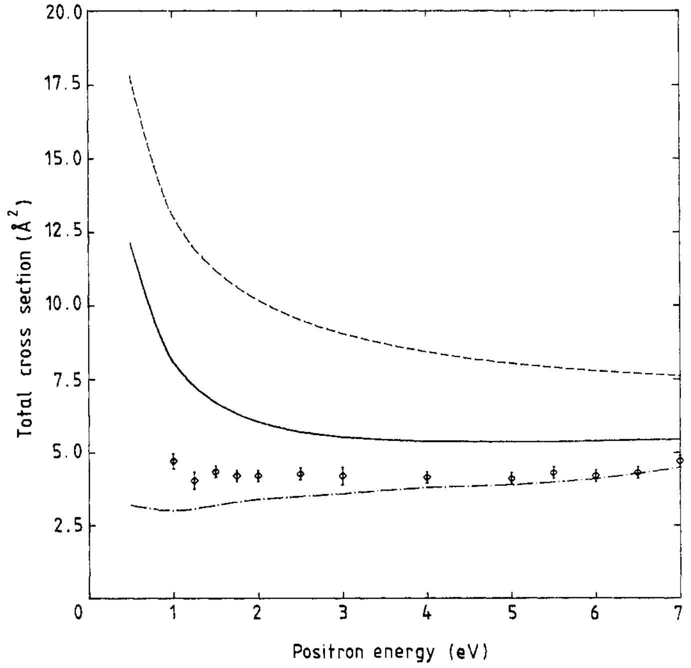

Figure 1. Total cross sections $\langle\sigma_t\rangle$ averaged over a distribution of rotational states at 300 K: - - -, static plus MEAN; ——, SP plus MEAN; – · – ·, Jain (1986a). The experimental points, including error bars, are from Kwan *et al* (1983).

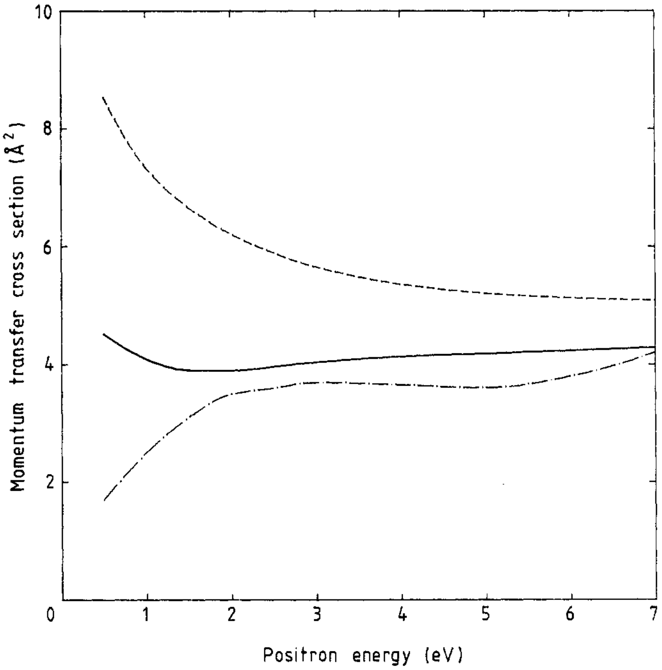

Figure 2. Momentum transfer cross sections $\langle\sigma_m\rangle$ averaged over a distribution of rotational states at 300 K: – – –, static plus MEAN; ——, SP plus MEAN; – · – ·, Jain (1896a).

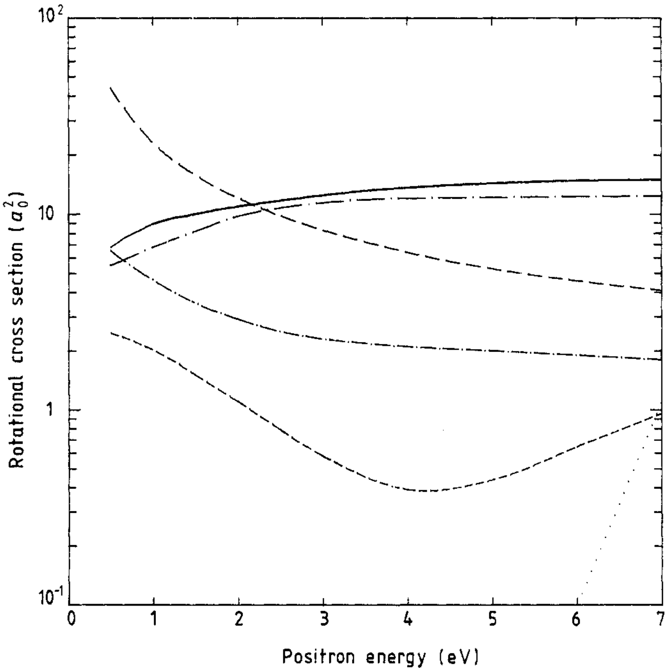

Figure 3. Rotational excitation cross sections $\sigma(J\text{-}J')$ for excitation from $J=0$ to the rotational state J'. SP plus MEAN results: ——, $\sigma(0\text{-}0)$; — —, $\sigma(0\text{-}1)$; – – –, $\sigma(0\text{-}2)$. Jain (1986a): — · —, $\sigma(0\text{-}0)$; – · – ·, $\sigma(0\text{-}1)$; · · · · · ·, $\sigma(0\text{-}2)$.

In conclusion, we have performed *ab initio* molecular R-matrix calculations for the low-energy scattering of positrons by a CO target. We find that the cross sections we obtain are very sensitive to the details of the model used in the calculations. For example, we find a large difference between the calculations which neglect and include short-range polarisation effects. This suggests that the good agreement obtained by Jain (1986a) and experiment may well be fortuitous as his calculations neglect these polarisation effects which depend sensitively on the interaction of the positron with the target electrons.

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