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Total cross section measurement for the metastable a $^3\Pi$ state in CO

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Abstract. An absolute integral cross section measurement for the electron-impact excitation of the CO(a $^3\Pi$) state is presented, which has been normalized to the theoretical work of Morgan and Tennyson. A comparison is made with previous experimental work and current theory, and a new determination for the magnitude of the cascade contribution into the a $^3\Pi$ state has been made.

1. Introduction

In this work, a total cross section measurement of the CO(a $^3\Pi$) state is made for incident electron-impact energies in the range from 6 to 70 eV. This electronic state is of considerable atmospheric interest. For example, emission from the a $^3\Pi$ state gives rise to the Cameron bands which have been observed by the Mariner space probes (Barth *et al* 1971). Fox and Dalgarno (1979) have shown that the electron-impact excitation of CO is one of the most important mechanisms for the excitation of the a $^3\Pi$ state in the Martian atmosphere. Carbon monoxide is also a major environmental pollutant.

Excitation of the a $^3\Pi$ state can proceed by direct excitation with a threshold energy of 6.01 eV from the ground electronic state X $^1\Sigma_g^+$ or indirectly by cascade. There is also significant population of the a $^3\Pi$ state by cascade from higher molecular levels which has an onset at 9.3 eV.

In addition to the a $^3\Pi$ state, carbon monoxide is known to possess several metastable electronic states, e.g. a′ $^3\Sigma^+$, e $^3\Sigma^-$, d $^3\Delta$, I $^1\Sigma^+$ and D $^1\Delta$, and experimental evidence (e.g. Cermak 1966 and Mason and Newell 1988) has been reported in support of the existence of two as yet unclassified, long-lived metastable states in the region of 10 eV. In the detection of the metastable flux of CO molecules it is possible to discriminate between the components due to the a $^3\Pi$ state and the '10 eV' states by using detecting surfaces which have different detection quantum efficiencies for the constituent metastable components.

Previous experimental determinations of this cross section which measured the metastable flux produced from electron-impact excitation of CO (e.g. Borst and Zipf 1971, Wells *et al* 1973) have detected both the a $^3\Pi$ and the '10 eV' states. The resulting cross section shapes were consequently found to be dependent on the relative detection efficiency of the surface employed for the detection of the a $^3\Pi$ and the '10 eV' states.

A further mode of discrimination between the metastable states produced is available through the time-of-flight detection method employed. A lifetime analysis was made of the metastable spectra by fitting the TOF spectra collected to a modified Maxwell–Boltzmann

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distribution (e.g. Borst and Zipf 1971). In this work, time-of-flight metastable spectra measured for incident electron energies less than 10 eV give lifetime values of 800 ± 200 μs characteristic of the $a\,^3\Pi$ state. In contrast, time-of-flight metastable spectra measured for electron energies greater than 10 eV yield lifetime values of 400 ± 200 μs, indicating the presence of shorter lived metastable species in the total flux.

The relative total cross section measurement of the $a\,^3\Pi$ state in CO made in the present work is placed on an absolute scale by normalization to the theoretical *R*-matrix calculations of Morgan and Tennyson (1993). The magnitude of the cascade contribution is also determined.

2. Experiment

A diagram of the electron spectrometer and the metastable detector used in this work are given in figure 1. Details of the electron optics and the experimental procedure have already been given by Mason and Newell (1987) and the operational characteristics of the surface detector by Furlong and Newell (1995), consequently only a brief outline of the apparatus will be given here. The monochromated electron gun produced electron beams at the interaction region of several nanoamperes with an energy resolution of typically 60 meV. The primary electron beam was collected and monitored in the Faraday cup.

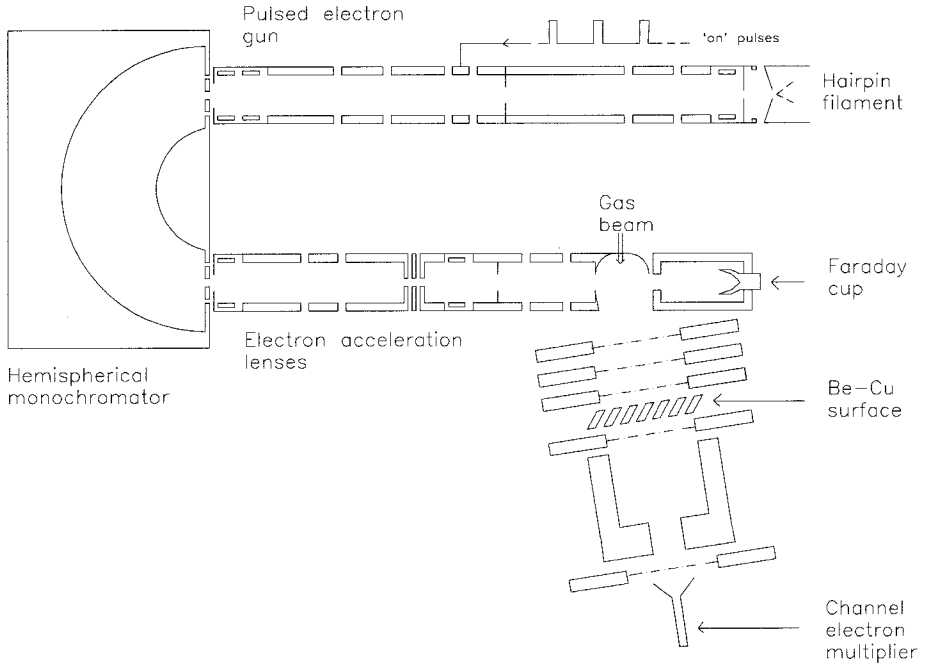

Figure 1. Schematic diagram of the electron spectrometer.

The spectrometer was operated in the time-of-flight mode by applying a negative 15 V, 100 μs pulse to a lens in the electron gun, which held the beam 'off'. The electron beam was pulsed 'on' by removing the negative 15 V pulse for a pre-set period; the 'on-time' for the electrons to pass through the interaction region was normally set to 15 μs. For incident electron energies above 20 eV, contributions from dissociatively-produced $O(^5S)$ atoms

became significant and overlapped with the leading edge of the metastable CO velocity distribution (see also Wells *et al* 1978). In order to avoid any artificial increase in the CO cross section measurement, the channels on a multichannel analyser which recorded the O(^{5}S) signal and the CO(a $^3\Pi$) were identified. The incident electron beam energy was calibrated by operating the apparatus in the excitation mode by scanning the primary beam energy and measuring the threshold excitation cross section in CO and normalizing the electron-beam energy to the 10.044 eV, $^2\Sigma^+$, core-excited Feshbach resonance (Brunt *et al* 1978); this allowed a determination of the contact potential to be made.

One of the main sources of error in a cross section measurement is the long term instability of the gas beam and the electron beam. The electron beam was monitored in this experiment using the Faraday cup. However, the number density of the gas beam was not measured absolutely; instead only variations in the number density of the gas beam were monitored by recording the pressure in the gas line and in the experimental chamber. Variations in the gas pressure over a twelve-hour period were observed to be only 5%.

The surface detector used in the present work employed a beryllium–copper (Be–Cu) surface (figure 1) from which the metastable species caused secondary electron ejection. The Be–Cu surface was positioned 2.35 cm away from the interaction region. The path length was determined by measuring a TOF spectrum for the metastable species N_2 ($A\,^3\Sigma_u^+$), at an incident electron energy of 8.0 eV. Since the lifetime of this species is long, i.e. $\tau = 1.4$ s (Shemansky and Carleton 1969), no significant inflight decay of the metastables takes place and this allowed the path length to be determined to an accuracy ± 0.20 cm.

The gas beam, produced by a hypodermic needle, intersects the electron beam at 90°. The detector is positioned at 19° with respect to the straight-through gas beam path to allow for recoil effects on the gas beam due to momentum transfer from the scattered electrons which varies from 19° for helium to 4° for carbon monoxide (Furlong 1993). The gas beam intensity distribution and the large acceptance angle of the detector ensured full collection of the metastable molecules produced (see Mason and Newell 1987). However, the background gas of the target species produces a gas cell in the interaction region from which scattering also occurs. This means that the observed signal is derived from a 'gas beam plus cell' configuration. Consequently, for each cross section measurement made for a 'gas beam plus cell' configuration, a corresponding measurement of a 'cell only' configuration was made and was subtracted from the 'gas beam plus cell' contribution following the method of Newell *et al* (1981).

In order to check the transmission effects of the electron beam over the energy range 20–70 eV and the collection efficiency of the detector a total cross section measurement was made for the excitation of the 2^3S and the 2^1S metastable species in helium. These results are normalized at 25 eV to 6.24×10^{-18} cm^2 (Mason and Newell 1987). Good agreement in the shape of the metastable helium cross section was obtained compared to the cross section measurement of Mason and Newell (1987) using a channeltron detector, see figure 2.

3. Results and discussion

The present results for the metastable production in CO are given in figure 3 and table 1, the present measurements have been normalized at 8.5 eV to 1.698×10^{-16} cm^2 (Morgan and Tennyson 1993). Theoretical and experimental determinations of the peak magnitude of the a $^3\Pi$ metastable cross section are given in table 2. Early theoretical determinations were based on the Born approximation (e.g. Chung and Lin 1974) and on the semiempirical calculations for existing experimental measurements of the cross section (e.g. Sawada *et*

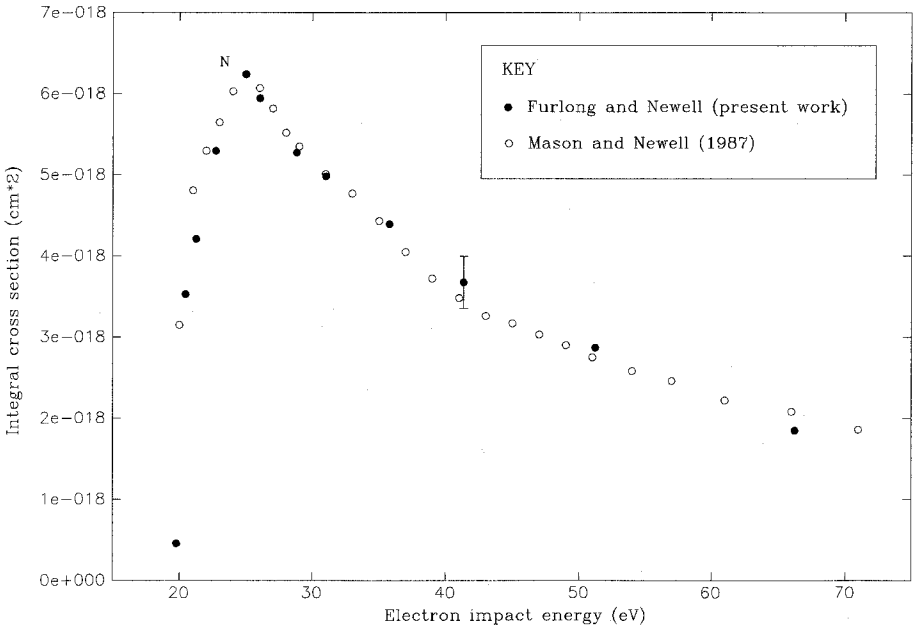

Figure 2. Comparison of the present integral cross section for the $2\,^3S$ and the $2\,^1S$ states in helium with those of Mason and Newell (1987).

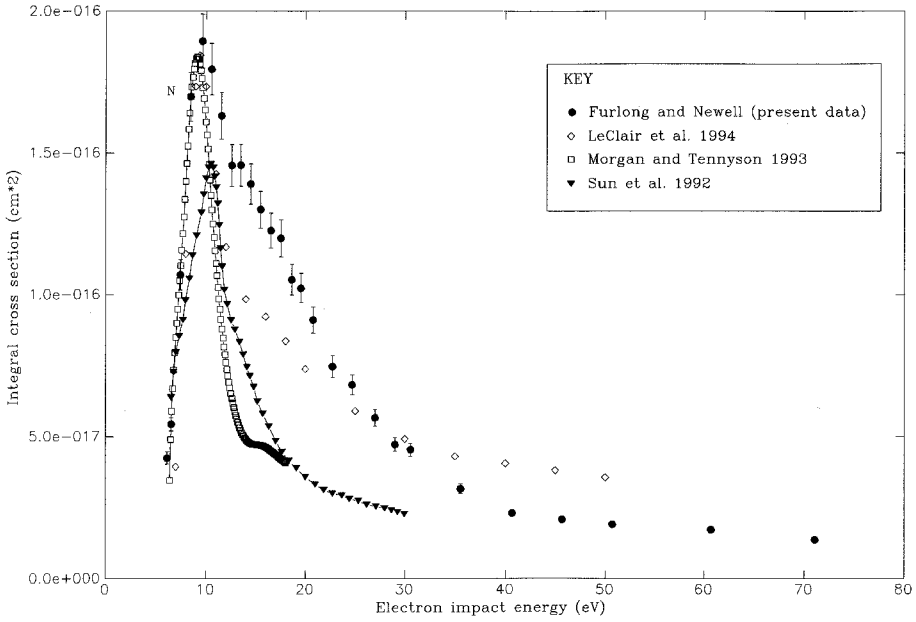

Figure 3. Total integral cross section measurement for the a $^3\Pi$ state in CO. Full circles represent the present data normalized to Morgan and Tennyson (1993) at 8.5 eV to 1.698×10^{-16} cm^2 (see feature N); open diamonds represent the experimental data of LeClair *et al* (1994) normalized to the peak cross section of the present results; open squares represent the calculation of the absolute cross section of Morgan and Tennyson (1993); inverted full triangles represent the calculation of the absolute cross section of Sun *et al* (1992).

Table 1. Compilation of previous experimental and theoretical determinations for the magnitude of the a $^3\Pi$ integral cross section in CO.

Electron energy (eV)	Cross section (10^{-16} cm^2)
6.14	0.425 ± 0.022
6.55	0.543 ± 0.023
7.46	1.070 ± 0.054
8.49	1.696 ± 0.086
9.65	1.892 ± 0.096
10.56	1.793 ± 0.091
11.55	1.629 ± 0.083
12.59	1.454 ± 0.074
13.50	1.455 ± 0.074
14.50	1.389 ± 0.071
15.49	1.299 ± 0.065
16.53	1.225 ± 0.062
17.53	1.272 ± 0.065
18.63	1.052 ± 0.054
19.56	1.022 ± 0.052
20.77	0.910 ± 0.046
22.72	0.745 ± 0.038
24.67	0.681 ± 0.035
26.98	0.566 ± 0.029
29.01	0.471 ± 0.024
30.57	0.453 ± 0.023
35.54	0.317 ± 0.016
40.68	0.231 ± 0.012
45.66	0.208 ± 0.011
50.70	0.192 ± 0.009
60.69	0.172 ± 0.001
71.09	0.136 ± 0.001

al 1972). However, these were soon superseded by relatively simple two-state model calculations using the distorted-wave method (e.g. Mu-Tao and McKoy 1982), and using the Schwinger multichannel variational method (e.g. Weatherford and Huo 1990). More recently, Sun *et al* (1992) have used the Schwinger multichannel variational method for an eight-state model at a single fixed geometry, although they have not necessarily included all eight states in a given calculation. A recent application of the *R*-matrix method (Morgan and Tennyson 1993) to the CO molecule is the most rigorous calculation to date. In their work, the *R*-matrix method is used to calculate the electron-impact excitation for the seven lowest electronically-excited states of CO in the energy range 6–18 eV, and their calculations have been carried out for a range of internuclear distances $1.8 \geqslant R \geqslant 3.0\ a_0$. They suggest that the tail of the $^2\Pi$ resonance at 1.8 eV could influence the shape of the a $^3\Pi$ cross section. A comparison between the present experimental results and those of LeClair *et al* (1994), and the calculations of Morgan and Tennyson (1993) and Sun *et al* (1992) is shown in figure 3. Good agreement is obtained from threshold up to 10 eV, above which cascade contributions into the a $^3\Pi$ state and the unidentified '10 eV' metastable states begin to dominate the present experimental cross section shape and any contribution from the '10 eV' states. The present work is also in reasonable agreement with the cross section measurement of Wells *et al* (1973).

Ajello (1971) made an emission cross section measurement of the Cameron band system

Table 2. Present integral cross section measurements for the CO(a $^3\Pi$) state. The results are normalized at 8.5 eV to 1.698×10^{-16} cm^2 (Morgan and Tennyson 1993).

Peak cross section (10^{-16} cm^2)	Energy[a] (eV)	Method	Reference
0.0009	9.5	Theory	Massey *et al* (1969)
1.2	10.0	Experimental	Carlton (1966)[b]
1.2 ± 0.9	11.0	Emission	Ajello (1971)
0.0695	10.1	Semiempirical	Sawada *et al* (1972)
1.29	10	Born approx.[c]	Chung and Lin (1974)
0.56	12.2	Born approx.[d]	Chung and Lin (1974)
1.4	6.0	Distorted-wave	Mu-Tao and McKoy (1982)
1.45	10.5	Multichannel Schwinger	Sun *et al* (1992)
1.84	9.1	*R*-matrix	Morgan and Tennyson (1993)

[a] Energy at which the cross section process is a maximum.
[b] See Collins (1973).
[c] Using Okhurs modification.
[d] Using the Rudge modification.

(a $^3\Pi \longrightarrow$ X $^1\Sigma^+$) in CO from threshold to 300 eV. However, the uncertainty in the measured shape of the cross section below 15 eV was estimated to be 35%. These measurements have since been shown to have been flawed by Erdman and Zipf (1983). Spectral contamination of the (1, 4) Cameron band used by Ajello to normalize the entire Cameron band cross section, revisions of the magnitude of the CO(a $^3\Pi$) lifetime, and the subsequent underestimate of the number of metastable molecules lost from the field of view of Ajello's detector are now known to be contributing factors which have not been accounted for in his determination.

LeClair *et al* (1994) have recently measured the relative a $^3\Pi$ integral cross section by electron-impact excitation. In their work they apply the TOF technique by pulsing their electron beam and timing the arrival of the metastable products. The metastable molecules are detected using a surface of solid xenon positioned 26.6 cm away from the collision region. Interestingly, they measure the lifetime of the a $^3\Pi$ state to be 80 μs; this is abnormally low compared to the present value of 800 μs, and that of Borst and Zipf (1971) of 1 ms. LeClair *et al* attribute this observed value as due to collisional quenching of the excited metastable molecules by the background gas. The results of their measurement have been normalized to the present data at the peak of the cross section, and are shown for comparison in figure 3. No shoulder is seen in their cross section above incident electron energies of 10 eV. Although they suggest that the solid xenon detector discriminates against the 10 eV species, quenching, as for the a $^3\Pi$ state, could remove them.

Subtraction of the calculated cross section for the a $^3\Pi$ state (Morgan and Tennyson 1993) from the present normalized results should reveal the cascade contribution. The result of this subtraction procedure is illustrated in figure 4 and is compared with the '10 eV' metastable cross section measurement of Mason and Newell (1988). Both cross sections are similar in shape, although the Mason and Newell cross section is two orders of magnitude smaller, suggesting that cascade into the a $^3\Pi$ species is the dominant 'excitation' mechanism in this cross section beyond the threshold region and that the present measurement (figure 3) is effectively the a $^3\Pi$ cross section. The differences in shape displayed in figure 4 are due to different detection efficiencies for the 10 eV and the a $^3\Pi$ metastable states in both experiments. The metastable flux produced by the '10 eV' state has been associated with the direct excitation of the I $^1\Sigma^+$ and D $^1\Delta$ states from the X $^1\Sigma^+$ ground state or by decay of the A $^1\Pi$ into the I $^1\Sigma^+$ and D $^1\Delta$ states; both these possibilities have been discarded by

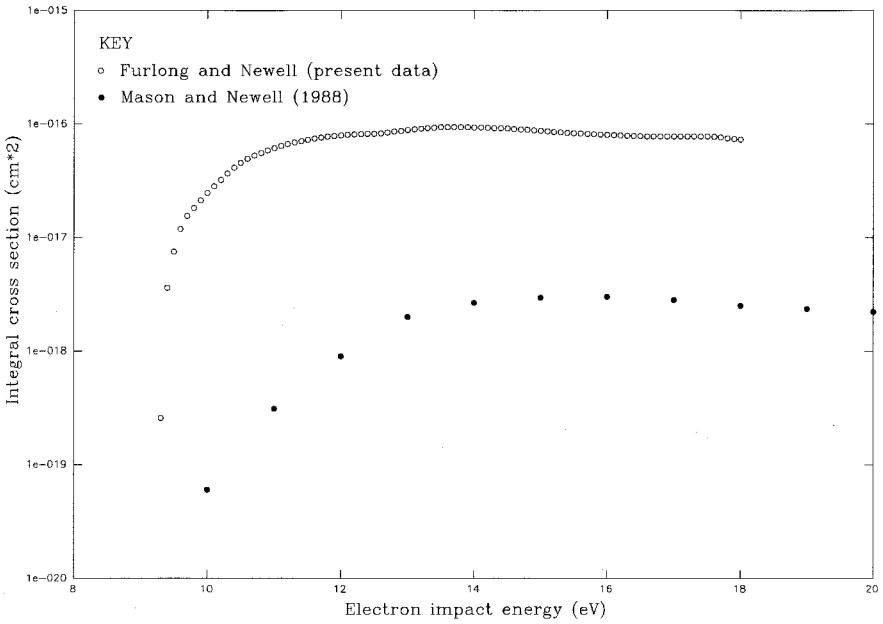

Figure 4. Comparison of the cascade contributions into the a $^3\Pi$ state (this work) and the 10 eV cross section measured by Mason and Newell (1988).

Rosenkrantz and Kirby (1989) and the states remain unclassified.

4. Conclusion

The total metastable cross section for the a $^3\Pi$ state in CO has been measured using a TOF technique in the energy range from threshold to 70 eV. For incident electron energies above 10 eV, cascade contributions into the a $^3\Pi$ species dominate the shape of the cross section. Good agreement on the shape of the a $^3\Pi$ cross section has been shown to exist between the present results and those of Morgan and Tennyson (1993), Sun *et al* (1992), and LeClair *et al* (1994), in the energy range from threshold to 10 eV. An indirect determination of the cascade contribution into the a $^3\Pi$ metastable species has also been made, and was found to be two orders of magnitude larger than the contribution from the '10 eV' species (Wells *et al* 1973, Mason and Newell 1988).

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