

Electron impact excitation of a higher lying metastable state of carbon monoxide

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Abstract. A higher lying '10 eV' metastable state of CO has been isolated for the first time from the influence of the $a^3\Pi$ state. Accurate evaluations of the observed lifetime have been made for a wide range of incident energies and established as $80 \pm 10 \mu\text{s}$. The total excitation cross section of the state has been measured under high electron resolution and the threshold accurately determined as lying at 9.45 eV with a possible second threshold at 10.45 eV. The $I^1\Sigma^-$ is affirmed as the most likely candidate for this higher lying metastable state.

1. Introduction

The role of the metastable states of CO in such diverse media as lasers, gas discharges, plasmas (McDaniel and Nighan 1982) and coal-fired MHD generators (Land 1978) has increased the interest in recent years in the measurement of their cross sections. Carbon monoxide is known to sustain several metastable states including the astrophysically important $a^3\Pi$ state lying 6.006 eV above the ground state ($X^1\Sigma^+$), with the forbidden Cameron bands $a^3\Pi-X^1\Sigma^+$ being the main feature in the spectra of the Martian atmosphere obtained by the Mariner space probes. See figure 1 for the relevant electronic states in CO. A higher lying metastable state with an excitation energy of approximately 10 eV has been observed by several investigators but controversy has arisen in the interpretation of these results. Olmsted *et al* (1965) using a silver-magnesium alloy surface detector observed a rapidly rising cross section above the $a^3\Pi$ cross section, and estimated the lifetime of this 10 eV state to be of the order of 100 μs ; they proposed that it might be the $b^3\Sigma^+$ state. Cermak (1966) using a Penning-ionisation detection technique confirmed the presence of such a 10 eV metastable state and proposed that the metastable flux arose from two metastable states, one with an energy between 9.2 and 10.2 eV (M_1 state), the other with an energy greater than or equal to 10.2 eV (M_2 state). Borst and Zipf (1971) derived the excitation cross section of the M_1 state by subtracting the electron impact excitation cross section for the $a^3\Pi$ state, observed by Ajello (1971), from their measured total excitation cross section. They estimated the lifetime of this M_1 state to be 150 μs , which precluded its classification as the $b^3\Sigma^+$ state which has a lifetime of 60 ns (Rogers and Anderson 1970); however the threshold established at 10.4 eV is close to that of the $b^3\Sigma^+$ state. Wells *et al* (1973) in the most rigorous investigation to date located a metastable threshold at 9.5 ± 0.4 eV and determined the state's lifetime to be $97 \pm 15 \mu\text{s}$. The peak

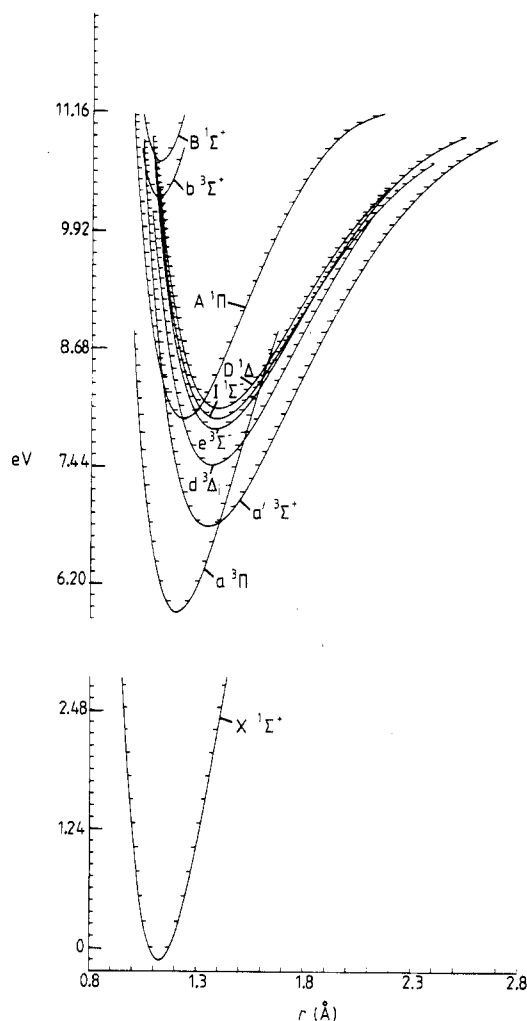


Figure 1. Some electronic states of the CO molecule. Produced from data given by Tilford and Simmons (1972).

cross section of this still unidentified state was estimated to be $3 \times 10^{-18} \text{ cm}^2$ at 15 eV, a not insignificant value, and if correct should underline the importance of such species in a variety of atmospheric processes (Massey and Bates 1982). Wells *et al* also discounted a $b^3\Sigma^+$ classification due both to the observed cross section shape and the lifetime, but proposed the $D^1\Delta$ and $I^1\Sigma^-$ states as alternative candidates.

Recent theoretical calculations for the total excitation cross sections of electronic states in CO (see e.g. Chung and Lin 1974, Mu-Tao and McKoy 1982) have suggested that the observed state is unlikely to be the $D^1\Delta$ state as the calculated cross section shape is different from that experimentally observed. In addition, the failure of Trajmar *et al* (1971) and Swanson *et al* (1975) to observe any energy loss features that could be attributed to $X^1\Sigma^+ - I^1\Sigma^-$ or $D^1\Delta$ excitation led to the proposal that the observed metastable flux arose from indirect excitation. The mechanism suggested was the direct excitation of the dipole-allowed $A^1\Pi$ state followed by decay both to the ground state

and to the $D^1\Delta$ and $I^1\Sigma^-$ metastable states. The intermediate $A^1\Pi$ state cross section shape would then be reflected in the observed metastable cross section. Since the interpretation of the previous experiments has been complicated by the presence of the much more intense $a^3\Pi$ species, it is now necessary to perform an experiment which 'isolates' the higher lying metastable state and allows its properties to be investigated independent of the Cameron band ($a^3\Pi-X^1\Sigma^+$).

2. Experimental method

The experimental arrangement used consists of an electron gun which produces a beam of $1\ \mu\text{A}$ at an incident energy of 6 eV on an electrostatic hemispherical monochromator. The monochromated electron beam is then accelerated to the required impact energy and intersected at right angles with a molecular carbon monoxide gas beam produced by a hypodermic needle. Spectroscopic-grade gas was used. Since there is a net momentum transfer to the metastable molecular beam it is necessary to place the metastable detector at an angle which accommodates the effect of the momentum transfer to the metastable molecules to ensure that all those produced are detected. The channel electron multiplier (CEM) is therefore placed at a scattering angle $\theta = 73^\circ$ with respect to the incident gas beam direction. A full discussion of the apparatus and method has been given by Mason and Newell (1986, 1987a).

The metastable species are detected through an Auger de-excitation process in which an electron is ejected from the surface of the detector upon which it impinges. If a surface is selected with a work function that is higher than the $a^3\Pi$ CO metastable state other higher lying metastable states may be preferentially detected.

Recent experiments (Brunt *et al* 1978, Mason and Newell 1987b) have demonstrated that only metastable states with excitation energies greater than approximately 8 eV could be detected using a commercial channel electron multiplier (CEM). The use of such a CEM as a detector for CO metastable molecules could therefore be used to 'isolate' the higher lying '10 eV' M states and enable a direct study to be made of the lifetimes and the cross sections of these states, with an excitation threshold determination also possible free of all the background problems associated with the $a^3\Pi$ state that exist in the earlier work.

Although the $v=0$ level of the $a^3\Pi$ state occurs at 6.006 eV, the higher lying vibrational levels ($v>11$) will lie at approximately 8 eV and consequently will have sufficient energy to be detected by the CEM. The cross section for these high vibration levels ($v=11$) of the $a^3\Pi$ state is approximately 10^{-2} of that for the $v=0$ level but probably comparable to the cross section for the excitation of the $I^1\Sigma^-$ and $D^1\Delta$ states. However, the longer lifetime, 1 ms (Borst and Zipf 1971), of the $a^3\Pi$ state will exclude this flux from that being detected in the TOF spectra (see figure 2(a)) which shows a lifetime of 70–80 μs . The metastable TOF spectra are generated using a 10 V 250 μs pulse applied to a gun lens in order to modulate the electron beam. The resultant TOF spectrum as recorded at the CEM consists of photons which arrive as a prompt pulse, followed by scattered electrons which arrive at the detector within 30 ns of the trailing edge of the primary electron pulse, and finally the metastable molecules and ions which have flight times of approximately 100 μs . The positive ions are removed by the application of a small positive voltage at the entrance of the detector. The data are stored as a TOF spectrum in a multichannel analyser, and then integrated over a finite time range and normalised to unit electron current.

The present work has isolated the higher lying M state(s) and allowed both the lifetime and threshold energy to be determined; the total cross section has also been evaluated.

3. Results and discussion

3.1. Lifetime determination

The lifetime of a metastable species may be determined from a careful study of their TOF distribution at the detector (Borst and Zipf 1971, Mason and Newell 1987b). In the case of a metastable molecule travelling from the collision chamber to the detector without decay the velocity distribution of metastables $D(V)$ is purely Maxwellian (Mason and Newell 1987a) (assuming a completely diffuse gas source and negligible momentum recoil after the collision) and is given by

$$D(V) dV = AV^2 \exp(-mV^2/2kT) dV \quad (1)$$

where A is a normalisation constant, m is the molecular mass, k is Boltzmann's constant and T is the temperature of the gas in the collision region.

The TOF distribution $P(t)$ is obtained by substituting $V = lt^{-1}$, where l is distance between the collision region and the detector and t is the time of arrival at the detector. Thus

$$P(t) dt = C(l/t^4) e^{-B/t^2} dt \quad (2)$$

where $B = ml^2/2kt$ and C is another normalisation constant.

However, if a certain fraction of the metastables decay in flight before reaching the detector (because the metastable lifetime is of the order of the transit time to the detector), then the measured TOF distribution for a *single* metastable species decaying with a lifetime τ is given by

$$P_\tau(t) = C'(l/t^4) e^{-B/t^2} e^{-t/\tau} \quad (3)$$

(assuming that UV photons from decaying metastables on their way to the detector can be neglected).

Excitation of CO metastables by a pulsed electron beam will therefore allow the lifetime τ_1 to be determined from the TOF spectrum. If a second metastable species of different lifetime (τ_2) but with a cross section of similar magnitude is also excited then the TOF distribution will change, requiring the use of a more general form of equation (3) (Mason and Newell 1987b).

Monitoring $P(t)$ as a function of incident electron impact energy may therefore resolve the uncertainty as to the number of high lying metastable states in CO. The determination of the lifetimes of such state(s) is also essential if a meaningful spectroscopic classification is to be attempted.

In the present work the TOF spectra for the production of metastable carbon monoxide molecules was studied at selected energies from threshold to 80 eV and equation (3) was used to determine τ for the high lying species observed. For incident energies between threshold and 35 eV τ was estimated to be $80 \pm 10 \mu\text{s}$ (figure 2(a)), with the only deviation from the computer-calculated curve and the experimental data being observed at low flight times and this difference in signal is probably due to in-flight-decay photons. At incident electron energies above 40 eV a slight decrease in τ to $70 \pm 10 \mu\text{s}$ was indicated (figure 2(b)), but contributions from dissociatively produced non-thermal $\text{O}(^5\text{S})$ atoms (detected as a sharp peak at smaller TOF) may

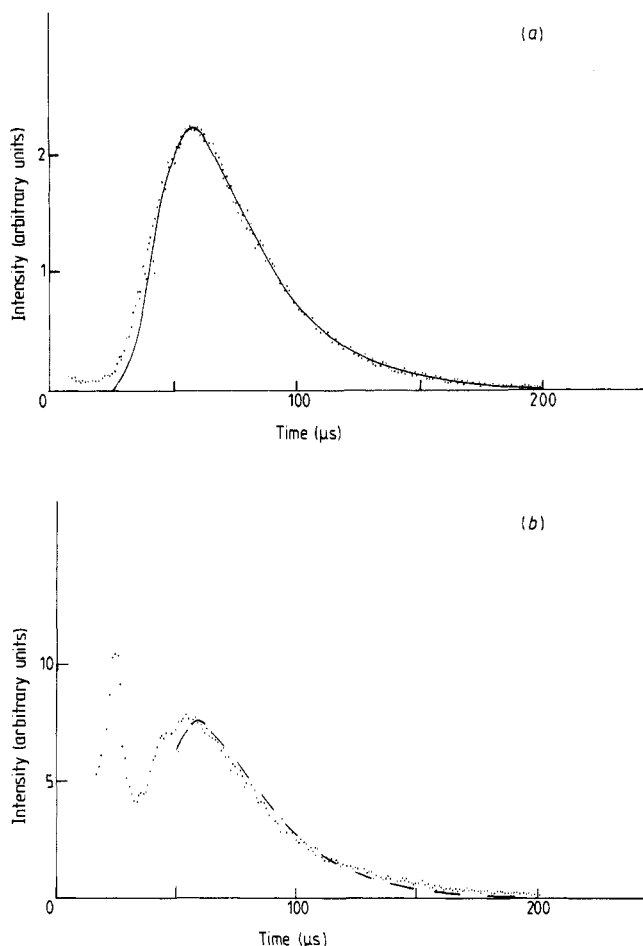


Figure 2. Metastable TOF spectra. (a) Taken at 20 eV incident electron energy; dots, present experimental data; —, computed curve for a $80\ \mu\text{s}$ lifetime. (b) Taken at 40 eV incident electron energy; dots, present experimental data; —, computed curve for a $70\ \mu\text{s}$ lifetime. The sharp peak at low flight times is due to non-thermal oxygen atoms produced by dissociation.

produce somewhat erroneous results at these energies. However, these lifetime values agree reasonably well with those derived by Wells *et al* (1973) who reported a value of $97 \pm 15\ \mu\text{s}$ for the '10 eV' state with the measured lifetime decreasing to $65 \pm 20\ \mu\text{s}$ at 45 eV.

Wells *et al* suggested that this apparent change in τ at 45 eV indicated that the total cross section was at this energy dominated by Cermak's M_2 metastable state, whereas the M_1 metastable state dominated the cross section at 20 eV. The M_1 and M_2 assignments were consequently proposed as the $I^1\Sigma^-$ state and the $D^1\Delta$ state, respectively. Other metastable states ($a'^3\Sigma^+$, $e^3\Sigma^-$, $d^3\Delta$) which arise from the same $1\pi-2\pi$ transition as the $I^1\Sigma^-$ and $D^1\Delta$ states will not contribute to the metastable flux due to the long flight time ($80\ \mu\text{s}$) in the present apparatus and the short lifetimes of these states of 5, 3.7 and $4\ \mu\text{s}$ respectively. In-flight decay will remove this flux. In addition, the measured lifetime, $70-80\ \mu\text{s}$, of the detected metastable signal confirms

that the a, e and d states are not contributing. Since lifetime measurements of the resolved $I^1\Sigma^-$ and $D^1\Delta$ states are not available it is not possible to decide the relative contributions from each state to the present metastable signal.

The present lifetime measurements do not preclude the presence of the two such states $I^1\Sigma^-$ and $D^1\Delta$; however, the measured lifetime at energies above 45 eV does not change dramatically as in the work of Wells *et al* but rather is relatively constant at $80 \pm 25 \mu\text{s}$ up to 80 eV. We detect no significant change in the measured lifetime that could be definitely ascribed to the dominant influence of either the $I^1\Sigma^-$ or $D^1\Delta$ state cross sections; indeed the possible excitation of different vibrational modes with varying lifetimes within each single state is also unresolved.

However, considering the relative cross sections discussed in § 3.2 we feel that the measured lifetime is dominated by the $I^1\Sigma^-$ state and its different vibrational excitations.

3.2. Total cross section

Integration of the TOF spectrum stored on the PHA provides a monitor of the metastable cross section under investigation. The total metastable excitation cross section for states lying 8 eV or more above the ground state of the carbon monoxide molecule is shown in figure 3 and table 1 for electron impact energies between 8 and 60 eV; above 60 eV contributions from dissociatively produced $O(^3S)$ atoms make the data less reliable. A comparison with the earlier works of Wells *et al* (1973), Borst and Zipf (1971) and Cermak (1966) is also made in figure 3. Although it is possible to determine the number density of the gas beam it has not been possible to make the present data absolute since the detection efficiency of the CEM is unknown for the CO metastable states involved. Consequently, all the data in figure 3 are normalised to the maximum value of Wells *et al*. It is seen that the present results are in reasonable quantitative agreement with Cermak's M_1 metastable excitation curve and in better agreement with the data of Wells *et al* and Borst and Zipf. If two states are contributing to the observed metastable flux it might be expected that at some energy the total cross section would show a 'break' where the two cross section contributions change as in the N_2 metastable

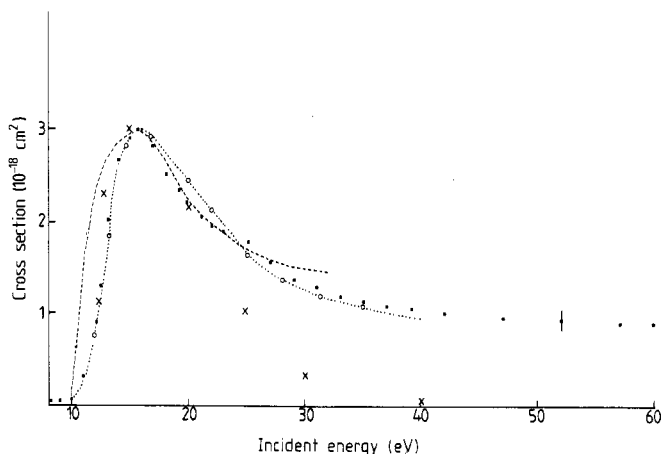


Figure 3. Total excitation cross section for the high lying metastable flux in CO. ■■■, Present data; ○--○--, Wells *et al* (1973); ×××, Borst and Zipf (1971); ---, Cermak (1966). The error bar shown represents the error on each of the present data points. See text for discussion.

Table 1. Total cross section for the 10 eV state(s) in CO.

Energy (eV)	Cross section ($\times 10^{-18}$ cm ²)
10	0.06 ± 0.02
11	0.31 ± 0.05
12	0.90 ± 0.07
13	2.00 ± 0.13
14	2.66 ± 0.16
15	2.95 ± 0.18
16†	3.00 ± 0.18
17	2.81 ± 0.17
18	2.50 ± 0.16
19	2.34 ± 0.16
20	2.21 ± 0.15
21	2.05 ± 0.14
22	1.95 ± 0.14
23	1.89 ± 0.13
25	1.79 ± 0.13
27	1.56 ± 0.12
29	1.38 ± 0.12
31	1.30 ± 0.11
33	1.19 ± 0.11
35	1.14 ± 0.11
37	1.10 ± 0.10
39	1.06 ± 0.10
42	1.00 ± 0.10
47	0.95 ± 0.10
52	0.94 ± 0.10
57	0.90 ± 0.10
60	0.90 ± 0.10

† Normalisation point to data of Wells *et al* (1973).

curves of Borst (1972). No such structure has been observed, even under high-resolution conditions (see § 3.3); indeed above 30 eV where Wells *et al* predict such a change to occur the observed cross section is smoothly varying. It is unlikely that one cross section and its cascade contribution would fall at a rate to compensate for the other's rise. The present results, while not precluding the existence of two states, would indicate that one state has the dominant cross section in agreement with the previously discussed lifetime data.

The shape of the observed cross section should assist in the clarification of the metastable state being detected. However, although the cross sections of the D ¹Δ and I ¹Σ⁻ states have not been determined experimentally, Chung and Lin (1974) and Mu-Tao and McKoy (1982) have calculated the total excitation cross section for the D ¹Δ state. They report a cross section that rises from threshold to a peak at 35 eV before falling only gradually, and this is not in agreement with the observed cross section.

The states which are most likely to be responsible for the measured metastable flux are the valence states associated with the (1σ²2σ²3σ²1π5σ²2π) excited electronic configuration. These states are ¹Σ⁺ a' ³Σ⁺ I ¹Σ⁻ e ³Σ⁻ D ¹Δ d ³Δ, and with the exception of the ¹Σ⁺ all the states are dipole forbidden to the ground state X ¹Σ⁺ of CO. However, since the singlet-to-triplet selection rule is not vigorously obeyed in CO and there exist quite strong band perturbations both between these states and with the A ¹Π state, all

of the five forbidden transitions $X^1\Sigma^+-(a', I, e, D, d)$ have been observed in single-photon UV absorption spectroscopy. Although all of these transitions are weak, it was noted by Simmons and Tilford (1966) that the $D^1\Delta$ excitation was much weaker than the a' or $I^1\Sigma^-$ excitation. Indeed in the energy loss spectra of Daviel *et al* taken at low incident electron energy and at two scattering angles ($30^\circ, 80^\circ$) only the a', d, e transitions were detected even though the experimental conditions favoured the excitation of forbidden transitions. The signal-to-noise ratio in these spectra indicates a possible upper limit on the intensity of the $I^1\Sigma^-$ transition of approximately 0.1 of the a' intensity, which is 0.1 of the $A^1\Pi$ intensity. Since the excitation cross section of the $A^1\Pi$ state is at a maximum of $2 \times 10^{-16} \text{ cm}^2$ in the calculations of Mu-Tao and McKoy (1982), then the relative intensity in the spectra of Daviel *et al* (1982) would indicate an upper limit of approximately 10^{-18} cm^2 in the cross section of the $I^1\Sigma^-$ state, and this value is in reasonable agreement with the presently observed value of $3 \times 10^{-18} \text{ cm}^2$. If, however, the experimental data of Mumma *et al* (1971) and Ajello (1971) is used then the $A^1\Pi$ cross section is only reduced to $4 \times 10^{-17} \text{ cm}^2$, yielding a value for the maximum cross section of the $I^1\Sigma^-$ excitation of $2 \times 10^{-19} \text{ cm}^2$ again based on an upper limit.

The a', e, d metastable states, although more intense than the $I^1\Sigma^-$ and $D^1\Delta$ states will not contribute to the metastable flux detected due to their short lifetimes. Distinguishing between the $I^1\Sigma^-$ and $D^1\Delta$ states on energy level grounds is also made difficult as the minima of both potential energy curves occur at the same internuclear separation with a 845 cm^{-1} (105 meV) difference in the $v=0$ level of each state. However, although in the first Born approximation the $X-I^1\Sigma^-$ and $D^1\Delta$ transitions are both considered forbidden the optical absorption spectra shows that the $X-I^1\Sigma^-$ transition is allowed and this excitation is probably responsible for the high-energy part of the cross section in figure 3 with the $D^1\Delta$ state contributing to the peak in the threshold region.

The electron impact excitation of higher lying Σ and Π states could result in cascade into the $I^1\Sigma^-$ and $D^1\Delta$ states. In addition, higher lying vibrational levels of the $A^1\Pi$ state could populate the $D^1\Delta$ state when the Franck-Condon (FC) overlap is favourable. Swanson, who also noted the absence of $D^1\Delta$ and $I^1\Sigma^-$ states in energy loss spectra, suggested that the metastable flux was dominated by cascade. However, considering the UV absorption work together with the energy loss data and the magnitude of the present cross section we feel that cascade is only a secondary process at the lower incident electron energies which may become more important at the higher electron energies.

3.3. Threshold excitation cross section

A study of the metastable excitation cross section close to threshold using a highly resolved incident electron beam ($\leq 40 \text{ meV FWHM}$) should reveal the excitation threshold energy and perhaps provide evidence of other state excitations. In the present threshold spectra, figure 4, the well established 10.044 eV resonance (Brunt *et al* (1978) and Newman *et al* (1983)), is clearly observed, as feature B, and thus provides an accurate normalisation point for the incident electron energy scale which locates the threshold excitation energy, feature A, at $9.45 \pm 0.05 \text{ eV}$.

It is interesting to compare the present results with those of Brunt *et al* (who also used a CEM detector) and Olmsted *et al* both of whom believed their results to be dominated by the '10 eV' states. Olmsted *et al*, using a low-resolution electron beam,

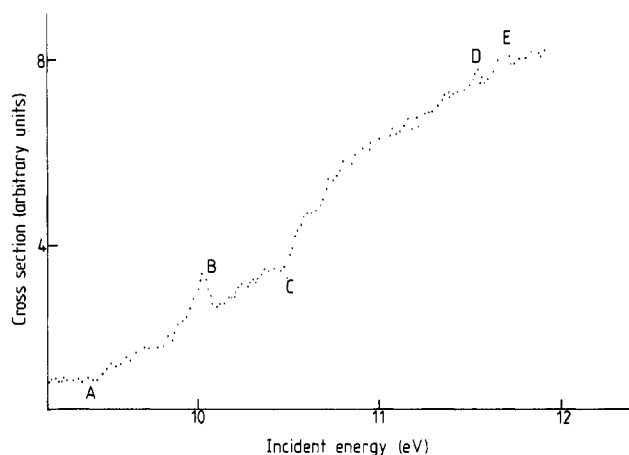


Figure 4. Threshold excitation of the high lying metastable flux in CO. See text for discussion of the features A to E.

saw some structure between 10 and 10.5 eV, which may now be ascribed to the 10.044 eV resonance, followed by a strongly rising cross section with an onset at approximately 10.5 eV. Their lower signal intensity below 10.3 eV may indicate some onset at 9.9 eV in agreement with Cermak. Brunt *et al* who carefully calibrated their energy scale with a mixture of argon and carbon monoxide gases saw the 10.044 eV resonance and a series of smaller Feshbach resonances between 14 and 15 eV close to their observed cross section maximum at 15 eV, a peak which is in good agreement with the present data (see figure 3). Below 10 eV they observed a gently rising cross section from 6.5 eV indicating perhaps that their channeltron was sensitive to the a $^3\Pi$ metastable species in contrast with the present data where there is no structure below the 9.45 eV threshold (figure 4). Above 10 eV they found a steeply rising cross section in agreement both with the present data and that of Olmsted *et al*.

The present data indicate a second possible threshold at 10.45 eV (feature C) and this could be interpreted as the onset of Cermak's M_2 state but, as Newman *et al* have demonstrated, for the a $^3\Pi$ state such discontinuities in the total cross section may also occur when higher lying vibrational levels of the already contributing state are excited. In this case the sharp increase could be produced by a rapid change in the FC factors between the X $^1\Sigma^+$ and I $^1\Sigma^-$ or D $^1\Delta$ states. The discontinuity could also be explained by cascade contributions from the A $^1\Pi$ state being superimposed upon the direct cross section, and indeed the $v = 16$ level of A $^1\Pi$ also lies at 10.45 eV. Other known levels in the energy region, b $^3\Sigma^+$ (10.39 eV) and B $^1\Sigma^+$ (10.78 eV), will not contribute to the signal as the b $^3\Sigma^+$ state is short lived and the B $^1\Sigma^+$ is optically coupled to the ground state.

There is no evidence in figure 4 for the excitation threshold of the D $^1\Delta$ state which should occur at 9.555 eV; the other fine-structure features D and E superimposed on the observed cross section are too weak to quantify reliably.

4. Conclusions

In this work we have successfully isolated the higher lying metastable states from the a $^3\Pi$ state and determined the threshold excitation energy as 9.45 ± 0.05 eV. This

present, three-pronged investigation using lifetime determinations, total cross sections measurement and the observation of threshold features together with the work in electron energy loss spectroscopy and UV absorption spectroscopy, has enabled the most probable mode for the direct excitation of the higher lying metastable state to be established as the $X^1\Sigma^+-I^1\Sigma^-$ transition.

Acknowledgments

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References

- Ajello J 1971 *J. Chem. Phys.* **55** 3158-68
Borst W L 1972 *Phys. Rev. A* **5** 648-56
Borst W L and Zipf E C 1971 *Phys. Rev. A* **3** 979-89
Brunt J N H, King G C and Read F H 1978 *J. Phys. B: At. Mol. Phys.* **11** 173-92
Cermak V 1966 *J. Chem. Phys.* **44** 1318-23
Chung S and Lin C C 1974 *Phys. Rev. A* **9** 1954-64
Daviel S, Wallbank B, Comer J and Hicks P J 1982 *J. Phys. B: At. Mol. Phys.* **15** 1929-37
Land J E 1978 *J. Appl. Phys.* **49** 5716-21
Mason N J and Newell W R 1986 *J. Phys. E: Sci. Instrum.* **19** 722-6
—— 1987a *J. Phys. B: At. Mol. Phys.* **20** 1357-77
—— 1987b *J. Phys. B: At. Mol. Phys.* **20** 3913-21
Massey H S W and Bates D R 1982 *Applied Atomic Collision Physics* vol 1 *Atmospheric Physics and Chemistry* (New York: Academic) pp 294-342
McDaniel E W and Nighan W L 1982 *Applied Atomic Collision Physics* vol 3 *Gas Lasers* (New York: Academic) pp 118-29
Mumma M J, Stone E J and Zipf E C 1971 *J. Chem. Phys.* **54** 2627-34
Mu-Tao L and McKoy V (1982) *J. Phys. B: At. Mol. Phys.* **15** 3971-83
Newman D S, Zubeck M and King G C 1983 *J. Phys. B: At. Mol. Phys.* **16** 2247-63
Olmsted J, Newton A S and Street K 1965 *J. Chem. Phys.* **42** 2321-7
Rogers J and Anderson R 1970 *J. Quant. Spectrosc. Radiat. Transfer* **10** 515-7
Simmons J D and Tilford S G 1966 *J. Chem. Phys.* **45** 2965-8
Swanson N, Celotta R J, Kuyatt C E and Cooper J U 1975 *J. Chem. Phys.* **62** 4880-8
Tilford S G and Simmons J D 1972 *J. Phys. Chem. Ref. Data* **1** 147-87
Trajmar S, Williams W and Cartwright D C 1971 *7th Int. Conf. on the Physics and Electronics of Atomic Collisions* (Amsterdam: North-Holland) Abstracts pp 1066-8
Wells W C, Borst W L and Zipf E C 1973 *Phys. Rev. A* **8** 2463-8