Electron impact excitation cross sections for carbon monoxide

Lee Mu-Tao† and Vincent McKoy

A A Noyes Laboratory of Chemical Physics‡, California Institute of Technology, Pasadena, California 91125, USA

Abstract. We present distorted-wave cross sections for excitation of the A $^1\Pi$, a $^3\Pi$, a$'$ $^3\Sigma^+$, D $^1\Delta$ and d $^3\Delta$ states of CO by electrons in the 20 to 50 eV energy range. In these studies both the initial and final distorted waves are obtained in the static-exchange field of the ground electronic state. Differential and integral cross sections are presented and compared with available experimental data and with other calculations. The calculated differential cross sections for the A $^1\Pi$ and a $^3\Pi$ states agree poorly in magnitude, but better in shape, with available experimental data. In general the distorted-wave cross sections differ substantially from those of plane-wave-type theories such as the Born–Ochkur–Rudge approximation.

1. Introduction

The electronic excitation of molecules by electrons in the low and intermediate energy range is a very important process in many fields of physics and chemistry. However, to date, there has been limited progress in the experimental determination of these cross sections (Cartwright *et al* 1977a, b, Chutjian *et al* 1977, 1983, Trajmar *et al* 1968, 1971, Finn and Doering 1976, Linder and Schmidt 1971) as well as in the development of new theoretical methods (Chung and Lin 1978, Holley *et al* 1981, Rescigno *et al* 1975, 1976, Fliflet and McKoy 1980, Hazi 1981) for studying these cross sections. Until quite recently, Born-type approximations (Arrighini *et al* 1980, Chung and Lin 1972, 1974, Chung *et al* 1975, Cartwright 1970, 1972, Khare 1966, 1967) were the only practical method for calculating these inelastic cross sections. On the experimental side, N_2 is the only molecule for which the electronic excitation cross sections have been extensively studied at low and intermediate energies (Cartwright *et al* 1977a, b, Chutjian *et al* 1977, 1983, Finn and Doering 1976). In view of the significant experimental effort and difficulties involved in the measurement of these cross sections for molecules, it is clearly of interest to develop theoretical methods with some degree of reliability which can be applied routinely at least for linear molecules.

Recently, we have used the distorted-wave method (DW) to study the electronic excitation cross sections in H_2 (Lee *et al* 1982) and N_2 (Lee and McKoy 1982a, b).

† Permanent address: Departamento de Quimica, Universidade Federal de São Carlos, São Carlos, 13560, SP Brasil.
‡ Contribution No 6608.

The results were encouraging in light of their comparison with available experimental data. The DW integral cross sections (Lee *et al* 1982) as well as those of Fliflet and McKoy (1980) agreed quite well with the available experimental data for excitation of the b $^3\Sigma_u^+$ (Corrigan 1965), B $^1\Sigma_u^+$ (Srivastava and Jensen 1977) and C $^1\Pi_u$ (Yung *et al* 1982) states. The DW integral cross sections (Fliflet and McKoy 1980) were similar to the two-state close-coupling (CC) results of Chung *et al* (1975) for the B $^1\Sigma_u^+$ state but differed substantially from their CC cross sections for the b $^3\Sigma_u^+$. In the case of N_2, the method successfully reproduced the shape and magnitude of the experimental differential inelastic cross sections for excitation of several states. Such studies also serve to reveal the limitations of the DW method and to identify states where the assumptions of the distorted-wave method may fail.

In this paper, we report the results of similar distorted-wave studies for electronic excitation of CO. These studies can provide a further test of this method. Moreover, a comparison of the cross sections for CO and N_2 can be useful. Cross sections for low-energy electron–CO scattering are also required for modelling plasmas containing CO, as well as in gas-discharge lasers and in coal-fired MHD generators (Land 1978). These results are also useful in interpreting observations of dayglow emissions from the upper atmosphere of Mars and Venus.

Electronic excitation cross sections for several states of CO have been calculated by Chung and Lin (1974) using the Born–Ochkur–Rudge (BOR) approximation. Experimentally, some differential cross sections (DCS) in the low-energy range have been measured by Rice (1968) and by Cartwright and Trajmar (1981). Integral cross sections for excitation of the A $^1\Pi$ (Ajello 1971, Aarts and de Heer 1970, Mumma *et al* 1971) and a $^3\Pi$ (Ajello 1971) states have been measured by the emission method. Integral cross sections for excitation of several electronic excited states have also been estimated by the semi-empirical method (Sawada *et al* 1972).

In this paper, we present the DW cross sections for excitation of the A $^1\Pi$, a $^3\Pi$, a' $^3\Sigma^+$, D $^1\Delta$ and d $^3\Delta$ states in the 20–50 eV energy range. In § 2, we briefly outline the relevant theory. Details of the calculations and comparisons with the available experimental and theoretical data are presented in § 3.

2. Theory

Using the Born–Oppenheimer and Franck–Condon approximations, and treating the target rotational levels as essentially degenerate, the differential cross sections for electronic excitation by electron impact can be written as:

$$\frac{d\sigma}{d\Omega}(n \leftarrow 0; E, \hat{r}') = SM_n \sum_{\nu'} \frac{k_{\nu'}}{k_0} q_{\nu'0} \frac{1}{8\pi^2} \int d\hat{R}' |f_{k_0}(n \leftarrow 0; \boldsymbol{R}', \hat{r}')|^2 \tag{1}$$

where E is the impact energy, k_0 and $k_{\nu'}$ the momenta of the incoming and outgoing electrons, respectively, $q_{\nu'0}$ the Franck–Condon factor for the $\nu = 0$ level of the initial electronic state and ν' the vibrational level of the excited state. The factor S results from summing over final levels and averaging over initial spin sublevels. For singlet excitations S equals $\frac{1}{2}$ and for singlet to triplet excitations S equals $\frac{3}{2}$. For linear molecules M_n is the orbital angular momentum projection degeneracy factor of the final state (1 for a Σ state and 2 for a Π state). The laboratory-frame scattering

amplitude f_{k_0} can be related to the fixed-nuclei dynamical coefficients as follows:

$$f_{k_0}(n \leftarrow 0; \boldsymbol{R}', \hat{r}') = \sum_{ll'mm'} a_{ll'mm'}(n \leftarrow 0; k_0, R) D_{m''m}^{(l')*}(\hat{R}) D_{0m'}^{(l')}(\hat{R}) Y_{lm''}(\hat{r}') \tag{2}$$

where $D_{m''m}^{(l')}(\hat{R}')$ is the rotational harmonic and the fixed-nuclei dynamical coefficients, $a_{ll'mm'}$, can be approximated by the fixed-nuclei partial-wave components of the electronic portion of the DW transition matrix elements as:

$$a_{ll'mm'}(n \leftarrow 0, k_0, R) = -\tfrac{1}{2}\pi [4\pi(2l'+1)]^{1/2} i^{l-l'} \langle k_n lm, n | T_{el} | k_0 l'm', 0 \rangle \tag{3}$$

where $\langle k_n lm, n | T_{el} | k_0 l'm', 0 \rangle$ is the DW transition matrix element. In this DW approach, $|k_n lm\rangle$ and $|k_0 l'm'\rangle$ represent partial-wave components of the final and initial Hartree–Fock continuum spin orbitals of the ground-state potential respectively and n and 0 designate the excited and initial electronic states of the target. Further details are discussed by Fliflet and McKoy (1980).

3. Calculations and results

In this work, the elastic static-exchange continuum wavefunctions are obtained by the iterative Schwinger variational method (Lucchese and McKoy 1979, Watson *et al* 1980). The static-exchange potential is generated using the ground-state SCF wavefunction of CO, with the electronic configuration of $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$. The Hartree–Fock wavefunction at the equilibrium internuclear separation of 2.132 au was obtained by a SCF calculation using a standard [9s5p] primitive Cartesian Gaussian function contracted to a [4s3p] basis set (Dunning 1970). With this basis set, the total energy of the ground state is -112.6869 au, close to the HF limit of -112.7860 au (Huo 1965).

In these studies we obtained the continuum wavefunctions for $l \leq 10$ and $m \leq 2$. In the calculations, the partial-wave expansion of the direct and exchange potentials are carried out up to $l = 38$ and $l = 19$ respectively. Only one iteration was needed in the Schwinger iterative procedure.

Calculations have been carried out in the 20–50 eV range. To determine the energy of the scattered electron for a given incident energy, we used the experimental values (Krupenie 1966) of the vertical excitation energy from the $\nu = 0$ vibrational level of the initial electronic state.

3.1. Excitation to the triplet states

The a$'^3\Sigma^+$ and d$^3\Delta$ excited states are essentially characterised by the single-electron transition from the occupied 1π orbital to the unoccupied 2π orbital, whereas the a$^3\Pi$ state corresponds to the transition from the 5σ to 2π orbital. The experimental vertical excitation energies for the a$'^3\Sigma^+$, d$^3\Delta$ and a$^3\Pi$ states are 8.2, 9.1 and 6.3 eV (Krupenie 1966) respectively. For these states, the 2π orbital is taken as an eigenfunction of the V_{N-1} potential formed by removing an electron from the 1π orbital for the a$'^3\Sigma^+$ and d$^3\Delta$ states and from the occupied 5σ orbital for the a$^3\Pi$ state. The calculations were carried out using the computer codes developed by Goddard and co-workers (Hunt and Goddard 1974). With the same Gaussian basis set as in the ground-state SCF calculation, we obtain vertical excitation energies of 7.65, 8.55 and 5.80 eV for these states respectively.

Electron impact excitation of the triplet states in CO involves only the exchange part of the distorted-wave matrix elements. These matrix elements are again calculated by use of the single-centre expansion of the distorted waves, the target orbitals and the Coulomb interaction. In this expansion, sufficient terms are included to ensure the convergence of all matrix elements. The resulting radial two-electron integrals are evaluated numerically by Simpson's rule. The single-centre expansion of the distorted-wave matrix elements converges rapidly for exchange-type excitation processes. In this calculation, we included partial-wave matrix elements for $l, l' \leq 10$ and $m, m' \leq 2$. No higher order corrections were included. We estimate that the contribution from those higher partial-wave matrix elements to the differential cross sections to be less than 5% at the impact energies of this work.

For excitations of the $a'^3\Sigma^+$ and $a^3\Pi$ states, we used the Franck–Condon factors calculated by Nicholls (1962). However, for the transition $X^1\Sigma \rightarrow d^3\Delta$, we are not aware of any published Franck–Condon factors. Hence for this transition, we calculated the Franck–Condon factors using the published RKR potentials for both the ground and excited states (Krupenie and Weissman 1965), using the Numerov method (Cooley 1961) to integrate the radial equation.
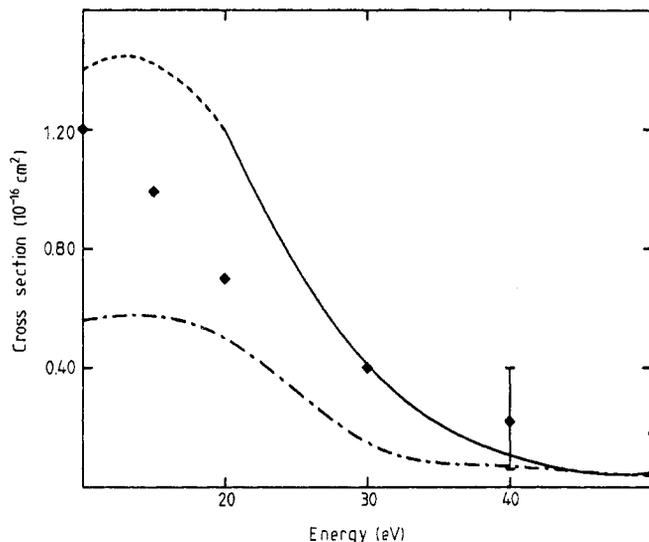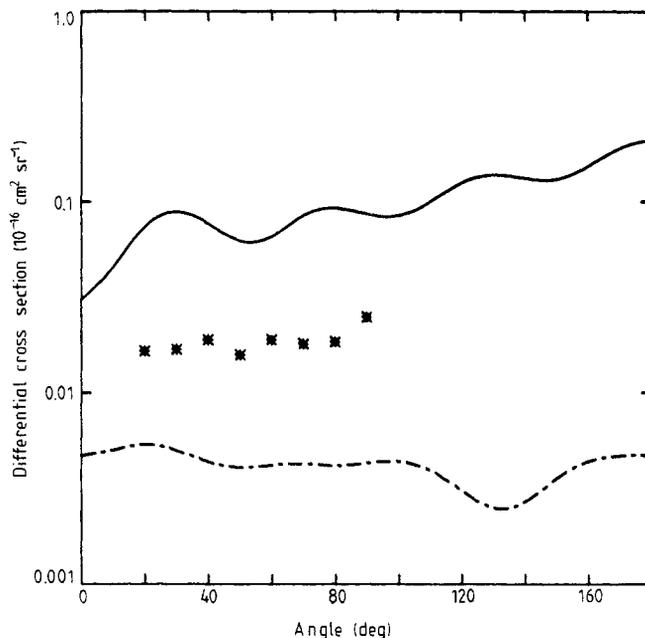

Figure 1. Integral cross section for the excitation of the $a^3\Pi$ state: the calculated DW results (full curve); the extrapolated DW results (broken curve, see text); the BOR results of Chung and Lin (1974) (chain curve) and experimental data of Ajello (1971) (diamonds).

In figure 1, we compare the integral cross section for the excitation of the $a^3\Pi$ state obtained by the DW method with those measured by emission experiments (Ajello 1971) along with the theoretical results obtained by the Born–Ochkur–Rudge (BOR) approximation (Chung and Lin 1974). The agreement between the DW cross sections and emission results is reasonable at the incident energies about 20 eV. Below that energy the shape resonance in the elastic scattering wavefunction leads to a large unphysical value of the DW inelastic cross section similar to the N_2 case (Lee and McKoy 1982a, b). The resonance-like feature in these DW inelastic cross sections is simply a consequence of the $^2\Pi$ shape resonance, which occurs around 3.8 eV, in

e–CO collisions at the static-exchange level. In the present DW model the final-state elastic wave is strongly affected by the resonance behaviour at 3.8 eV. This enhancement is a serious limitation of the present DW model. In figure 1 and other figures the broken lines below 20 eV do not correspond to DW values but are shown just to indicate the probable shape of the cross section in that region. The BOR approximation shows a smaller cross section at lower energies. As expected, the DW and BOR cross sections agree well as the energy increases.

In figure 2, we show the DW differential cross sections at 20 and 50 eV, along with the experimental measurements of Cartwright and Trajmar (1981) at 20 eV. Although it reproduces the shape of the experimental DCS quite well, the DW method overestimates the magnitude of the DCS by a factor of four. This overestimation of the DCS at 20 eV is probably caused by the influence of the elastic shape resonance at low energies and hence we can expect better agreement with experiment at higher incident energies.
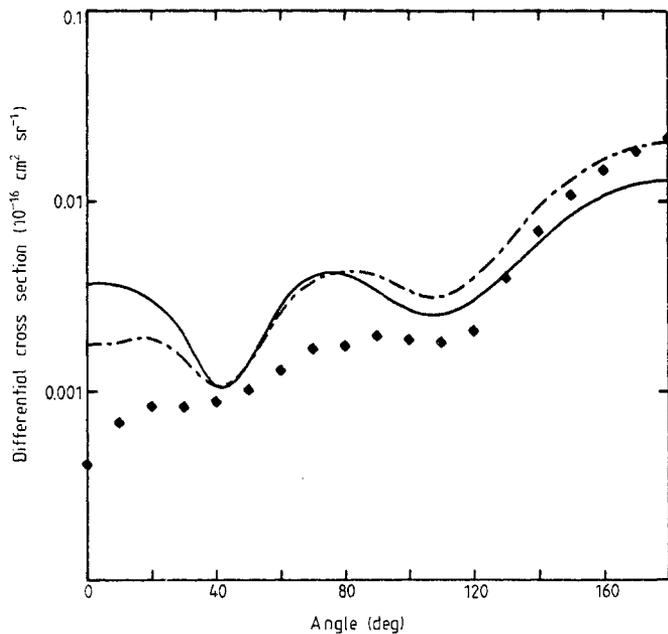

Figure 2. DCS for the excitation of the a $^3\Pi$ state: the DW results at 20 eV (full curve); the experimental data of Cartwright and Trajmar (1981) at 20 eV (stars); the DW results at 50 eV (chain curve).

In figure 3, we compare our DW integral cross sections for excitation of the a' $^3\Sigma^+$ state with the BOR results (Chung and Lin 1974). In this case, the BOR method gives considerably larger cross sections than the DW method. Although there are no experimental measurements available for this state, the analysis of the measured electron transport coefficient data (Land 1978) suggests that the BOR data should be reduced by a factor of 0.35. This reduced BOR cross section is also shown in figure 3. The agreement between this reduced BOR data and the DW cross section is quite good. In figure 3, we have also shown the DW (Lee and McKoy 1982a, b) and experimental (Cartwright *et al* 1977a, b) integral cross sections for excitation of the A $^3\Sigma_u^+$ state of N$_2$. One sees that the energy dependence of the N$_2$ cross sections is
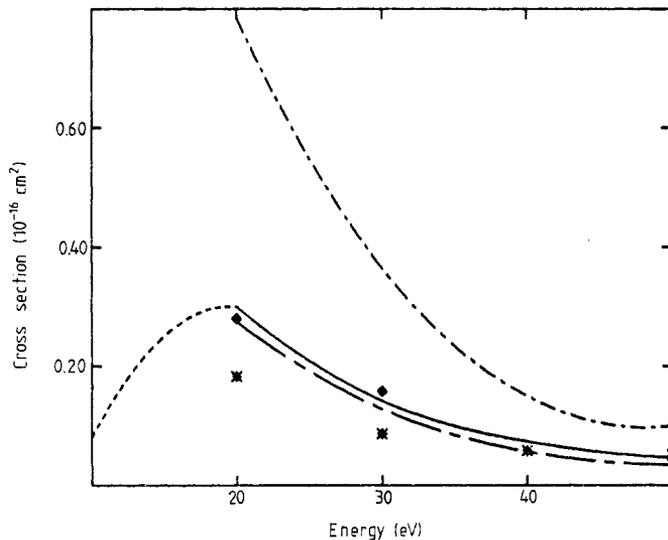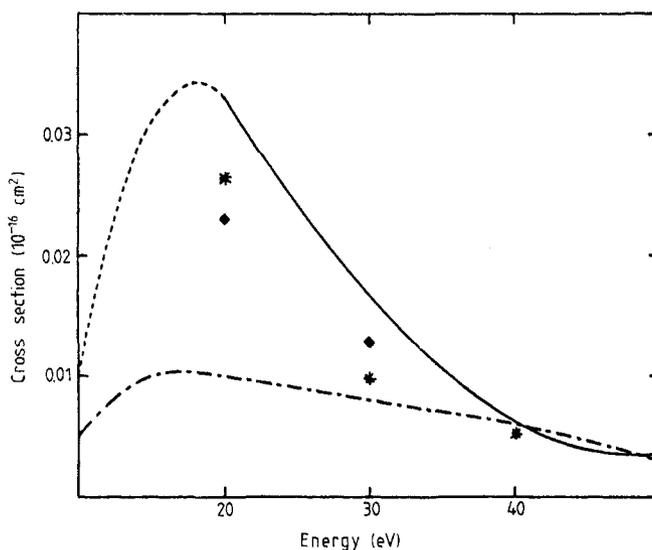
Figure 3. Integral cross section for the excitation of the $a'\,^3\Sigma^+$ state: the calculated DW results (full curve); the extrapolated DW results (broken curve, see text); the BOR results of Chung and Lin (1974) (chain curve); the BOR results multiplied by 0.35 as suggested by Land (1978) (long and short dashed curve); the DW results for excitation of the $A\,^3\Sigma_u^+$ state of N_2 (Lee and McKoy 1982a) (diamonds) and the corresponding experimental data for N_2 (Cartwright *et al* 1977b) (stars).

Figure 4. DCS for excitation of the $a'\,^3\Sigma^+$ state: the DW results at 50 eV (full curve); the DW result for the corresponding excitation in N_2 (chain curve, see text), the experimental DCS of the corresponding excitation in N_2 (Cartwright *et al* 1977b) (diamonds).

similar to that of CO, while the magnitude of the cross section in N_2 is smaller by a factor of two at 20 eV, but getting closer to the CO cross section at 50 eV.

In figure 4, we show the differential cross section for excitation of the a' $^3\Sigma^+$ state of CO at 50 eV. Again there are no experimental DCS available for this state. We have also plotted the DW (Lee and McKoy 1982a, b) and experimental (Cartwright *et al* 1977a, b) DCS for excitation of the A $^3\Sigma_u^+$ state in N_2 at the same energy. The agreement between these two sets of theoretical cross sections is quite good both in shape and magnitude. The same comparison has been done for elastic scattering of electrons by N_2 and CO (Bromberg 1969, 1970, Dubois and Rudd 1976, Tanaka *et al* 1978) showing that the angular distributions of elastically scattered electrons are very similar for these two gases. This similarity in behaviour is reasonable for the elastic scattering cross section since N_2 and CO are isoelectronic. It is interesting to observe that similar behaviour also occurs in the inelastic cross sections.

Figure 5. Integral cross sections for excitation of the d $^3\Delta$ state: the calculated DW results (full curve); the extrapolated DW results (broken curve); the BOR results of Chung and Lin (1974) multiplied by ten (chain curve); the DW results of the corresponding excitation in N_2 (diamonds); the experimental data for the corresponding excitation in N_2 (stars).

In figure 5 we show that DW integral cross section for excitation of the d $^3\Delta$ state along with the BOR cross sections of Chung and Lin (1974). No experimental data are available for this state. The agreement between these two sets of theoretical data is poor. Part of this poor agreement could be due to the fact that in their BOR calculation Chung and Lin (1974) used the virtual 2π orbital of the ground-state Hartree–Fock calculation for the excited 2π orbital of d $^3\Delta$ state. Again comparison shows that the DW integral cross sections for CO are quite similar to those for excitation of the W $^3\Delta_u$ state in N_2 for incident energies above 15 eV, i.e., away from the elastic shape resonance region. The DCS for excitation of the d $^3\Delta$ state at 50 eV is shown in figure 6. In this case, there are also no experimental measurements available. Comparison with the DW (Lee and McKoy 1982a, b) and experimental (Cartwright *et al* 1977a, b) DCS for excitation of the W $^3\Delta_u$ state in N_2 at the same energy shows these two DCS are similar, particularly in the forward and backward direction.
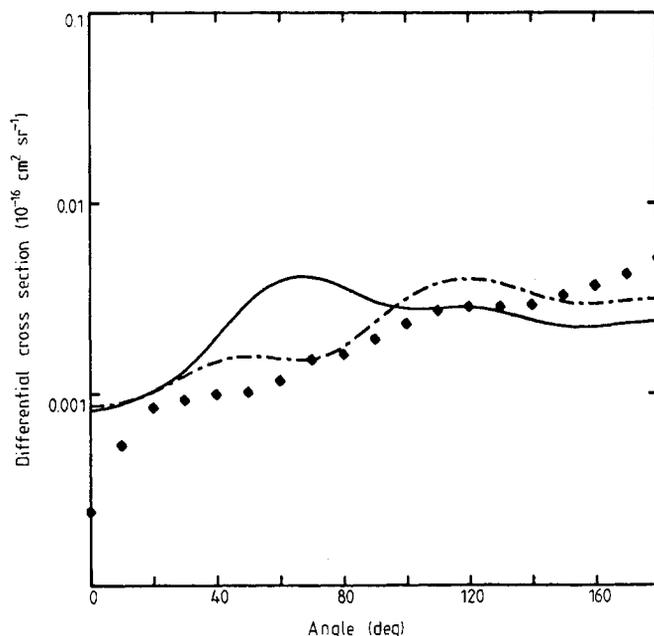
Figure 6. DCS for excitation of the d $^3\Delta$ state: the labels are the same as in figure 4.

3.2. Excitation of the singlet states

The A $^1\Pi$ and D $^1\Delta$ excited states essentially correspond to the single-electron transition from the occupied 5σ and 1π orbitals to the unoccupied 2π orbital respectively. The experimental excitation energies for the A $^1\Pi$ and D $^1\Delta$ states are 8.35 and 10.4 eV respectively. For these states, single-configuration wavefunctions are also obtained in the same way as for the triplet excited states and with the same basis set as in the SCF calculation. We obtained vertical excitation energies of 9.10 and 9.95 eV for the A $^1\Pi$ and D $^1\Delta$ states respectively.

In these singlet–singlet excitation processes, both the direct and exchange parts of the partial-wave transition matrix elements are included with l, $l' \leqslant 10$ and m, $m' \leqslant 2$. The contribution from higher partial-wave terms to the direct matrix elements are included in the Born approximation in the same way as described by Fliflet and McKoy (1980). No higher-order corrections are carried out in the exchange matrix elements.

For excitation of the A $^1\Pi$ state, we also used the Franck–Condon factors calculated by Nicholls (1962). For the excitation of the D $^1\Delta$ state, we calculated the Franck–Condon factors using the RKR potential curve for both the ground and excited states (Krupenie and Weissman 1965, Simmons and Tilford 1966).

In figure 7, we compare the DW integral cross sections for excitation of the A $^1\Pi$ state with the BOR results (Chung and Lin 1974) and the experimental data obtained by the emission method (Ajello 1971, Mumma *et al* 1971). The agreement between these two sets of theoretical results is good for impact energies above 30 eV. However, both results overestimate the cross sections by a factor of three, compared with the experimental data from the emission measurements. Below 30 eV, the resonance-like feature is again observed and causes a large enhancement of the cross sections in the DW method.
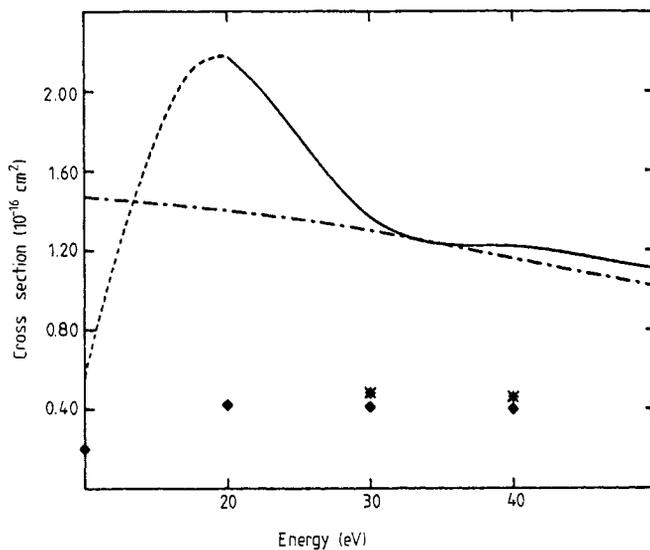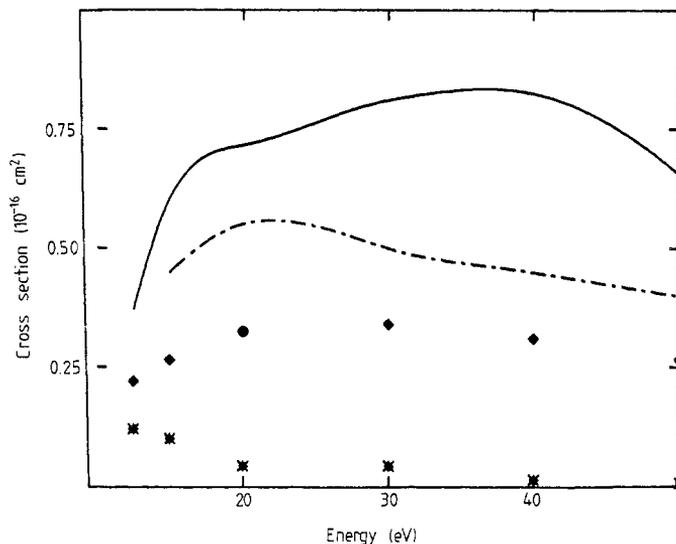
Figure 7. Integral cross sections for excitation of the A $^1\Pi$ state: the calculated DW results (full curve); the extrapolated DW results (broken curve); the BOR results of Chung and Lin (1974) (chain curve); the experimental data of Ajello (1971) (diamonds) and Mumma *et al* (1971) (stars).
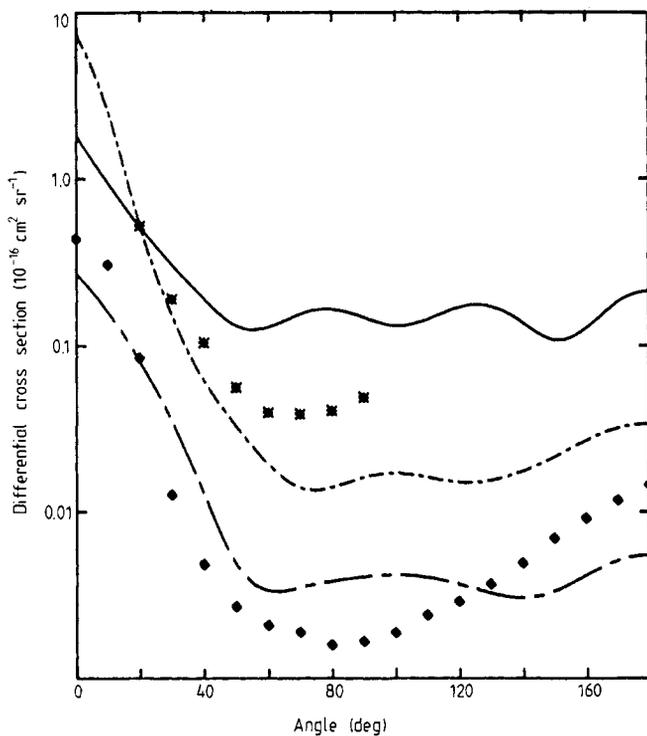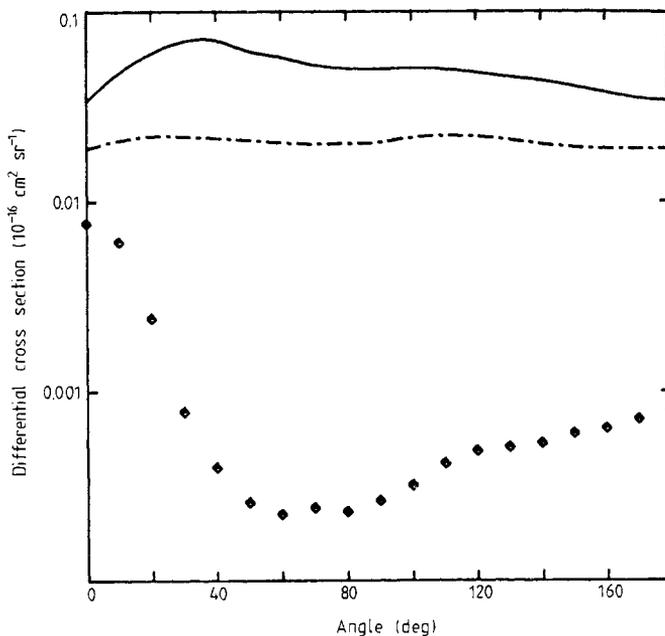

Figure 8. DCS for excitation of the A $^1\Pi$ state: the DW results at 20 eV (full curve) and 50 eV (chain curve); the experimental data at 20 eV (Cartwright and Trajmar 1981) (stars); the DW (Lee and McKoy 1982b) (long and short dashed curve) and experimental DCS (Chutjian *et al* 1983) (diamonds) for the corresponding excitation in N_2 at 50 eV.

In figure 8, we show the DW DCS for this excitation at 20 and 50 eV. At 20 eV, we compare our DCS with the experimental results of Cartwright and Trajmar (1981) in the angular range between 20 and 90°. The DW theory again reproduces the shape of the experimental DCS. However, the theory overestimates its magnitude. As in the excitation of the A $^3\Pi$ state, this overestimation is caused by the enhancement of the cross section due to the shape resonance in the $^2\Pi$ channel in the elastic scattering.

Figure 9. Integral cross sections for excitation of the D $^1\Delta$ states: the labels are the same as in figure 5.

Figure 10. DCS for excitation of the D $^1\Delta$ state: the labels are the same as in figure 6.

We expect that better agreement might be obtained at higher impact energies. At 50 eV, we compare the DCS for this excitation with the DW (Lee and McKoy 1982a, b) and experimental (Cartwright *et al* 1977a, b) DCS of the corresponding excitation (i.e., $X\,^1\Sigma_g^+ \to a\,^1\Pi_g$) in N_2. In this case, the shape of these two sets of theoretical DCS is very similar, although the magnitude of the DCS in CO is much larger.

In figure 9, we show the DW integral cross sections for excitation of the $D\,^1\Delta$ state along with the BOR results of Chung and Lin (1974). The agreement between these results is again very poor. The comparison with the DW integral cross sections for excitation of the $w\,^1\Delta_u$ state in N_2 shows the same angular dependence but the cross section for CO is larger in general by a factor of two. This difference between the present DW results and those of the BOR can be partly due again to the use of the 2π virtual orbital of the ground state in the $w\,^1\Delta_u$ state in the BOR calculation. However, comparison with the data of N_2 suggests that interchannel coupling may be important in the excitation of this state.

The DCS for excitation of the $D\,^1\Delta$ state at 50 eV is compared with the DW (Lee and McKoy 1982a, b) and experimental (Cartwright *et al* 1977a, b) DCS of the corresponding excitation of N_2 in figure 10. The poor agreement between the calculated and measured cross sections for this state of N_2 has been discussed previously (Lee and McKoy 1982a).

4. Conclusion

We have applied the distorted-wave approximation to calculate the electron impact cross sections for several states of CO. Comparison with measured cross sections for the $a\,^3\Pi$ and $A\,^1\Pi$ states shows that, although the DW method overestimates the magnitude of the DCS by a factor of four, it does much better in reproducing the shape of the DCS. There are no experimental data on the DCS available for any other states of CO. The DW integral cross section for the $A\,^1\Pi$ is also about three times larger than the measured cross sections. In general, however, the DW cross sections differ substantially from those predicted by the BOR approximation. As expected the difference between these DW and BOR cross sections decreases with increasing impact energies. Comparison of these cross sections with those of the corresponding excitations in N_2 show, that in most cases, the shapes of the angular distribution are similar for these two systems. In general, the DCS of CO are larger. As in the case of N_2, the large enhancement of the DW inelastic cross sections caused by the shape resonance in the $^2\Pi$ elastic out-going distorted wave is observed. These resonance-like enhancements limit the applicability of the DW theory at energies near threshold. Simple procedures for removing these resonance-like enhancements and to extend the DW method to more complicated molecules (e.g., CO_2) are now in progress.

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