Electron excitation of electronic states of the CO molecule*

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The electron-impact excitation cross sections of the $A^1\Pi$, $E^1\Pi$, $B^1\Sigma^+$, $C^1\Sigma^+$, $D^1\Delta$, $a^3\Pi$, $c^3\Pi$, $b^3\Sigma^+$, $j^3\Sigma^+$, $a'^3\Sigma^+$, and $d^3\Delta$ states of the CO molecule have been calculated for the incident electron energies over the range of threshold to 1000 eV for the singlet states and up to 100 eV for the triplet states by means of the Born approximation with Ochkur's and Rudge's modification for treating electron-exchange scattering. The wave functions of the various electronic states used in this calculation were determined by the self-consistent-field procedure with the Gaussian-type orbitals as basis functions. The calculated generalized oscillator strengths of the $A^1\Pi$, $E^1\Pi$, and $C^1\Sigma^+$ state are in reasonable agreement with the experimental values of Lassettre *et al.*, but a larger discrepancy is found for the $B^1\Sigma^+$ state. The total cross sections calculated by this scheme show satisfactory agreement with experiment (30% at 300 eV) for the $A^1\Pi$ state and are generally within the range of uncertainty of the experimental data for $a^3\Pi$. For the $B^1\Sigma^+$ and $b^3\Sigma^+$ states the theoretical cross sections differ very significantly from the experimental data of Skubenich which, however, are in serious disagreement with measurements reported from two other laboratories.

I. INTRODUCTION

The excitation properties of electron-atom collision processes have been studied quite extensively by using various theoretical formalisms; comparisons of the results of different theoretical formalisms with each other, as well as with experimental data, have been made.[1-4] On the other hand, theoretical studies of the corresponding molecular problem, i.e., electron excitation of the electronic states of molecules, are in a comparatively primitive stage. Progress in the theory of electron-molecule excitation has been impeded mainly by the computational difficulties associated with multicenter integrals. However, recent works have shown that by expressing the molecular wave functions in terms of Gaussian-type orbitals (GTO), the computational difficulty can be resolved so that the electron-excitation cross sections of the electronic states of molecules may be computed readily by means of the Born approximation.[5-7] With the availability of the Hartree-Fock self-consistent-field (SCF) method for calculating electronic wave functions of molecules, it becomes practical to make extensive theoretical investigations of electron excitation of electronic states of diatomic molecules. Thus, for the case of the N_2 molecule, we have calculated excitation cross sections for 12 electronic states and compared them with the available experimental data.[5]

Measurements of excitation cross sections of electronic states of the CO molecule have been reported by several groups.[8-16] Interest in excitation of CO was further accentuated as a result of the observations of Mars's atmosphere by Mariner 6 and 7. Particularly, the Fourth Positive System ($A^1\Pi$) and the Cameron Bands ($a^3\Pi$) are of special interest because they are among the prominent features of the ultraviolet emission bands observed in Mars's atmosphere.[17] On the other hand, the problem of *ab initio* theoretical calculations of such cross sections has received much less attention in the literature, although calculations of the generalized oscillator strengths of the $A^1\Pi$ state by means of the Tamm-Dancoff and random phase approximations have been reported by Szabo and Ostlund.[18]

We have conducted a comprehensive theoretical study of electron excitation of CO by means of the Born-type approximation. In this paper we present theoretical excitation cross sections of the $A^1\Pi$, $E^1\Pi$, $B^1\Sigma^+$, $C^1\Sigma^+$, $D^1\Delta$, $a^3\Pi$, $c^3\Pi$, $b^3\Sigma^+$, $j^3\Sigma^+$, $a'^3\Sigma^+$, and $d^3\Delta$ states of the CO molecule over the range of threshold to 1000 eV for the singlet states and threshold to 100 eV for the triplet states. As explained in our previous paper on N_2, although the plane-wave approximation is inherently a high-energy one, the use of the Ochkur or Rudge modification of the Born-Oppenheimer approximation may possibly provide sufficient improvement so as to extend the validity of the Born-Oppenheimer method to much lower energies. Indeed, in the case of excitation to the $C^3\Pi_u$ state of N_2, a reasonable agreement has been found between the Born-Rudge cross sections and the experimental values. For incident electron energies higher than 100 eV, the theoretical excitation cross sections for all the triplet states reported in this paper diminish

characteristically as the inverse cube of the incident-electron energy. Cross sections for energies above 100 eV can therefore be obtained from the values at 100 eV by extrapolation.

II. RESUME OF THEORY

The present problem of electron excitation of the CO molecule differs little from that of N_2 molecule. Since the theoretical formulation for the N_2 problem has already been presented,[5] we shall outline here only the key points pertinent to our discussions. Let us consider the excitation of a heteronuclear diatomic molecule from the ground electronic and vibrational state (00) to an excited state (nv). The rotational structure of the molecule will be ignored; instead, we shall average the excitation cross sections over the orientation of the molecule with respect to the direction of the incident electron. Under the one-configuration approximation for the molecular wave functions, the excitation process may be described as a transition of an electron from one molecular orbital ϕ_λ of the ground configuration to another ϕ_μ of a particular excited configuration. (For the $B\,^1\Sigma^+$, $C\,^1\Sigma^+$, and $a'\,^3\Sigma^+$ states the wave functions are of the multiconfiguration form; extension of the theory described in this section to the multiconfiguration case can be made in a straightforward manner and will not be detailed here.) For a diatomic molecule with a closed-shell structure in the ground configuration, the transition amplitude is

$$\mathscr{S}_{on}(K,\Theta,\Phi,R) = -\sqrt{2}\int \phi_\mu^*(\vec{r},\vec{R})e^{i\vec{K}\cdot\vec{r}}\phi_\lambda(\vec{r},\vec{R})d\vec{r}\,,$$

$$(1)$$

with

$$\vec{K} = \vec{k}_{00} - \vec{k}_{nv}\,,\tag{2}$$

where $\vec{k}_{00}$ and $\vec{k}_{nv}$ are the incident and scattered wave vectors, respectively, and Θ and Φ specify the orientation of the molecular axis relative to $\vec{K}$. The molecular orbitals are functions of the electron coordinates $\vec{r}$ and depend parameterically on the internuclear distance R. By using the Born approximation the direct-excitation collision amplitude is

$$f_{nv}(\theta\phi) = 2K^{-2}\int\!\!\int\mathscr{S}_{on}(K,\Theta,\Phi,R)\chi_{nv}^*(R)\chi_{00}(R)R^2\,dR\,,$$

$$(3)$$

$$f_{nv}(\theta\phi) \cong 2K^{-2}\mathscr{S}_{on}(K,\Theta,\Phi,R_0)\int \chi_{nv}^*(R)\chi_{00}(R)R^2\,dR\,,$$

$$(4)$$

where χ_{00} and χ_{nv} are the vibrational wave functions of the initial and final states, respectively.

In going from Eq. (3) to Eq. (4), we have used the "Franck-Condon factor approximation" by which we have suppressed the dependence of $\mathscr{S}_{on}$ on R, and evaluated $\mathscr{S}_{on}$ at the equilibrium internuclear separation R_0 of the ground state. This procedure is quite satisfactory in the case of excitation from the ground vibrational state whose wave function has a very localized form. From the experimental data of Holland[19] for the $a\,^1\Pi_g$ state of N_2 and of Mumma, Stone, and Zipf[11] for the $A\,^1\Pi$ state of CO, the Franck-Condon factor approximation is found to work rather well. To test this approximation from the theoretical standpoint, we have computed differential cross sections $(A\,^1\Pi)$ corresponding to the $|\vec{K}|$ values [as defined in Eq. (2)] ranging from 0 to 1 with and without the Franck-Condon factor approximation. For excitation to the first eight vibrational levels $(v=0-7)$ of the $A\,^1\Pi$ state, the discrepancy in the differential cross sections due to the Franck-Condon factor approximation does not exceed 6%.

The exchange-excitation collision amplitude of the Born-Oppenheimer approximation has been modified by Ochkur[20] and subsequently by Rudge,[21] with the results

$$g_{nv}^+(\theta\phi) = -(K^2/\sqrt{2}T^2)f_{nv}(\theta\phi)\,,$$
$$g_{nv}^-(\theta\phi) = -(\sqrt{3}K^2/\sqrt{2}T^2)f_{nv}(\theta\phi)\,,$$

$$(5)$$

where g_{nv}^+ and g_{nv}^- are, respectively, the exchange amplitude of the singlet and triplet excitation, and

$$T^2 = k_{00}^2 \quad\text{(Ochkur)}\,,$$
$$T^2 = (k_{nv} - i\epsilon^{1/2})^2 \quad\text{(Rudge)}\,,$$

$$(6)$$

ϵ being the ionization energy of the initial state.

From the collision amplitudes we obtain the differential cross sections for singlet and triplet excitations as

$$I_{nv}^S(\theta\phi) = \frac{\omega_n k_{nv}}{4\pi k_{00}}\int d\Omega\,|f_{nv} + g_{nv}^+|^2$$

$$= \frac{\omega_n k_{nv}q_{nv}}{\pi k_{00}}\int d\Omega\,|(K^{-2} - \tfrac{1}{2}T^{-2})\mathscr{S}_{on}(K,\Theta,\Phi,R_0)|^2\,,$$

$$(7)$$

$$I_{nv}^T(\theta\phi) = \frac{3\omega_n k_{nv}q_{nv}}{\pi k_{00}}\int d\Omega\,|-\tfrac{1}{2}T^{-2}\mathscr{S}_{on}(K,\Theta,\Phi,R_0)|^2\,,$$

$$(8)$$

respectively, where q_{nv} is the Franck-Condon factor defined as

$$q_{nv} = |\int \chi_{nv}^*(R)\chi_{00}(R)R^2\,dR|^2\,,\tag{9}$$

ω_n is the degeneracy of the final state, and the integration over Ω results from averaging of the orientation of the molecular axis with respect to $\vec{K}$. Integration of Eqs. (7) and (8) with respect to $(\theta\phi)$ gives the excitation cross sections to the

individual electronic-vibrational levels from which the total cross section $Q(0 \to n)$ of excitation to an electronic state may be obtained, i.e.,

$$Q(00 \to nv) = 2\pi q_{nv} \int_{K_{min}}^{K_{max}} I_{nv}(K) K \, dK , \qquad (10)$$

$$Q(0 \to n) = \sum_{v} Q(00 \to nv) . \qquad (11)$$

Here, we have made the familiar change of variables to K, K_{min} and K_{max} being $(k_{00} - k_{nv})$ and $(k_{00} + k_{nv})$, respectively, and

$$I_{nv}^{S}(K) K \, dK = \frac{\omega_n K \, dK}{\pi k_{00}^2} \int d\Omega \, | (K^{-2} - \tfrac{1}{2} T^{-2}) \mathcal{E}_{on}(K, \Theta, \Phi, R_0)|^2 , \qquad (12)$$

$$I_{nv}^{T}(K) K \, dK = \frac{3\omega_n K \, dK}{\pi k_{00}^2} \int d\Omega \, | -\tfrac{1}{2} T^{-2} \mathcal{E}_{on}(K, \Theta, \Phi, R_0)|^2 .$$

It is useful to introduce the quantity

$$G_{on}(K) = \frac{2\omega_n}{4\pi K^2} \int | \mathcal{E}_{on}(K, \Theta, \Phi, R_0)|^2 \, d\Omega \qquad (13)$$

as an intermediate step for calculating the differential and total cross sections. In terms of $G_{on}(K)$, the differential cross sections in Eq. (12) may be expressed as

$$I_{nv}^{S}(K) K \, dK = (2 \, dK/k_{00}^2 K) G_{on}(K) | 1 - \tfrac{1}{2} K^2 / T^2 |^2 , \qquad (14)$$

$$I_{nv}^{T}(K) K \, dK = (3K^3 \, dK/2k_{00}^2) G_{on}(K) / | T^2 |^2 . \qquad (15)$$

Since it is through $G_{on}(K)$ functions that the cross sections depend on the molecular wave function, $G_{on}(K)$ functions serve a useful purpose in appraising the sensitivity of cross sections on the accuracy of wave functions. In the case of *singlet-to-singlet excitation*, the $G_{on}(K)$ function is simply equal to the generalized oscillator strength divided by the vertical excitation energy. Finally, the optical oscillator strength is obtained as the limiting value of the generalized oscillator strength at $K = 0$.

III. WAVE FUNCTIONS

The electronic states of the CO molecule considered in this paper arise primarily from the following electronic configurations[22-25]:

$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$,

$X^1\Sigma^+$ (ground) ;

$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)(2\pi)$,

$A^1\Pi, a^3\Pi$ (valence) ;

$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^3(5\sigma)^2(2\pi)$,

$^1\Sigma^+, a'\,^3\Sigma^+, D\,^1\Delta, d\,^3\Delta, I\,^1\Sigma^-, e\,^3\Sigma^-$ (valence) ;

$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)(3p\pi)$,

$E^1\Pi, c^3\Pi$ (Ry) ;

$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)(3s\sigma)$,

$B^1\Sigma^+, b\,^3\Sigma^+$ (Ry) ;

$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)(3p\sigma)$,

$C^1\Sigma^+, j\,^3\Sigma^+$ (Ry) .

The identifications of most of the states are contained in the review work of Krupenie.[22] Discussion of the $c^3\Pi$ and $j^3\Sigma^+$ states may be found in Refs. 23 and 24. The valence $^1\Sigma^+$ $[(1\pi)^3(2\pi)]$ state has not been observed (or identified) to our knowledge.

The wave functions used in this paper are computed by the self-consistent-field method[26,27] with GTO basis functions. We have adopted the technique of contracted Gaussians,[27] and our basis set consists of contracted GTO's (three s type and two p type) centered at each atom as given by Dunning,[28] and two s-type and two p-type floating GTO's located at the center of the nuclear charges. The equilibrium internuclear separation of the ground state $(R_0 = 2.132a_0)$ is used throughout. For each of the $X^1\Sigma^+$, $A^1\Pi$, $a^3\Pi$, $E^1\Pi$, $c^3\Pi$, $b^3\Sigma^+$, and $j\,^3\Sigma^+$ states, we have performed separate SCF calculations to obtain the wave functions appropriate for the particular state. In the cases of the (5σ) $(3s\sigma)$ and (5σ) $(3p\sigma)$ configurations, application of the general SCF scheme given in Ref. 26 to the singlet states $(B^1\Sigma^+$ and $C^1\Sigma^+)$ is complicated by the presence of two partially occupied shells of the same symmetry, although this difficulty does not exist for the triplet states $(b^3\Sigma^+$ and $j^3\Sigma^+)$. An alternative procedure is therefore adopted to find the wave functions of the $B^1\Sigma^+$ and $C^1\Sigma^+$ states. Here, we solve the SCF problems appropriate for the $(5\sigma)(6\sigma)^3\Sigma^+$, (5σ) $\times (7\sigma)^3\Sigma^+$, $(5\sigma)(8\sigma)^3\Sigma^+$, and $(5\sigma)(9\sigma)^3\Sigma^+$ states $(6\sigma$ and 7σ being $3s\sigma$ and $3p\sigma$, respectively), and use the 6σ, 7σ, 8σ, and 9σ orbitals so obtained to construct the zeroth-order functions of the corresponding $^1\Sigma^+$ states. The wave functions of the $B^1\Sigma^+$ and $C^1\Sigma^+$ states are then determined from a configuration-interaction (CI) calculation for the $^1\Sigma^+$ states covering five excited configurations $[(1\pi)^3(2\pi)$ and the four $(5\sigma)(n\sigma)]$ by using those zeroth-order functions as basis. The difficulty of having two partially occupied shells of the same symmetry is also encountered in the $(1\sigma)^2 \cdots (1\pi)^3$ $\times (5\sigma)^2 (2\pi)$ configuration. Thus, we again apply a CI procedure to find the wave function of the $a'\,^3\Sigma^+$ state. On the other hand, of all the configurations listed in the first paragraph of this section, only

$(1\pi)^3(2\pi)$ contains Δ states; to carry out a CI analysis for the $D^1\Delta$ and $d^3\Delta$ states would therefore require a considerable amount of work of obtaining wave functions of configurations involving δ orbitals. Since our main interests lie in the excitation of the Σ^+ and Π states for which experimental data are available, an extensive CI calculation for the Δ states is not deemed worthwhile at this stage. Instead, we shall simply approximate the 2π orbital of the Δ states by the corresponding unoccupied orbital resulting from the SCF calculation of the $X^1\Sigma^+$ ground state. The Σ^- states have zero-excitation cross section under the Born approximation and will not be dealt with here. In most cases, the molecular orbitals (1σ), (2σ), ... of an excited state are not orthonormal to those of the ground state. The problem of non-orthonormality can be removed by means of a transformation similar to the ones described by King et al.[29]

Nesbet[30] has published a set of SCF molecular orbitals of the CO molecule. We will have occasions to use his functions to test the sensitivity of the theoretical cross sections with respect to the choice of wave functions. In Nesbet's paper the SCF calculations were reported for the ground configuration only; thus, to calculate excitation cross sections we have to approximate the excited-state functions by using the unoccupied orbital of the ground state. Because Nesbet's wave functions are expressed in terms of the Slater-type orbitals, we have curve-fitted them into the Gaussian form to facilitate the numerical work.

IV. RESULTS

A. $G_{on}(K)$ functions

Since the differential cross sections are directly related to $G_{on}(K)$ as shown in Eqs. (14) and (15), the $G(K)$ functions as defined in Eq. (13) lend themselves very well to the studies of variations of the computed cross sections due to the use of different sets of wave functions. In this section we shall examine the behaviors of the $G(K)$ functions for the various transitions.

1. $5\sigma \rightarrow 2\pi$

The $5\sigma \rightarrow 2\pi$ transition is responsible for excitation of the $A^1\Pi$ and $a^3\Pi$ states. We present in Fig. 1 the $G(K)$ functions [curves (i) and (ii)] calculated by using the 5σ orbital of the ground state $X^1\Sigma^+$ coupled with (i) the 2π orbital of the $A^1\Pi$ state and (ii) the 2π orbital of the $a^3\Pi$ state. The small difference between these two curves is a reflection that the 5σ and 2π orbitals of the $A^1\Pi$ state differ slightly from those of $a^3\Pi$. It has been a rather common practice to approximate the ex-

cited orbital of an *excited* state by the corresponding unoccupied orbitals of the ground state. To test this approximation we have used the unoccupied 2π orbital of the $X^1\Sigma^+$ ground state to calculate $G(K)$, and the results are shown in Fig. 1 as curve (iii). In addition, we have repeated the same calculation [curve (iv) in Fig. 1] by using the 5σ and unoccupied 2π orbitals associated with $X^1\Sigma^+$ reported by Nesbet.[30] From the close resemblance of curves (iii) and (iv) we expect that the sensitivity of the computed cross sections on the choice of different SCF wave functions (of the $X^1\Sigma^+$ state) is not likely to be large. However, both curves (iii) and (iv) show much larger (~50%) values than do curves (i) and (ii). This is understandable since the 2π orbital of an excited configuration may be considerably different from that of the ground configuration. The large difference in $G(K)$ suggests that the use of the unoccupied orbitals could lead to an appreciable error in the theoretical cross sections.

Szabo and Ostlund[18] made a theoretical calculation of the generalized oscillator strengths of the $A^1\Pi$ state by means of the Tamm-Dancoff (TDA)
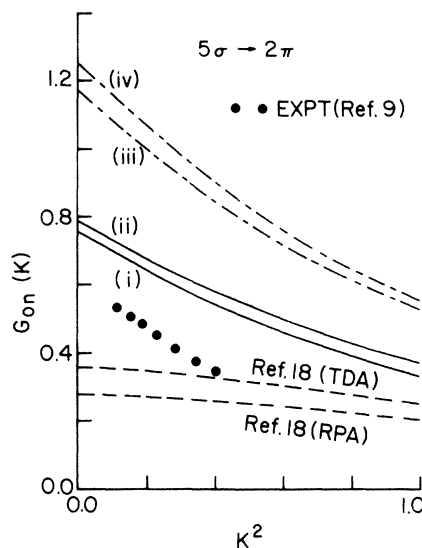

FIG. 1. Theoretical values of $G_{on}(K)$ [defined in Eq. (13)] for the $5\sigma \rightarrow 2\pi$ transition computed by using the 5σ orbital of $X^1\Sigma^+$ coupled with (i) 2π orbital of $A^1\Pi$ (solid line), (ii) 2π orbital of $a^3\Pi$ (solid line). For comparison we also show *approximate* $G_{on}(K)$ computed by using 5σ and *unoccupied* 2π orbitals of the $X^1\Sigma^+$ state wave functions (iii) of the present work (long-short dashed line), and (iv) of Ref. 30 (long-short dashed line). Included are also the theoretical calculations of Szabo and Ostlund in Ref. 18 by means of the Tamm-Dancoff (TDA) and random phase (RPA) approximations (even dashed line). The experimental data of Lassettre and Skerbele in Ref. 9 are shown as circles.

and random phase approximations (RPA) along with the molecular orbitals calculated by Ransil[31] with the minimal basis set. In Fig. 1 we see that the TDA and RPA results of Ref. 18 are much smaller in magnitude and have flatter shape. In Ref. 18 the authors pointed out the inadequacy of representing the diffuseness of the excited state ($A\,^1\Pi$) by using the minimal basis set as was used in their calculation. They further quote that by enlarging the basis set the values of the optical oscillator strength increased substantially by both TDA and RPA methods. It is our opinion that the discrepancy between the present work and that of Ref. 18 probably originates, to a large measure, from the different way by which the excited-state wave function is represented. As mentioned before, in calculating the curve (i) we have used the wave functions of the $A\,^1\Pi$ state obtained from *ab initio* SCF calculation appropriate for the $A^1\Pi$ state.

Lassettre and his co-workers[8,9] reported generalized oscillator strengths of the $A\,^1\Pi$ state determined from the electron-impact energy loss experiments. We have included in Fig. 1 the recent data [reduced to $G(K)$] of Lassettre and Skerbele,[9] which are on the average smaller by a factor of 0.727 than the earlier data of Lassettre and Silverman.[8] Lassettre and Skerbele suggest that the cause of this difference is due to an error probably related to the measurement of pressure. Compared with the present theoretical curve (i), the more recent values of Ref. 9 are smaller typically by a factor of 0.75. However, a reasonably good agreement is seen for the shape of $G(K)$ function between the present theory and the experiment. From $G(K=0)$ we obtain the theoretical optical oscillator strength of 0.232, which may be compared with experimental value of 0.195 of Ref. 9. Hesser[32] has determined the optical oscillator strength as 0.094 from the lifetime measurement. However, reanalyses of his data have been reported in Refs. 9 and 11, indicating new values of 0.17 and 0.15, respectively.

2. $5\sigma - 3p\pi$

The $G(K)$ functions for the $5\sigma \to 3p\pi$ transitions appropriate for the $E\,^1\Pi$ and $c\,^3\Pi$ states are shown in Fig. 2. Unlike the case of the $A\,^1\Pi$ and $a\,^3\Pi$ states, the $G(K=0)$ for the $c\,^3\Pi$ state is about 40% larger than the $G(K=0)$ for the $E\,^1\Pi$ state. From $G(K=0)$ we obtain the optical oscillator strength of the $E\,^1\Pi$ state as 0.105, which is nearly identical with the experimental value of 0.101 reported by Lassettre and Skerbele.[9]

3. $1\pi - 2\pi$

When an electron in a degenerate 1π orbital is

promoted to another degenerate 2π orbital, four different assignments may be made, i.e., a Σ^+, a Σ^-, and a doubly degenerate Δ state. The triplet Σ^+ state is designated as $a'\,^3\Sigma^+$, but we have found no identification for the optically allowed $^1\Sigma^+$ state. The other states ($D\,^1\Delta$, $d\,^3\Delta$, $I\,^1\Sigma^-$, $e\,^3\Sigma^-$) are all dipole-forbidden states. For the symmetry forbidden Σ^- states the transition amplitude vanishes identically under the Born approximation, and in order to calculate the theoretical cross sections of these states, it would be necessary to include indirect coupling potentials via other intermediate states. This would require much more complex computational procedures, and we shall exclude these states from consideration in this paper.

In **Fig. 3** we show the $G(K)$ function appropriate for the $a'\,^3\Sigma^+$ state and one for the $D\,^1\Delta$ and $d\,^3\Delta$ states. As $K^2 \to 0$ the $G(K)$ curve tends to a constant value for $a'\,^3\Sigma^+$ state and to zero (proportional to K^2) for Δ states. The wave functions for the $D^1\Delta$ and $d^3\Delta$ states were constructed from the same set of molecular orbitals (derived from the SCF calculation of the ground state); consequently, these two Δ states have the same $G(K)$ curve. A similar calculation of $G(K)$ of the Δ states based on Nesbet's functions (SCF solution appropriate for $X^1\Sigma^+$) gives results which are about 10% smaller than the ones shown in Fig. 3. While this agreement may be taken as an indica-
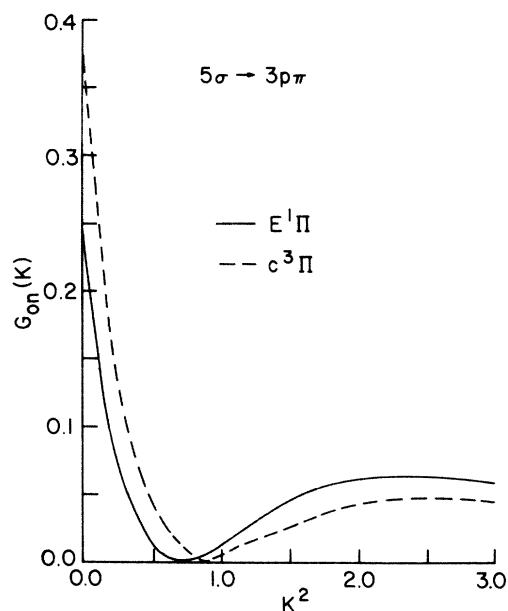

FIG. 2. Theoretical values of $G_{on}(K)$ [defined in Eq. (13)] for the $5\sigma \to 3p\pi$ transition appropriate for the $E^1\Pi$ state (solid line) and for the $c\,^3\Pi$ state (dashed line).

tion of convergence as far as the SCF calculation of the ground $X^1\Sigma^+$ state is concerned, the inherent approximation of using the unoccupied 2π orbital may lead to a considerably larger error. There are no experimental or theoretical data that we are aware of to compare with the present calculations.

4. $5\sigma \rightarrow 3p\sigma$ and $5\sigma \rightarrow 3s\sigma$

The $5\sigma \rightarrow 3p\sigma$ transition gives rise to the Rydberg $C^1\Sigma^+$ and $j^3\Sigma^+$ states, while the Rydberg $B^1\Sigma^+$ and $b^3\Sigma^+$ states result from the $5\sigma \rightarrow 3s\sigma$ transition. In Figs. 4 and 5 we show the $G(K)$ functions of these transitions which are appropriate for the respective singlet states. The $G(K)$ function of the $b^3\Sigma^+$ state is somewhat (15%) larger than its singlet counterpart, whereas the $C^1\Sigma^+$ and $j^3\Sigma^+$ states have nearly identical $G(K)$ curves. The $^1\Sigma^+$ states, being optically allowed states, yield $G(K)$ approaching constant values as $K^2 \rightarrow 0$. However, the $G(K)$ of the $B^1\Sigma^+$ state exhibits a maximum near $K^2 = 0.34$, as shown in Fig. 5, which is somewhat puzzling at the first glance. This peculiar behavior can be understood by making comparison with the similar transition of the isoelectronic N_2 molecule. When the $3\sigma_g \rightarrow 3s\sigma_g$ transition is made of the homonuclear N_2 molecule

the resulting state is an optically forbidden $a''^1\Sigma_g^+$ state, the $G(K)$ function[5] of which is also shown in Fig. 5. Since the $B^1\Sigma^+$(CO) and $a''^1\Sigma^+$(N$_2$) states are the corresponding Rydberg states of the same isoelectronic sequence, the excitation properties of these two states may reasonably be expected to resemble each other. However, because of the presence of inversion symmetry in one case and absence in the other, the $a''^1\Sigma_g^+$(N$_2$) and $B^1\Sigma^+$(CO) states are, respectively, optically forbidden and allowed states. Such a distinction between the two states is exhibited in the $G(K)$ functions at small values of K^2.

Skerbele and Lassettre[10] reported the generalized oscillator strengths of the $C^1\Sigma^+$ and $B^1\Sigma^+$ states from the electron-impact energy loss experiment at 300, 400, and 500 eV. We have included their experimental results obtained at 500 eV in Figs. 4 and 5. Since the reported experimental values of Skerbele and Lassettre are for excitation to the $v = 0$ level only, in order to account for $v = 1$ level of the upper states, we have scaled up the experimental values by 1.04 and 1.13 in accordance with the experimental optical oscillator strengths of the $C^1\Sigma^+$ and $B^1\Sigma^+$ states given by Lassettre and Skerbele.[9] Comparison between theory and experiment shows a fairly good agreement for the $C^1\Sigma^+$ state. For the $B^1\Sigma^+$ state the discrepancy is much larger. In addition to the general feature of the maximum in $G(K)$, the experiment of Ref. 10 also
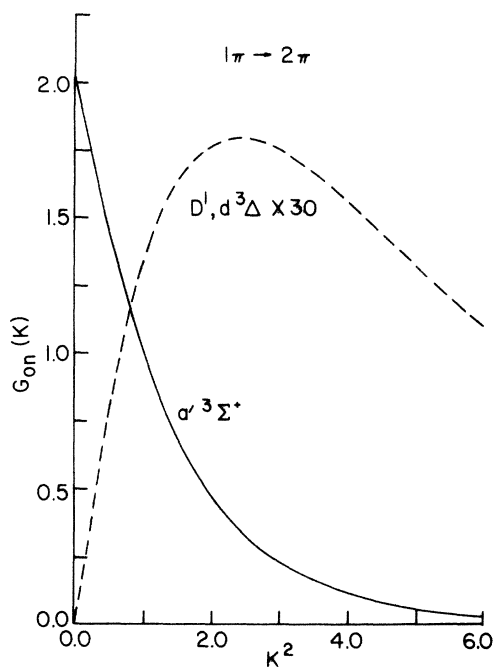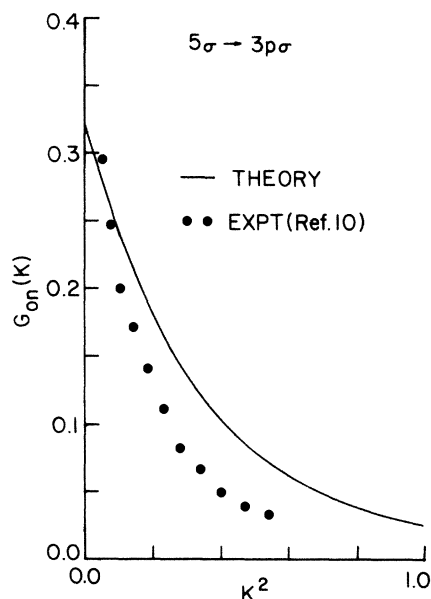

FIG. 3. Values of G_{on} (K) [defined in Eq. (13)] for the $1\pi \rightarrow 2\pi$ transitions computed by using the wave functions of present work appropriate for the $a'^3\Sigma^+$ state (solid line), and for both the D^1 and $d^3\Delta$ states enlarged by a factor of 30 (dashed line).

FIG. 4. Theoretical values of G_{on} (K) [defined in Eq. (13)] for the $5\sigma \rightarrow 3p\sigma$ transition (solid line), along with the experimental values of Skerbele and Lassettre in Ref. 10 (circles).

shows a rising of $G(K)$ below $K^2 \cong 0.02$ which is not found in our calculation.

From $G(K = 0)$ we obtain optical oscillator strengths of 0.136 and 0.0098 for the $C\,^1\Sigma^+$ and $B\,^1\Sigma^+$ states, respectively, as compared with the corresponding experimental values of 0.17 ± 0.021 and 0.017 ± 0.0034 by Lassettre and Skerbele.[9] From the lifetime measurements Hesser[32] reported optical oscillator strengths as 0.12 ($C\,^1\Sigma^+$) and 0.0073 ($B\,^1\Sigma^+$), which are in better agreement with our results.

B. Excitation cross sections of singlet states

Since the Born approximation is intended to be applicable primarily at high incident-electron energies, our investigation of excitation of the singlet states is mainly aimed at high-energy region, although for the sake of completeness we present our results down to much lower energies. The exchange effect is taken into consideration by means of Ochkur's method, as our previous work[5] has suggested a preference of it over the Rudge scheme for singlet-singlet excitation.

1. $A^1\Pi$ state (fourth positive system)

In Fig. 6 we show the excitation function of the $A\,^1\Pi$ state. The wave functions used here are identical to those associated with curve (i) discussed in Sec. IV A 1. The solid line represents the results with exchange by Ochkur's modification and the dashed line is results without ex-

change. At high energies the difference is negligible; for example, at 100 eV the two curves differ by only 3%. (Unless otherwise specified, all the singlet cross sections presented in this paper are computed by means of the Born-Ochkur method.)

Mumma, Stone, and Zipf[11] investigated experimentally the excitation of the $A\,^1\Pi$ state in the energy range of threshold to 350 eV by monitoring several emission bands. These authors found the absolute total cross sections of $A\,^1\Pi$ to be 5.0 $\times 10^{-17}$ (peak) and 2.13×10^{-17} cm^2 at 25 and 300 eV, respectively. They also found that the Franck-Condon factor approximation holds quite well for this excitation process. Measurements of excitation cross sections of the $A\,^1\Pi$ state have also been performed by Ajello.[12] The experimental excitation functions of Refs. 11 and 12 are in good agreement (typically within 10%), although in the latter work the peak cross section of 4.4×10^{-17} cm^2 was placed at 23 eV. The results of Mumma et al.[11] are included in Fig. 6. Aarts and De Heer[13] also reported the emission cross sections of the (01) band of the $A\,^1\Pi$-$X^1\Sigma^+$ system. Since the total cross sections of $A\,^1\Pi$ are not given, we normalized their data to our theoretical cross section at 1000 eV (Fig. 6) in order to compare the shape of the excitation functions. No cascade
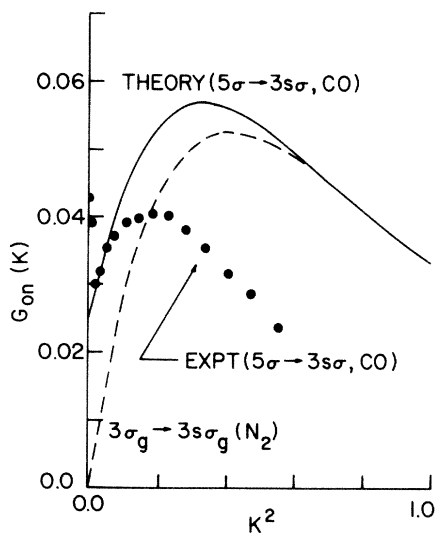

FIG. 5. Theoretical values of $G_{on}(K)$ [defined in Eq. (13)] for the $5\sigma \rightarrow 3s\sigma$ transition of CO (solid line), along with the experimental values of Skerbele and Lassettre in Ref. 10 (circles). Also included is the $G_{on}(K)$ function for the $3\sigma_g \rightarrow 3s\sigma_g$ transition of N_2 in Ref. 5 (dashed line).
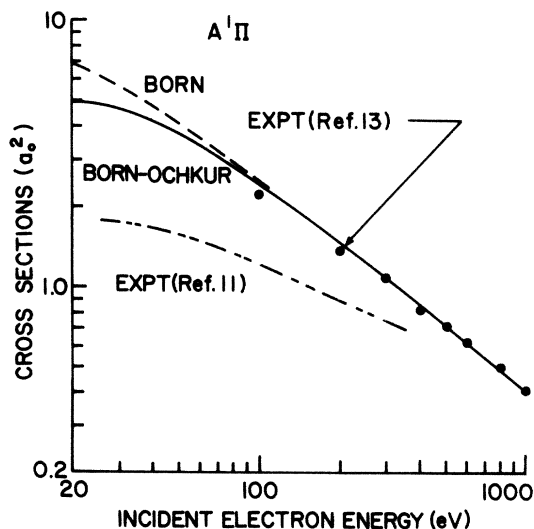

FIG. 6. Excitation functions of the $A\,^1\Pi$ state (fourth positive system) computed by using Ochkur's exchange (solid line), and without exchange (dashed line). Also included are the experimental excitation function of Mumma, Stone, and Zipf in Ref. 11 (long-short-short dashed line) and the experimental relative cross sections from the emission data of Aarts and De Heer in Ref. 13 (circles) as normalized to the theoretical cross section at 1000 eV.

correction was made in all three experiments; however, the cascade to the $A\,^1\Pi$ state is given as about 1.5% of the direct excitation cross sections in Ref. 13.

There appears to be an appreciable difference in the shape of the excitation function between the two sets of experimental results shown in Fig. 6. The shape of the excitation function reported by Aarts and De Heer agrees quite well with our calculations. The absolute cross sections of Ajello and of Mumma, Stone, and Zipf are below the Born-theoretical values. At 300 eV the experimental cross sections are about 30% smaller than the theoretical ones, but the difference becomes larger at lower energies.

2. $B^1\Sigma^+$, $C^1\Sigma^+, E^1\Pi$, and $D^1\Delta$ states

The excitation functions of the $B\,^1\Sigma^+$ and $C\,^1\Sigma^+$ states are shown in Fig. 7 and those of $E\,^1\Pi$ and $D\,^1\Delta$ in Fig. 8. Also included in Fig. 7 are the emission cross sections of the $B\,^1\Sigma^+$ and $C\,^1\Sigma^+$ states by Aarts and De Heer[13] normalized to our Born cross sections at 1000 eV. The shapes of the excitation functions of the $B\,^1\Sigma^+$ and $C\,^1\Sigma^+$ states agree rather well between the present work (theory) and the experiment by Aarts and De Heer. Trajmar, Williams, and Cartwright[16] have present-

ed experimental data of differential cross sections of several states including $A\,^1\Pi$, $E\,^1\Pi$, $B\,^1\Sigma^+$, and $C\,^1\Sigma^+$ at 20 eV with scattering angles in the range of 0–120°. However, the energy of the incident electrons (20 eV) is too low to test the Born cross sections of these singlet states. Experimental cross sections of the $B\,^1\Sigma^+$ state in the energy range of threshold to 100 eV have been reported by Skubenich and Zapesochny,[14, 15] whose data disagree rather drastically with our theory and the corresponding experimental results of Aarts and De Heer.[13] Furthermore, we note that Trajmar, Williams, and Cartwright[16] found their integral cross section (total cross section) of the $B\,^1\Sigma^+$ state at 20 eV to be about a factor of 2 larger than the one reported by Skubenich.

We are not aware of any other works on the $E\,^1\Pi$ and $D\,^1\Delta$ states to compare the present theoretical results with. It should be pointed out that since the wave function of the $D\,^1\Delta$ state was constructed by using the unoccupied 2π orbital resulting from SCF calculation for the $X^1\Sigma^+$ state ⌊rather than the $(1\pi)^3 (5\sigma)^2 (2\pi)$ configuration⌋, the theoretical cross sections of $D\,^1\Delta$ may be subject to a higher degree of uncertainty than those of the other singlet states.

C.   Excitation cross sections of triplet states

Unlike the case of the singlet states, the electron exchange is solely responsible for excitation of the triplet states. Therefore, the computed cross sections depend more sensitively on how the exchange amplitude is treated. We have calculated
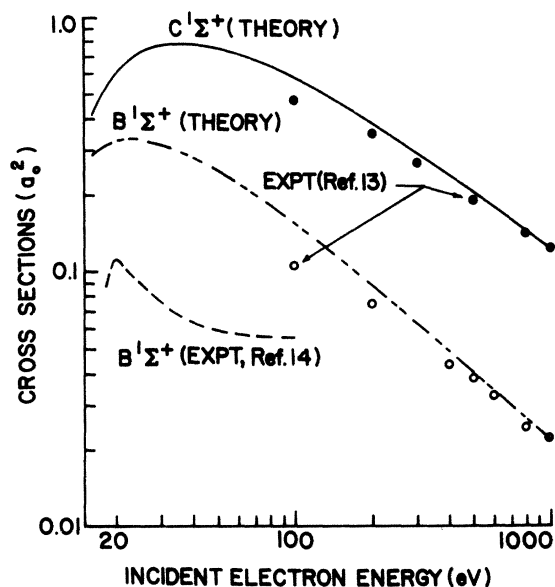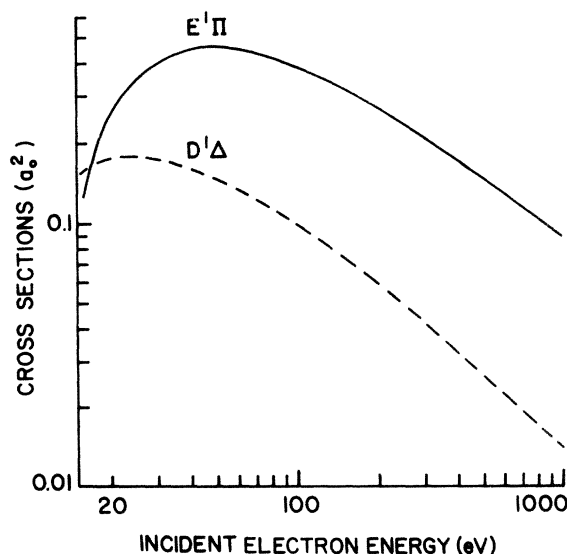

FIG. 7. Theoretical excitation functions of the $C^1\Sigma^+$ state (solid line) and the $B^1\Sigma^+$ state (long-short-short dashed line). Also included are the experimental relative cross sections from the emission data of Aarts and De Heer (Ref. 13) of the $C^1\Sigma^+$ state (solid circles) and of the $B^1\Sigma^+$ state (open circles), and the experimental excitation function of the $B^1\Sigma^+$ state (even dashed line) of Skubenich in Ref. 14.

FIG. 8. Theoretical excitation functions of the $E^1\Pi$ state (solid line) and of $D\,^1\Delta$ state (dashed line).

the excitation cross sections of the triplet states by using the modification by Rudge[21] and by Ochkur[20] of the Born-Oppenheimer approximation. Although the relative merits of the two modifications are not very clear at this time, a critical comparison by Crothers[33] of the two versions is suggestive of favoring Rudge's modification in the case of singlet-triplet excitation. In a previous research on electron-N_2 excitation processes[5] we found that the results by Rudge's modification agree better with the experiments. For these reasons we shall adopt Rudge's modification as the prime tool of investigating excitation cross sections of the triplet states.

1. $a^3\Pi$ state (Cameron band)

In Fig. 9 are shown the cross sections of the $a^3\Pi$ state computed by using Rudge's modification as well as Ochkur's. We see that Ochkur's modification gives much larger cross sections than Rudge's. This large difference is entirely due to the different values which T^2 assumes in Eq. (6).
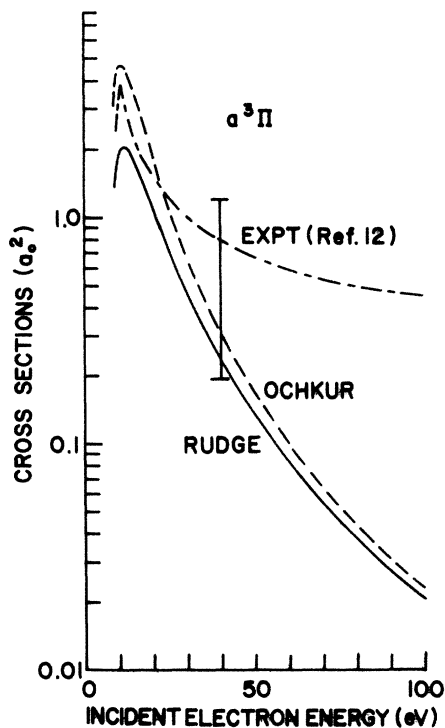

FIG. 9. Excitation function of the a $^3\Pi$ state (Cameron band) computed by using Rudge's exchange (solid line), and Ochkur's exchange (even dashed line), and the experimental excitation function (long-short dashed line) of Ajello in Ref. 12. We have drawn an error bar corresponding to the stated 75% uncertainty of the experimental data.

From Eqs. (6) and (8) we see that if the vertical excitation energy ΔE is equal to the ionization energy ϵ, the two versions would give identical results. However, in the present case, ΔE and ϵ are 6 eV and 14 eV, respectively, and this accounts for the difference in the computed cross sections.

The experimental excitation function reported by Ajello[12] is included in Fig. 9. The theoretical cross sections calculated by using Rudge's modification, though appearing to lie below the experimental curve, are within the stated 75% uncertainty of the experimental data except at energies above 40 eV. Trajmar, Williams, and Cartwright[16] reported experimental differential cross sections of a number of states including $a^3\Pi$, $b^3\Sigma^+$, and $a'^3\Sigma^+$ in the $0°-110°$ range of scattering angle at 20 eV of incident electron energy. We have attempted to integrate their data over the scattering angle to estimate the total cross sections. Unfortunately, the combination of the experimental error bars as indicated in Ref. 16, and the uncertainty involved in extrapolating the differential cross sections beyond $110°$ is so unfavorable that we fail to arrive at an estimate of sufficient reliability to make comparison with theory.

2. $b^3\Sigma^+$, $d^3\Delta$, $j^3\Sigma^+$, $c^3\Pi$, and $a'^3\Sigma^+$ states

The present theoretical cross sections of the $b^3\Sigma^+$ state are displayed in Fig. 10 along with
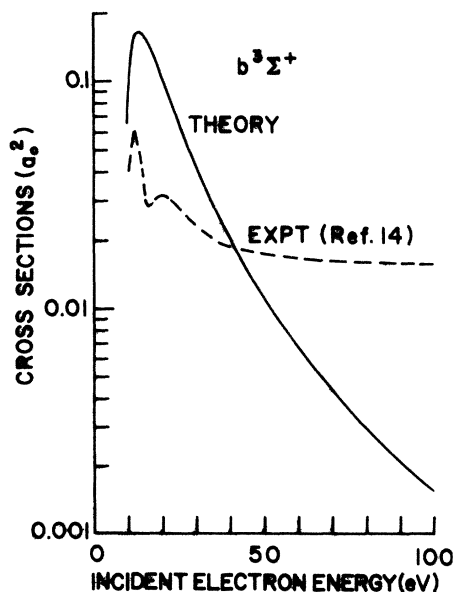

FIG. 10. Theoretical excitation function of the $b^3\Sigma^+$ state (solid line) and the experimental excitation function (dashed line) of Skubenich in Ref. 14.

the corresponding experimental values of Sku-
benich.[14] The discrepancy between the present
theoretical work and the experiment of Skubenich
is rather large; the experimental cross sections
are as much as 3 times smaller in the low-energy
region, and the shape of the excitation functions
also differs substantially. We might note here
that Trajmar et al.[16] found their integrated cross
section (total cross section) of the $b\,^3\Sigma^+$ state to
be about twice as large at 20 eV than the one re-
ported in Ref. 14.

We have also computed the excitation cross sec-
tions of the $a'\,^3\Sigma^+$, $j\,^3\Sigma^+$, $c\,^3\Pi$, and $d\,^3\Delta$ states,
which are shown in Fig. 11. We are unable to
find in the literature any experimental or theo-
retical data with which we can compare our cross
sections. As in the case of the $D\,^1\Delta$ state, the
use of the unoccupied 2π orbital of $X\,^1\Sigma^+$ may re-
sult in a larger uncertainty of the cross sections
of the $d\,^3\Delta$ state.

V. CONCLUSION

We have computed electron-excitation cross
sections of 11 electronic states of the CO mole-
cule by means of Born-type approximations. A
comprehensive comparison of the theoretical
cross sections with experiments is made difficult
by the lack of experimental data for many of the
states, as well as some disagreement of the mea-
sured cross sections reported by different labora-
tories. Nevertheless, on a more limited basis,
we found that the theoretical shape of the excita-
tion functions of the $A\,^1\Pi$, $B\,^1\Sigma^+$, and $C\,^1\Pi$ states
agree well with the emission cross sections mea-
sured by Aarts and De Heer,[13] and the calculated
absolute cross sections of the $A\,^1\Pi$ are in reason-
able agreement with experiment[11] (30% at 300 eV).
For the $B\,^1\Sigma^+$ state our calculated cross sections
show quite substantial discrepancy with the mea-
surements of Skubenich[14] which, however, are in
serious disagreement with the experimental data
of Aarts and De Heer[13] and of Trajmar, Williams,
and Cartwright.[16] As for the triplet states, the
theoretical cross sections are within the range of
uncertainty of the experimental data[12] (at energies
below 40 eV) for $a\,^3\Pi$, but differ quite substantially
from the measured values of the $b\,^3\Sigma^+$ state re-
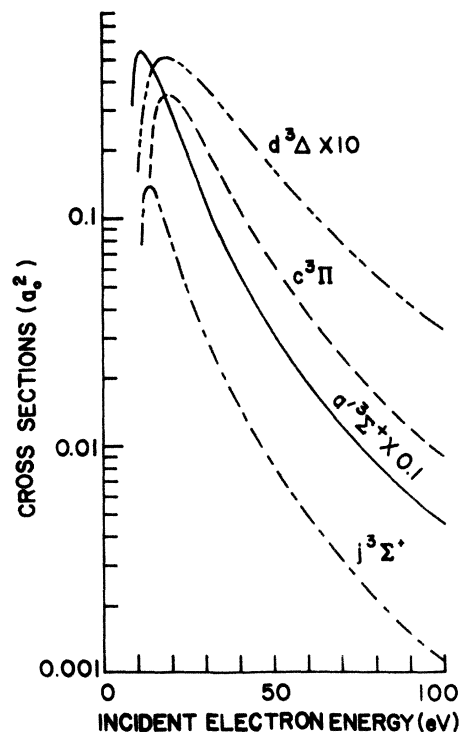ported by Skubenich[14] which, like the case of $B\,^1\Sigma^+$,

FIG. 11. Theoretical excitation functions of the
$a'\,^3\Sigma^+$ state reduced by 0.1 (solid line), of the $d\,^3\Delta$ state
enlarged by 10 (long-short-short dashed line), of the $c\,^3\Pi$
state (even dashed line), and of the $j\,^3\Sigma^+$ state (long-short
dashed line).

differ very significantly from the results of
Trajmar et al.[16]

It is clear that more experimental works are
needed in order to make a more extensive com-
parison with the theoretical calculations and to
arrive at a clearer assessment of the accuracy
of the Born-type approximations when applied to
electron excitation of electronic states of mole-
cules. Nevertheless, by means of the Born-type
approximation and with the aid of GTO technique,
we do have a simple scheme for calculating ex-
citation cross section of electronic states of mole-
cules, and the results for both CO and N_2 are
sufficiently encouraging that one may perhaps
expect the Born-type theory for molecules to have
about the same degree of applicability and use-
fulness as it has for electron-atom excitation.

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