

# Equations of motion method: Inelastic electron scattering for helium and CO<sub>2</sub> in the Born approximation\*

Clyde W. McCurdy, Jr. and Vincent McKoy

Arthur Amos Noyes Laboratory of Chemical Physics,<sup>†</sup> California Institute of Technology, Pasadena, California 91109  
(Received 12 November 1973)

We have applied the equations of motion method to the computation of generalized oscillator strengths in helium and CO<sub>2</sub>. The equations of motion approach yields excitation energies without the computation of separate ground and excited state wavefunctions and is ideally suited for computing matrix elements of the operator used in the Born approximation. Our results for helium agree well with more extensive calculations [Y. Kim and M. Inokuti, *Phys. Rev.* **175**, 176 (1968)]. We compare our generalized oscillator strengths for CO<sub>2</sub> with experiment, and discuss assignments including the peaks at 8.61 and 9.16 eV in the experimental energy loss spectrum. We also compute a valence-like  $^1\Sigma_u^+$  state below the first ionization potential with a large oscillator strength ( $f=0.64$ ), which may be responsible for the proposed continuum absorption between 11–14 eV in CO<sub>2</sub>.

## I. INTRODUCTION

We have previously discussed the equations of motion (EOM) method as an approach for directly calculating spectroscopic properties of molecules, e.g., transition energies and optical intensities.<sup>1,2</sup> The EOM is a theory specifically designed for calculating relative and response properties of atoms and molecules and does not entail the calculation of highly accurate wavefunctions and absolute energies for each electronic state. We solve the equations of motion for the operator  $O_\lambda^*$  which generates the excited state  $|\lambda\rangle$  from the ground state  $|0\rangle$ , and express transition amplitudes and matrix elements between the ground and excited states in terms of this operator. In the EOM approximation including single particle-hole ( $1p-1h$ ) and two-particle-two-hole ( $2p-2h$ ) components in  $O_\lambda^*$  gives results for transition energies and intensities in N<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub>,<sup>3</sup> C<sub>6</sub>H<sub>6</sub>,<sup>4</sup> and H<sub>2</sub>CO<sup>5</sup> which are in good agreement with experiment.

The calculation of Born differential cross sections and generalized oscillator strengths requires the computation of the matrix elements of a simple operator between the ground and excited electronic states. The equations of motion approach is ideally suited for calculating such quantities with a minimum of computational effort. In this paper we present results of calculations on generalized oscillator strengths of helium and carbon dioxide. Our results for helium agree well with the very extensive calculations of Kim and Inokuti.<sup>6</sup> Our results on carbon dioxide are compared with experiment, and assignments in the CO<sub>2</sub> spectrum are discussed. In particular, we can identify the experimental generalized oscillator strengths of Lassetre and Shiloff<sup>7</sup> for transitions at 8.61 and 9.16 eV with that of the  $^1\Pi_g$  state of CO<sub>2</sub>.

In the following two sections we briefly outline the theory of the Born approximation and the equations of motion method. Sections V and VI give the results for helium and carbon dioxide.

## II. BORN APPROXIMATION

Consider a process in which an electron of mass  $m$ , charge  $e$ , and initial momentum  $\hbar\mathbf{k}$  is scattered inelastically by a stationary atom or molecule into solid angle

element  $d\omega$  in the center of mass coordinate system. The final momentum of the electron is  $\hbar\mathbf{k}'$ , and the target atom or molecule is left in excited state  $n$ . The differential cross section in the Born approximation is<sup>8</sup>

$$d\sigma_n = (2me^2/\hbar^2 K^2)^2 (k'/k) |\epsilon_n(K)|^2 d\omega, \quad (1)$$

where  $\hbar\mathbf{K} = \hbar(\mathbf{k} - \mathbf{k}')$  is the momentum transfer vector. If the target is an  $N$  electron atom the matrix element  $\epsilon_n(K)$  is<sup>9</sup>

$$\epsilon_n(K) = \int \varphi_n^* \sum_{j=1}^N e^{i\mathbf{K}\cdot\mathbf{r}_j} \varphi_0 d^3r_1 \dots d^3r_N, \quad (2)$$

where  $\varphi_0$  and  $\varphi_n$  are the ground and excited state eigenfunctions of the atom in terms of the electronic coordinates  $\mathbf{r}_i$ . For a molecular target with  $M$  nuclei and  $N$  electrons  $\epsilon_n(K)$  is given by

$$\epsilon_n(K) = \int \psi_n^* \sum_{j=1}^N e^{i\mathbf{K}\cdot\mathbf{r}_j} \psi_0 d^3r_1 \dots d^3r_N d^3R_1 \dots d^3R_M, \quad (3)$$

where  $\psi_0$  and  $\psi_n$  are the ground and excited state eigenfunctions of the molecule and depend on both the electronic coordinates  $\mathbf{r}_i$  and nuclear coordinates  $R_i$ .

Several simplifying assumptions can be applied to Eq. (3). First we make the Born-Oppenheimer separation and neglect rotational-vibrational coupling.<sup>8</sup> Since rotational levels are not usually resolved in current experiments, a sum over final and an average over initial rotational states can be performed yielding an average over molecular orientations.<sup>8-10</sup> The expression for  $\epsilon_n(K)$  is now an integral involving vibrational and electronic wavefunctions only. We will not consider vibrational levels explicitly in our calculations, and a sum over final vibrational states gives an expression for scattering into all vibrational levels of the excited electronic configuration.<sup>9</sup> The expression for  $\epsilon_n(K)$  for molecular targets becomes

$$\epsilon_n(K) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi |\langle u_n | \sum_{j=1}^N e^{i\mathbf{K}\cdot\mathbf{r}_j} | u_0 \rangle|^2 \sin\theta d\theta d\psi, \quad (4)$$

$u_0$  and  $u_n$  are the ground and excited electronic eigenfunctions, respectively. The inner integration in Eq. (4) is over electronic coordinates only. In Eq. (4) the Euler angles  $\theta$  and  $\psi$  between a system of coordinates

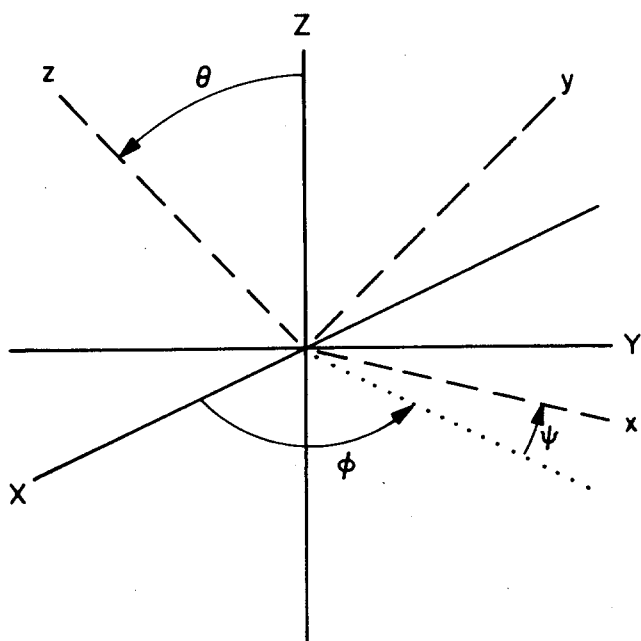


FIG. 1. Definition of the Euler angles used in Eq. (4) and (5).

fixed in the molecule and a space-fixed frame (in which the momentum transfer vector  $\hbar\mathbf{K}$  lies along the  $Z$  axis) are defined in Fig. 1. The dependence of the electronic matrix element on  $\theta$  and  $\psi$  appears explicitly in  $\mathbf{K} \cdot \mathbf{r}_j$  as

$$\mathbf{K} \cdot \mathbf{r}_j = K(x_j \sin\theta \sin\psi + y_j \sin\theta \cos\psi + z_j \cos\theta), \quad (5)$$

where  $x_j$ ,  $y_j$ , and  $z_j$  are electronic coordinates in the molecule-fixed frame. The integration over molecular orientations must in general be performed numerically. This is discussed further in Sec. IV. It should be noted that  $\epsilon_n(\mathbf{K})$  in Eq. (2) or (4) is a function of only the magnitude of  $\mathbf{K}$ .

The generalized oscillator strength, which is directly related to the differential cross section, is more useful in the comparison of experimental and theoretical results.<sup>11</sup> If  $\Delta E_n$  is the transition energy between the ground and excited states, and  $R$  and  $a_0$  denote the Rydberg energy and Bohr radius, respectively, the generalized oscillator strength  $f_n(K)$  is defined by<sup>8</sup>

$$f_n(K) = \frac{\Delta E_n/R}{(Ka_0)^2} |\epsilon_n(K)|^2. \quad (6)$$

This quantity is independent of incident energy at energies for which the Born approximation is valid, and approaches the familiar optical oscillator strength as the momentum transfer  $K$  goes to zero. For further details of the application of the Born approximation to electron-molecule scattering, including sum rules satisfied by  $f_n(K)$ , the reader is referred to the excellent review on the subject by Inokuti.<sup>8</sup>

### III. EQUATIONS OF MOTION METHOD

The equations of motion method has been discussed in detail elsewhere,<sup>1,2</sup> and only a brief summary of the theory will be given here. The operator  $O_\lambda^\dagger$  which generates excited state  $|\lambda\rangle$  from the ground state  $|0\rangle$  can be shown to be exactly a solution of the equation of motion<sup>12</sup>

$$\langle 0 | [\delta O_\lambda, H, O_\lambda^\dagger] | 0 \rangle = \omega_\lambda \langle 0 | [\delta O_\lambda, O_\lambda^\dagger] | 0 \rangle, \quad (7)$$

for all variations  $\delta O_\lambda^\dagger$  in the amplitudes specifying  $O_\lambda^\dagger$ . In Eq. (7)  $\omega_\lambda$  denotes the excitation frequency and the double commutator is defined as

$$2[A, B, C] = [[A, B], C] + [A, [B, C]]. \quad (8)$$

If  $O_\lambda^\dagger$  is restricted to single particle-hole ( $1p-1h$ ) form, Eq. (7) becomes the matrix equation for the amplitudes  $\{Y_{m\nu}\}$  and  $\{Z_{m\nu}\}$ .

$$\begin{bmatrix} A & B \\ -B^* & -A^* \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \end{bmatrix} = \omega_\lambda \begin{bmatrix} D & 0 \\ 0 & D \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \end{bmatrix}. \quad (9)$$

The elements of the matrices  $A$ ,  $B$ , and  $D$  are given elsewhere.<sup>1</sup> It has been shown that the theory including two-particle-two-hole ( $2p-2h$ ) components is equivalent to the  $1p-1h$  theory with a renormalized interaction.<sup>2</sup> In addition an approximate perturbative scheme has been developed for calculating the correction to the transition energies due to the effect of the  $2p-2h$  components.<sup>2</sup> In the  $1p-1h$  theory the matrix element  $M_{0\lambda}$  of any one electron operator between state  $|\lambda\rangle$  and the ground state  $|0\rangle$  is given (to second order in the correlation coefficients of the ground state) by<sup>3</sup>

TABLE I. Basis functions.

Exponent	S		P	
	Coefficient		Coefficient	
Helium				
3293.69	0.004615	4.50000	1.0	
488.894	0.036575	1.45337	1.0	
108.772	0.197834	0.34627	1.0	
30.1799	0.827072	0.11191	1.0	
9.78905	1.0	0.04216	1.0	
3.52226	1.0	0.01702	1.0	
1.35244	1.0	0.01127	1.0	
0.55261	1.0	0.00510	1.0	
0.24092	1.0			
0.10795	1.0			
0.04837	1.0			
0.02167	1.0			
0.00971	1.0			
0.00300	1.0			
0.00100	1.0			
Oxygen				
2200.0	0.009108	8.3560	0.221135	
332.20	0.066636	1.7190	0.872694	
76.930	0.288115	0.3814	1.0	
21.740	0.730114	0.0400	1.0	
6.7730	1.0			
1.1030	0.454600			
0.3342	0.605065			
0.0480	1.0			
Carbon				
994.70	0.011529	4.2970	0.209524	
160.00	0.075741	0.8699	0.881228	
39.910	0.291275	0.2036	1.0	
11.820	0.716418	0.0300	1.0	
3.6980	1.0			
0.6026	0.410040			
0.1817	0.648033			
0.0360	1.0			

TABLE II. Transition energies and optical oscillator strengths for helium.

State	$\Delta E^a$	$\Delta E^a$	$\Delta E^b$	$f_n$	$f_n^c$
	(1 <i>p</i> -1 <i>h</i> )	(1 <i>p</i> -1 <i>h</i> ) + (2 <i>p</i> -2 <i>h</i> )	Exptl		
2 <sup>3</sup> S		20.00	19.82		
2 <sup>1</sup> S	22.22	20.88	20.61		
2 <sup>3</sup> P		21.24	20.96		
2 <sup>1</sup> P	22.78	21.51	21.22	0.2643	0.276
3 <sup>3</sup> S		22.91	22.72		
3 <sup>1</sup> S	24.47	23.14	22.92		
3 <sup>3</sup> P		23.22	23.01		
3 <sup>1</sup> P	24.63	23.32	23.09	0.0735	0.0734

<sup>a</sup>Basis set is [12s18*p*] and energies are in eV. See text.

<sup>b</sup>C. E. Moore, Natl. Bur. Stand. Circ. No. 467 (1949).

<sup>c</sup>B. Schiff and C. L. Pekeris, Phys. Rev. 134, A638 (1964).

$$M_{0\lambda} = \langle 0 | M | \lambda \rangle = \sqrt{2} \sum_{m\gamma} \{ Y_{m\gamma}^*(\lambda) M_{m\gamma} + Z_{m\gamma}^*(\lambda) M_{m\gamma} \}, \quad (10a)$$

$$M_{m\gamma} = M_{m\gamma}^0 + \sum_6 M_{m\delta}^0 \rho_{\gamma\delta}^{(2)} - \sum_n M_{n\gamma}^0 \rho_{mn}^{(2)}. \quad (10b)$$

$M_{m\gamma}^0$  is the matrix element between a hole orbital  $\gamma$  and a particle orbital  $m$ , and  $\rho_{ij}^{(2)}$  is the contribution to the density matrix which is quadratic in the correlation coefficients. We will make use of Eq. (10) in computing  $\epsilon_n(K)$  of Eqs. (2) and (4) in the 1*p*-1*h* approximation. The 2*p*-2*h* amplitudes will have only a small effect on the matrix elements of single particle operators, and hence we neglect 2*p*-2*h* contributions to  $M_{0\lambda}$ .

#### IV. COMPUTATIONAL DETAILS

The first step in the calculation of the generalized oscillator strengths is to carry out a Hartree-Fock calculation on the ground state of the target atom or molecule to generate a particle-hole basis. The SCF calculations were done in a basis of Gaussian orbitals. A [12S/8P] basis for the calculation on helium was constructed using exponents suggested by Huzinaga<sup>13</sup> as well as additional diffuse S functions and one additional valence P Gaussian. Contraction coefficients for the S functions were obtained from calculations by Guberman.<sup>14</sup> For the calculation on CO<sub>2</sub> a valence [3S/2P] basis of contracted Gaussian orbitals was constructed from the (7S/3P) set suggested by Whitman and Hornback.<sup>15</sup> This basis was augmented by a (1S/1P) set of diffuse functions. The basis functions in our calculations are given in Table I.

With the particle-hole basis from the SCF calculation, the 1*p*-1*h* equations of motion are solved for the  $Y(\lambda)$  and  $Z(\lambda)$  amplitudes and the 1*p*-1*h* approximation to the transition energies, and the 2*p*-2*h* corrections to the transition energies are computed. Then the matrix elements for the generalized oscillator strength are calculated using Eq. (10). The matrix elements of  $\exp(i\mathbf{K} \cdot \mathbf{r})$  can be expressed in terms of integrals involving Gaussian orbitals on different centers A and B

$$N_A N_B I_x I_y I_z = \int dV \exp(i\mathbf{K} \cdot \mathbf{r}) \varphi_A \varphi_B, \quad (11)$$

where  $\varphi_A$  and  $\varphi_B$  are Gaussian orbitals at centers A and B, and  $N_A$  and  $N_B$  are normalization constants.  $I_x$ ,  $I_y$ , and  $I_z$  denote the integrals over  $x$ ,  $y$ , and  $z$ , i. e.,

$$I_x = \int_{-\infty}^{\infty} dx' (x' - A_x)^l (x' - B_x)^m \times \exp[iK_x x' - \zeta_A (x' - A_x)^2 - \zeta_B (x' - B_x)^2] dx', \quad (13)$$

where  $A_x$  and  $B_x$  are the  $x$  coordinates of centers A and B;  $\zeta_A$  and  $\zeta_B$  are Gaussian exponents and the vector  $q = (\sin\theta \sin\psi, \sin\theta \cos\psi, \cos\theta)$ . This integral can be performed to give<sup>16</sup>

$$I_x = \left(\frac{\pi}{\lambda}\right)^{1/2} \exp\left[iK_x p_x - \frac{(K_x p_x)^2 + 4\zeta_A \zeta_B (A_x - B_x)^2}{4\lambda}\right] \times \sum_{k=0}^l \binom{l}{k} \left(\frac{\zeta_B (B_x - A_x)}{\lambda}\right)^{l-k} \sum_{j=0}^m \binom{m}{j} \left(\frac{\zeta_A (A_x - B_x)}{\lambda}\right)^{m-j} \times \left(\frac{i}{2\lambda^{1/2}}\right)^{k+j} H_{k+j} \left(\frac{K_x p_x}{2\lambda^{1/2}}\right), \quad (14)$$

where  $\lambda = (\zeta_A + \zeta_B)$ ,  $p_x = (\zeta_A A_x + \zeta_B B_x)/\lambda$ ,  $H_n$  is a Hermite polynomial, and  $\binom{n}{k}$  is a binomial coefficient.

To compute the generalized oscillator strength for molecules an integration over molecular orientations is required. For the linear geometry of CO<sub>2</sub>, we may perform the  $\psi$  integration analytically to obtain a factor of  $2\pi$ . The  $\theta$  integration was performed using 8-point Gauss-Legendre quadrature in  $\cos\theta$ .

#### V. HELIUM

Helium provides a test case for the equations of motion approach to high-energy inelastic electron scattering uncomplicated by the necessity of numerical averaging

TABLE III.  $f_n(K)/\Delta E_n$  for helium.<sup>a</sup>

$K^{2b}$	2 <sup>1</sup> S	3 <sup>1</sup> S	2 <sup>1</sup> P	3 <sup>1</sup> P
0.018	1.3840(-3)	3.0402(-4)	2.5670(-1)	7.1774(-2)
0.071	5.1150(-3)	1.1489(-3)	2.3535(-1)	6.7041(-2)
0.160	1.0112(-2)	2.3480(-3)	2.0423(-1)	5.9854(-2)
0.284	1.5074(-2)	3.6483(-3)	1.6841(-1)	5.1105(-2)
0.444	1.8934(-2)	4.7921(-3)	1.3264(-1)	4.1786(-2)
0.640	2.1120(-2)	5.5876(-3)	1.0035(-1)	3.2820(-2)
0.871	2.1572(-2)	5.9512(-3)	7.3365(-2)	2.4864(-2)
1.138	2.0595(-2)	5.9019(-3)	5.2148(-2)	1.8253(-2)
1.440	1.8654(-2)	5.5277(-3)	3.6244(-2)	1.3050(-2)
1.778	1.6214(-2)	4.9447(-3)	2.4760(-2)	9.1340(-3)
2.151	1.3648(-2)	4.2639(-3)	1.6702(-2)	6.2894(-3)
2.560	1.1205(-2)	3.5718(-3)	1.1171(-2)	4.2797(-3)
3.004	9.0255(-3)	2.9254(-3)	7.4327(-3)	2.8892(-3)
3.484	7.1668(-3)	2.3551(-3)	4.9346(-3)	1.9415(-3)
4.000	5.6319(-3)	1.8717(-3)	3.2770(-3)	1.3024(-3)
4.551	4.3938(-3)	1.4738(-3)	2.1811(-3)	8.7411(-4)
5.138	3.4120(-3)	1.1532(-3)	1.4572(-3)	5.8808(-4)
5.760	2.6427(-3)	8.9877(-4)	9.7840(-4)	3.9719(-4)
6.418	2.0049(-3)	6.9904(-4)	6.6076(-4)	2.6962(-4)
7.111	1.5829(-3)	5.4339(-4)	4.4915(-4)	1.8411(-4)
7.840	1.2268(-3)	4.2267(-4)	3.0746(-4)	1.2654(-4)
8.604	9.5288(-4)	3.2927(-4)	2.1204(-4)	8.7599(-5)
9.404	7.4208(-4)	2.5707(-4)	1.4739(-4)	6.1098(-5)
10.240	5.7972(-4)	2.0125(-4)	1.0330(-4)	4.2950(-5)
11.111	4.5447(-4)	1.5805(-4)	7.3007(-5)	3.0438(-5)
12.018	3.5761(-4)	1.2454(-4)	5.2042(-5)	2.1749(-5)
12.960	2.8250(-4)	9.8500(-5)	3.7415(-5)	1.5669(-5)
13.938	2.2407(-4)	7.8196(-5)	2.7127(-5)	1.1381(-5)
14.951	1.7845(-4)	6.2317(-5)	1.9829(-5)	8.3321(-6)
16.000	1.4270(-4)	4.9857(-5)	1.4608(-5)	6.1468(-6)

<sup>a</sup>Notation is, e.g., 1.3840(-3) = 1.3840 × 10<sup>-3</sup>.

<sup>b</sup>In atomic units.

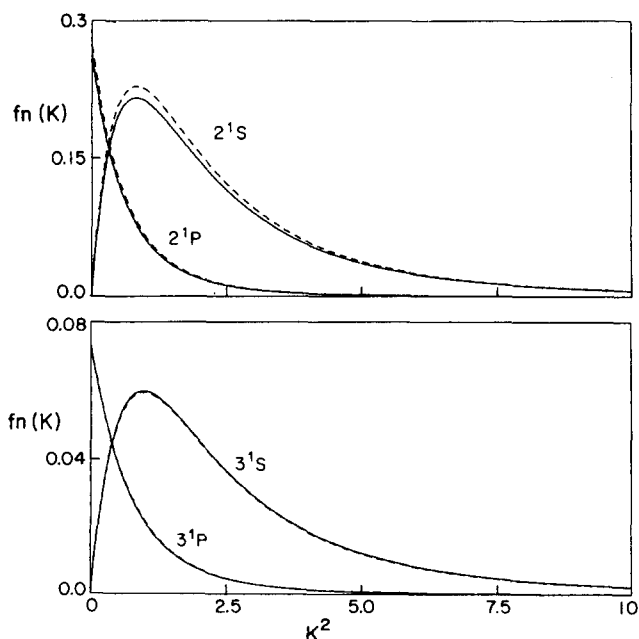
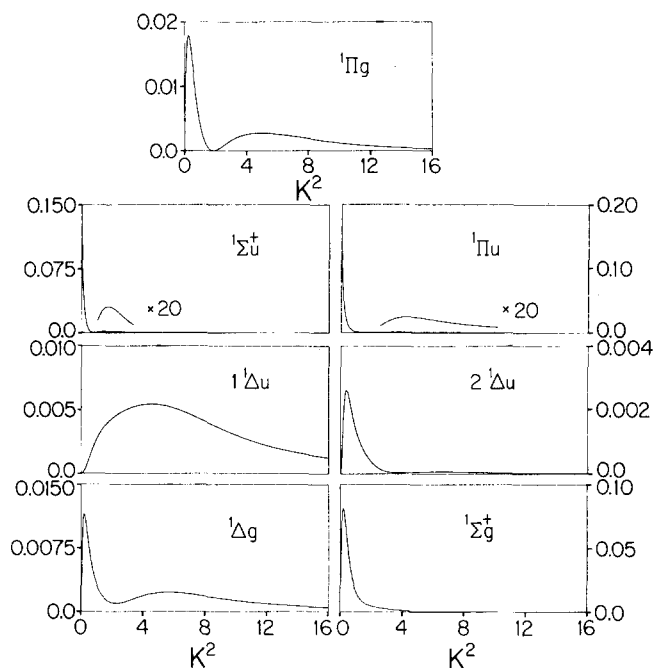
TABLE IV. Comparison at selected points with calculations using accurate Weiss CI wavefunctions for helium.

$K^2$ (a. u.)	$2^1S$		$3^1S$	
	This work <sup>a</sup>	Kim and Inokuti <sup>b</sup>	This work <sup>a</sup>	Kim and Inokuti <sup>b</sup>
0.25	$1.3903 \times 10^{-2}$	$1.4683 \times 10^{-2}$	$3.3284 \times 10^{-3}$	$3.3168 \times 10^{-3}$
1.00	$2.1235 \times 10^{-2}$	$2.2493 \times 10^{-2}$	$5.9738 \times 10^{-3}$	$5.9352 \times 10^{-3}$
4.00	$5.6319 \times 10^{-3}$	$5.9528 \times 10^{-3}$	$1.8717 \times 10^{-3}$	$1.8502 \times 10^{-3}$
9.00	$8.4059 \times 10^{-4}$	$8.6148 \times 10^{-4}$	$2.9085 \times 10^{-4}$	$2.7911 \times 10^{-4}$
$K^2$ (a. u.)	$2^1P$		$3^1P$	
	This work <sup>a</sup>	Kim and Inokuti <sup>b</sup>	This work <sup>a</sup>	Kim and Inokuti <sup>b</sup>
0.25	$1.7753 \times 10^{-1}$	$1.8596 \times 10^{-1}$	$5.3385 \times 10^{-2}$	$5.3618 \times 10^{-2}$
1.00	$6.2049 \times 10^{-2}$	$6.5431 \times 10^{-2}$	$2.1381 \times 10^{-2}$	$2.1671 \times 10^{-2}$
4.00	$3.3277 \times 10^{-3}$	$3.4485 \times 10^{-3}$	$1.3024 \times 10^{-3}$	$1.3116 \times 10^{-3}$
9.00	$1.7661 \times 10^{-4}$	$1.7346 \times 10^{-4}$	$7.3088 \times 10^{-5}$	$6.7427 \times 10^{-5}$

<sup>a</sup>EOM results with  $[12s/8p]$  basis.<sup>b</sup>Reference 6.

over orientations. No particle states were truncated from the particle basis for helium prior to performing the EOM calculation. The results of the EOM calculation are compared with experiment and other theoretical results in Table II, and the agreement for both transition energies and optical oscillator strengths is quite good. The generalized oscillator strengths were computed over a grid of thirty points between zero and sixteen atomic units in  $K^2$ , and are shown in Table III as  $f_n(K)/\Delta E$ . Our results agree well with a similar calculation on helium by Schneider.<sup>17</sup>

Measurements of absolute cross sections are difficult to make, and consequently experimental data are often scaled to a known optical limit or normalized to a theoretical calculation.<sup>18</sup> However, for helium the definitive calculations of Kim and Inokuti<sup>6</sup> provide an excellent standard of comparison. Kim and Inokuti<sup>6</sup> have used accurate Weiss CI wavefunctions to compute gen-

FIG. 2. Comparison of EOM generalized oscillator strengths (solid lines) for helium with the results of Kim and Inokuti<sup>6</sup> (dashed).  $K^2$  is in atomic units.FIG. 3. Calculated generalized oscillator strengths for CO<sub>2</sub>.  $K^2$  is in atomic units.

eralized oscillator strengths for transitions from the ground state to the  $2^1S$ ,  $3^1S$ ,  $2^1P$ , and  $3^1P$  states as well as for a number of other transitions. The accuracy of their results is demonstrated by close agreement with experiment as well as by agreement of their results using the "length" and "velocity" formulas for the generalized oscillator strength. The results of our calculations using the equations of motion method are compared in Table IV with the results of Kim and Inokuti at representative points, and in Fig. 2 our results are plotted with those of Kim and Inokuti.<sup>6</sup> In calculating  $f_n(K)$  using Eq. (6) we use the transition energy  $\Delta E_n$  in the  $1p-1h$  approximation to be consistent with the fact that the  $Y_{mp}$  and  $Z_{mp}$  amplitudes are computed using only  $1p-1h$  components. Agreement is good; an average deviation of less than 5% is found for the four transitions for  $K^2 < 9$  a. u.

TABLE V. SCF molecular orbital eigenvalues for CO<sub>2</sub>.<sup>a</sup>

MO	$\epsilon_v^b$	MO	$\epsilon_m$	MO	$\epsilon_m$
1	1σ <sub>u</sub> -20.7220	12	5σ <sub>g</sub> 0.0389	26	8σ <sub>g</sub> 0.5437
2	1σ <sub>g</sub> -20.7204	13	2π <sub>ux</sub> 0.0577	27	5π <sub>ux</sub> 1.0049
3	2σ <sub>g</sub> -11.5469	14	2π <sub>uy</sub> 0.0577	28	5π <sub>uy</sub> 1.0049
4	3σ <sub>g</sub> -1.5737	15	4σ <sub>u</sub> 0.0667	29	7σ <sub>u</sub> 1.0414
5	2σ <sub>u</sub> -1.5414	16	6σ <sub>g</sub> 0.1390	30	8σ <sub>u</sub> 1.2242
6	4σ <sub>g</sub> -0.7967	17	2π <sub>gx</sub> 0.1450	31	3π <sub>gx</sub> 1.8319
7	3σ <sub>u</sub> -0.7456	18	2π <sub>gy</sub> 0.1450	32	3π <sub>gy</sub> 1.8319
8	1π <sub>ux</sub> -0.7437	19	3π <sub>ux</sub> 0.1728	33	6π <sub>ux</sub> 2.0289
9	1π <sub>uy</sub> -0.7437	20	3π <sub>uy</sub> 0.1728	34	6π <sub>uy</sub> 2.0289
10	1π <sub>gx</sub> -0.5460	21	5σ <sub>u</sub> 0.1734	35	9σ <sub>u</sub> 2.0469
11	1π <sub>gy</sub> -0.5460	22	4π <sub>ux</sub> 0.2047	36	9σ <sub>g</sub> 2.0710
		23	4π <sub>uy</sub> 0.2047	37	10σ <sub>g</sub> 13.0305
		24	7σ <sub>g</sub> 0.2294	38	11σ <sub>g</sub> 23.0554
		25	6σ <sub>u</sub> 0.2808	39	10σ <sub>u</sub> 24.3690

<sup>a</sup>In a  $([3s/2p] + R(1s/1p))$  basis of contracted Gaussians, with  $R_{C-O} = 2.192$  a. u. This basis gives a ground state  $E_{SCF} = -187.29846$  a. u.<sup>b</sup>In atomic units.

TABLE VI. EOM calculation of singlet excited states of CO<sub>2</sub>.

Transition	$\Delta E^{a,b}$		$f_0^c$	$\Delta(\langle x^2 \rangle + \langle y^2 \rangle)^d$	Dominant <sup>d</sup> Components
	$\Delta E^a$ ( $1p-1h$ )	( $2p-2h$ ) <sup>+</sup>			
$^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$	11.63	8.53		1.24	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow ^1\Delta_u$	11.98	8.56		1.36	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow ^1\Pi_g$	11.87	8.62		15.3	$1\pi_g \rightarrow \sigma_g^*$
$^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$	13.87	10.29	0.116	35.5	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow ^2^1\Delta_u$	13.91	10.42		35.3	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow ^1\Pi_u$	14.20	10.97	0.1680	22.4	$1\pi_g \rightarrow \sigma_u^*$
$^1\Sigma_g^+ \rightarrow ^1\Delta_g$	15.56	12.60		20.9	$1\pi_g \rightarrow \pi_g^*$
$^1\Sigma_g^+ \rightarrow ^1\Sigma_g^+$	16.09	12.63		24.0	$1\pi_g \rightarrow \pi_g^*$
$^1\Sigma_g^+ \rightarrow ^1\Sigma_g^-$	15.42	12.78		15.1	$1\pi_g \rightarrow \pi_g^*$

<sup>a</sup>In electron volts.<sup>b</sup>Best approximation to transition energies.<sup>c</sup>Optical oscillator strength assuming Franck-Condon factor of unity for vertical excitation.<sup>d</sup>Difference in ground and excited state expectation value of  $x^2 + y^2$  [in (a. u.)<sup>2</sup>].

## VI. CARBON DIOXIDE

Tables V, VI, and VII give orbital energies of CO<sub>2</sub> from the Hartree-Fock calculation and the results of the equations of motion calculation on transition energies and optical oscillator strengths. In the EOM calculation hole states with energies less than -10 Hartrees and particle states above 10 Hartrees were truncated from the particle-hole basis. There are many features in the carbon dioxide uv absorption<sup>19</sup> and electron impact<sup>20</sup> spectra with uncertain assignments. The transition energies from the EOM calculation can aid in the identification of several of these features. However, transition energies do not constitute a complete description of the spectrum, and the generalized and optical oscillator strengths for the singlet-singlet transitions can also play an important part in determining assignments.

The generalized oscillator strengths calculated for seven states of CO<sub>2</sub> are given in Fig. 3 and Table VIII. Of these seven states only the  $1^1\Delta_u$  is completely va-

TABLE VII. EOM calculation of triplet excited states of CO<sub>2</sub>.

Transition	$\Delta E^a$		$\Delta(\langle x^2 \rangle + \langle y^2 \rangle)^b$	Dominant components
	( $1p-1h$ ) <sup>+</sup>	( $2p-2h$ )		
$^1\Sigma_g^+ \rightarrow ^3\Sigma_u^+$	7.35		1.00	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow ^3\Delta_u$	8.06		1.09	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow ^3\Sigma_u^-$	8.39		1.24	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow ^3\Pi_g$	8.40		12.2	$1\pi_g \rightarrow \sigma_g^*$
$^1\Sigma_g^+ \rightarrow ^2^3\Delta_u$	10.43		34.7	$1\pi_g \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow ^3\Pi_u$	10.99		20.1	$1\pi_g \rightarrow \sigma_u^*$
$^1\Sigma_g^+ \rightarrow ^3\Sigma_g^+$	11.33		2.28	$1\pi_u \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow ^3\Delta_g$	12.42		5.99	$1\pi_u \rightarrow \pi_u^*$
$^1\Sigma_g^+ \rightarrow ^3\Sigma_g^-$	12.67		15.5	$1\pi_g \rightarrow \pi_g^*$

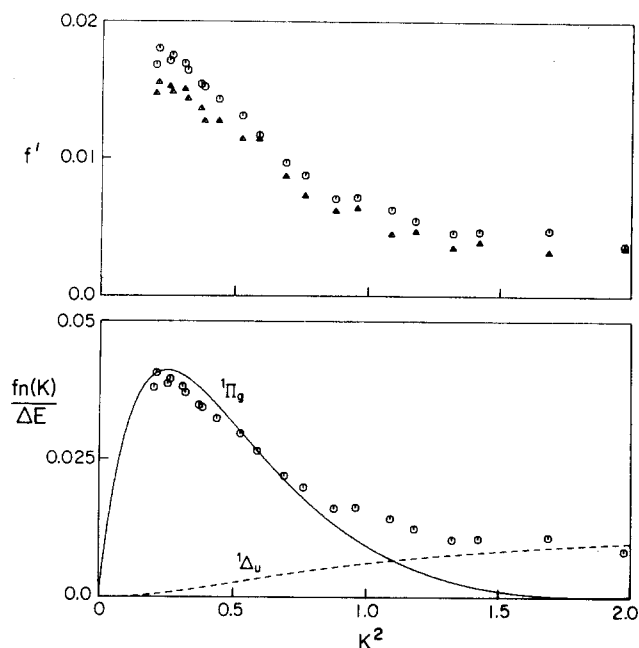
<sup>a</sup>In electron volts.<sup>b</sup>Difference in ground and excited state expectation value of  $x^2 + y^2$  [in (a. u.)<sup>2</sup>].

FIG. 4. Upper: Experimental differential generalized oscillator strengths for CO<sub>2</sub> measured at 8.61 eV (triangles) and 9.16 eV (circles) by Lassette and Shiloff.<sup>7</sup> Lower: Comparison of theoretical results for the  $^1\Pi_g$  (solid) and  $^1\Delta_u$  states with the differential generalized oscillator strength of the 9.16 eV peak times 0.76.

lence like, and there is no minimum in the generalized oscillator strength for this state.<sup>21</sup> The  $f_n(K)$  for the other states, with the exception of the  $^1\Sigma_g^+$  state, show minima of different depths.

The assignment of the  $1^1\Delta_u$  and  $^1\Pi_g$  states in the optical and electron impact spectra is a problem of current interest. In the uv absorption spectrum the peaks observed at 9.31 and 8.41 eV<sup>22</sup> have been variously assigned as two components of the  $^1\Pi_g$  transition split by vibrational effects,<sup>7</sup> as the  $^1\Pi_g$  and  $^1\Delta_u$ , respectively,<sup>22</sup> and together as the  $^1\Delta_u$ .<sup>23</sup> Lassette and Shiloff<sup>7</sup> have reported the differential generalized oscillator strength  $f'$  for peaks in the electron impact energy loss spectrum at 8.61 and 9.16 eV,<sup>7</sup> and their data is plotted in Fig. 4. The integral of  $f'$  over a peak in the energy loss spectrum gives the generalized oscillator strength for that transition assuming only one transition contributes to the peak.<sup>11</sup> As an approximation one may assume that the ratio  $b$  of peak area to height is constant over scattering angle so that the generalized oscillator strength is  $f \approx bf'$ , where  $f'$  is measured at the maximum of the peak.<sup>11</sup> Lassette and Shiloff<sup>7</sup> find that as the scattering angle increases the two peaks at 9.16 and 8.61 eV merge into one peak at 9.12 eV.<sup>7</sup> Thus they were unable to determine a value of  $b$  for each peak separately. It should be noted from Fig. 4, however, that the two differential generalized oscillator strengths are qualitatively very much the same. Lassette and Shiloff<sup>7</sup> assert on the basis of this evidence and an argument relating the shape of the envelope of the 9.12 eV transition to vibronic effects, that the two peaks observed are components of the  $^1\Pi_g$  transition.

The theoretical results for the generalized oscillator

TABLE VIII.  $f_n(K)/\Delta E_n$  for CO<sub>2</sub>.<sup>a</sup>

$K^2$ <sup>b</sup>	$1^1\Delta_u$	$1^1\Pi_g$	$1^1\Sigma_u^+$	$2^1\Delta_u$	$1^1\Pi_u$	$1^1\Delta_g$	$1^1\Sigma_g^+$
0.01	1.373(-6)	2.209(-3)	1.044(-1)	2.426(-5)	1.491(-1)	1.465(-3)	9.770(-3)
0.04	1.280(-5)	7.768(-3)	8.254(-2)	9.694(-5)	1.191(-1)	4.891(-3)	3.290(-2)
0.09	5.895(-5)	1.415(-2)	5.583(-2)	5.752(-4)	8.311(-2)	8.226(-3)	5.588(-2)
0.16	1.791(-4)	1.834(-2)	3.229(-2)	1.339(-3)	5.179(-2)	9.938(-3)	6.782(-2)
0.25	4.144(-4)	2.052(-2)	1.584(-2)	2.170(-3)	2.975(-2)	9.802(-3)	6.629(-2)
0.36	7.868(-4)	1.926(-2)	6.426(-3)	2.542(-3)	1.626(-2)	8.481(-3)	5.569(-2)
0.49	1.284(-3)	1.603(-2)	2.003(-3)	2.470(-3)	8.629(-3)	6.759(-3)	4.211(-2)
0.64	1.863(-3)	1.197(-2)	4.365(-4)	2.129(-3)	4.434(-3)	5.131(-3)	2.978(-2)
0.81	2.471(-3)	8.001(-3)	2.376(-4)	1.714(-3)	2.142(-3)	3.795(-3)	2.034(-2)
1.00	3.059(-3)	4.685(-3)	5.467(-4)	1.336(-3)	9.112(-4)	2.777(-3)	1.378(-2)
1.21	3.600(-3)	2.226(-3)	9.917(-4)	1.024(-3)	2.948(-4)	2.032(-3)	9.475(-3)
1.44	4.080(-3)	7.728(-4)	1.318(-3)	7.682(-4)	4.430(-5)	1.504(-3)	6.735(-3)
1.69	4.496(-3)	9.911(-5)	1.466(-3)	5.559(-4)	1.609(-5)	1.152(-3)	5.014(-3)
1.96	4.855(-3)	5.845(-5)	1.432(-3)	3.801(-4)	1.231(-4)	9.499(-4)	3.910(-3)
2.25	5.164(-3)	4.330(-4)	1.261(-3)	2.409(-4)	3.071(-4)	8.806(-4)	3.146(-3)
2.56	5.433(-3)	1.016(-3)	1.015(-3)	1.399(-4)	5.225(-4)	9.248(-4)	2.548(-3)
2.89	5.665(-3)	1.640(-3)	7.527(-4)	7.566(-5)	7.304(-4)	1.057(-3)	2.027(-3)
3.24	5.861(-3)	2.196(-3)	5.171(-4)	4.267(-5)	9.002(-4)	1.246(-3)	1.553(-3)
3.61	6.017(-3)	2.629(-3)	3.300(-4)	3.244(-5)	1.013(-3)	1.458(-3)	1.131(-3)
4.00	6.124(-3)	2.922(-3)	1.959(-4)	3.595(-5)	1.064(-3)	1.661(-3)	7.762(-4)
5.76	5.913(-3)	3.015(-3)	1.395(-5)	6.739(-5)	8.502(-4)	2.016(-3)	1.004(-4)
7.84	4.748(-3)	2.232(-3)	6.535(-6)	5.533(-5)	5.172(-4)	1.655(-3)	6.020(-5)
10.24	3.309(-3)	1.313(-3)	6.912(-6)	3.252(-5)	2.825(-4)	1.128(-3)	5.800(-5)
12.96	2.156(-3)	6.712(-4)	5.214(-6)	1.785(-5)	1.392(-4)	7.182(-4)	2.753(-5)
16.00	1.384(-3)	3.359(-4)	2.806(-6)	1.031(-5)	6.726(-5)	4.486(-4)	1.359(-5)

<sup>a</sup>Notation is, e. g., 1.373(-6) = 1.373 × 10<sup>-6</sup>.<sup>b</sup>In atomic units.

strengths of the  $1^1\Pi_g$  and  $1^1\Delta_u$  transitions are compared in Fig. 4 with the experimental  $f'$  data for the 9.16 eV peak. Since no  $b$  value is given by Lassettre and Shiloff, a value found by least squares analysis was used for purposes of qualitative comparison. Also because the computed transition energies and the energies of the experimental peaks differ slightly, the oscillator strengths were divided by their associated transition energies to make comparison easier. It can be seen from Fig. 4 that the theoretical  $f_n(K)$  of the  $1^1\Pi_g$  state is qualitatively much the same as the  $f'$  for both the 9.16 and 8.61 eV peaks, whereas that of the  $1^1\Delta_u$  is not. Lassettre and Shiloff<sup>7</sup> perform an extrapolation of the  $f'$  curves to obtain maxima at  $K^2 \approx 0.2$  a. u.,<sup>2</sup> in good agreement with the calculated maximum at about 0.25 of the  $1^1\Pi_g$  state. The maximum in the theoretical  $f_n(K)$  for the  $1^1\Delta_u$  state is at a much higher value of momentum transfer,  $K^2 \approx 4.5$  a. u.<sup>2</sup>

The above comparison strongly supports the assertion of Lassettre and Shiloff<sup>7</sup> that the generalized oscillator strengths they observe at 8.61 and 9.16 eV are due (at least predominantly) to the  $1^1\Pi_g$  transition. However, the uv absorption spectrum of these two peaks show markedly different vibrational structure.<sup>22</sup> This fact leads Rabalais *et al.*,<sup>22</sup> to assign the 8.41 eV peak in the optical spectrum to the  $1^1\Delta_u$  transition and the 9.31 eV peak to the  $1^1\Pi_g$ . The unambiguous assignment of these two peaks in the CO<sub>2</sub> spectrum must await higher resolution electron impact measurements as well as careful vibrational analysis of the optical spectrum. Tentatively we can assign at least the 9.31 eV peak in the optical spectrum to the  $1^1\Pi_g$  and speculate that the 8.4 eV peak contains contributions from both the  $1^1\Pi_g$  and  $1^1\Delta_u$  transitions.

The two lowest optically allowed transitions of CO<sub>2</sub> occur at 11.08 and 11.4 eV, and these peaks have been assigned by different investigators to the  $1^1\Sigma_u^+$  and  $1^1\Pi_u$  states and vice versa.<sup>20,22,24</sup> The transition energies from the EOM calculation suggest assigning these peaks as  $1^1\Sigma_u^+$  at 11.08 eV and  $1^1\Pi_u$  at 11.4 eV. The calculated optical oscillator strength of 0.116 for the  $1^1\Sigma_u^+$  state agrees well with the experimental value for the 11.08 eV transition of 0.12.<sup>25</sup> Lassettre and Shiloff<sup>7</sup> have measured the generalized oscillator strength for the 11 eV transition. They note that there may be a weak maximum in the  $f_n(K)$  of this peak at  $K^2 \approx 2$  a. u.<sup>2</sup> Our theoretical  $f_n(K)$  for the  $1^1\Sigma_u^+$  state shows a maximum at  $K^2 \approx 1.75$  a. u.<sup>2</sup> in agreement with the location of the

TABLE IX. Assignments in the CO<sub>2</sub> spectrum.

State	$\Delta E^a$ ( $1p-1h$ ) + ( $2p-2h$ )	$\Delta E^a$ Experimental	% Error <sup>b</sup>	$f$	$f_{exp}$
$3^1\Sigma_u^+$	7.35	7.5 <sup>c</sup>	2%		
$3^1\Delta_u$	8.06	8.0 <sup>c</sup>	1%		
$1^1\Delta_u$	8.56	8.41 <sup>d</sup>	2% <sup>e</sup>		
$1^1\Pi_g$	8.62	9.31 <sup>d</sup>	7%		
$1^1\Sigma_u^+$	10.29	11.08 <sup>d</sup>	7%	0.116	0.12 <sup>f</sup>
$1^1\Pi_u$	10.97	11.4 <sup>e</sup>	4%	0.1680	

<sup>a</sup>In electron volts.<sup>b</sup>Relative to experimental value.<sup>c</sup>Reference 28.<sup>d</sup>Reference 22.<sup>e</sup>Reference 7.<sup>f</sup>Reference 25.<sup>g</sup>Tentative assignment, see Sec. VI.

maximum tentatively identified experimentally, while the  ${}^1\Pi_u$  generalized oscillator strength has a maximum only beyond 4 a. u.<sup>2</sup> Otherwise both theoretical generalized oscillator strength curves are qualitatively the same as the experimental results for the transition at 11 eV. Although the above comparison is not conclusive it tends to substantiate the assignment of the 11.08 eV peak in the optical spectrum as the  ${}^1\Sigma_u^+$  transition.

Krauss *et al.*<sup>26</sup> and Lawrence<sup>27</sup> have suggested that there is an underlying continuum absorption in CO<sub>2</sub> in the range 11–14 eV due to a transition to a valencelike interloper state of  ${}^1\Sigma_u^+$  symmetry. Our calculations yield a valencelike  ${}^1\Sigma_u^+$  state occurring with a vertical transition energy of approximately 12–12.5 eV (from results of two independent calculations), which has an optical oscillator strength  $f=0.64$ . We cannot definitely assign this state to the continuum absorption without first computing its energy surface. However it seems likely this state corresponds to the valence  ${}^1\Sigma_u^+$  state calculated by Krauss *et al.*<sup>26</sup> using an approximate SCF method.

The threshold electron impact spectrum of CO<sub>2</sub> has been measured by Hubin-Franskin and Collin by the SF<sub>6</sub> scavenger technique.<sup>28</sup> The energies of transitions seen in this spectrum are displaced by a few tenths of an electron volt from their counterparts in the optical spectrum. Peaks are observed in the threshold spectrum at 8.55 and 9.3 eV corresponding to the 8.41 and 9.31 eV transitions in the optical spectrum. Just below these transitions a peak is observed at 8.0 eV whose intensity decreases markedly for energies just above threshold suggesting that this peak is due to a transition to a triplet state. From the EOM transition energies we may tentatively assign this peak to the  ${}^3\Delta_u$  state which is calculated to lie at 8.06 eV. The next transition of lower energy observed in the threshold electron impact spectrum is at 7.5 eV, and we may assign it in a similarly tentative manner to the  ${}^3\Sigma_u^+$  state.

The assignments in the CO<sub>2</sub> spectrum which we have made are tabulated and the calculated transition energies compared with experiment in Table IX.

## VII. CONCLUSIONS

We have discussed calculations on the excited states of helium and carbon dioxide, including the computation of generalized and optical oscillator strengths, as an application of the equations of motion method. Generalized oscillator strengths calculated for helium using the EOM agree well with other theoretical calculations. We have discussed assignments in the electronic spectrum of carbon dioxide including the  ${}^1\Pi_g$ ,  ${}^1\Delta_u$ ,  ${}^1\Sigma_u^+$ , and  ${}^1\Pi_u$  states. The error in the calculated transition energies of the states we have assigned is less than 10% in all cases. The comparison of our theoretical generalized oscillator strengths with those measured for carbon dioxide by Lassetre and Shiloff<sup>7</sup> proves helpful in making spectral assignments.

## ACKNOWLEDGMENTS

The authors would like to thank W. A. Goddard for supplying the SCF computer programs, and John Rose and David Huestis for computational assistance. One of us (CWM) thanks the National Science Foundation for support and the California Institute of Technology for the award of an Earl C. Anthony Fellowship.

\*Supported by a grant from the National Science Foundation.

†Contribution Number 4792.

<sup>1</sup>T. Shibuya and V. McKoy, *Phys. Rev. A* **2**, 2208 (1970).

<sup>2</sup>T. Shibuya, J. Rose, and V. McKoy, *J. Chem. Phys.* **58**, 500 (1973).

<sup>3</sup>J. Rose, T. Shibuya, and V. McKoy, *J. Chem. Phys.* **58**, 74 (1973).

<sup>4</sup>J. B. Rose, T. Shibuya, and V. McKoy, "Electronic Excitations of Benzene from the Equations of Motion Method," *J. Chem. Phys.* **60**, xxx (1974).

<sup>5</sup>D. L. Yeager and V. McKoy, "The Equations of Motion Method: The Excited States of Formaldehyde," *J. Chem. Phys.* **60**, xxx (1974).

<sup>6</sup>Y. Kim and M. Inokuti, *Phys. Rev.* **175**, 176 (1968).

<sup>7</sup>E. N. Lassetre and J. C. Shiloff, *J. Chem. Phys.* **43**, 560 (1965).

<sup>8</sup>M. Inokuti, *Rev. Mod. Phys.* **43**, 297 (1971).

<sup>9</sup>F. H. Read and G. L. Whiterod, *Proc. Phys. Soc. Lond.* **82**, 434 (1963).

<sup>10</sup>D. C. Cartwright and A. Kupperman, *Phys. Rev.* **163**, 86 (1967).

<sup>11</sup>E. N. Lassetre and A. S. Francis, *J. Chem. Phys.* **40**, 1208 (1964).

<sup>12</sup>D. J. Rowe, *Rev. Mod. Phys.* **40**, 153 (1968).

<sup>13</sup>S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

<sup>14</sup>S. Guberman, Ph. D. thesis, California Institute of Technology (1972).

<sup>15</sup>D. R. Whitman and C. J. Hornback, *J. Chem. Phys.* **51**, 398 (1968).

<sup>16</sup>K. J. Miller and M. Krauss, *J. Chem. Phys.* **47**, 3754 (1967).

<sup>17</sup>B. Schneider, *Phys. Rev. A* **2**, 1873 (1970).

<sup>18</sup>E. N. Lassetre, M. Krasnov, and S. Silverman, *J. Chem. Phys.* **40**, 1242 (1964).

<sup>19</sup>R. S. Nakata, K. Watanabe, and F. M. Matsunaga, *Sci. Light* **14**, 54 (1965).

<sup>20</sup>U. Y. Foo, C. E. Brion, and J. B. Hasted, *Proc. R. Soc. A* **322**, 535 (1971).

<sup>21</sup>M. Krauss and S. R. Mielczarek, *J. Chem. Phys.* **51**, 5241 (1969).

<sup>22</sup>J. W. Rabalais, J. M. MacDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.* **71**, 73 (1971). Professor Lassetre has kindly pointed out that the observations of Rabalais *et al.* are consistent with the interpretation that both peaks are due to the  $\pi_g$  state (private communication).

<sup>23</sup>A. D. Walsh, *J. Chem. Soc.* **1953**, 2266.

<sup>24</sup>V. D. Meyer and E. N. Lassetre, *J. Chem. Phys.* **42**, 3436 (1965).

<sup>25</sup>E. C. Y. Inn, K. Watanabe, and M. Zeilikoff, *J. Chem. Phys.* **21**, 1648 (1953).

<sup>26</sup>M. Krauss, S. R. Mielczarek, D. Neumann, C. E. Kuyatt, *J. Geophys. Res.* **76**, 3733 (1971).

<sup>27</sup>G. M. Lawrence, *J. Chem. Phys.* **56**, 3435 (1972).

<sup>28</sup>M. J. Hubin-Franskin and J. E. Collins, *Bull. Soc. R. Sci. Liege* **40**, 361 (1971).