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Electron impact cross sections for $v = 0 \rightarrow 1$ vibrational excitation in CO at electron energies of 3 to 100 eV†

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Abstract. Normalised, absolute differential cross sections have been measured for electron-impact excitation of the $v = 0 \rightarrow 1$ pure vibrational transition in CO. Integral and momentum-transfer cross sections have been obtained from these differential results. Incident electron energies were in the range 3 to 100 eV, and the range of scattering angles 10 to 135°. Comparison of the results is made with pure $v = 0 \rightarrow 1$ cross sections in N_2, as well as with a recent two-potential theory for electron scattering from diatomic molecules. The present CO cross sections are remarkably similar to those in N_2, indicating that the long-range effect of the small CO dipole moment is negligible in promoting vibrational excitation. Moreover, a significant peak in the integral and momentum-transfer cross sections is observed at 20 eV. This results from a broad, resonant excitation process in the $v = 1$ channel, and confirms earlier measurements taken at only two scattering angles. Comparison is made of the low-energy integral cross sections with a recent set of swarm data for vibrational excitation.

1. Introduction

Cross sections and electron-excitation rates for the interaction of low-energy electrons with the CO molecule are needed in modelling various plasmas of which CO is an important component, such as the CW and high-pressure pulsed laser discharge (Jeffers and Wiswall 1971, Rockwood *et al* 1973). The presence of CO in the interstellar medium (Oppenheimer and Dalgarno 1975, Langer 1976, Dalgarno and Black 1976) together with energetic electrons produced by stellar UV or cosmic-ray ionisation points out the importance of knowing not only thermal e–CO cross sections, but also inelastic cross sections for higher energy electrons. It is these inelastic collisons which 'cool down' energetic electrons to thermal energies where important electron–positive-ion recombinations become dominant.

In this paper we report normalised, absolute scattering cross sections for the vibrationally inelastic $v = 0 \rightarrow 1$ excitation in CO. Measurements were made at incident electron energies (E_0) between 3 and 100 eV. The differential cross sections at each E_0 were also integrated to give absolute integral and momentum-transfer cross sections.

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In addition to the plasma-modelling applications mentioned above, the present results have interesting ties with e–molecule scattering theories. Earlier, a series of experimental–theoretical comparisons for pure vibrational $v = 0 \rightarrow 1$ excitation in N_2 were published (Truhlar *et al* 1976, 1977). The question naturally arises as to the effect on vibrational cross sections of a slight charge asymmetry and dipole moment introduced in going from $N_2(\mu_e = 0\ \text{D})$ to $CO(\mu_e = 0{\cdot}11\ \text{D})$. As will be shown, the present results imply that the major effect in the scattering appears to arise from shorter range forces in CO, rather than from the longer range dipole potential.

2. Experimental methods

The apparatus used in the present measurements has been described previously (Chutjian 1974, 1979). Briefly, a beam of CO effusing from a multichannel array is crossed with a beam of mono-energetic electrons of desired energy E_0. Elastically and inelastically scattered electrons at a particular scattering angle (θ) are energy-analysed and detected. The resolution in these measurements was 45–60 meV (FWHM). This was sufficient to separate clearly the $v = 0 \rightarrow 1$ excitation from $v = 0 \rightarrow 0$ (elastic) and $v = 0 \rightarrow 2$ excitations, but insufficient to resolve any rotational structures.

As in earlier studies on N_2 the experimental quantity measured was the ratio $R_1(E_0, \theta)$ of peak heights or integrated areas of the $v = 0 \rightarrow 1$ cross section $\sigma_{01}(E_0, \theta)$ relative to the elastic-scattering cross section $\sigma_{00}(E_0, \theta)$; i.e. $R_1(E_0, \theta) = \sigma_{01}(E_0, \theta)/\sigma_{00}(E_0, \theta)$. Checks of this ratio for the presence of a parent-beam contribution were made at small scattering angles ($\theta < 30°$) by pumping away the CO target gas to a background pressure of 5×10^{-8} Torr and measuring the parent-beam intensity. The lowest scattering angles at which $R_1(E_0, \theta)$ is reported are those where the correction for parent-beam effects was 20% or less. To place the vibrational cross section ratio on the absolute scale, the value of $R_1(E_0, \theta)$ was multiplied by the elastic CO differential cross section (Tanaka *et al* 1978) at each E_0 and θ to give the normalised, absolute value of $\sigma_{01}(E_0, \theta)$.

As in previous measurements the true zero scattering angle was determined as that angle about which the elastic scattering intensity was symmetric. The estimated error in this determination is ±2°. The energy scale was calibrated to an estimated accuracy of ±0·1 eV by noting the nominal energy position of the 10·04 eV CO resonance at $\theta = 80°$ (Sanche and Schulz 1971, Comer and Read 1971, Swanson *et al* 1975).

3. Results and discussion

Values of $R_1(E_0, \theta)$ at each E_0 and θ are given in table 1. Errors in these values were estimated from the reproducibility of two to four separate measurements of R_1 taken on different days, under different spectrometer conditions. This error was 15% at 3 eV, and 13% at 5–100 eV. Values of σ_{01} are given in table 2 and plotted in figures 1 and 2. Errors in σ_{01} were taken as the quadrature sum of the errors in R_1 and σ_{00}. This latter error was (Tanaka *et al* 1978) 22% at 3 eV, 11% at 5 and 9 eV, and 20% at 20–100 eV. This gave a quadrature error in σ_{01} of 27% at 3 eV, 17% at 5 and 9 eV and 20% at 20–100 eV.

Also plotted in figure 1 are the differential cross sections for $v = 0 \rightarrow 1$ pure vibrational excitation in N_2 (Truhlar *et al* 1976, 1977) at 5, 10 and 30 eV, while N_2 data

Table 1. Ratios $R_1(E_0, \theta)$ in units of 10^{-3} for $v = 0 \rightarrow 1$ vibrational excitation in CO at the indicated impact energies (E_0) and scattering angles (θ). Extrapolated values are given in parentheses. Errors in $R_1(E_0, \theta)$ are 15% (3 eV) and 13% (5–100 eV).

θ \ E_0	3	5	9	20	30	50	75	100
5	—	—	—	—	—	—	(0·76)	—
10	(43)	(27)	8·95	3·08	1·03	0·639	0·400	—
15	34·6	26·5	4·44	2·80	0·845	0·381	0·387	—
20	26·1	18·8	2·44	2·86	0·708	0·285	0·389	0·564
25	21·0	13·2	1·79	2·95	0·653	0·250	0·540	0·698
30	17·9	8·19	1·19	3·51	0·725	0·331	1·11	1·98
35	14·5	5·83	1·07	4·37	0·900	0·622	1·70	3·08
40	12·6	4·45	1·00	5·33	1·18	1·01	2·71	4·68
50	11·0	3·30	1·13	11·2	2·43	2·21	3·96	5·77
60	12·2	3·27	1·54	16·2	4·90	3·70	4·52	5·14
70	16·5	4·09	1·97	24·2	8·92	5·34	5·22	4·20
80	23·0	5·00	2·33	33·1	13·6	6·84	5·24	4·05
90	26·1	5·56	2·48	28·6	14·7	7·49	4·88	5·37
100	30·1	5·91	2·02	23·2	11·8	6·83	3·91	6·88
110	32·5	5·98	1·64	21·5	9·05	4·86	3·64	8·37
120	34·0	6·08	1·35	18·2	7·48	3·69	3·21	9·30
130	33·6	6·96	1·92	15·7	6·21	2·96	2·96	9·30
140	(34)	(10)	(2·6)	(15)	(5·4)	(2·8)	(2·6)	(8·2)

at 50 and 75 eV are shown in figure 2. Also shown in figure 2 are theoretical N_2 results of Choi *et al* (1979) and CO results of R T Poe (1979, private communication) using a two-potential theory for e–CO vibrational excitation.

Since plasma modellers often require integral and momentum-transfer cross sections we present in figures 3 and 4 these integrated results for CO. Assignment of errors to the integrated data took into account an estimated error in extrapolating the differential cross section from 10° to 0°, and 135° to 180°. This error, when combined in quadrature with the differential cross section error, gave an overall error in σ_I and σ_M of 28% at 3 eV, 22% at 5 and 9 eV, and 24% at 20–100 eV. Theoretical results (figure 3) in the two-potential theory are also presented. Also shown in figure 4 is an adjusted set of cross sections in the range 1·514–3·816 eV which are consistent with CO swarm measurements (Land 1978).

Several conclusions can be drawn from the results shown in figures 1–4. From figures 1 and 2 the close resemblance, both in shape and magnitude, of the differential cross sections for CO and N_2 implies that, at these energies, and at least in the angular range measured (see below), the effect of the small CO dipole moment is practically negligible in promoting vibrational excitation in this molecule. The major effect appears to arise in both species from shorter range potentials, such as polarisation and quadrupole, rather than to the long-range dipole potential. Further, there is generally good agreement between results in the two-potential theory and experiment (figure 2) with theory successfully accounting for the trends in the low angle ($\theta < 80°$) differential cross section.

The second interesting effect may be seen in figure 3 by the pronounced hump in the σ_I and σ_M at 20 eV. This effect was seen earlier (Chutjian *et al* 1972) at scattering angles of 40° and 80°, and was also noted in N_2 (Pavlović *et al* 1972). The present

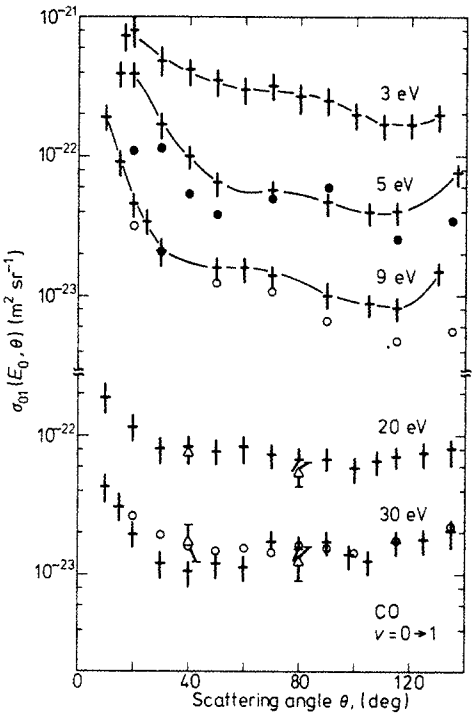

Figure 1. Differential cross sections for the $v = 0 \rightarrow 1$ vibrational excitation in CO at the indicated impact energies. Crosses represent present measurements for CO. Full circles (●) are data for $v = 0 \rightarrow 1$ excitation in N_2 at 5 eV, and open circles (○) are data for N_2 at 10 eV (below 9 eV CO data) and 30 eV. Open triangles are previous CO data using the ratios $R_1(E_0, \theta)$ of Chutjian *et al* (1972) and recently reported $\sigma_{00}(E_0, \theta)$ of Tanaka *et al* (1978).

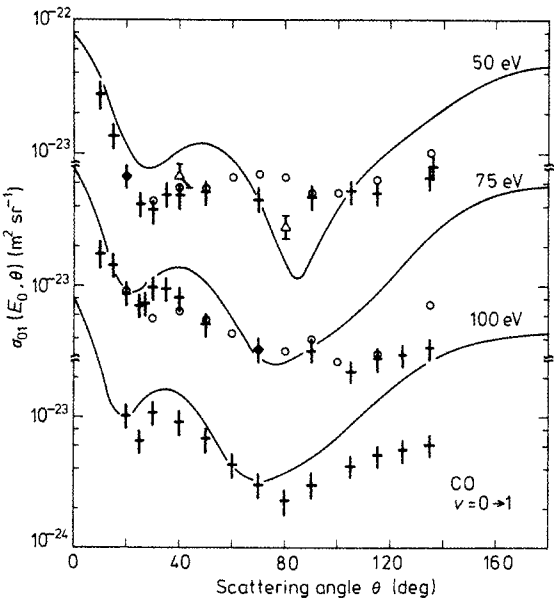

Figure 2. Same as figure 1, but at 50, 75 and 100 eV impact energies. The full curves are results of the two-potential theory for e–CO vibrational excitation.

Table 2. Absolute differential $\sigma_{01}(E_0, \theta)$, integral σ_I and momentum-transfer σ_M cross sections for $v = 0 \rightarrow 1$ vibrational excitation in CO at the indicated impact energies (E_0) and scattering angles (θ). Units are $10^{-23}\,m^2\,sr^{-1}$. Extrapolated values are given in parentheses. Errors in $\sigma_{01}(E_0, \theta)$ are 27% (3 eV), 17% (5 and 9 eV) and 20% (20–100 eV). Errors in both σ_I and σ_M are 28% (3 eV), 22% (5 and 9 eV) and 24% (20–100 eV).

θ \ E_0	3	5	9	20	30	50	75	100
0	(64)	(34)	(38)	(26)	(6·9)	(5·8)	(3·7)	(4·4)
5	(70)	(37)	(28)	(22)	(5·6)	(4·1)	(2·7)	(3·2)
10	(73)	(39)	18·8	18·2	4·58	2·81	1·84	(2·0)
15	(75)	42·6	9·14	14·4	3·10	1·34	1·33	(1·2)
20	72·0	37·0	4·84	11·6	2·04	0·680	0·840	0·954
25	58·5	26·8	3·36	9·20	1·43	0·413	0·708	0·686
30	50·3	17·2	2·10	8·04	1·21	0·374	0·895	1·06
35	43·7	12·7	1·88	7·78	1·08	0·460	1·07	1·03
40	40·6	10·1	1·75	8·10	1·02	0·492	0·813	0·946
50	34·6	6·54	1·60	7·85	1·12	0·514	0·534	0·704
60	30·3	5·40	1·62	7·93	1·24	0·492	0·391	0·433
70	30·8	5·73	1·44	7·38	1·57	0·450	0·333	0·305
80	28·0	5·30	1·28	6·78	1·61	0·424	0·324	0·245
90	25·1	4·67	1·04	6·51	1·59	0·448	0·281	0·293
100	20·8	4·14	0·910	6·04	1·42	0·489	0·259	0·381
110	16·9	3·89	0·868	6·73	1·34	0·510	0·246	0·443
120	17·7	4·38	0·894	7·26	1·63	0·546	0·286	0·542
130	19·8	5·64	1·48	7·78	1·93	0·651	0·326	0·608
140	(23)	(8·6)	(2·2)	(8·2)	(2·1)	(0·79)	(0·36)	(0·66)
150	(26)	(11)	(2·8)	(8·5)	(2·3)	(0·98)	(0·38)	(0·70)
160	(29)	(14)	(3·4)	(8·9)	(2·5)	(1·1)	(0·40)	(0·74)
170	(31)	(16)	(3·8)	(9·2)	(2·7)	(1·3)	(0·41)	(0·76)
180	(32)	(17)	(4·2)	(9·4)	(2·8)	(1·4)	(0·42)	(0·79)
σ_I	365	104	24·1	96·7	20·6	7·57	5·42	7·03
σ_M	300	85·0	20·3	93·4	21·9	7·97	4·21	6·48
σ_I^a	—	—	—	—	—	13·8	16·3	17·2
σ_M^a	—	—	—	—	—	16·8	21·3	22·2

[a] Theoretical results of R T Poe (1979, private communication).

integrated cross section results confirm earlier CO results at the two scattering angles. In both cases the hump was interpreted as resonances associated with doubly excited states of CO and N_2. In N_2 the resonances were said to arise from states having two holes in the N_2 core $KK(\sigma_g 2s)^2\,(\sigma_u 2s)^2\,(\pi_u 2p)^4\,(\sigma_g 2p)^2$ and three electrons in the first two excited orbitals ($\pi_g 2p$) and ($\sigma_u 2p$). The resonances in CO would arise from two holes in the analogous orbitals $KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^2$ with three electrons in the orbitals (2π) and (6σ). However, recent calculations in N_2 (K Onda and D G Truhlar 1979, private communication, Dehmer *et al* 1979) show the enhancement to arise simply from a single-particle shape resonance associated with the ($\sigma_u 2p$) orbital. This one-electron picture would also apply to CO with the particle in the (6σ) orbital. Further confirmation of the resonance in CO comes from the differential cross sections in figure 1. The angular distribution at 20 eV exhibits a minimum at about $\theta = 35°$, followed by a local maximum at about 55° and a slightly deeper minimum at 90°. This shape is characteristic of an f-wave ($l = 3$) resonance (see, for example, Read 1968), a

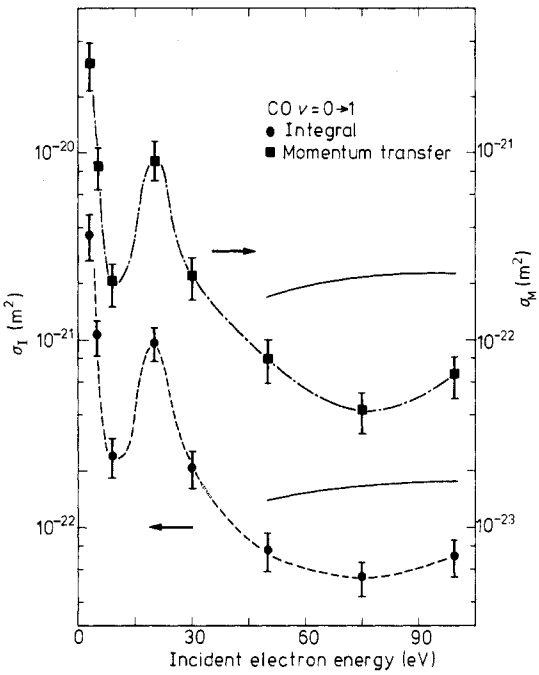

Figure 3. Integral (σ_I) and momentum transfer (σ_M) cross sections for $v = 0 \rightarrow 1$ vibrational excitation in CO. Broken curves are drawn for ease of viewing. The full curve at 50–100 eV is the result of the two-potential theory of R T Poe (1979, private communication) and Choi *et al* (1979).

result consistent with both theoretical calculations (Dehmer *et al* 1979, K Onda and D G Truhlar 1979, private communication) and verifying experimental data at 19·5 eV (Tronc and Azria 1979).

It is interesting to note that for both N_2 and CO the Σ_u or Σ shape resonance lies at surprisingly high energies (greater than a few eV), and is unusually broad (greater than 0·1 eV).

Also shown in figure 3 are the results of R T Poe (1979, private communication, CO results) (see also Choi *et al* 1979, N_2 results) in the two-potential theory. This theory includes contributions from a short-range shielded Coulomb potential of the carbon and oxygen atom centres, and a permanent plus induced long-range potential consisting of dipole, quadrupole and induced polarisation terms. One finds fair agreement between experiment and theory at the three energies (50, 75 and 100 eV) where calculations exist. Theory is a factor of two to four higher than experiment, and gives a distinctly different shape of σ_I and σ_M against E_0. One possible source of discrepancy could lie in the form of the extrapolation of the experimental differential cross sections to zero degree scattering angle. We have examined several 'reasonable' extrapolations, using also the theoretical differential cross sections as a guide. In addition, an extrapolation using the shape (momentum transfer)$^{-2}$ as given by the Bethe theory (Inokuti 1971) for small momentum transfers was used. This form was joined to the lowest angle data points and extrapolated to zero degrees. The maximum deviation was found for σ_I, and was 30% using the momentum-transfer extrapolation. The deviation in σ_M was less than 1% since the low-angle differential cross section is greatly

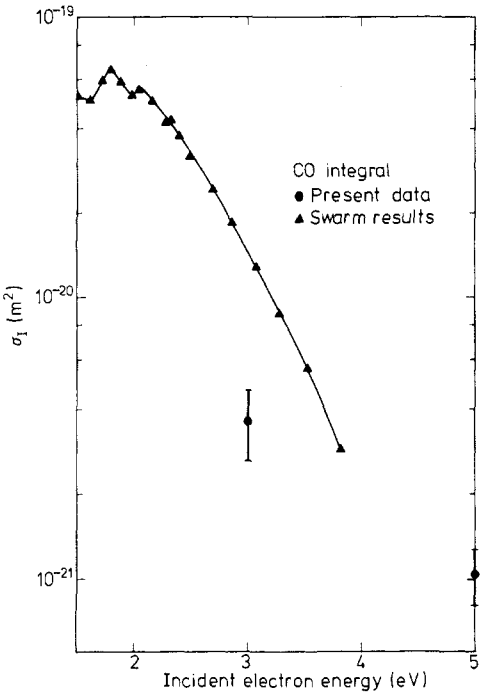

Figure 4. Present integral cross sections for $v = 0 \rightarrow 1$ excitation at 3 and 5 eV compared with a set of extended swarm results for the $v = 0 \rightarrow 1, \ldots, 10$ excitations made consistent by Land (1978).

disfavoured by the $\sin\theta(1-\cos\theta)$ factor in the calculation of σ_M. One therefore concludes that the source of the experimental–theoretical discrepancy very likely lies in the theory. This is true for σ_I, and especially for σ_M which responds hardly at all to small-angle adjustments in the differential cross section.

Finally, we show in figure 4 another comparison of the present 3 and 5 eV results for σ_I with a recent extension of swarm data for the *sum* of vibrational excitations from $v = 0$ to higher levels (Land 1977, 1978). The extension was made from the highest energy swarm results (0·7 eV, see Land 1978 and references therein) to 3·8 eV using the shape of Ehrhardt *et al* (1968) and Boness and Schulz (1973) extrapolated and adjusted in magnitude to meet the swarm data at 0·7 eV.

One finds that the present 3 eV result for σ_I lies below the extended data by a factor of about four. The discrepancy cannot be accounted for by possible errors in extrapolating the present differential cross sections to 0° and 180°. The contribution of the high-angle extrapolation to $\sigma_I(140–180°)$ is 11% in the present data, while the low-angle (20–0°) extrapolation contributes 8%. One would thus require high- and low-angle extrapolations exceeding by a factor of about 20 that actually used in order to raise the present 3 eV value of σ_I to the extended data. Again this seems unlikely in view of the fairly isotropic behaviour of the 3 eV differential cross sections (see figure 1) and the discontinuous shape such an abrupt extrapolation would incur. Nor does the discrepancy lie in neglect, in the present data, of integral cross sections for the excitations $v = 2–10$. One can estimate these transitions to contribute about another 25% to σ_I (Ehrhardt *et al* 1968, Boness and Schulz 1973), reducing the discrepancy now to a factor of three. A similar difficulty was encountered (Land 1978) in attempting

to reconcile earlier crossed-beam data (Ehrhardt *et al* 1968, Boness and Schulz 1973) with the extended swarm data. The crossed-beam results had to be raised by a factor of 1·9 to reconcile the two sets. We also note that the present integral cross section at 3 eV is $3{\cdot}65 \times 10^{-17}$ cm^2 which compares with a value of approximately 7×10^{-17} cm^2 as read from figure 8 of Ehrhardt *et al* (1968).

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