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Electron scattering from vibrationally excited CO₂

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Abstract. The total cross section for electron scattering from vibrationally excited (principally 010) CO_2 molecules has been measured in the energy range 0.12–2.0 eV with a time of flight electron spectrometer. The vibrationally excited molecules were produced by thermal excitation of the gas contained in a scattering cell at a temperature of 300 °C. The cross section for scattering from these excited molecules was deduced by comparison with similar measurements performed at room temperature. At energies below 2 eV the excited-state cross section is considerably larger than that for scattering from ground-state CO_2. The ground-state measurements are in excellent agreement with other recent experimental and theoretical work. No other experimental or theoretical data exist for the excited-state cross section.

1. Introduction

Collisions of low-energy electrons with vibrationally excited molecules play an important role in determining the behaviour of gas discharges and plasmas (see, for example, Phelps 1979). However, because of difficulties in producing and characterising vibrationally excited targets in sufficient number densities very little quantitative experimental work has been done in this field. Indeed, to our knowledge, only a handful of such experiments have been carried out. For CO_2 this work has been directed towards measurements of dissociative attachment from vibrationally excited states (Spence and Schulz 1969, Chantry 1972, Srivastava and Orient 1983) whilst for N_2 and O_2 several high-resolution electron energy loss (gain) measurements have been made for both vibrationally and electronically excited molecules (White and Ross 1976, Hall and Trajmar 1975). In the case of O_2, Hall and Trajmar found that low-energy excitation cross sections from the metastable a $^1\Delta_g$ state were up to an order of magnitude larger than corresponding excitations from the ground state.

Theoretical interest in these problems has also been rather limited, although of particular interest to the present work is the calculation of Davis and Schmidt (1972) which indicates that significant enhancement of electron–molecule collision cross sections may occur if the molecule is in a vibrationally excited level with an associated electric dipole moment.

The principal motivation for the present work was the electron swarm study of Haddad and Elford (1979). These authors found that the momentum transfer cross section for electron scattering by CO_2, derived from the analysis of drift velocity measurements, was strongly temperature dependent at energies below 1 eV. They attributed this enhanced scattering at high temperatures to an increased population of thermally vibrationally excited molecules, principally in the first bending vibration

(010), which has a threshold of 0.083 eV. As this molecular vibration has an associated electric dipole moment, the increase in the cross section observed at low energies may well be a result of the electron–dipole interaction. Such effects have often been observed in low-energy electron scattering from polar molecules.

The aim of the present measurements was to both confirm and quantify the results of Haddad and Elford in a single-collision experiment. It was also believed that if the electron–vibrational-dipole interaction was responsible for this enhanced scattering a total cross section measurement would be a more sensitive means of investigating it. This is because the long-range dipole interaction results in increased scattering in the forward direction and thus manifests itself more in the total cross section than in the momentum transfer cross section, which is weighted towards backward scattering events.

The experimental apparatus and procedures and possible sources of systematic errors are discused in § 2. The absolute total cross sections for scattering from both ground- and excited-state CO_2 are presented and discussed in § 3 and, where possible, comparison is made with other experimental and theoretical work.

2. Experimental apparatus and procedures

The time of flight (TOF) electron spectrometer used for the present studies has been described in detail in a previous publication (Buckman and Lohmann 1986a) and only a brief outline of the experiment will be given here, although those aspects relevant to the production and characterisation of the vibrationally excited molecular target will be discussed in more detail.

A well focused, high-energy (100–200 eV) electron beam is pulsed by sweeping it across a small aperture with a RF (170 kHz) square-wave pulse applied to a pair of deflection plates. The pulsed electron beam is then retarded in energy by a series of electrostatic lenses before entering a 255 mm long attenuation cell containing the gas of interest. Those unscattered electrons which emerge from the cell are accelerated and detected in a channeltron electron multiplier. The energy of the electrons within the scattering cell is determined from their measured time of flight, and the total cross section is derived at each energy by measuring the transmitted electron intensity both with and without gas in the scattering cell and by applying the Lambert–Beer relationship.

The vibrationally excited CO_2 molecules were produced by heating the scattering cell to a temperature of 300 °C. At this temperature approximately 19.2% of the molecules in the gas are in vibrationally excited levels (see table 1), with approximately 15.2% in the first bending (010) mode.

Table 1. Fractional populations of the first four vibrational levels of CO_2 at 37 and 300 °C.

T (°C)	000	010	020 100	030
37	0.9545	0.043	0.0019	0.0001
300	0.8090	0.1519	0.0282	0.0064

The molybdenum scattering cell was heated resistively by passing a current through a number of coaxial heating elements (Thermocoax) mounted on its outer surface. The heaters and their associated wiring within the vacuum system were arranged such that no induced magnetic field resulted during operation. This was confirmed by observing no significant effect on either the electron count rates or the shape of the energy spectrum at the lowest electron energy (0.120 eV) when the heaters were operational. During the measurements, the temperature of the scattering cell was measured by three platinum resistance thermometers mounted along its length and monitored by the microcomputer controlling the experiment. The microcomputer was programmed to adjust the power of the heater supplies to ensure that a constant temperature was maintained. The operation of this control loop every 10 s and the high thermal capacity of the scattering cell resulted in the temperature being maintained to within 0.1 °C of the desired set point. The temperature measurement was accurate to ±1 °C.

The absolute pressure of the gas in the scattering cell was measured with a spinning rotor viscosity gauge (SRG). As the gauge head was maintained at 37 °C, which was the normal operating temperature of the scattering cell, a correction for thermal transpiration effects was required when the scattering cell was operated at 300 °C. To account for these effects, which with a temperature differential of 263 °C are of the order of 30%, we have used the empirical expression developed by Takaishi and Sensui (1963). As thermal transpiration effects are often apparatus specific, we tested the applicability of this expression to our apparatus by making cross section measurements at a fixed energy (14 eV) in argon at both 37 and 300 °C. After application of the correction to the high-temperature data the resulting cross sections agreed to within the experimental uncertainty of ±3%. As the thermal transpiration correction is also gas dependent, we duplicated this procedure with CO_2 at energies of 14 and 20 eV where the effect of the initial vibrational-state population was expected to be negligible and again found no significant differences between the cross sections.

As the experiment involves dynamic gas flow through the scattering cell it was also necessary to demonstrate that the CO_2 was in thermal equilibrium with the cell when it was operated at 300 °C. Non-thermalisation at low pressures may manifest itself in two ways: firstly as an apparent increase in the scattering cross section due to an underestimation of the gas number density, and secondly as a real decrease in the cross section due to a reduction in the number of excited molecules in the gas sample. A test for these effects was carried out by making cross section measurements at a number of different pressures in the range 5×10^{-4}–3×10^{-3} mbar—the pressure range used for the measurements presented here—and at energies of 14 and 0.30–0.50 eV. Again no significant difference was noted in the measured cross sections as a function of the gas pressure, indicating that the gas was in thermal equilibrium with the cell. As it is also possible that these effects could be compensated for by a decrease in the cross section as a function of pressure by multiple scattering, similar tests were carried out in a gas sample at 37 °C to establish that single-collision conditions applied in this pressure range.

The cross section for scattering from the vibrationally excited molecules was derived from measurements performed at 37 and 300 °C but with otherwise identical conditions. The measured cross sections at 37 and 300 °C can be expressed as

$$\sigma_{t_m}(37) = N_g(37)\sigma_{t_g} + N_{ex}(37)\sigma_{t_{ex}} \tag{1}$$

$$\sigma_{t_m}(300)N_g(300) = \sigma_{t_g} + N_{ex}(300)\sigma_{t_{ex}} \tag{2}$$

where $N_g(T)$ and $N_{ex}(T)$ are the fractional populations of ground- and excited-state molecules at temperature T and σ_{t_g} and $\sigma_{t_{ex}}$ are the cross sections for scattering from the ground and excited states of CO_2. By inserting the appropriate values from table 1 we obtain the following expression for the excited-state scattering cross section in terms of the measured cross sections at 37 and 300 °C:

$$\sigma_{t_{ex}} = 5.307(\sigma_{t_m}(300)/0.809 - \sigma_{t_m}(37)/0.9545). \tag{3}$$

The uncertainty in the room temperature measurements is typically ±3% whilst for the high-temperature measurements the increased uncertainty in the pressure measurement (±3%) due to thermal transpiration leads to an overall uncertainty in the cross section of 4–5% (see Buckman and Lohman (1986a) for a complete discussion of experimental uncertainties). This results in an uncertainty of about ±30% in the derived cross section for scattering from the vibrationally excited molecules. It should be noted that this rather large uncertainty comes about principally because of the relatively low fraction of molecules that are in excited states.

3. Results and discussion

The absolute total cross sections for electrons scattered from vibrationally excited (principally 010) CO_2 are given in table 2 at a number of energies between 0.120 and 2.0 eV and shown in figure 1. As there are no other experimental or theoretical results available for comparison with this cross section we can only make a comparison with the cross section for scattering from CO_2 at a temperature of 37 °C. For convenience we will refer to the latter as the 'ground-state cross section'. The excited-state cross section ($\sigma_{t_{ex}}$) exhibits the same general energy dependence as that for the ground state (σ_{t_g}), showing a very rapid increase towards lower energies, but it is considerably larger than the ground-state cross section throughout the energy range shown in figure 1. The maximum relative difference occurs at about 2.5 eV where $\sigma_{t_{ex}}$ is 2.4 times larger

Table 2. Total cross sections for electrons scattered by vibrationally excited CO_2. Absolute uncertainties (1 SD) are typically ±30%.

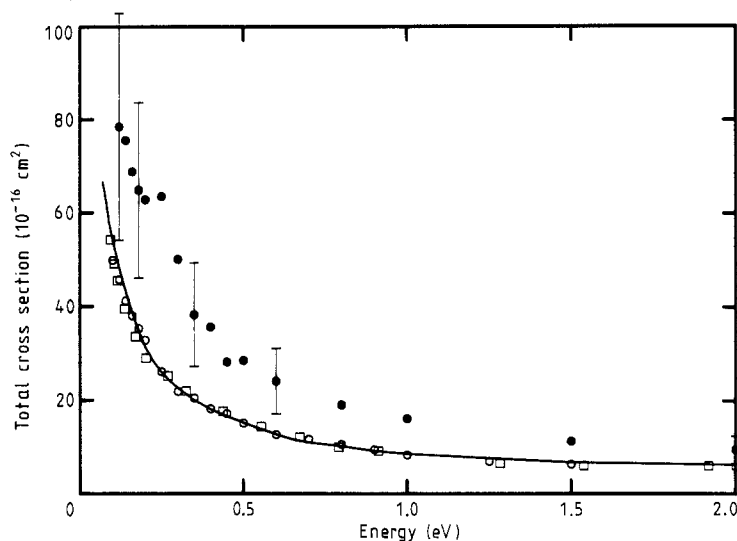| Energy (eV)	Q_t (10^{-16} cm^2)
0.12	78.5
0.14	75.5
0.16	68.8
0.18	64.9
0.20	62.8
0.25	63.6
0.30	50.1
0.35	38.3
0.40	35.7
0.45	28.2
0.50	28.5
0.60	24.1
0.80	19.1
1.00	16.2
1.50	11.3
2.0	9.5

Figure 1. Absolute total cross sections for electron scattering from CO_2 in the energy range 0–2.0 eV. ●, present results for vibrationally excited CO_2: ○, present results for ground-state CO_2; □, Ferch *et al* (1982); ——, theory of Morrison *et al* (1977).

than σ_{t_g}. As the incident energy increases the relative difference between the two cross sections decreases until at 2.0 eV there is substantial overlap of the error bounds on the two measurements. Measurements at higher energies (3.0, 3.8 and 14 eV) revealed no significant differences between the excited-state and ground-state cross sections. It should be noted that the ground-state cross section contains a contribution due to about 4.5% of the molecules being in the first excited state (see table 1). The true ground-state cross section can be readily calculated from equation (1), but in the interests of clarity it is not shown in figure 1 as the largest deviation between it and σ_{t_m} (37) is about 6% at 0.25 eV.

These measurements of the effect of temperature (or initial vibrational state population) on the scattering cross sections are in good qualitative agreement with the conclusions of Haddad and Elford (1979) based on electron swarm studies. Although not published in their original study, these authors derived a momentum transfer cross section (σ_{mom}) for electron scattering in CO_2 at 300 °C which shows significant low-energy enhancement of the cross section over that observed at room temperature (Elford 1986). In particular they observed a similar maximum in the difference between the ground and excited state σ_{mom} at about 0.25 eV.
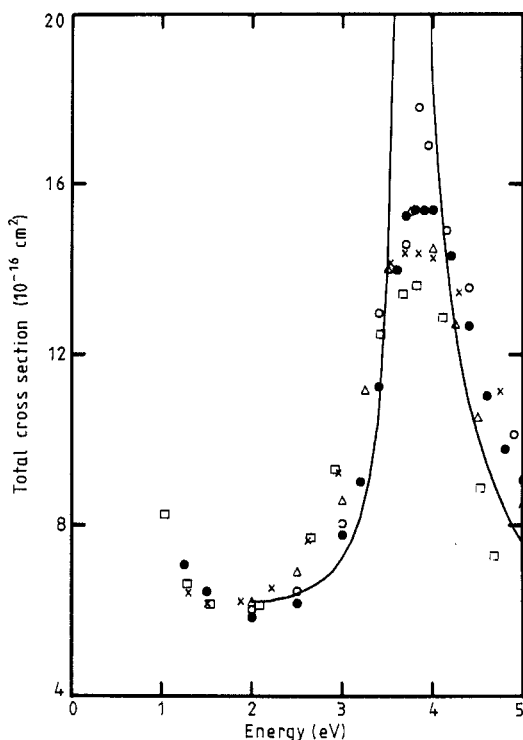
Also shown in figure 1 are the total cross section measurements of Ferch *et al* (1981) for ground-state CO_2 and the coupled-channels static exchange polarisation calculation of Morrison *et al* (1977). The agreement between the two experiments and between experiment and theory is excellent over the whole energy range. The present ground-state total cross sections are also given in table 3.

The total scattering cross sections for ground-state CO_2 for energies in the range 2.0–5.0 eV which encompasses the $^2\Pi_u$ resonance are shown in figure 2. Comparison is also made with several previous experimental cross sections. In general the agreement is good, although there are some discrepancies between the present results and the two most recent experimental investigations (Ferch *et al* 1981, Hoffmann *et al* 1982).

Table 3. Absolute scattering cross sections for CO_2 in its ground vibrational state. The uncertainty at each energy is ±3% (1 SD).

Energy (eV)	Q_t (10^{-16} cm^2)
0.10	49.92
0.12	45.79
0.14	41.28
0.16	38.07
0.18	35.35
0.20	32.86
0.25	26.16
0.30	21.95
0.35	20.56
0.40	18.28
0.45	17.25
0.50	15.27
0.60	12.79
0.70	11.80
0.80	10.67
0.90	9.57
1.00	8.44
1.25	7.07
1.50	6.44
2.0	5.84
2.5	6.16
3.0	7.76
3.2	9.01
3.4	11.24
3.6	13.97
3.7	15.24
3.8	15.38
3.9	15.37
4.0	15.38
4.2	14.31
4.4	12.66
4.6	11.03
4.8	9.78
5.0	9.05

At energies above 2.0 eV there are some significant differences (>5%) between the present results and those of Ferch *et al.* Some of these differences on the wings of the resonance can be resolved by shifting either data set by 100-200 meV, and as the energy uncertainty for both of these experiments is about 100 meV at energies above 2.0 eV, such an explanation is not unreasonable. However, this explanation cannot account for the difference between the cross sections at the resonance peak, the present result being some 13% higher than that found by of Ferch *et al*, a difference which is well outside the combined uncertainties of the two data sets. Equally puzzling is a similar discrepancy between the present cross section and that of Hoffmann *et al* (1982), although in this case the present result is 14% lower than that of Hoffman *et al* at the resonance peak. It is unlikely that any of these differences can be due to energy resolution. The present results are in good agreement with those of Szmytkowski and Zubek (1978), particularly with regard to the magnitude of the cross section at the resonance peak.

Figure 2. Total cross section for CO_2. ●, present results; □, Ferch *et al* (1982); ○, Hoffman *et al* (1982); △, Szmytkowski and Zubek (1978); ×, Bruche (1927); ——, theory of Morrison *et al* (1977).

Also shown in figure 2 are the measurements of Bruche (1927) which are in good general agreement with most of the recent experiments and which further highlight the remarkable accuracy of many of the cross section measurements from the 1920s and 1930s. The experimental data of Sueoka and Mori (1984) (not shown in figure 2) are in poor agreeemnt with the present data and other recent experimental results in the energy range 1.5–5.0 eV. These measurements, performed with a retarding-potential TOF technique, predict a maximum at the resonance peak that is about 30% lower than the present cross section.

The calculated cross section of Morrison *et al* (1977) is also shown in figure 2. With the exception of the overestimation of the resonance cross section it is in reasonable agreement with the experimental results. As has been discussed previously (Morrison *et al* 1977, Ferch *et al* 1981), this overestimation is most likely due to the neglect of nuclear motion in the calculation. Similar differences between experiment and theory have also been noted for the low-energy shape resonances in N_2 (Kennerly 1980) and CO (Buckman and Lohmann 1986b).

4. Conclusions

We have measured the low-energy total electron scattering cross section for CO_2 at temperatures of 37 and 300 °C and found a significant increase in the cross section at energies below 2.0 eV due to the presence of molecules thermally excited to vibrational

states, principally the first bending mode (010). The increase is attributed to a combination of enhanced elastic, inelastic and superelastic scattering due to the electric dipole moment associated with this first bending vibration. The derived excited-state cross section has an absolute uncertainty of ±30%. We also present scattering cross sections from ground-state CO_2 for electrons with energies up to 5 eV. These data have an absolute uncertainty of ±3% and are generally in good agreement with previous measurements and theory.

To our knowledge these are the first quantitative measurements of scattering cross sections for vibrationally excited molecules. The magnitude of the enhancement of the cross section in this case suggests that such effects should be considered when modelling the behaviour of low-pressure discharges, particularly in species possessing low-energy (<100 meV) vibrational modes which can be readily thermally excited and which have associated electric dipole moments.

Acknowledgments

References

Brüche E 1927 *Ann. Phys., Lpz* **83** 1065
Buckman S J and Lohmann B 1986a *J. Phys. B: At. Mol. Phys.* **19** 2547
—— 1986b *Phys. Rev.* A **34** 1561
Chantry P J 1972 *J. Chem. Phys.* **57** 3180
Davis H T and Schmidt L D 1972 *Chem. Phys. Lett.* **16** 260
Elford M T 1986 Private Communication
Ferch J, Masche C and Raith W 1981 *J. Phys. B: At. Mol. Phys.* **14** L97
Haddad G N and Elford M T 1979 *J. Phys. B: At. Mol. Phys.* **12** L743
Hall R I and Trajmar S 1975 *J. Phys. B: At. Mol. Phys.* **8** L293
Hoffman K R, Dababneh M S, Hsieh Y-F, Kauppila W E, Pol V, Smart J H and Stein T S 1982 *Phys. Rev.* A **25** 1393
Kennerly R E 1980 *Phys. Rev.* A **21** 1876
Morrison M A, Lane N F and Collins L A 1977 *Phys. Rev.* A **15** 2186
Phelps A V 1979 *Electron-Molecule Scattering* ed S C Brown (New York: Wiley) p 81
Spence D and Schulz G J 1969 *Phys. Rev.* **188** 280
Srivastava S K and Orient O J 1983 *Phys. Rev.* A **27** 1209
Sueoka O and Mori S 1984 *J. Phys. Soc. Japan* **53** 2491
Szmytkowski C and Zubek M 1978 *Chem. Phys. Lett.* **57** 105
Takaishi T and Sensui Y 1963 *Trans. Faraday Soc.* **59** 2503
White M D and Ross K J 1976 *J. Phys. B: At. Mol. Phys.* **9** 2147