The vibrational excitation of hot molecules by low energy electron impact

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Abstract. We report vibrational excitation functions and angular distributions for electron scattering from the ground vibrational quantum (000), the bending vibrational quantum (010) and the unresolved first bending overtone (020) and symmetric stretch (100) modes of the ground-electronic state in hot (750 K) carbon dioxide (CO₂) molecules. The excitation function measurements were carried out at incident electron energies in the range of 1–9 eV, and at the electron scattering angles of 30°, 60°, 90° and 120°.

1. Introduction

Experimental studies on the excitation processes of molecules by low energy electron impact have usually been performed under conditions near room temperature. However, it is very rare that the system or the phenomenon under study e.g. in nature or in a laboratory, corresponds to such an ideal system. In low temperature plasmas (400-1000 K), it has been pointed out that vibrationally excited (hot) molecules play important roles in the behaviour of that plasma. While there have been several investigations, both experimental and theoretical [1] (and references therein), into electron impact excitation of room temperature CO₂, where the predominant scattering occurs from the ground vibrational quantum (000) of the ground electronic state (¹Σ₉⁺), studies into electron scattering from hot CO₂ are still quite limited. We believe that the first quantitative experiment to study low-energy electron scattering from vibrationally excited CO₂ molecules was by Buckman et al. [2], in which total cross sections (TCSs) as a function of temperature were determined using a linear attenuation time-of-flight (TOF) spectrometer. In that work Buckman et al. observed a substantial increase in the TCS at electron energies below 2 eV, which they attributed to enhanced scattering due to the electric dipole moment of the bending (010) mode. No significant change in the TCS was observed at higher energies. Ferch et al. [3] repeated the experiment of Buckman et al., also using a TOF spectrometer, and confirmed the earlier result of direct dipole scattering but also found, in contrast, a pronounced change (increase) in the TCSs at energies from about 3 to 5 eV, where the ³Π₈ resonant state of CO₂ is formed. The resonance contribution from the vibrationally excited (hot) molecules, again mainly in the (010) mode, was also observed to shift to lower energies, compared to the ground-state case, by about 0.3 eV. This point is important and is used later in our analysis. More recently, Strakeljahn et al. [4] confirmed the results from Ferch et al. With respect to angular distribution measurements for electron scattering from hot CO₂, we are aware of only the data from Johnstone et al. [5], at an impact energy...
of 4 eV and scattering angle of 30°, and the somewhat more extensive results from Johnstone et al. [6], now at 3.8 eV, but for the scattered electron angles 20°, 30°, 40°, 60° and 80°. These latter results obtained the first inelastic cross sections for scattering from the (010)* → (020)(100) modes and for superelastic scattering of the (010)* mode to the ground-state (000) level. Note that the asterisk here and throughout this paper denotes scattering from an excited vibrational mode of the CO₂ molecule. Nonetheless the available data in the literature remains quite limited. Indeed part of the rationale for the present study was to try to significantly extend the superelastic and inelastic vibrational cross sections that are available. This is not only important for providing benchmark data against which sophisticated theoretical calculations can be compared, but is also vital when trying to study the role of electron-driven processes on Venus and Mars where CO₂ is one of the two dominant atmospheric species [7]. In recent years, the vibrational excitation functions for the inelastic and superelastic transitions of hot CO₂ were reported by our group [8] for the first time. In this paper, angular distributions of vibrational DCSs in hot CO₂ are now reported.

2. Experimental and analysis details

The experimental apparatus consists of a typical crossed-beam method in conjunction with the relative flow technique [9]. The present experiments were performed with an overall energy resolution of about 30 meV, and with an incident current of the order of a few nA in the impact energy range from 1 eV to 9 eV. The absolute scale is set using the relative flow technique with helium and its well-established cross sections [10] as the standard gas. Note that the relative flow method is corrected for the effect of the target gas temperature on the gas flux by using \( J \propto P/\sqrt{T} \), where \( J \) is the gas flux, \( P \) the target gas pressure and \( T \) the temperature of the target gas. The impact energy scale was calibrated against the He resonance at 19.367 eV, as well as the \(^2\Pi_g\) resonance of N₂ (\( v=1 \)) at 0.97 eV [11]. We believe this is accurate to ±10 meV.

We employed a gas resistive heating method (see Figure 1) to produce hot CO₂. The CO₂ gas is heated using a cylindrical cell made of solid Cu, which incorporates a 4 mm long nozzle of 0.6 mm diameter. The cell itself has an internal diameter of 10 mm and a length of 12 mm, with a quartz fibre. The cell is heated by wrapping a resistive coaxial sheath wire around it, and can reach temperatures up to about 850 K. A magnetic shield, placed around the cell, prevents the field generated by the heater, around which there is wrapped a pipe with flowing water that provides an outer cooling jacket, from penetrating into the interaction region. A thermocouple was set in to a small hole on the cell, and can serve to monitor the cell temperature. From an earlier experiment [12] that produced a gas phase C₆₀ beam, it has been confirmed that the gas temperature of the cell can be estimated approximately to be the same as that for the CO₂ beam at the collision centre (~1.5–2 mm from the cell nozzle exit).

![Figure 1. Schematic diagram of our hot CO₂ source.](image)
While sweeping the electron impact energies over the range 1–9 eV, the excitation function experiments were carried out at the respective energy loss values of 0.083 eV and -0.083 eV and at the scattering angles of 30°, 60°, 90° and 120°. Furthermore they were measured at the temperatures of 300, 550 and 750 K. Our experimental results therefore include cross sections from a variety of initial states whose populations depend on the Boltzmann distribution (see Table 1). The result of this process is thus, at each θ, an unresolved absolute excitation function for the (010)*→(000) and (020)*(100)*→(010)* superelastic transitions, and an unresolved absolute excitation function for the (000)→(010) and (010)*→(020)(100) inelastic transitions. We attempt to uniquely deconvolve their respective contributions by using the following assumptions in conjunction with a least squares fit. In the deconvolution, in all relevant cases, we assume that the Principle of Detailed Balance [13] holds. This assumption is expected to be valid, following the work of Johnstone et al. [6]. In the case of the bending mode this means that the condition:

\[ E_0 g_i \sigma_{i0}(E_0, \theta) = (E_0 - \Delta E_i) g_i \sigma_{i0}(E_0 - \Delta E_i, \theta) \]  \hspace{1cm} (1)

must be maintained in the deconvolution process. Note that in Eq. (1) above \( g_i \) is the degeneracy of the mode, \( \Delta E_i \) is the energy of the vibrational quantum excited, \( \sigma_{i0} \) is shorthand notation for the inelastic cross section for the (000)→(010) transition, while \( \sigma_{i0} \) denotes the superelastic cross section for the (010)*→(000) transition.

In Figure 2 we therefore show the absolute excitation function results from this process, as measured at \( \theta=90^\circ \), for the (000)→(010), (010)*→(020)(100), (010)*→(000) and (020)*(100)*→(010)* transitions. The overall errors on these excitation functions are in the range 20–70 % and include contributions from the statistical accuracy of the data, an uncertainty in our experimental calibration procedures including our normalisation to set the absolute scale, and an uncertainty reflecting the uniqueness of our least squares fit deconvolutions.

| Table 1. Population fractions of the vibrational modes in the initial state of CO₂, determined from a standard Boltzmann distribution [14]. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Vibrational     | Energy          | \( g_i \)       | Population      | Population      |
| mode            | (meV)           |                 | fractions (%)   | fractions (%)   |
| (000)           | 0.00            | 1               | 91.8632         | 66.4394         | 49.8724         |
| (0110)          | 82.75           | 2               | 7.4819          | 23.1840         | 27.7222         |
| (0200)          | 159.37          | 1               | 0.1931          | 2.3018          | 4.2357          |
| (0220)          | 165.54          | 2               | 0.3042          | 4.0416          | 7.7001          |
| (1000)          | 172.11          | 1               | 0.1180          | 1.7592          | 3.4779          |
| (0310)          | 239.59          | 2               | 0.0173          | 0.8472          | 2.4485          |
| (0330)          | 248.38          | 2               | 0.0123          | 0.7038          | 2.1371          |
| (1110)          | 257.50          | 2               | 0.0087          | 0.5806          | 1.8558          |
| (0001)          | 291.26          | 1               | 0.0012          | 0.1424          | 0.5504          |

3. Results and discussion

It is clear from Figure 2 that the \(^3\Pi_u \) resonance plays a significant role in enhancing the measured cross sections for all the excitation functions measured as a part of this study. It is also clear that there are no detailed theoretical calculations against which we can compare the present excitation functions. The resonance energy of (010)*→(020)(100) is shifted to about 0.4 eV on the lower energy side compared to (000)→(010), and the cross sections are decreased in magnitude to about half. The
resonance energy of \((020)^*(100)^*\rightarrow(010)^*\) is also shifted to the lower energy side compared to \((010)^*\rightarrow(000)\). In the comparison of the transitions \((010)^*\rightarrow(020)(100)\) and \((010)^*\rightarrow(000)\), from the same initial state, shown by solid line in Figure 2, we find they have similar cross sections, and their peak resonance energies are now only about 0.2 eV different. We note that for the \((010)\) mode the molecule undergoes a 5 degree deformation from its equilibrium geometry. However, even this small deformation can account for the 0.2 eV energy shift noted above. This is explained by the Renner-Teller effect as follows: the \(\text{CO}_2\) state is split to the bent \(^2\Lambda_1\) and linear \(^2\Sigma_1\) states with the shift in the resonance energies being dependent on this effect. At the scattering angles of \(30^\circ\), \(60^\circ\), \(90^\circ\) and \(120^\circ\) (not shown), we observed that the peak resonance energies all had the same shift as that at the scattering angle of \(90^\circ\). This observation is in agreement with the resonance energy shift of the TCS results of Ferch et al. [3] and Strakeljahn et al. [4]. Moreover, in the TCS, cross sections from the vibrationally-excited state are about 1.5 times larger than those from the ground vibrational state. On the other hand, in our DCS results, cross sections for vibrational excitation from vibrationally-excited states are not larger than those from the ground vibrational state. Therefore, we suggest that the increased magnitude in the TCS from excited \(\text{CO}_2\) is more dependent on the elastic process. This is consistent with results for elastic scattering from excited \(\text{CO}_2\) from Johnstone et al. [6].

![Figure 2](image2.png)

**Figure 2.** Vibrational excitation functions for the \((000)\rightarrow(010)\) and \((010)^*\rightarrow(020)(100)\) inelastic transitions and \((010)^*\rightarrow(000)\) and \((020)^*(100)^*\rightarrow(010)^*\) superelastic transitions of \(\text{CO}_2\) at impact energies of 1–9 eV and at a scattering angle of \(90^\circ\). In each case the line simply serves to highlight the observed energy dependence.

![Figure 3](image3.png)

**Figure 3.** Angular distributions of vibrational excitation DCS for the inelastic and superelastic transitions of \(\text{CO}_2\), at an impact energy of 3.8 eV and at scattering angles in the range \(30^\circ–120^\circ\).
scattering angles of the present work, cross sections for \((010)^*\rightarrow(020)(100)\) and \((010)^*\rightarrow(000)\) are at about the same magnitude and are about half of those cross sections for \((000)\rightarrow(010)\). The comparison between the present work and Johnstone et al.’s data showed that the cross sections of \((000)\rightarrow(010)\) and \((010)^*\rightarrow(000)\) are in good agreement within error. But, on the \((010)^*\rightarrow(020)(100)\) transition, the cross sections of Johnstone et al.’s data are larger than the present results at 60° and 90°. A general observation from these results is that cross sections at the impact energy of the resonance energy region show strong enhancement at around 90°. This suggests d-wave like scattering is important here in the reaction mechanism description [15].

4. Conclusions
We have reported absolute excitation functions and angular distributions for the \((000)\rightarrow(010)\) and \((010)^*\rightarrow(020)(100)\) inelastic and \((010)^*\rightarrow(000)\) and \((020)^*\rightarrow(010)^*\) superelastic transitions for electron scattering from hot CO2. We hope that the present measurements will now stimulate theorists to investigate the processes we have studied in more detail. Finally we believe that the branching ratio between the resonant vibrational excitation cross sections for ground-state and hot CO2 scattering, which are the most effective processes for the thermalisation of lower energy electrons, provides important information for the modelling of upper atmospheric phenomena.

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